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On the effect of hot water vapor on MX-80 clay

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October 2000

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Abstract

Earlier experiments with smectite clay exposed to hot water vapor have indicated that the expandability may be largely lost. If such conditions prevail in a HLW repository the buffer clay may deteriorate and lose its isolating potential. The present study aimed at checking this by hydrothermal treatment at 90 to 110°C of rather dense MX-80 clay with subsequent oedometer testing for determining the hydration rate, swelling pressure and hydraulic conductivity, which are all expected to be quite different from those of untreated clay if the expandability is actually reduced. The results show that the swelling pressure of MX-80 clay is not noticeably altered by exposing it to vapor with a temperature of up to 110°C for one month while the hydraulic conductivity is increased by about 10% due to some permanent microstructural alteration. The overall change in physical properties of MX-80 clay under the prevailing laboratory conditions is not very significant.

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Summary

In the hydration period the buffer smectite clay will be exposed to steam that emanates from vaporised porewater. Earlier experiments with smectite clay exposed to hot water vapor have indicated that the expandability is largely lost. If such conditions prevail in a HLW repository the buffer clay may deteriorate and lose a large part of its waste-isolating ability. The present study comprised autoclave treatment for 30 days at 90 to 110°C of MX-80 clay with a water content of 7.5% and a dry density of 1900 kg/m^3. Water was contained in cups placed on the free upper surface of the samples in the cells to an amount that would be sufficient for complete hydration of the mineral surfaces. The clay underwent expansion and strong aggregation, particularly at the upper end. After opening the cells, small specimens were taken for microscopy and the remainder used for oedometer testing for determining the swelling pressure and hydraulic conductivity. The microscopy showed that relatively big voids remained after hydration because of a reduced gel-forming potential by silica-cementation. The hydration rate and swelling pressure were on the same order of magnitude as those of untreated clay, which is assumed to be due to easy breakdown of most of the cementation. The hydraulic conductivity increased by 10% for the investigated temperature range due to some remaining cementation. The conclusion was that the isolating properties of MX-80 clay will not be altered to a practically important extent by vapor attack under the investigated hydrothermal conditions.

Sammanfattning

I bevätningsskedet utsätts buffertleran för vattenånga som härrör från förångat porvatten. Tidigare experiment med smektitlera som exponerats för het vattenånga har visat att en stor del av svällningsförmågan kan förloras (”Coutureeffekten”). Om sådana förhållanden råder i ett slutförvar för HLW kan bufferten försämras och förlora en stor del av sin förmåga att isolera avfallet. Den aktuella undersökningen innebar hydrotermalbehandling i 30 dagar vid 90 till 110°C av MX-80 lera med 7.5 % vattenkvot och en torrdensitet av 1900 kg/m^3. Fritt vatten fanns tillgängligt i behållare på lerkropparnas fria överyta i cellerna i sådan mängd att full hydratisering av mineralytorna skulle kunna ske. Leran expanderade och aggregering uppkom, särskilt i den övre delen. Efter öppning av cellerna togs små provbitar för mikroskopi och återstoden användes för ödometertestning för att bestämma svällningstryck och hydraulisk konduktivitet. Mikroskopin visade att relativt stora porer kvarstod efter vattenmättnaden som följd av att kiselcementering gav reducerad gelbildningsförmåga. Hydratiseringstakten och svällningstrycket blev emellertid av samma storleksordning som för obehandlad lera, vilket tolkas som att en stor del av cementeringen lätt bröts ned. Den hydrauliska konduktiviteten ökade ca 10 % för det undersökta temperaturområdet på grund av viss kvarstående cementering. Slutsatsen är att MX-80 lera inte får sina isoleringsegenskaper försämrade i praktiskt betydelsefull omfattning av ångpåverkan under de undersökta hydrotermala förhållandena.

1 Scope of study

In 1985 a laboratory study on the influence of hot water vapor on the expandability of smectite clay was reported by Rex Couture /1/. He showed that reaction of Na bentonite with water vapor at 150 to 250°C results in rapid irreversible loss of most of the expandability, while it is known that reaction of bentonite saturated with water at temperatures ranging between 100 and 150°C produces limited loss in swelling capacity. Couture concluded that the loss of expandability is related to the influence of pressurized water vapor but gave no explanation of the mechanism.

The conditions in the deposition holes of a KBS-3 repository imply that steam will be produced in the buffer clay near the hot canisters. When the joints between the large buffer blocks become tight by absorption of water supplied by the surrounding rock, a closed system of interconnected voids is formed around the canisters (Figure 1-1). This space is filled with air and water vapor and the relative humidity will be 100% at a late stage of wetting when water has moved in from the rock and the wetting front is close to the hot canister surface. Hence, depending on whether vapor can escape from the buffer clay and what the temperature will be in the vapor-filled space, the buffer will be exposed to steam pressurized to 70 to 143 kPa for the temperature interval 90 to 110°C. This state is similar to the hydrothermal conditions that prevail in the final phase of orogenetic processes, in which precipitation of clay minerals and zeolites is known to take place. It is hence possible that the effect that Couture noticed may be due to precipitation of cementing minerals. The present study is intended to investigate this possibility.

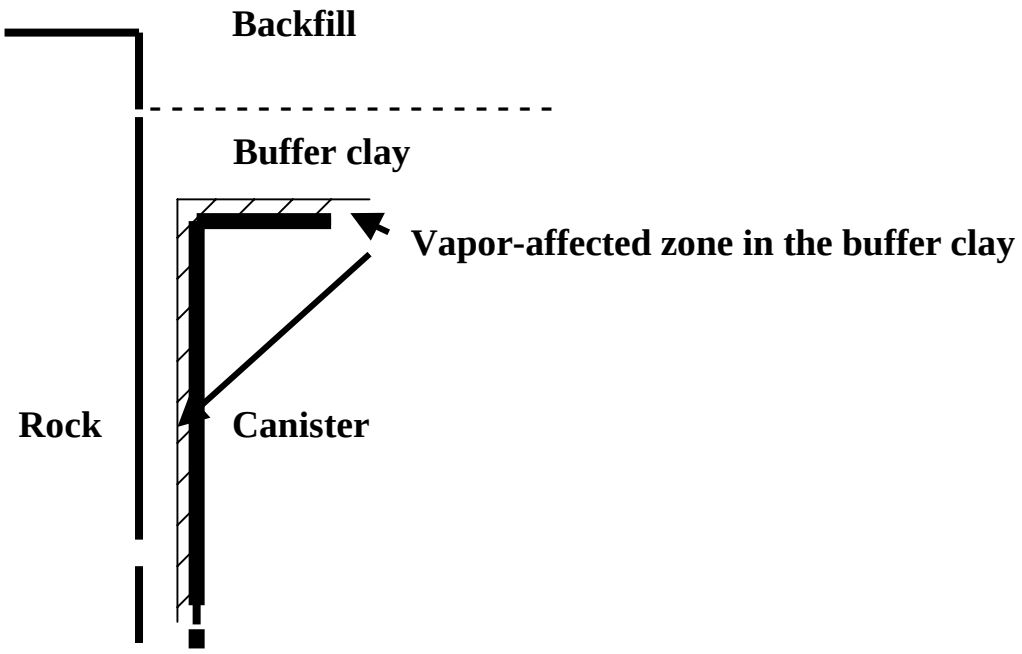


Figure 1-1. *Vapor-filled zone in the buffer clay close to canisters.*

2 Test plan

2.1 Purpose of test

The present study was planned to be a short-term pilot investigation of the effect of pressurized water vapor on MX-80 buffer clay with a first aim to find out whether changes in expandability and hydraulic conductivity will take place at all under experimental conditions that are representative of those in a KBS-3 deposition hole. A second aim was to identify the physico/chemical processes that lead to such changes if they take place.

2.2 Preparation of samples

Isostatically compacted MX-80 samples with a water content of 7.5% and a dry density of 1900 kg/m^3 had been stored for about 2 years under ordinary room atmosphere conditions. The fracture-free samples were trimmed to cylindrical form for fitting into the vapor pressure cells. After vapor treatment small specimens were taken for subsequent microstructural analysis and the remainder extruded from the cells and transferred to oedometers for saturation with distilled water and concurrent measurement of swelling pressure and hydraulic conductivity.

The material used for preparing the compacted samples two years before the present study had the form of granulated powder with 90 weight percent passing the 0.5 mm sieve, 50% passing the 0.2 mm sieve, and 10% passing the 0.1 mm sieve. The compacted samples contained voids with normal size distribution and a maximum diameter of about 20 μm /2/.

2.3 Investigation of samples after oedometer testing

After complete saturation with distilled water and testing of the hydraulic conductivity and swelling pressure for a sufficiently long time to make sure that sufficient homogenisation had been reached, specimens were cut out for subsequent microstructural investigation with the aim of finding possible changes produced by the exposure to pressurized water vapor.

3 Experimental

3.1 Vapor treatment

3.1.1 General

were simulated by exposing homogeneous, unsaturated MX-80 clay to steam under pressure in closed cells that were bigger than the clay samples and hence allowed the clay to hydrate and expand. The temperature was maintained at 90, 100 and 110°C in separate tests and the vapor pressure measured. The hydrothermal treatment lasted for 30 days.

3.1.2 Equipment

The stainless steel cells for vapor treatment had 30 mm diameter and 40 mm height. About 10 mm free space remained between the clay sample and the lid and here a metal cup with about 20 g of distilled water was placed for providing steam. This amount of water together with the water contained in the clay roughly corresponded to the theoretical capacity of the interlamellar and basal surface areas to absorb water. The clay samples were free to expand in the cells, a schematic section of which is shown in Figure 3-1.

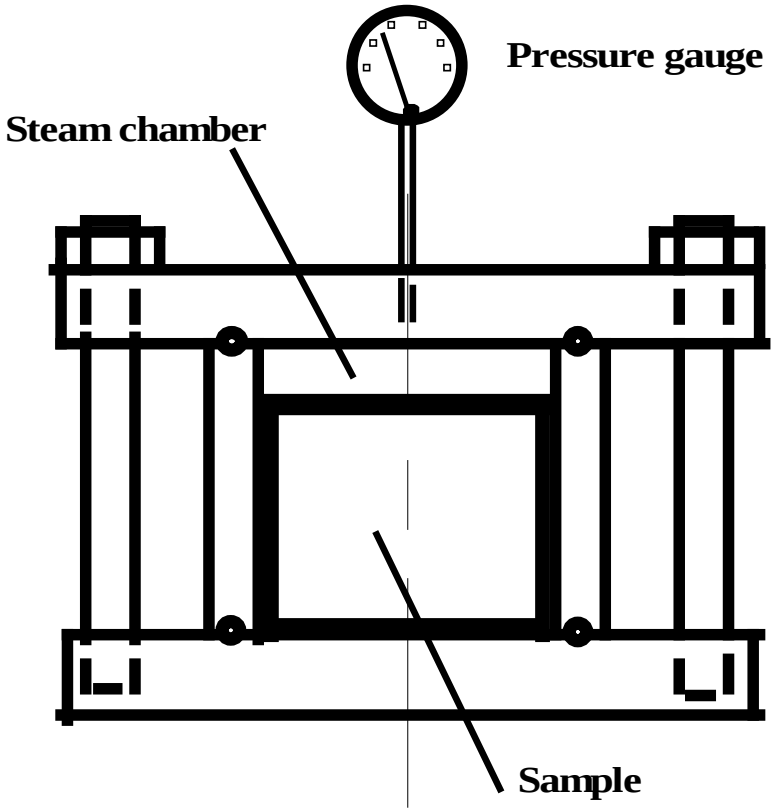


Figure 3-1. *Schematic picture of steam chamber with 30 mm diameter and 40 mm height.. The chamber contained a small metal cup with water that evaporated and created vapor at a pressure that was recorded.*

3.1.3 Test procedure

The cells were tightly closed after applying the clay samples and the water cups, and were then placed in an oven with the gas pressure gauge placed outside for taking readings.

3.2 Determination of hydraulic conductivity and swelling pressure

3.2.1 Equipment

The vapor-treated samples were pushed into 30 mm diameter oedometers with stainless steel filters (10 μm pore size). The axial space between the filter of the piston and that of the base plate varied between 27 and 29 mm in the tests, which hence became the ultimate height of the clay samples, which could expand in the hydration phase. The in- and outlets of the oedometers were connected to burettes for measuring the water flux in the saturation and percolation stages with an accuracy of better than 5E-13 m/s.

The swelling pressure was recorded by use of Entran MM35 pressure cells.

3.2.2 Test procedure

The 90 and 100°C samples were placed in the oedometers such that saturation and percolation took place from below, i.e. from the homogeneous, dense ends, while water was supplied from the rough, aggregated end in the test with the sample that had been treated with 110°C vapor. In the latter case water saturation was achieved more rapidly because of the very high porosity of the aggregated part as described in Chapter 5.2. Very small specimens were extracted for microstructural analysis from the rough upper ends before closing the oedometers.

3.3 Microstructural analyses

3.3.1 Specimens from vapor-treated material

On opening the cells it was noted that the vapor-treated clay samples had expanded into their open parts, creating a rough upper surface of the samples from which small specimens were taken for investigation by scanning electron microscopy using also EDX element analysis. This study, which aimed at finding out whether precipitates had been formed, was made by Dr Jörn Kasbohm, Greifswald University, Germany.

3.3.2 Specimens from water saturated material

General appearance of the samples

The saturated clay samples gave a very homogeneous impression when the cells were opened; they had expanded to fully occupy the oedometers and had the typical greenish appearance and ductile consistency of ordinary water saturated MX-80 bentonite. Since identification of possible small-scale heterogeneities requires microstructural analysis, specimens were extracted after determination of the hydraulic conductivity and swelling pressure for transmission electron microscopy. The preparation of the material was made by replacement of the water by ethylene alcohol, which was in turn replaced by a monomer consisting of 85% butyl methacrylate and 15% methacrylate to which 2% 2.4-dichlorbenzoylperoxide (EWM) had been added /3/. After polymerization 300 Å and 10000 Å (1 μm) sections were cut by ultramicrotomy for examination in a transmission electron microscope. The cutting and microscopy were made by Dr Jörn Kasbohm, Greifswald University. The applied way of preparing clay samples is known to largely preserve the general microstructural pattern /2,3/.

4 Predictions

4.1 Rate of hydration of MX-80 clay

Water saturation of heterogeneous clay samples is a complex process involving hydration and microstructural reorganization in the form of local expansion and consolidation in conjunction with breakage, deformation, displacement and rotation of stacks and aggregates of stacks. Experience has shown that water saturation of a confined, unsaturated but homogeneous MX-80 sample can be described as a diffusion process with an approximate diffusion coefficient of D=3 E-10 m^2/s /4/. Using this value and applying the diffusion code ANADIFF /5/ one obtains the water content distributions in Figure 4-1.

Theoretically, a confined cylindrical MX-80 sample wetted from one end will be fully water saturated to about 15 mm distance from this end after 30 days while it is expected to be saturated to somewhat more than 20 mm distance in 90 days. At 25 mm distance from the wetted end the degree of saturation will be about 95% in 90 days. This state gives practically the same swelling pressure and hydraulic conductivity as 100% saturation.

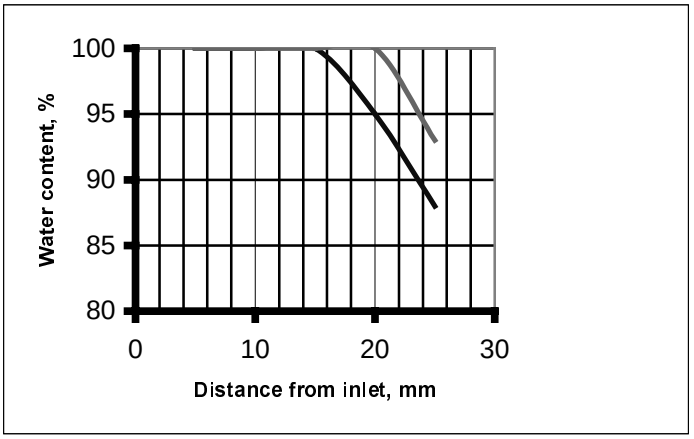


Figure 4-1. *Theoretical distribution of the water content. The left curve represents the conditions after 30 days and the right one the distribution after 90 days.*

4.2 Hydraulic conductivity of MX-80 clay

Figure 4-2 shows a generalized picture of the hydraulic conductivity of natural, untreated MX-80 bentonite saturated and percolated with distilled water /6/. The graph represents recordings taken within a few days or a week after complete saturation of the clay.

4.3 Swelling pressure of MX-80 clay

Figure 4-3 shows a generalized picture of the swelling pressure of ordinary, untreated MX-80 bentonite saturated with distilled water /6/. The graph represents recordings taken within a few days or a week after complete saturation of the clay.

4.4 Microstructure of MX-80 clay

4.4.1 Qualitative

Comprehensive microstructural investigations of MX-80 clay confined in oedometers and saturated under room temperature conditions have given the basis for microstructural modelling /2,7/. They have shown that the microstructure of clay with a density that is representative of the presently investigated material, i.e. around 1800 kg/m^3, is characterized by local, gel-filled voids with 1 to 20 μm diameter distributed in a very uniform, practically impermeable particle matrix (cf. Figure 4-4). These voids are interconnected and determine the bulk hydraulic conductivity and anion diffusivity.

4.4.2 Quantitative

According to the GMM model /2,6/ a cross section of untreated MX-80 clay with a density of 1850 kg/m^3 contains gel-filled voids according to Table 4-1, meaning that TEM micrographs of specimens thinner than about 1 μm and representing cross section areas of less than 1000 μm^2 are expected to show no voids with larger size than about 5 μm.

Table 4-1. Approximate frequencies of gel-filled voids of different size in differently sized cross sections through water saturated untreated MX-80 clay with different densities. A/B/C represent A=1–5 μm voids, B=5–20 μm voids and C=20–50 μm.

Clay density kg/m^3	Cross section area 62500 μm^2	Cross section area 1000 μm^2	Cross section area 500 μm^2	Cross section area 50 μm^2	Cross section area 15 μm^2
2130	168/0/0	3/0/0	1/0/0	0/0/0	0/0/0
1850	547/10/0	9/0/0	4/0/0	1/0/0	0/0/0
1570	3400/100/2	55/2/0	27/1/0	3/0/0	1/0/0

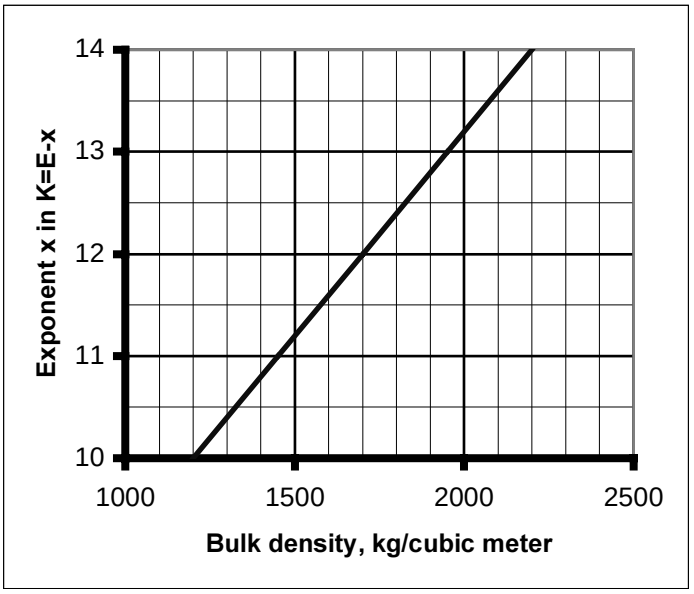


Figure 4-2. *Hydraulic conductivity K of water saturated MX-80 bentonite as a function of the bulk density for saturation and percolation with distilled water.*

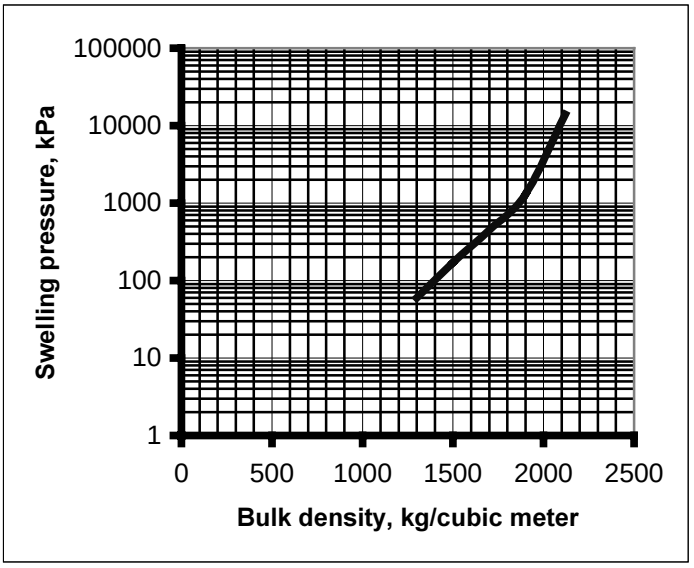


Figure 4-3. *Swelling pressure of MX-80 bentonite as a function of the bulk density for saturation with distilled water.*

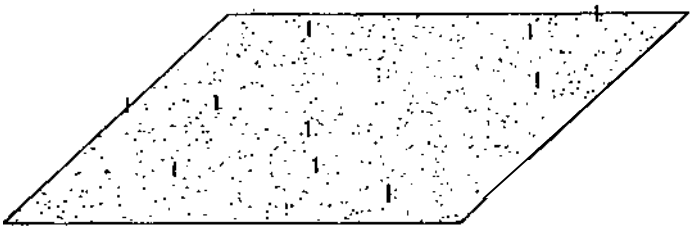


Figure 4-4. *Generalized picture of the frequency of gel-filled voids of different size in saturated MX-80 clay with a bulk density of 1850 kg/m^3 /7/. Dots represent 1–5 μm gel-filled voids and short bars 5–20 μm voids in a cross section with the dimensions 250x250 μm^2. The rest is practically impermeable.*

5 Test results

5.1 Observations during vapor treatment

5.1.1 Vapor pressure conditions

Theoretically, the total amount of water initially adsorbed by the clay and present in liquid form in the cells would have been sufficient for complete hydration of the clay mineral surfaces implying formation of maximum 3 water molecule layers in the expanded interlamellar space and on external surfaces of stacks of lamellae. However, heating was expected to cause vaporization of part of the water and hence cause somewhat less hydration.

The vapor pressure in the hydrothermal cells was recorded in the course of the vapor treatment. Theoretically, the vapor pressure would be 70 kPa at 90°C, 101 kPa at 100°C and 143 kPa at 110°C and pressures of this order of magnitude were also measured initially in the respective tests. However, the pressure dropped from the maximum values by about 75% in the 90°C test and by slightly less than 30% in the 100°C and 110°C tests (cf. Table 5-1). In all the tests there was a slight tendency of increased vapor pressure after about 3 weeks.

Table 5-1. Vapor pressure in kPa recorded in the experiments.

Time, hours	90°C	100°C	110°C
2	50	30	30
24	70	105	140
72	25	80	90
96	25	80	80
120	17	80	75
240	17	75	70
360	17	77	75
480	18	77	77
600	18	77	77
720	18	77	77

The initial increase in vapor pressure was due to the successive evaporation of the water in the cups, while the drop in pressure after reaching the maximum value was caused by absorption of water molecules from the vapor. The adsorption was significantly stronger at 90°C than at the higher temperatures, indicating that temperature controls hydration and dehydration of smectite clay.

The desorption after about 10 days was insignificant but statistically certified. It may have been due to a slight reduction in effective surface area caused by precipitation of silica and aluminum.

5.1.2 Macrostructural features

At the opening of the test cells it was noticed that the upper surface of all the samples had risen significantly and was crumbly and fractured (Figure 5-1). The clay was brittle and apparently dry down to about 5 millimeters depth while it was more homogeneous deeper down. Here, the clay had expanded and formed tight contact with the cell walls, which shows that hydration and expansion had taken place. The uppermost parts of the samples were somewhat smoothened and flattened before the piston was brought in contact with them at the preparation for the subsequent oedometer testing. The height of the samples was somewhat different causing a variation in theoretical net density after hydration, i.e. 1750 kg/m^3 for the 110°C sample, 1800 kg/m^3 for the 90°C, and 1850 kg/m^3 for the 100°C sample.

The vapor-exposed ends had a very uneven and fractured shape with 5–8 mm large aggregates separated by several millimeter-wide voids. The contact with the filters in the piston and base plate was hence very uneven, which was expected to delay or prevent homogenization of the clay had significant cementation taken place.

Figure 5-1. *Typical appearance of the vapor-treated samples with crumbled upper part.*

5.2 Hydraulic properties

5.2.1 Hydration

The conditions for water saturation yielding the rates in Figure 4-1 and implying almost complete hydration and homogenization of the samples located in the oedometers for 90 days, were not completely satisfied for the 90 and 100°C samples although the oedometer inlets were pressurized by 10 kPa for speeding up the saturation process. The reason is that these samples were oriented in the oedometers as in the hydrothermal cells, meaning that hydration and percolation took place from below, i.e. from the more homogeneous, dense ends. This implied that the dense part would have to be almost fully water saturated before hydration, expansion and reorganization of the very heterogeneous and porous upper parts could start. Transport of water through the saturated part would mainly be by flow, which would take place at a very low rate due to the low hydraulic gradient and conductivity. This was verified by the experiments (cf. Table 5-2).

For speeding up the saturation of the clay sample that had been treated with 110°C vapor this sample was oriented such in the oedometer that water was supplied from the rough, aggregated end. Water saturation was thereby achieved more rapidly as demonstrated by the fact that the swelling pressure was fully developed in about 8 weeks.

5.2.2 Hydraulic conductivity

The hydraulic conductivity was currently evaluated in the percolation phase, yielding the data in Table 5-2.

Table 5-2. Evaluated hydraulic conductivity at the end of the respective tests.

Vapor Temp. °C	Density kg/m³	Hydraulic conductivity, m/s
90	1800	6.1E-11
100	1850	2.2E-11
110	1750	1.7E-11

Comparison with the plottings in Figure 4-2 shows that the vapor-treated samples had a hydraulic conductivity that was 50 to 100 times higher than that of unheated clay with corresponding densities. For the samples with 1800 and 1850 kg/m^3 density the deviation is partly caused by overrating the inflow rate due to the concurrent uptake of water in the hydration process. Considering this contribution the conductivity is still more than 10 times higher than that of untreated MX-80 clay. For the almost fully saturated sample with a density of 1750 kg/m^3, i.e. the one that had been exposed to water vapor with 110°C temperature and for which hydration had been largely completed when the conductivity was evaluated, the value 1.7E-11 m/s is about 10 times higher than for untreated MX-80 clay.

A tentative explanation of the higher hydraulic conductivity of vapor-treated clay may be that the microstructure is less homogeneous than that of untreated MX-80 clay because of a reduced gel-production potential due to cementation processes.

5.3 Swelling pressure

The swelling pressure was recorded continuously in the hydration and percolation phases, yielding the data in Table 5-3.

Table 5-3. Recorded swelling pressure p_s in kPa at different stages of the tests. Time in weeks (w).

Vapor Temp. °C	Density kg/m³	p_s 1 w	p_s 2 w	P_s 3 w	P_s 4 w	P_s 5 w	P_s 6 w	P_s 7 w	P_s 8 w	P_s 9 w	P_s 10 w	P_s 11 w
90	1800	200	200	215	230	245	255	–	–	–	–	–
100	1850	200	360	320	310	400	495	525	570	605	650	680
110	1750	490	530	545	570	600	620	675	700	–	–	–

The table illustrates the aforementioned slow maturation rate. Thus, for the clay exposed to 90°C and having a density of 1800 kg/m³, the recorded swelling pressure after 6 weeks was 255 kPa but steadily increasing to a maximum value that is estimated to have been developed after more than 12 weeks. For the clay exposed to 100°C and having the density 1850 kg/m³ the recorded pressure was 680 kPa as compared to 1000 kPa for untreated clay. However, the pressure was still rising after 11 weeks and is estimated to have reached a maximum value beyond 12 weeks. For the clay that had been exposed to 110°C and having a density of 1750 kg/m³ the recorded pressure rose much quicker than in the other tests due to the altered percolation direction and became 700 kPa after 2 months as compared to about 700 kPa for untreated clay.

It is concluded from the recording of the swelling pressure of the clay sample that had been exposed to the most severe vapor treatment, i.e. by being heated to 110 °C steam, that the swelling pressure of MX-80 clay is not affected by vapor treatment under the applied experimental conditions.

5.4 Microstructural changes caused by exposure of MX-80 clay to hot vapor

5.4.1 Samples of clay exposed to hot vapor in hydrothermal cells

Figures 5-2 and 5-3 show the typical appearance of crumbles from the vapor-treated clay samples at 90°C as vizualised by scanning electron microscopy (SEM). The element analyses of the contacts between aggregates indicate excess silica, which points to cementation by precipitated Si that was set free from the smectite and accessory minerals at the hydrothermal treatment. The micrographs also showed a number of dense laminated aggregates that are believed to have resulted from contraction of similarly oriented stacks of montmorillonite lamellae.

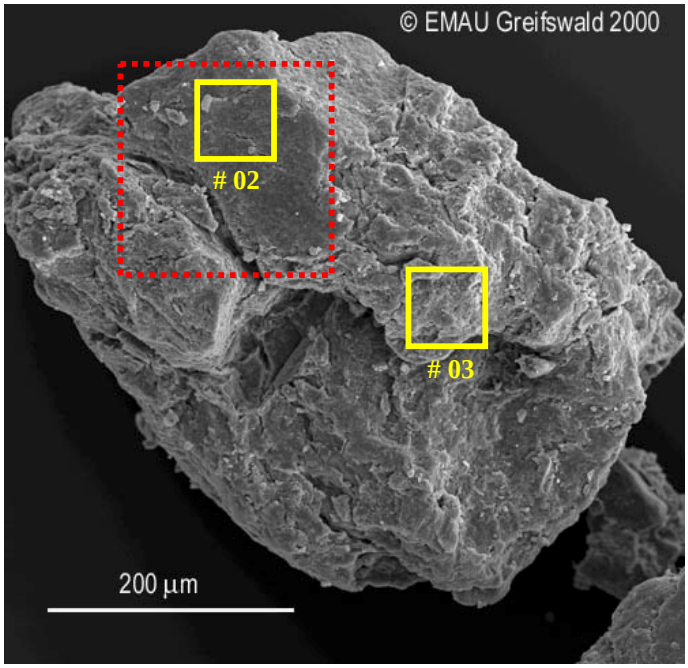
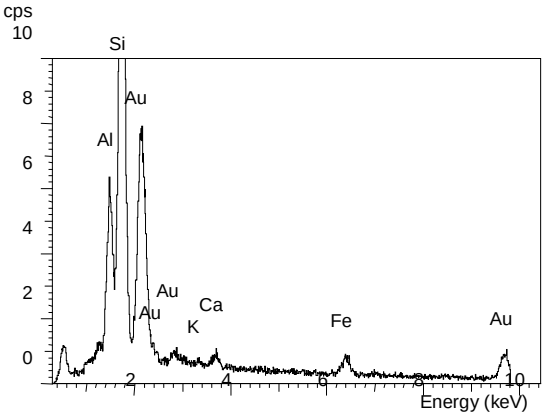


Image-File: Pusch 90° 01 200
Magnification: 200x
EDX-File: P9001.clp

90° specimen: aggregate of laminated, densely grouped montmorillonite lamellae.

yellow boxes: zoom areas for images #02 & #03
red box: EDX-area of P9001.clp



EDX-File: P9001.clp
Magnification: 9.000x

90° specimen: EDX of grain or compacted area of file, Pusch 90° 01 200'

Figure 5-2. *Crumble aggregate in MX-80 clay exposed to 90°C vapor. The element analyses show an approximately normal Si/Al ratio for montmorillonite.*

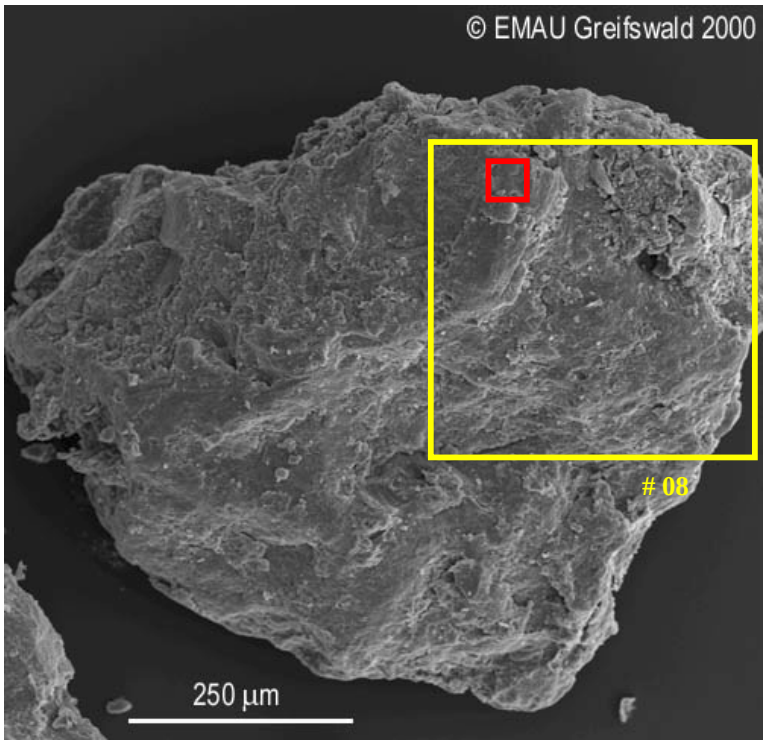
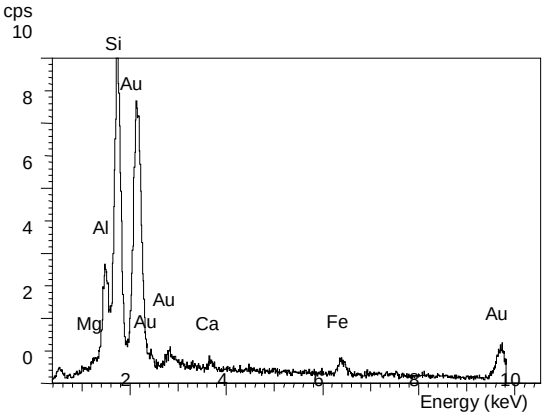


Image-File: Pusch 90° 06 130
Magnification: 130x
EDX-File: P9006.clp

90° specimen: other aggregate (Si-dominated)

yellow box: zoom area for image ***# 08***
red box: EDX-area of P9006.clp



EDX-File: P9006.clp
Magnification: 6.000x

90° specimen: EDX of clay aggregate Pusch 90° 06 130'

[Au caused by the SEM-coating of the specimen]

Figure 5-3. *Micrograph of aggregate in MX-80 clay exposed to 90°C vapor. The element analyses of the edge, representing contact with an adjacent aggregate, shows excess Si that may be due to silica precipitation.*

The clay exposed to 110°C vapor had similar excess Si concentration at aggregate edges as the 90°C sample but also showed larger laminated aggregates as examplified by Figure 5-4, indicating stronger, permanent contraction of several, similarly oriented stacks of montmorillonite lamellae. The element analyses of the contacts between aggregates indicate excess Si, which points to cementation by precipitated silica that was set free from the smectite and accessory minerals at the hydrothermal treatment.

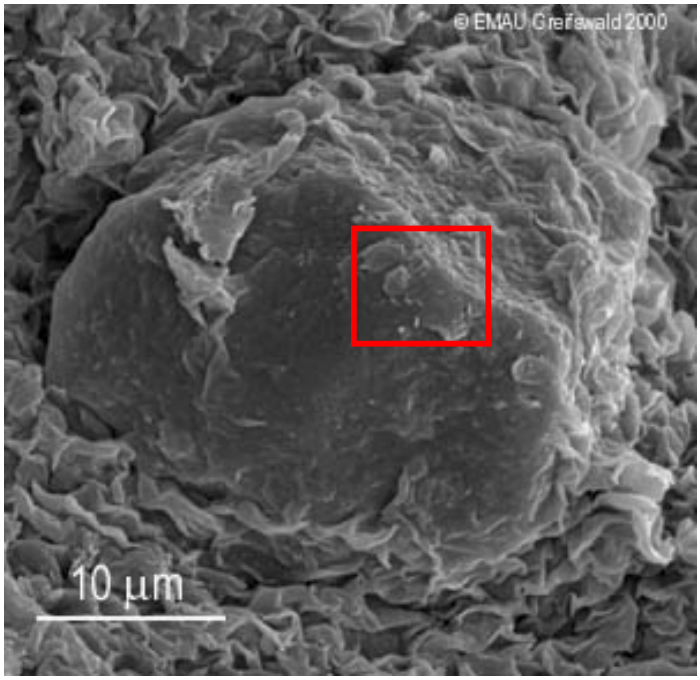
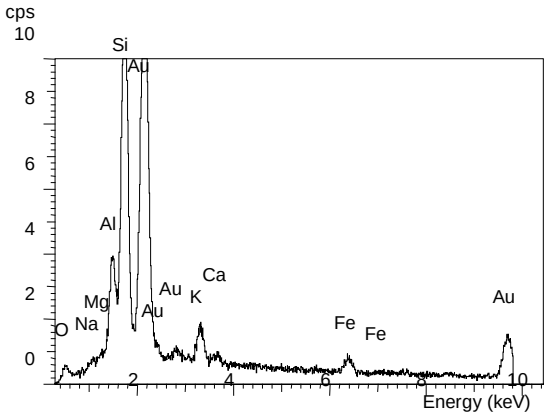


Image-File: Pusch 110° 05 3K
Magnification: 3.000x
EDX-File: P11005.clp

110° specimen: Aggregate in a Si-dominated matrix

red box: EDX-area of P11005.clp



EDX-File: P11005.clp
Magnification: 12.000x

110° specimen: EDX of clay aggregate, Pusch 110° 05 3K

Figure 5-4. *Micrograph of aggregate in MX-80 clay exposed to 110°C vapor. The aggregate, which is surrounded by a typical wavy matrix of clay particles, is made up of equally oriented densely arranged groups of montmorillonite lamellae. The element analyses of the edge of the aggregate shows some excess Si that may represent silica precipitates.*

5.4.2 Samples extracted from oedometers after testing of saturated clay

The study, which was confined to the clay exposed to 110°C and performed by transmission electron microscopy (TEM) of acrylate-treated specimens, showed the typical wavy pattern of montmorillonite stacks as untreated MX-80 clay with 1800 kg/m^3 bulk density. The only discernable difference was that the vapor-treated clay had denser aggregates and larger voids, indicating that some irreversible contraction of the stacks of montmorillonite lamellae had taken place.

Ultramicrotome sections with a thickness of 1.0, 0.3 μm (300 nm) and 0.1 μm (100 nm) were examined. These rather large specimen thicknesses were used for estimating the size of voids in three dimensions /8/. Typical micrographs of the 1 μm sections are shown in Figures 5-5 to 5-9.

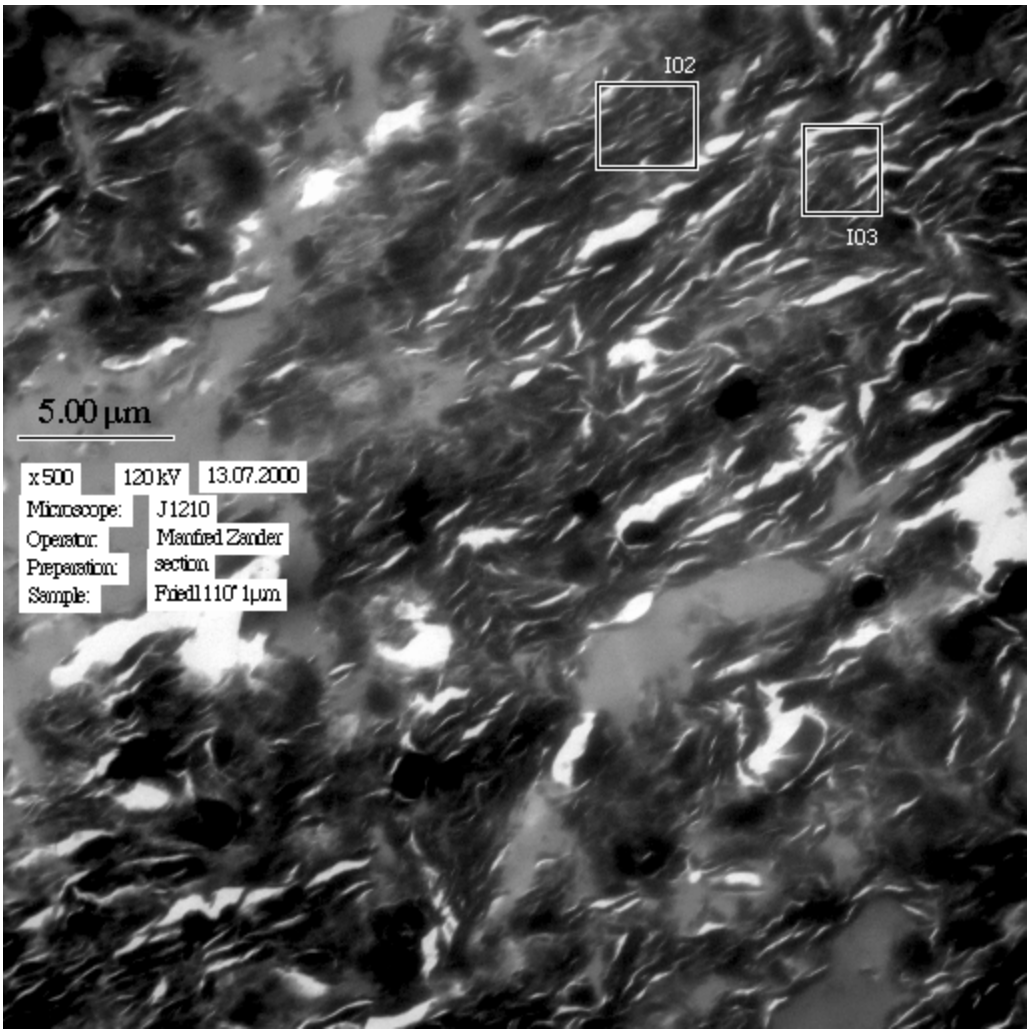


Figure 5-5. *TEM micrograph with 500 x magnification of 1 μm thick section of MX-80 clay exposed to 110°C vapor and then hydrated and homogenized in an oedometer to a density of 1750 kg/m³. Open and gel-filled voids are seen, two with a long diameter of 5–20 μm and thirty with a long diameter of 1–5 μm. The total cross section area is about 1000 μm².*

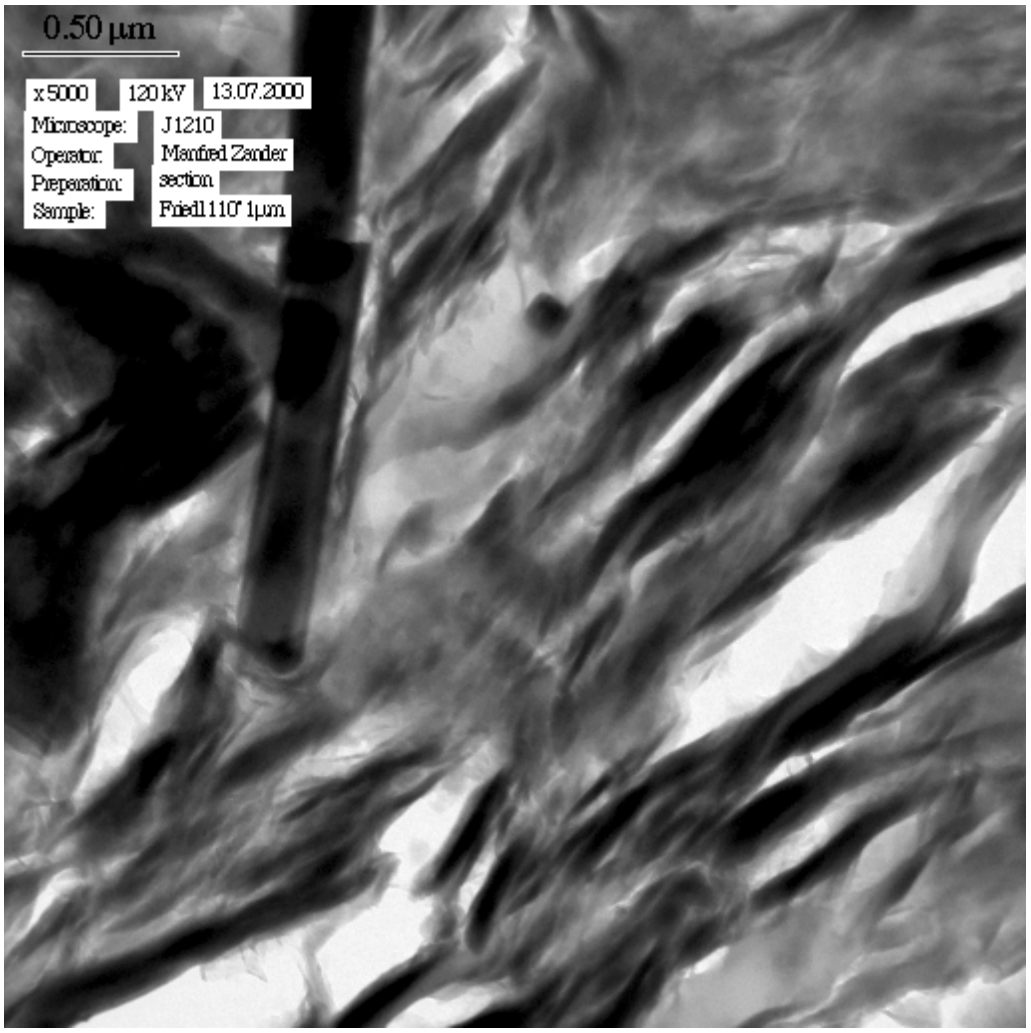


Figure 5-6. *TEM micrograph with 5000 x magnification of 1 µm thick section of MX-80 clay exposed to 110°C vapor and then hydrated and homogenized in an oedometer to a density of 1750 kg/m³. Two open or gel-filled voids are seen that belong to the size interval 1–5 µm. The total cross section area is about 15 µm². The compact nature of the stacks of lamellae is obvious.*

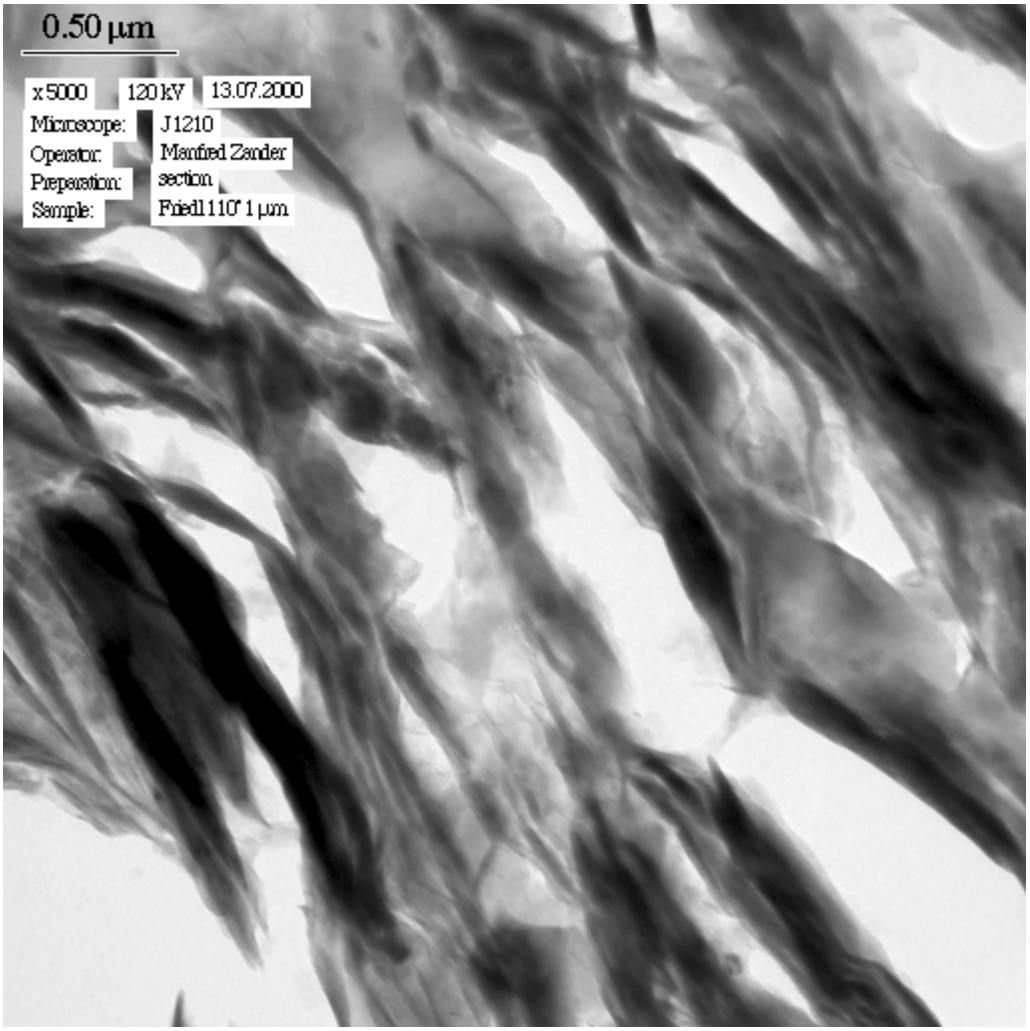


Figure 5-7. *TEM micrograph with 5000 x magnification of 1 µm thick section of MX-80 clay exposed to 110°C vapor and then hydrated and homogenized in an oedometer to a density of 1750 kg/m³. Four open or gel-filled voids are seen that belong to the size interval 1–5 µm. The total cross section area is about 15 µm². The compact nature of the stacks of lamellae is obvious.*

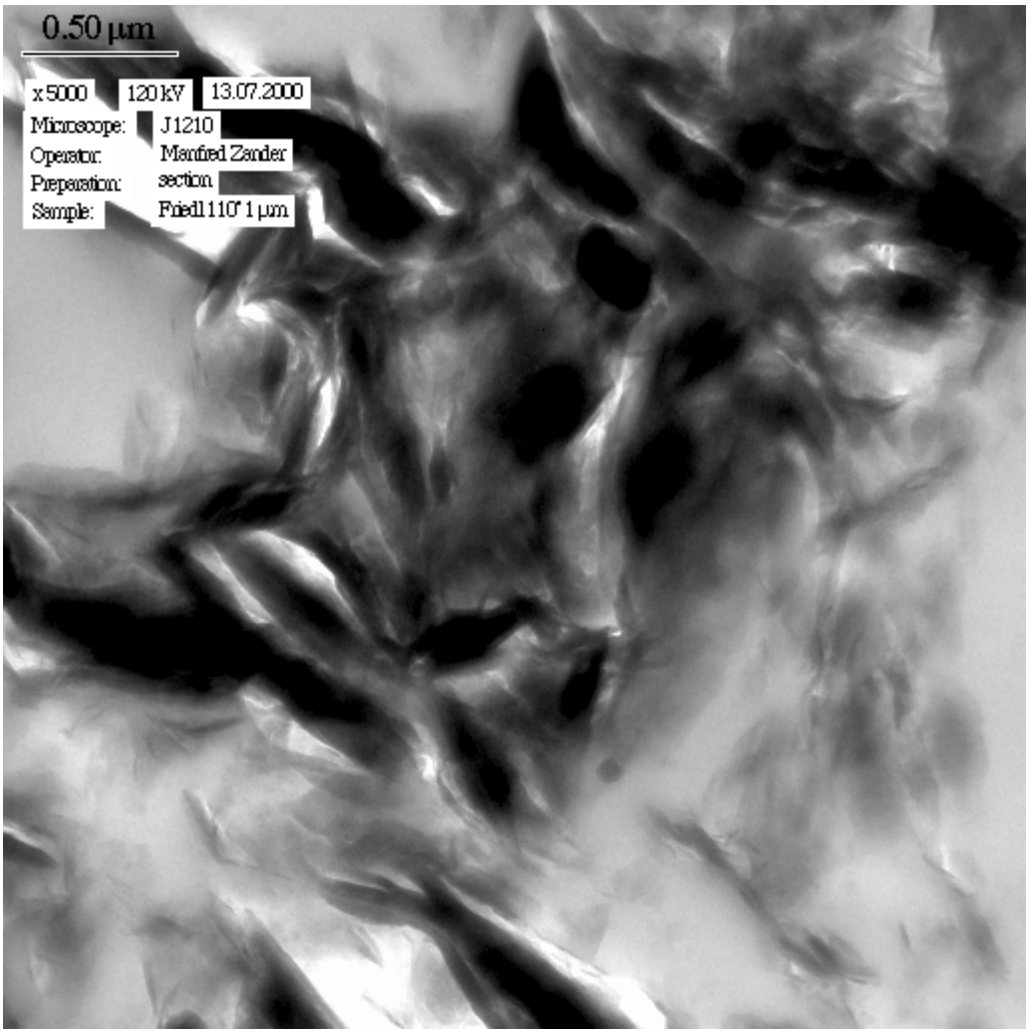


Figure 5-8. *TEM micrograph with 5000 x magnification of 1 µm thick section of MX-80 clay exposed to 110°C vapor and then hydrated and homogenized in an oedometer to a density of 1750 kg/m³. Three open or gel-filled voids are seen that belong to the size interval 1–5 µm. The total cross section area is about 15 µm². The compact nature of the stacks of lamellae is obvious.*

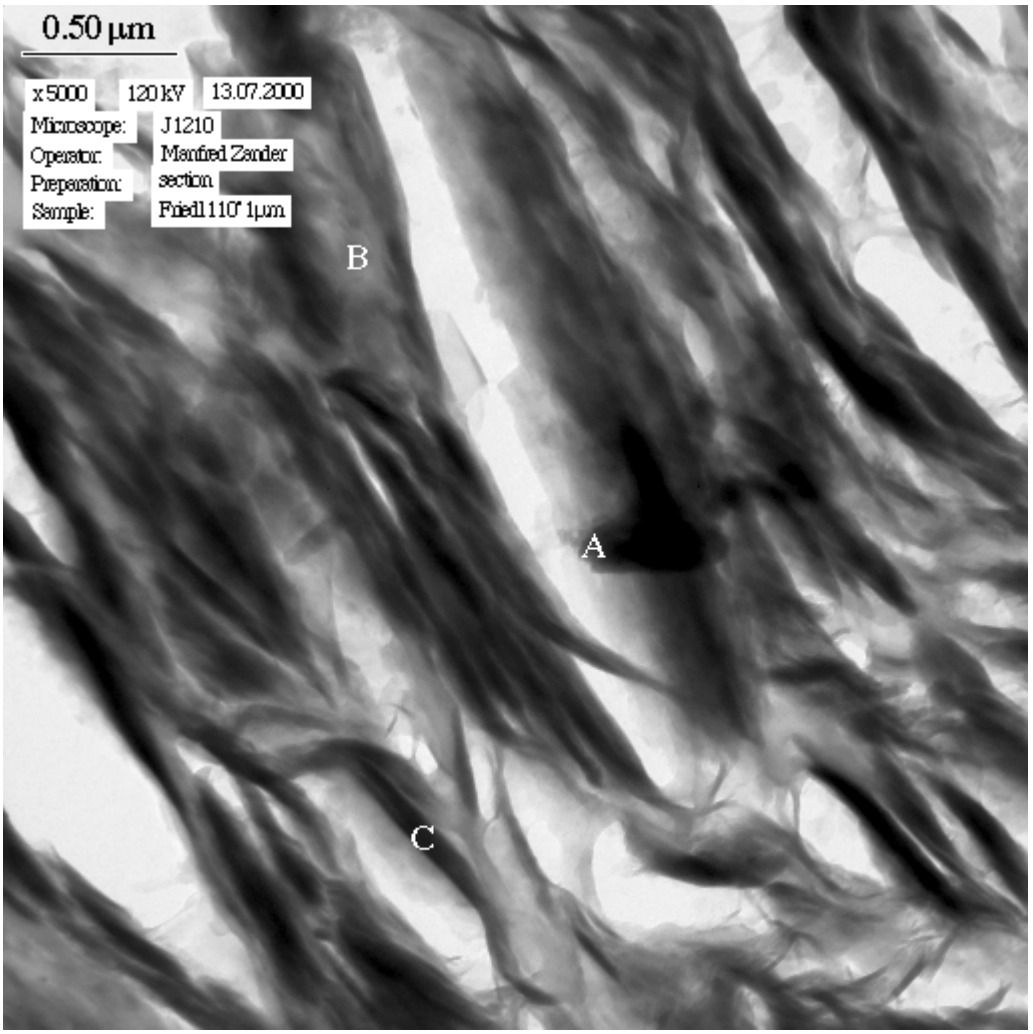


Image-File: PU01I03s.tif ***Magnification:*** 5.000x ***Thickness of section:*** 1 µm
(zoom of PU01I01s.tif)

Figure 5-9. *TEM micrograph with 5000 x magnification of 1 µm thick section of MX-80 clay exposed to 110°C vapor and then hydrated and homogenized in an oedometer to a density of 1750 kg/m³. Four open or gel-filled voids are seen that belong to the size interval 1–5 µm. The total cross section area is about 15 µm². The compact nature of the stacks of lamellae (A and C) is obvious.*

One concludes from the examination of the 1 µm thick sections that a couple of open or gel-filled voids with a long diameter of 5–20 µm and about 35 voids with a long diameter of 1–5 µm appear in a cross section area of about 1000 µm². 15 µm² cross sections show 2 to 4 voids of the latter type. Untreated MX-clay with a density of 1750 kg/m³ does not contain voids in the size interval 5–20 µm at all and the number of voids belonging to the size interval 1–5 µm is appreciably smaller (cf. Table 4-1). Thus, the number of 1–5 µm voids in untreated MX-80 clay with a density of about 1750 kg/m³ is expected to be less than 20 in a 1000 µm² cross section and – at maximum – 1 per 15 µm² cross section area. Hence, the vapor-treated clay contains larger voids between the aggregates, which appear to be denser than in untreated clay.

Typical micrographs of 0.1 µm sections are shown in Figures 5-10 to 5-13. Results from the examination of sections with 0.3 µm thickness are not reported here.

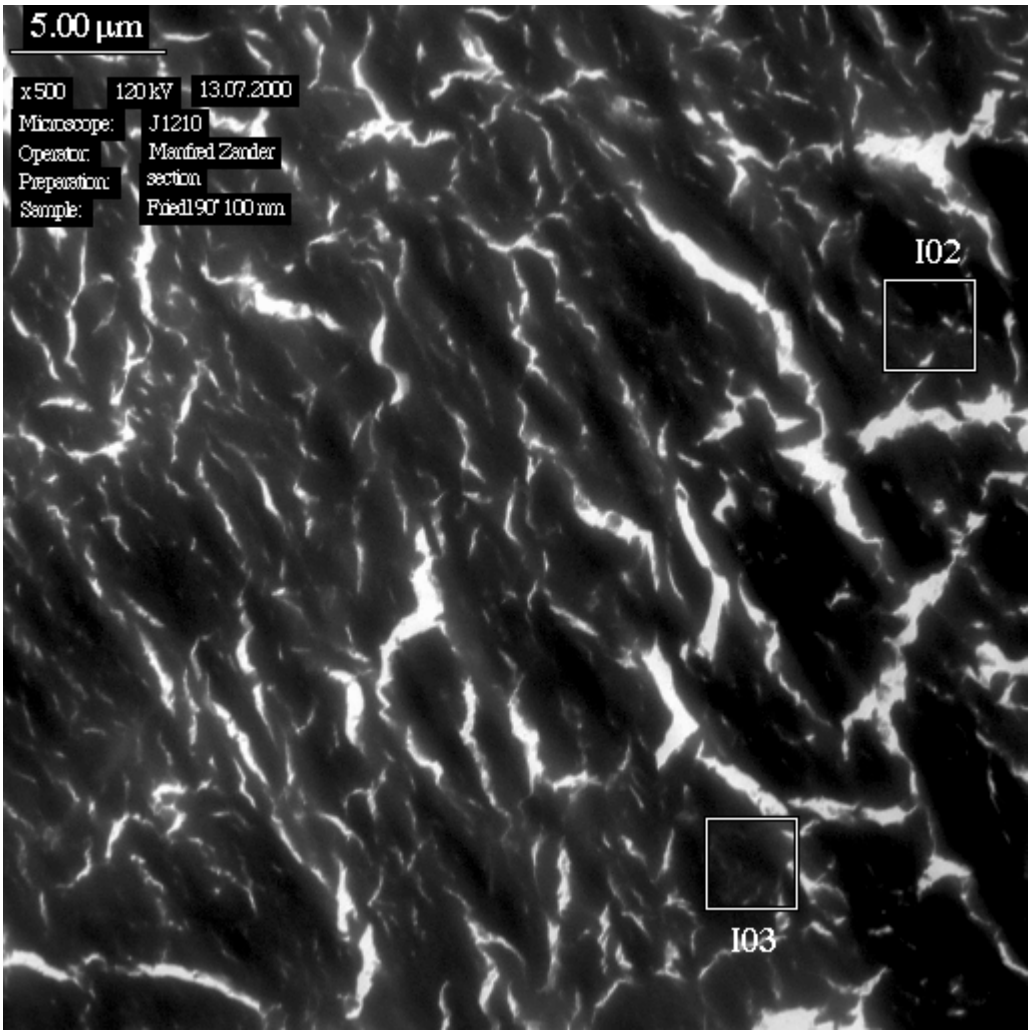


Figure 5-10. *TEM micrograph with 500 x magnification of 0.1 µm thick section of MX-80 clay exposed to 110°C vapor and then hydrated and homogenized in an oedometer to a density of 1750 kg/m³. Open and gel-filled voids are seen, three with a long diameter of 5–20 µm and about forty with a long diameter of 1–5 µm can be. The total cross section area is about 1000 µm².*

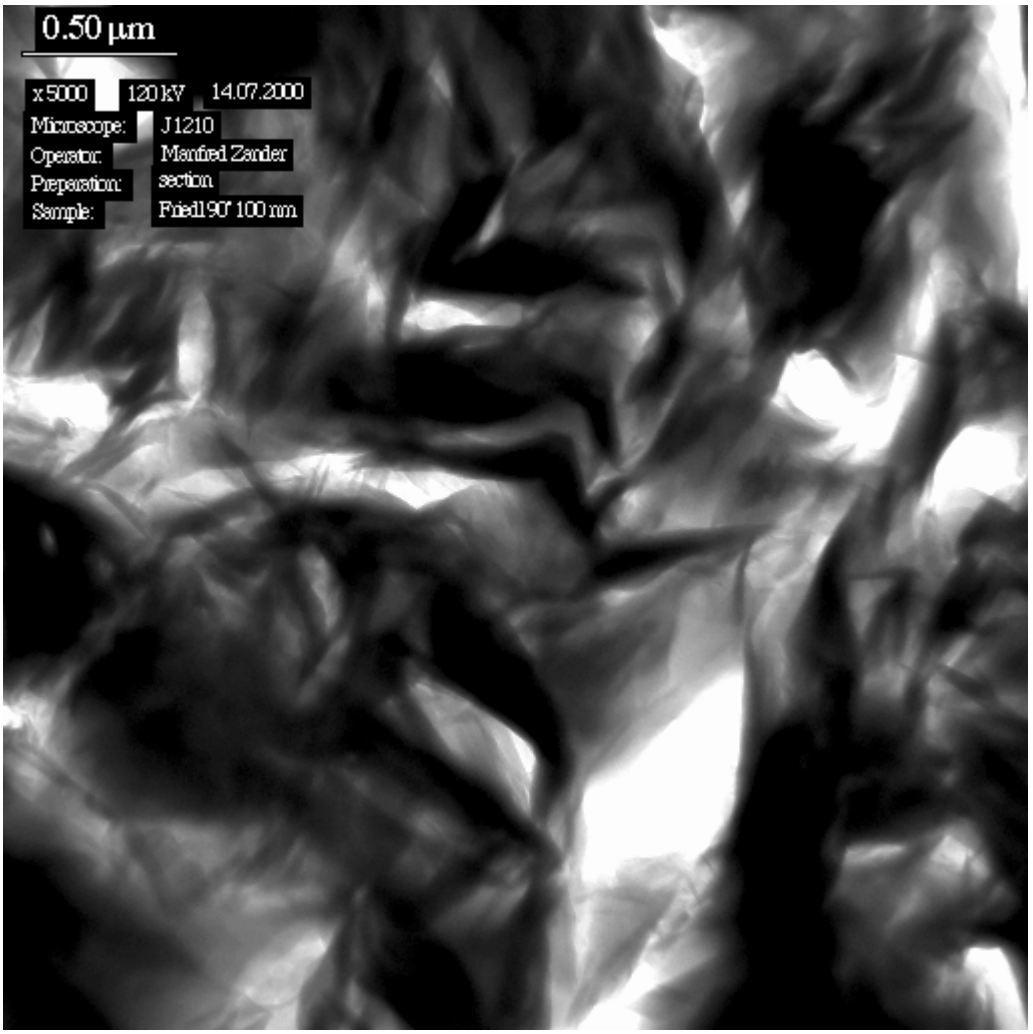


Figure 5-11. *TEM micrograph with 5000 x magnification of 0.1 µm thick section of MX-80 clay exposed to 110°C vapor and then hydrated and homogenized in an oedometer to a density of 1750 kg/m³. Six open or gel-filled voids are seen that belong to the size interval 1–5 µm. The total cross section area is about 15 µm². The compact nature of the stacks of lamellae is obvious.*

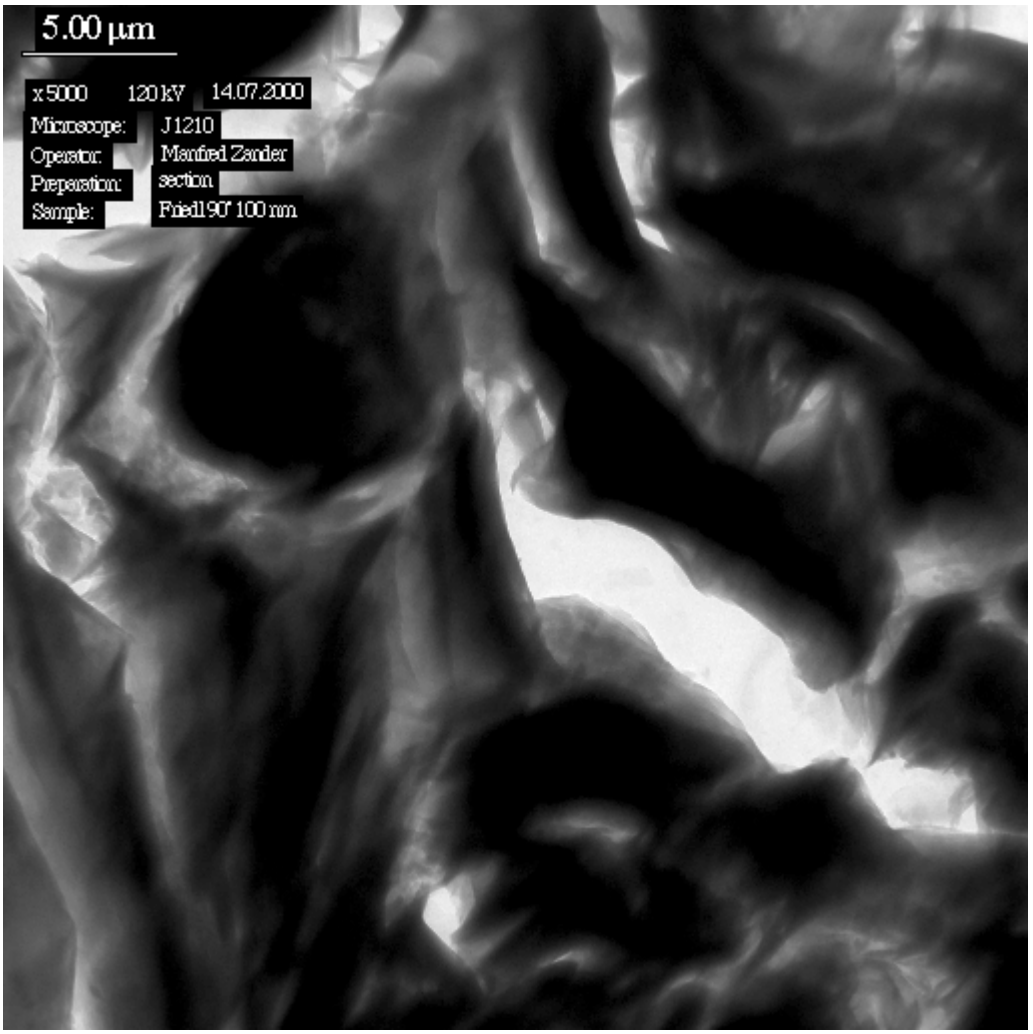


Figure 5-12. *TEM micrograph with 5000 x magnification of 0.1 µm thick section of MX-80 clay exposed to 110°C vapor and then hydrated and homogenized in an oedometer to a density of 1750 kg/m^3. Two open or gel-filled voids are seen that belong to the size interval 1–5 µm. The total cross section area is about 15 µm^2. The compact nature of the stacks oflamellae is obvious.*

The evaluation of the micrographs with 0.1 mm thickness gave the same conclusions as of those of 1 µm thickness, which indicates that many of the voids are disc-shaped with similar diameter in all directions. However, in accordance with theory the number of voids of all sizes is higher in the thinner sections /8/. Thus, certain cross sections covering areas on the order of 1000 µm^2 showed larger numbers of 5–20 µm voids as illustrated by Figure 5-12, in which one can identify half a dozen voids of this size. Since such a high frequency was not seen in the 1 µm thick sections some voids of this size may be very flat and enclosed in 1 µm thick clay matrix.

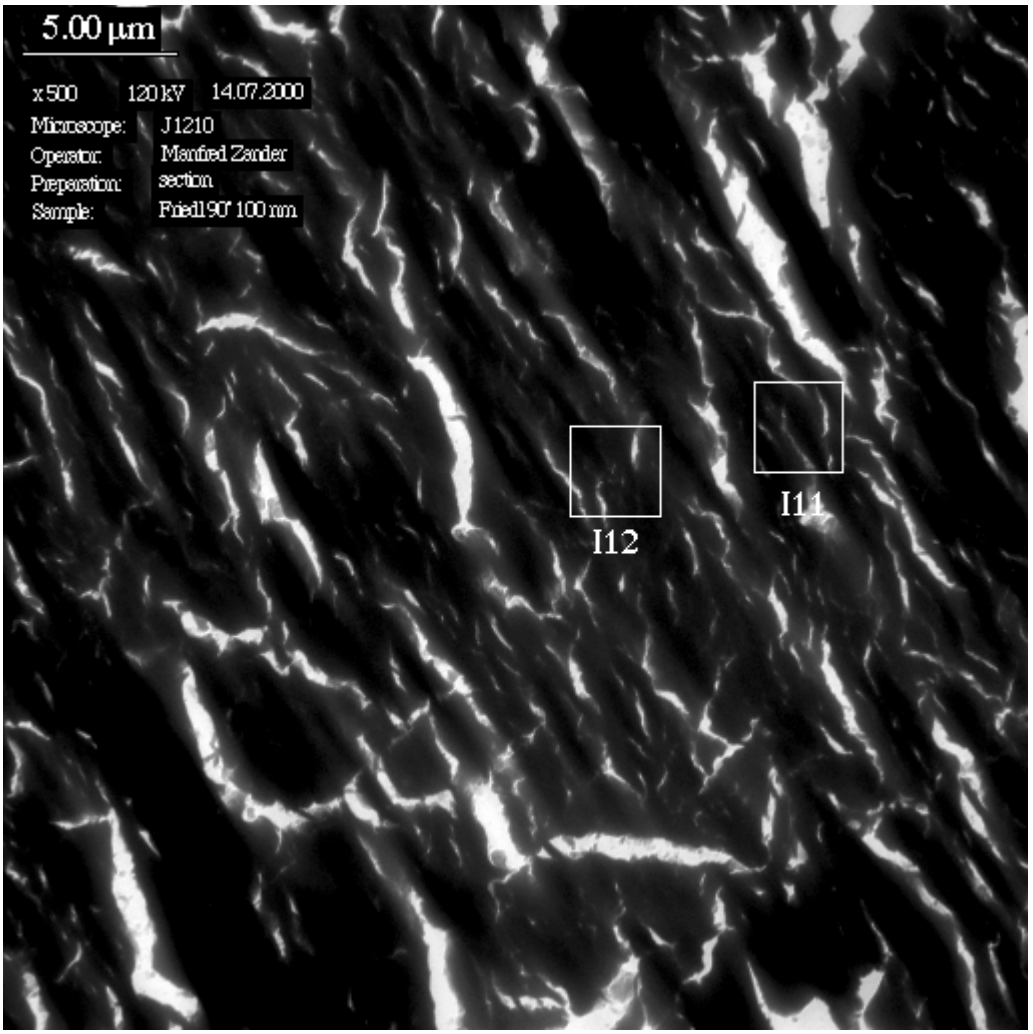


Figure 5-13. *TEM micrograph with 500 x magnification of 0.1 µm thick section of MX-80 clay exposed to 110°C vapor and then hydrated and homogenized in an oedometer to a density of 1750 kg/m³. Open and gel-filled voids are seen, three with a long diameter of 5–20 µm and about sixty with a long diameter of 1–5 µm. The total cross section area is about 1000 µm².*

5.4.3 Conclusions from the microstructural investigations

The following major conclusions were drawn:

1. It is probable that the excess silica observed on the surfaces of the aggregates was precipitated at the cooling subsequent to the hydrothermal treatment, which caused dissolution of smectite crystallites and accessory silicates.

2. Precipitated Si may have produced coherent particle aggregates by cementing them together. This would have reduced the potential to exfoliate thin stacks that normally yields effective gel formation in the voids between aggregates when unsaturated smectitic clay is water saturated.

3. The hydrothermal treatment seems to have caused contraction of similarly oriented stacks of montmorillonite lamellae, hence forming large and dense particle aggregates.

These conclusions are in line with an earlier proposed model /9,10/ for the impact of high temperature on MX-80 clay as illustrated in Figure 5-14.

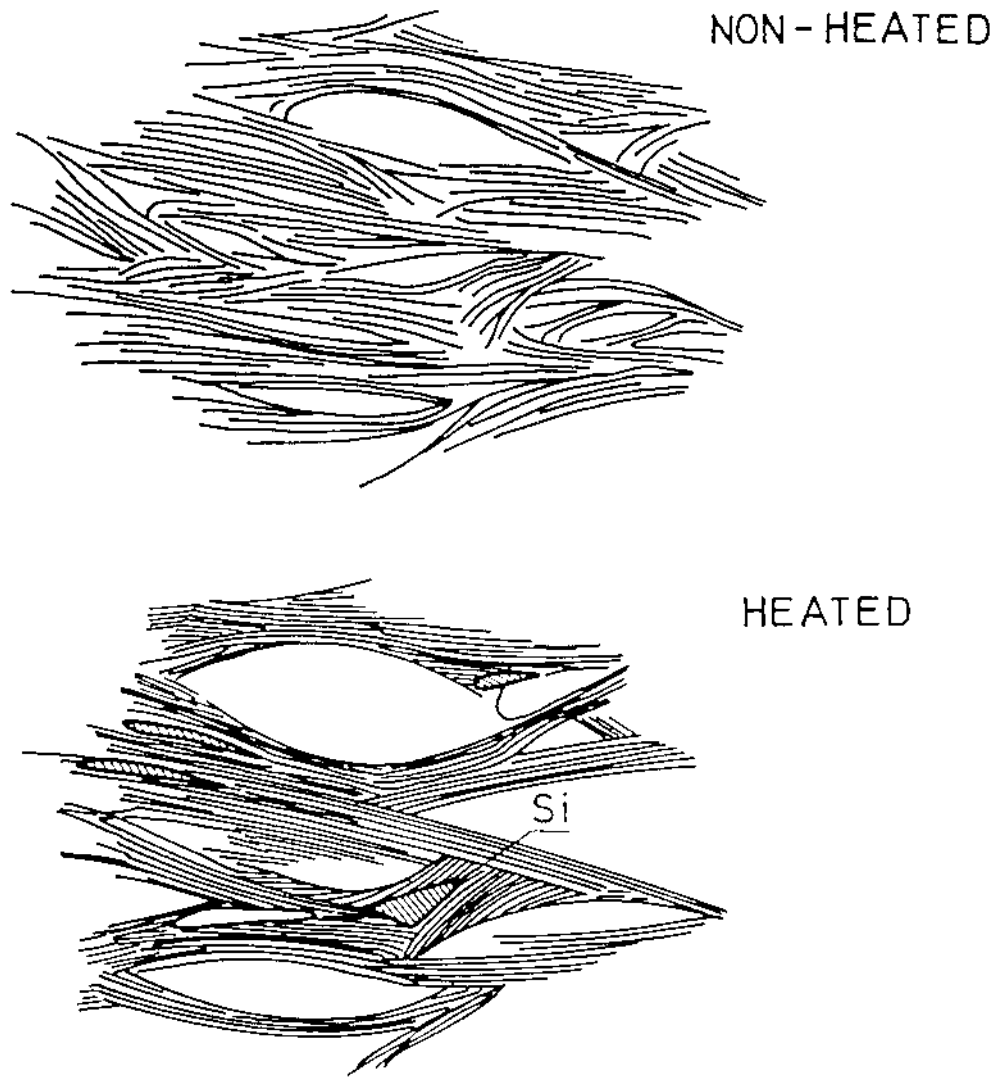


Figure 5-14. *Schematic illustration of microstructural changes and cementation by Si precipitation on heating of MX-80 clay under unsaturated conditions.*

6 Discussion and conclusions

6.1 General observations

The present study involved exposure of unsaturated MX-80 clay to hot vapor, resembling the hydrothermal conditions that prevail close to hot canisters in a KBS-3 repository. The vapor treatment lasted for 30 days and the results are hence valid only for this period. However, it is believed that most of the physico/chemical processes that took place in the hot phase, i.e. slight dissolution of silicates and reorganization of montmorillonite particles, were completed under the closed conditions that prevailed and that further significant changes would not be expected at prolonged treatment. It is therefore believed that the experiments illustrate the performance of the buffer clay also under longer periods of time.

The major findings are summarized below:

- The clay underwent expansion and strong aggregation under the hydrothermal conditions.

- The hydration rate and swelling pressure of the vapor-treated material were on the same order of magnitude as those of untreated clay, while the hydraulic conductivity increased by 10% for the investigated temperature range. This is believed to be due to a more heterogeneous microstructure than in untreated clay.

- Precipitated Si that was observed on the surfaces of the aggregates may have produced coherent particle aggregates by cementing them together. The silica was probably precipitated at the cooling subsequent to the hydrothermal treatment, which caused dissolution of smectite crystallites and accessory silicates.

- Cementation is believed to have reduced the potential to exfoliate thin stacks that normally yields effective gel formation in the voids between aggregates when unsaturated smectitic clay is water saturated. This is the major reason for the rise in hydraulic conductivity of vapor-treated MX-80 clay.

- The hydrothermal treatment seems to have caused contraction of similarly oriented stacks of montmorillonite lamellae, hence forming large and dense particle aggregates. Cementation of the aggregates prevented them to expand and produce clay gels in larger voids. The presence of larger voids is a second reason for the rise in hydraulic conductivity of vapor-treated MX-80 clay.

6.2 Major conclusion

The study supports Couture's results in the sense that hot vapor is shown to have an influence on physical properties of smectite clay. However, at temperatures relevant to the KBS-3 concept, i.e. less than 100°C the impact is small and confined to the clay within a few centimeters distance from the canister surface provided that physically closed conditions prevail. For obtaining such conditions and minimizing the risk of

drying, which would widen the vapor-influenced part of the clay buffer, early back-filling of the deposition tunnels is recommended since this produces fast build-up of piezometric pressures in the rock and tunnel backfill.

7 References

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