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Alteration of MX-80 by hydrothermal treatment under high salt content conditions

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Abstract

MX-80 clay saturated with or exposed to concentrated NaCl solutions at 110°C, i.e. conditions resembling those of the buffer clay close to the hot canisters in deposition holes, is concluded to have undergone slight mineralogical changes in a 30 days long hydrothermal period. They had the form of some collapse of montmorillonite stacks, conversion to beidellite, and possible neof ormation of sodium illite (brammalite). Also, stable aggregates were formed that were larger than in untreated MX-80. The mechanical stability of the aggregates is probably due to cementation by precipitation of silicious matter that was set free by beidellitization or by dissolution of the smectite component.

Sammanfattning

Om brammalit, dvs natriumillit, bildas av smektit i salt vatten vid hög temperatur kan sådan omvandling ske också i buffertleran runt kapslarna i ett förvar av typ KBS-3. Den aktuella studien omfattade två laboratorieförsök med MX-80 lera, ett med kompakterat lerpulver med torrdensiteten 1200 till 1300 kg/m³ och mättat med 10% and 20% NaCl-lösningar med åtföljande värmning till 110 °C under slutna förhållanden i 30 dagar. I det andra försöket kompakterades lerpulver i hydrotermalceller som värmdes till 110 °C under samma tid och var anslutna till kärl med 10% och 20% NaCl-lösningar. Den förstnämnda serien svarar mot förhållandena i buffertleran efter mättnad med Natrikt saltvatten och den andra mot förhållandena under mättnad med salt vatten. Alla laboratorieanalyser gjordes efter kort tids perkolering av hydrotermalproverna med destillerat vatten för att garantera vätskemättnad.

Resultaten från undersökningen av de fysikaliska egenskaperna hos lermaterialen visar att den hydrauliska konduktiviteten och svällningstrycket var av samma storleksordning som för obehandlad lera. Jämförelse med illitlera visar att denna har mer än hundra gånger högre genomsläpplighet än de hydrotermalt behandlade lerorna, vilket innebär att omvandlingen till illit hos dessa var obetydlig. Det är också uppenbart därför att illitlera uppvisar mycket låga svällningstryck medan de hydrotermalt påverkade materialen visade svällningstryck av samma storleksordning som obehandlad MX-80 lera.

XRD analys visade en tydlig skillnad i mineralsammansättning mellan de två försöksserierna. Medan leran som mättats med saltlösning före den hydrotermala behandlingen inte uppvisade annat än obetydlig nybildning av mixed-layer smektit-illit vid 20% NaCl-lösning, visade leran som i lufttorr form kontaktades med saltlösningar under hydrotermala förhållanden något mer påtagliga förändringar. I det fallet hade natriumillit eller permanent kollapsade lager bildats och Mg bedömdes ha migrerat från oktaederpositioner till interlamellära positioner i kristallgittret, en process som antyder partiell lösning av montmorillonit-komponenten. I leran som i lufttorr form kontaktades med saltlösningar under hydrotermala förhållanden var tjockleken hos montmorillonitpartiklarna betydligt större än den hos obehandlad MX-80, vilket kan bero på "Ostwald ripening" eller aggregering med åtföljande cementering genom utfällning av kiselkomponenter.

TEM EDX analys visade att Mg i oktahederskikten till en del ersatts av Al vilket givit en minskning av skikt-laddningen särskilt i leran som i lufttorr form kontaktades med saltlösningar under hydrotermala förhållanden. Kiselkomponenten, som delvis föreligger som kvarts och kristobalit, kan vara utfälld och härröra från tetrahederpositionerna i montmorillonitgittret där Al gått in och bildat beidellit, eller från lösning av montmorillonitmineralen.

Eftersom temperaturen var högre än i ett KBS-3 förvar och salthalten betydligt högre än vad man normalt finner på 500 m djup i svenskt kristallint berg kan degraderingsprocesserna vara mindre betydelsefulla i förvarets buffertlera. Å andra sidan rådde hydrotermala förhållanden endast under en månad i laboratoriestudien medan de verkar under mycket lång tid i slutförvaret.

Summary

If brammalit, i.e. sodium illite, is formed from smectite in Na-rich salt water at high temperature such conversion can also take place in the buffer clay that surrounds the canisters in a KBS-3 repository. The present study comprised two laboratory test series with MX-80 clay, one with compacted clay powder with a dry density of 1200 to 1300 kg/m³ and saturation with 10% and 20% NaCl solutions followed by heating to 110°C under closed conditions for 30 days. In the second series air-dry compacted clay powder in a cell was heated at 110°C for the same period of time and connected to vessels with 10% and 20% NaCl solutions. The first series represents the conditions in the buffer clay after saturation with Na-rich salt water while the second one corresponds to the conditions in the course of saturation with such water. All laboratory tests were made after short-term percolation with distilled water for making sure that the hydrothermally treated samples were fully fluid-saturated.

The results from the physical testing showed that the hydraulic conductivity and swelling pressure of the hydrothermally treated clay samples were on the same order of magnitude as for untreated clay. Comparison with illitic clays shows that the latter are at least a hundred times more permeable than the hydrothermally treated salt clays in the present study, which hence indicates that conversion to illite was insignificant. This is obvious also from the fact that while illitic clays have very low swelling pressures the hydrothermally treated clays exhibited swelling pressures on the same order of magnitude as untreated MX-80.

XRD analysis showed a clear difference in mineral constitution between the two test series. Thus, while no significant change from the typical mineralogy of untreated MX-80 was found for hydrothermal treatment of clay saturated with 10 and 20% NaCl solution, except for some very slight neof ormation of illite-smectite mixed layers or irreversible partially collapsed phases in the 20% NaCl solution, dry clay exposed to 20% NaCl solution showed changes although they were still limited. Here, formation of Na-illite or fully contracted layers took place and Mg was concluded to have migrated from octahedral lattice positions to interlamellar sites, implying partial dissolution. The thickness of the montmorillonite particles were comparable to that of untreated MX-80 montmorillonite for the hydrothermally treated clay saturated with NaCl solutions, while it was significantly larger for the air-dry clay exposed to such solutions at heating to 110°C. The larger thickness may be an example of “Ostwald ripening” or aggregation with simultaneous cementation by precipitated silicious matter.

TEM EDX analyses showed that partial replacement of octahedral Mg by Al yielding a drop in interlayer charge had occurred especially in the air-dry clay powder heated to 110°C under simultaneous exposure to NaCl solutions. Silicious matter, partly in the form of quartz or cristobalite, may have precipitated. The silica may have originated from tetrahedral positions in the montmorillonite lattice where aluminum can have replaced it, hence forming beidellite, or by dissolution of the smectite component.

Since the temperature was higher than in a KBS-3 repository and the salt content appreciably higher than what is normally found at 500 m depth in Swedish crystalline rock, the degrading processes may be less significant in the buffer clay. On the other hand, the hydrothermal conditions in the lab study prevailed only for a month while they will last for much longer time in the repository.

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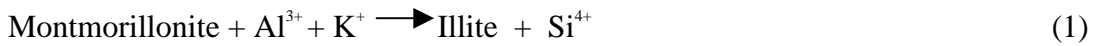
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1 Scope

According to the literature the non-expanding mineral sodium illite (brammalite) has been identified in nature and it has been proposed that this mineral may be formed from montmorillonite in an environment characterized by high NaCl concentration and high temperature. If this process takes place in the buffer clay embedding KBS-3 canisters it will cause a rise in hydraulic conductivity and a loss in expandability and self-sealing capacity. The present study was made to find out if such alteration can take place and what the physical properties of the reaction products would be.

2 Theoretical background

Solid solution-type conversion of the smectite species montmorillonite to illite has long been proposed as an important illitization process passing from 100% smectite (S) via mixed-layer (IS) minerals to 100% illite (I):



Aluminum replacing tetrahedral silicons is assumed to originate from octahedral positions or from external sources and the mineral formed is beidellite that is easily transformed to illite by uptake of potassium. The release of excess silica implies interaction with the local environment, i.e. the porewater in fully or partly fluid-filled voids.

In terms of Maegdefrau's general formula the mineral formed by replacement of tetrahedral silica by aluminum and interlamellar uptake of monovalent cations to balance the charge change would be:



where y is in the interval 1–2, M^{I} represents monovalent cations, M^{II} magnesium and divalent iron, and M^{III} aluminum or trivalent iron. Electrostatic forces, hydrogen bonds and mass forces keep the lamellae together. If potassium is available in sufficient amounts illite is believed to be formed, while absence of K^+ means that the smectite will be preserved as beidellite.

However, it has been proposed that high temperature and pressure may cause beidellite to collapse to the 10 Å paragonite-type mineral brammalite if it is saturated with sodium /1/. A requirement would be that the density is high or that partial dehydration takes place, both representing actual conditions in the hottest part of KBS-3 buffer in rock with Na-rich groundwater.

Dissolution/precipitation is an alternative illitization mechanism. One of many models of such conversion of smectite (S) to illite (I) was proposed by Pollastro in 1985, the idea being that the latter mineral is formed by dissolution of smectite in I/S aggregates /2/. A somewhat similar alteration mechanism was suggested by Nadeau et al /3/ at the same time and their ideas are supported, in principle at least, by comprehensive investigations of the Shinzan area in Japan by Inoue et al /4/, and by Gueven's studies /5/ of samples from deep clay sediments in conjunction with oil prospection. The latter study showed that heat-exposed smectite has two major physical forms: flaky or mossy appearance representing interstratified I/S, and lath-shaped minerals representing neo-formed illite that has grown in pores, and that is assumed to be formed by precipitation of Si and Al released from dissolved smectite and accessory minerals in conjunction with uptake of potassium.

Theoretically, neoformation of brammalite instead of illite may take place in the absence of potassium especially if the density of the clay matrix is high. An indication that brammalite may in fact be formed even when some potassium is present is Tardy's

and Touret's application of thermodynamics /6/, which shows that while potassium is preferred in interlamellar positions at high clay densities, sodium is preferred at low densities.

Natural analogues

Brammalite has been recognized in nature /7,8/ where it has been found to be related to low-grade metamorphism. In such a case it appeared as mixed layer montmorillonite/brammalite indicating that solid transition of stacks of montmorillonite to contain brammalite lamellae had taken place.

Laboratory experiments

It has recently been demonstrated that non-expandable 10 Å minerals can be formed rather quickly from montmorillonite at temperatures around 100°C in hydrothermal tests using strong NaCl solutions /9/.

3 Test program and equipment

3.1 Principle

If brammalite, i.e. sodium illite, is formed from montmorillonite in strong NaCl solution at high temperatures, such conversion may also take place in the buffer clay that surrounds the canisters in a KBS-3 repository. For investigating if hydrothermal conditions really yield brammalite and what the physical properties of the reaction products are, two laboratory test series were conducted. In one of the series clay powder was compacted to a dry density of 1190 and 1330 kg/m³ (1750 to 1840 kg/m³ at water saturation) and saturated with 10% and 20% NaCl solutions for subsequent heating to 110°C under confined conditions for 30 days. In the second series clay powder was compacted to a dry density of 1270 and 1350 kg/m³ (1800 to 1850 kg/m³ at water saturation) in hydrothermal cells that were heated to 110°C under confined conditions for 30 days while being connected to vessels with 10% and 20% NaCl solutions in separate tests. The first series is equivalent to the conditions in a deposition hole when the buffer has been saturated with very concentrated NaCl groundwater. The second series represents the conditions in deposition holes during saturation with very concentrated Na-rich groundwater.

3.2 Materials

3.2.1 Clay

MX-80 was used as clay component in the investigation. The powder used for preparing the clay materials had a water content of 9 to 11% and was compacted in the test cells to the desired dry density, i.e. about 1250 kg/m³.

3.2.2 Solutions

Pure NaCl (pro analysis) salt was dissolved in distilled water to 10 and 20% concentrations.

3.2.3 Equipment

Two types of cells were used, all of them having a diameter of 30 mm, the sample height being 16 mm. Acid-proof, sintered filters of stainless steel with 2 mm thickness separated the clay samples from the top and bottom of the cells. For the clay saturated with salt water the cells were closed leaving a small internal space for expansion of the porewater at the heating to 110°C. For the “dry” clays no such space was left at the top lids, which had lead-throughs for the tubings that connected the cells with the vessels with salt solutions.

In the testing of hydraulic conductivity and swelling pressure after the hydrothermal treatment the porewater flux was measured by use of burettes, maintaining a constant hydraulic gradient of 30–35. The swelling pressure was measured by use of ENTRAN MM35D-2 electronic pressure cells.

3.3 Test procedure

After completing the hydrothermal tests the samples were transferred to ordinary oedometers for percolation of distilled water with concomitant evaluation of the hydraulic conductivity and swelling pressure under room temperature conditions. Distilled water was used for dissolving possibly formed halite crystals which could otherwise affect the conductivity and mask the influence of mineral and microstructural alteration. The percolation of distilled water was expected to reduce the electrolyte concentration of the porewater but since the tests only ran for a few days no large changes in porewater concentration were anticipated. Still, the evaluated hydraulic conductivity and swelling pressure are conservatively assumed to be representative of appreciably lower porewater salinities than the 10 and 20% NaCl concentrations used in the hydrothermal phase, namely 2%. Fair comparison with untreated MX-80 clay is therefore made by referring to tests of such material with 2% NaCl porewater solution.

3.4 Recording and analyses

In the hydrothermal treatment of saturated clay the only variable recorded was the temperature in the oven in which the cells were placed. It varied by less than $\pm 0.5^{\circ}\text{C}$ throughout the 30 days heating period. In the treatment of “dry” clay the uptake of salt solutions was recorded as well.

In the subsequent phase of percolation with distilled water the hydraulic conductivity and swelling pressure were currently evaluated.

For identifying possible mineralogical changes the following investigations were made:

1. X-ray diffraction analysis of specimens extracted from the clay specimens that had been percolated with distilled water after the hydrothermal treatment. This would reveal possible conversion of montmorillonite to non-expanding minerals.
2. Transmission electron microscopy of dispersed clay for identifying possible changes in particle size, like aggregation or growth of particles.
3. Scanning microscopy of undisturbed specimens for identifying possible changes in microstructural arrangement.

4 Test results

4.1 Hydraulic conductivity and swelling pressure

4.1.1 Clay saturated with salt solution and heated to 110°C for 30 days

10% NaCl solution

The hydraulic conductivity and swelling pressure of the hydrothermally treated clay determined in the course of percolation with distilled water is given in Table 4-1, which also gives the corresponding data for ordinary untreated MX-80 percolated with distilled water as well as 2% NaCl solution. Table 4-2 gives the corresponding swelling pressures.

Table 4-1. Hydraulic conductivity (K in m/s) of hydrothermally treated clay saturated with 10% salt solution and then heated to 110°C for 30 days. Data of untreated MX-80 representing percolation with 2% NaCl solution are from /10/.

Property	Density at complete water saturation, kg/m ³	Hydrothermally treated MX-80 clay	Untreated MX-80 clay percolated with distilled water	Untreated MX-80 clay percolated with 2% NaCl solution
K, m/s	1840	9.8E-12	3E-13	2E-12

Table 4-2. Swelling pressure (p_s in MPa) of hydrothermally treated clay saturated with 10% salt solution and then heated to 110°C for 30 days. Data of untreated MX-80 representing percolation with 2% NaCl solution are from /11/.

Property	Density at complete water saturation, kg/m ³	Hydrothermally treated MX-80 clay	Untreated MX-80 clay percolated with distilled water	Untreated MX-80 clay percolated with 2% NaCl solution
p _s	1840	450	900	500 (estimated)

20% NaCl solution

The hydraulic conductivity and swelling pressure of the hydrothermally treated clay determined in the course of percolation with distilled water is given in Table 4-3, which also gives the corresponding data for ordinary MX-80 percolated with distilled water and 2% NaCl solution. Table 4-4 gives the corresponding swelling pressures.

Table 4-3. Hydraulic conductivity (K in m/s) of hydrothermally treated clay saturated with 20% salt solution and then heated to 110°C for 30 days. Data of untreated MX-80 representing percolation with 2% NaCl solution are from /10/.

Property	Density at complete water saturation, kg/m ³	Hydrothermally treated MX-80 clay	Untreated MX-80 clay percolated with distilled water	Untreated MX-80 clay percolated with 2% NaCl solution
K, m/s	1750	5.8E-12	8E-13	2E-11

Table 4-4. Swelling pressure (p_s in MPa) of hydrothermally treated clay saturated with 20% salt solution and then heated to 110°C for 30 days. Data of untreated MX-80 representing percolation with 2% NaCl solution are from /10/.

Property	Density at complete water saturation, kg/m ³	Hydrothermally treated MX-80 clay	Untreated MX-80 clay percolated with distilled water	Untreated MX-80 clay percolated with 2% NaCl solution
p_s	1750	200	550	200

One finds that the hydraulic conductivity and swelling pressure of the hydrothermally treated clay samples are on the same order of magnitude as for untreated clay percolated with 2% NaCl solution. Comparison with illitic clay shows that the latter are much more permeable /12/. Thus, for a typical illitic clay prepared by drying, grinding and compaction the hydraulic conductivity to a density at water saturation of 1750 kg/m³ is 4E-8 m/s, while the densities 1800 and 1850 kg/m³ yield approximately 2E-9 m/s and 8E-10 m/s, respectively. These values are more than a hundred times higher than for the hydrothermally treated salt clays in the present study, which hence indicates that illitization was insignificant. This is obvious also from the fact that while illitic clays exhibit very low swelling pressures the hydrothermally treated clays had swelling pressures on the same order of magnitude as untreated MX-80.

4.1.2 Clay prepared by compacting dry clay powder that was then heated to 110°C under simultaneous exposure to salt solutions for 30 days

At the extraction of the hydrothermally treated clay samples for subsequent percolation with distilled water it was found that they were not completely saturated with the respective salt solution. This is believed to be due to the fact that the vapor pressure was only slightly lower than the applied water pressure. It was also noticed that salt had precipitated in the tubings close to the hydrothermal cells where they had a temperature of 110°C while the rest of the tubings had a temperature of 25–30°C. These precipitations, which manifest the principle of salt accumulation in porous media that are undergoing wetting under a thermal gradient, may also have affected the degree of saturation by delaying it. After saturation with distilled water in the subsequent oedometer testing, the percolate was found to have about the same salinity as in the first test series, i.e. appreciably more than 2%.

10% NaCl solution

The hydraulic conductivity and swelling pressure of the hydrothermally treated clay determined in the course of the subsequent percolation with distilled water is given in Table 4-5, which also gives the corresponding data for ordinary MX-80 percolated with distilled water and 2% NaCl solution. Table 4-6 gives the corresponding swelling pressures.

Table 4-5. Hydraulic conductivity (K in m/s) of dry, hydrothermally treated clay exposed to 10% salt solution at 110°C for 30 days. Data of untreated MX-80 representing percolation with 2% NaCl solution are from /10/.

Property	Density at complete water saturation, kg/m ³	Hydrothermally treated MX-80 clay	Untreated MX-80 clay percolated with distilled water	Untreated MX-80 clay percolated with 2% NaCl solution
K , m/s	1850	6E-12	3E-13	2E-12

Table 4-6. Swelling pressure (p_s in MPa) of dry, hydrothermally treated clay exposed to 10% salt solution at 110°C for 30 days. Data of untreated MX-80 representing percolation with 2% NaCl solution are from /11/.

Property	Density at complete water saturation, kg/m ³	Hydrothermally treated MX-80 clay	Untreated MX-80 clay percolated with distilled water	Untreated MX-80 clay percolated with 2% NaCl solution
p_s	1850	450	1000	500 (estimated)

20% NaCl solution

The hydraulic conductivity and swelling pressure of the hydrothermally treated clay determined in the course of percolation with distilled water is given in Table 4-7, which also gives the corresponding data for ordinary MX-80 percolated with distilled water and 2% NaCl solution. Table 4-8 gives the corresponding swelling pressures.

Table 4-7. Hydraulic conductivity (K in m/s) of dry, hydrothermally treated clay exposed to 20% salt solution at 110°C for 30 days. Data of untreated MX-80 representing percolation with 2% NaCl solution are from /10/.

Property	Density at complete water saturation, kg/m ³	Hydrothermally treated MX-80 clay	Untreated MX-80 clay percolated with distilled water	Untreated MX-80 clay percolated with 2% NaCl solution
K , m/s	1800	6E-12	3E-13	6E-12

Table 4-8. Swelling pressure (p_s in MPa) of dry, hydrothermally treated clay exposed to 20% salt solution at 110°C for 30 days. Data of untreated MX-80 representing percolation with 2% NaCl solution are from /11/.

Property	Density at complete water saturation, kg/m ³	Hydrothermally treated MX-80 clay	Untreated MX-80 clay percolated with distilled water	Untreated MX-80 clay percolated with 2% NaCl solution
p_s	1800	450	900	225 (estimated)

It is concluded that the hydraulic conductivity and swelling pressure at percolation with distilled water of the hydrothermally treated clay samples are on the same order of magnitude as for untreated clay saturated and percolated with 2% NaCl solution. As for the first test series one concludes that there cannot have been significant changes in mineralogy caused by the hydrothermal treatment.

It should be added that the difference in physical properties between untreated MX-80 saturated with distilled water and salt water is due to coagulation effects, which naturally also affected the hydrothermally treated clays.

4.2 X-ray diffraction (XRD)

4.2.1 Non-oriented specimens

This study was performed at the Geological Department, University of Greifswald, Germany and is fully reported in the Appendix 1.

A typical X-ray diffraction graph of MX-80 clay saturated with 20% NaCl solution and heated at 110°C for 30 days and then percolated for a few days with distilled water is shown in Figure 4-1. This diagram does not show any change in mineralogy from that of ordinary untreated MX-80 and the same conclusion was drawn also from the hydrothermal treatment of clay saturated with 10% NaCl solution. Of particular importance is that the XRD study did not show the presence of illite or completely contracted layers. The montmorillonite is hence concluded to be intact with a symmetric peak at 13.4 Å and the major accessory minerals are the same as in untreated MX-80, i.e. quartz, cristobalite, and feldspar. There is also some halite that precipitated in the course of the NaCl treatment.

Figure 4-2 shows an X-ray diffraction graph of MX-80 clay compacted in air-dry form, then exposed to 20% NaCl solution while being heated at 110°C for 30 days, and subsequently percolated for a few days with distilled water.

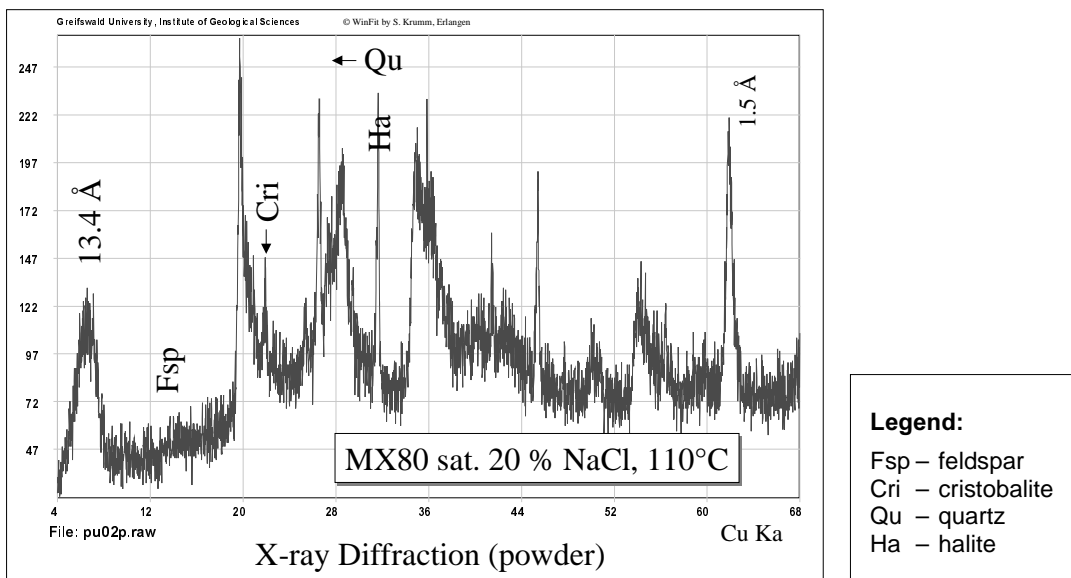


Figure 4-1. XRD spectrum of MX-80 clay saturated with 20% NaCl solution and heated at 110°C for 30 days and then percolated for a few days with distilled water.

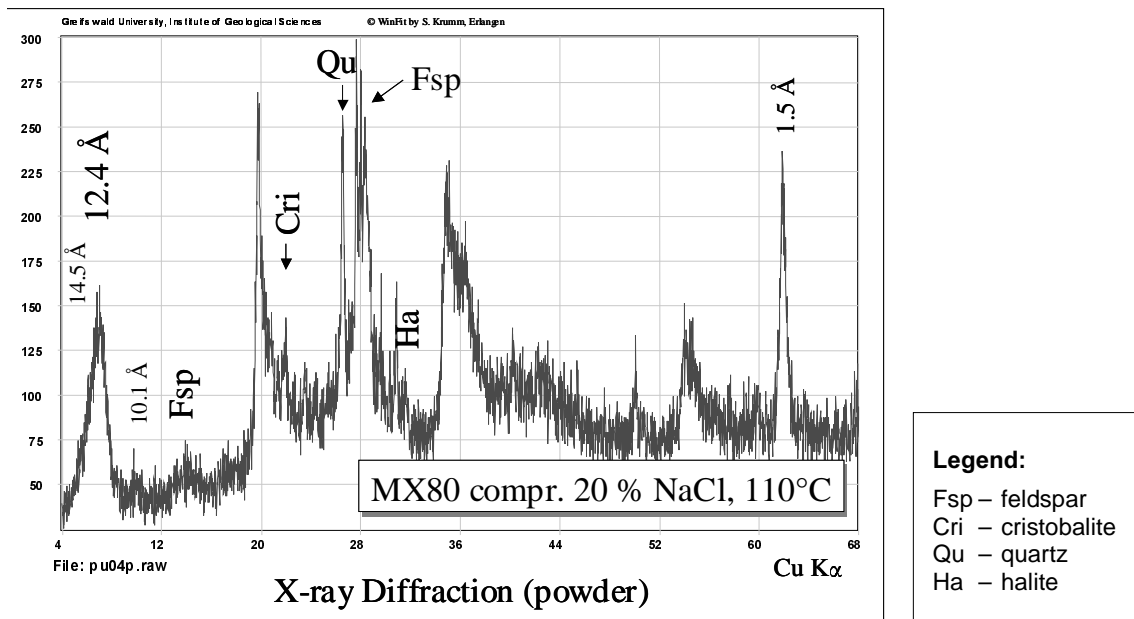


Figure 4-2. XRD spectrum of MX-80 clay compacted in air-dry form and then exposed to 20% NaCl solution while being heated at 110°C for 30 days, and finally percolated for a few days with distilled water.

The diagram in Figure 4-2 shows some minor deviations from the appearance of spectra of ordinary MX-80 clay:

- Some Na-illite or fully contracted layers are found (10.1 Å).
- The montmorillonite species has an asymmetric major peak composed of two symmetric peaks at 14.5 Å and 12.4 Å (mixture of mono- and bivalent cations in the interlayers, e.g. Na and Mg).
- Mg in the interlamellar space probably stems from the octahedral layers, meaning that intracrystalline dissolution has taken place.
- Accessory minerals are the same as in untreated MX-80 clay, i.e. quartz, cristobalite, feldspar. Also, there is some halite that precipitated in the course of the NaCl treatment.

The exposure of dry clay to 20% NaCl solution showed somewhat more, but still very limited formation of Na-illite or fully contracted layers and somewhat more obvious asymmetry of the main montmorillonite peak.

In conclusion, the XRD study of non-oriented specimens showed that air-dry MX-80 clay being contacted and moistened with NaCl-rich water undergoes slight mineralogical changes in the form of crystal lattice reorganization comprising transfer of Mg from the lattice to the interlamellar space, and formation of Na-illite or fully contracted layers. Since the test conditions resemble those of the buffer clay close to the hot canisters in deposition holes mineralogical changes of these types are expected in a repository.

4.2.2 Oriented mounts

This study was made for a second check of possible mineral changes and for estimating particle (stack) thicknesses. For the latter purpose the software WinFit (© by S Krumm, Erlangen) the “Coherent Scattering Domain”-distribution (CSD) was used for montmorillonite and illite. For oriented, glycol-saturated mounts one can take the CSD-values to represent the average particle thickness for these minerals. Only material representing minus 2 micrometers was used. The following major conclusions were drawn:

- For the clay saturated with NaCl solutions and heated to 110°C followed by percolation with distilled water, the thickness of the montmorillonite particles was comparable to that of untreated MX-80 montmorillonite. For the air-dry clay exposed to salt solutions at 110°C followed by percolation with distilled water, the thickness was larger, indicating Ostwald ripening (thickening of larger particles on the expense of small ones), growth of montmorillonite stacks by formation or intercalation of neoformed I/S or illite lamellae, or formation of very coherent dense aggregates. In both experiment series the thickness of montmorillonite seems to decrease with increasing concentration of NaCl in the solution. The CSD values, expressed in Å of glycol-saturated material were:

	Montmorillonite (17 Å)	Illite ? (10 Å)
Saturated, 10% NaCl-solution	95	>350
Saturated, 20% NaCl-solution	80	350
Air-dry, 10% NaCl-solution	210	355
Air-dry, 20% NaCl-solution	170	265

- For the clay saturated with 10% NaCl solution and heated to 110°C followed by percolation with distilled water, the montmorillonite constituent was characterized by unchanged swelling ability (16.9 Å in glycol-saturated oriented mounts) and the typical positions of the (002)- and (003)-peaks. For the clay that was hydrothermally treated with 20% NaCl solution, some neoformed/alternated illite-smectite mixed layers or irreversible partially collapsed phases were found. Since mixed-layers were not identified in the TEM study, it may be a matter of collapsed phases.
- For the air-dry clay exposed to salt solutions at 110°C followed by percolation with distilled water the montmorillonite peak at 15 Å was asymmetric, meaning that the interlamellar space was occupied by a mixture of bi- and monovalent cations. The presence of a second order montmorillonite peak at 8.5 Å composed of two peaks was identified by WinFit deconvolution. The bi-valent interlamellar ions, which dominate, are mainly Mg, indicating lattice dissolution since Mg can only have emanated from octahedral layers. Traces of illite or complete contracted layers were found as well. In the test with 10% NaCl solution traces of kaolinite (7.17 Å, 3.57 Å) were detected but this accessory mineral may have been present already in the raw material, which is known to have a somewhat varying mineral composition. The mineral matter is made up of montmorillonite, illite, I/S or complete collapsed montmorillonite, quartz, cristobalite, and feldspar.

The asymmetric second order peak of montmorillonite at 8.5 Å (glycol-saturated) indicates the presence of neoformed/alternated illite-smectite mixed layers or the existence of irreversible partially collapsed phases. Since mixed-layers were not identified in the TEM study, it may be a matter of collapsed phases.

The ion occupation of the interlamellar space is more complex than in the saturated series. Thus, adequate deconvolution of the spectra is only possible by assuming three or even four peaks, which indicates a higher degree of dissolution in the hydrothermal treatment of air-dry clay exposed to salt solutions. The 20% NaCl solution showed the strongest changes since more cations were available.

Figure 4-3 shows typical XRD graphs of material from the two test series with 20% NaCl, one with clay saturated with the salt solution and heated to 110°C, the other with air-dry clay heated to 110°C while being exposed to the salt solution. The tests with 10% NaCl showed similar but less obvious spectral differences.

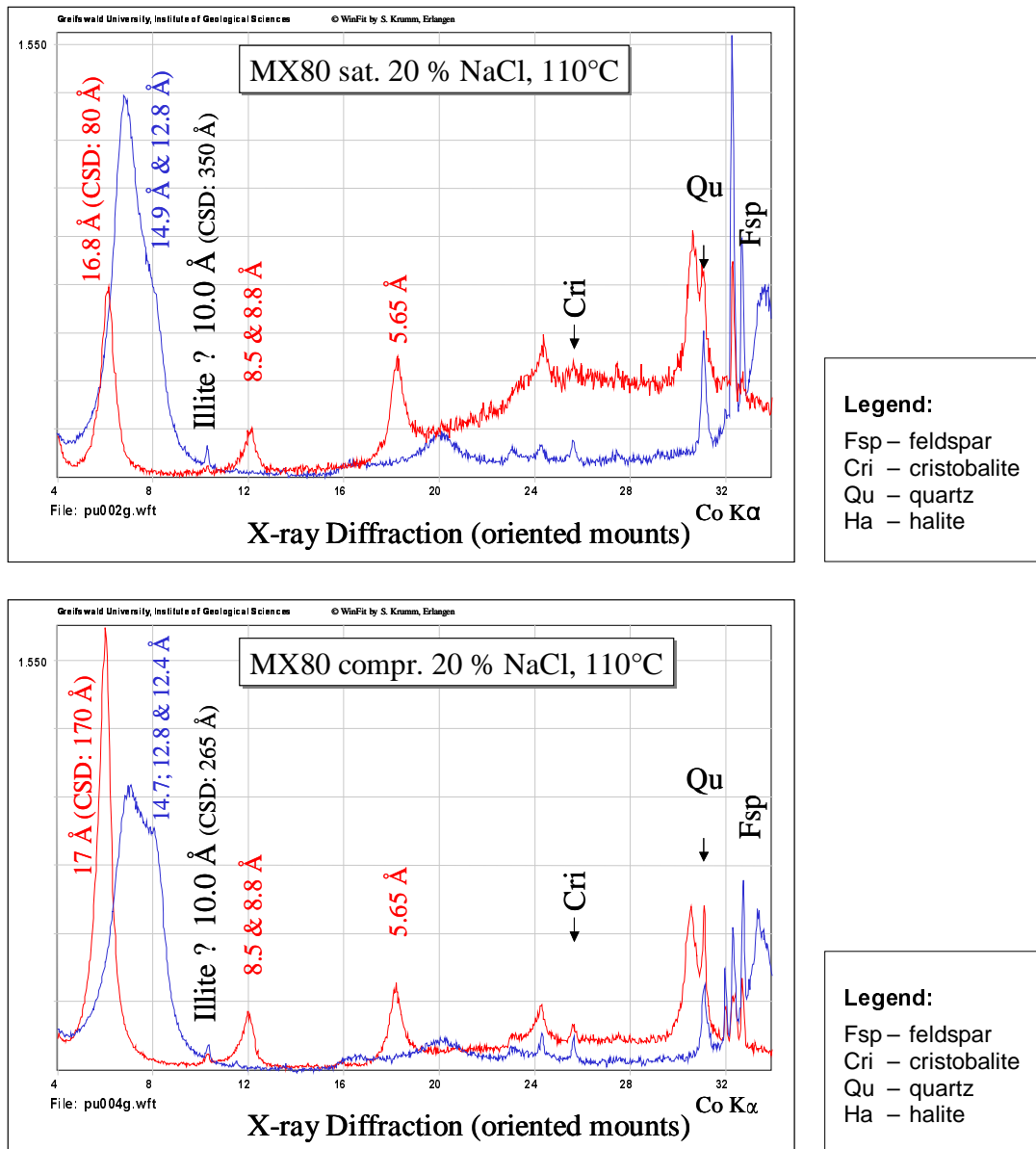


Figure 4-3. XRD spectra of oriented mounts of MX-80 clay. Upper: Clay that had been saturated with 20% NaCl solution and heated at 110°C for 30 days and then percolated for a few days with distilled water. Lower: air-dry clay exposed to 20% NaCl solution at 110°C followed by percolation with distilled water for a few days.

4.3 Transmission electron microscopy (TEM)

This study was performed at the Geological Department, University of Greifswald, Germany, using samples supplied by Geodevelopment AB. It referred to dispersed clay for identifying possible changes in particle size like aggregation or growth of certain particles on the expense of others.

The major conclusions from this study are compiled here.

4.3.1 Clay saturated with salt solution and heated to 110°C for 30 days

At 1000x magnification the appearance of large expansive aggregates and small, less expandable ones are obvious features in the tests with 10 and 20% NaCl solutions (Figure 4-4). An EDX analysis spectrum of area 102 is shown in Figure 4-5. It demonstrates replacement of octahedral Mg by Al yielding a drop in interlayer charge.

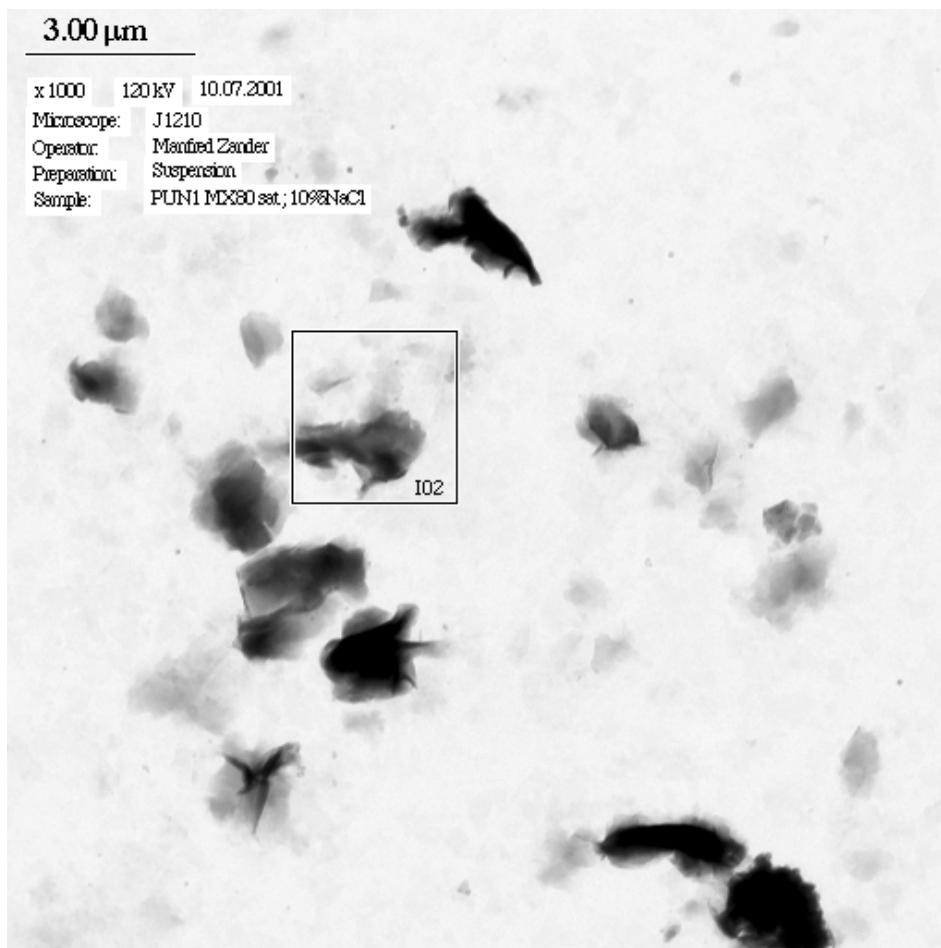


Figure 4-4. Overview of dispersed sample of material from the experiment with clay saturated with 10% NaCl solution. Like in untreated MX-80 the size of aggregates varies from a few micrometers down to a small fraction of a micrometer. An EDX analysis spectrum of area 102 is shown in Figure 4-5.

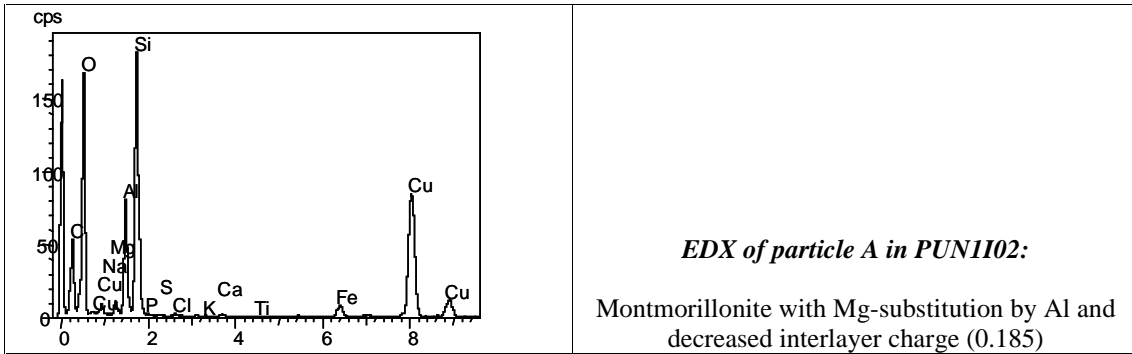


Figure 4-5. Example of crystal lattice change by substitution of Mg by Al yielding drop in charge.

4.3.2 Clay prepared by compacting dry clay powder that was then heated to 110°C under simultaneous exposure to salt solutions for 30 days

This test series gave more obvious changes of the clay material, especially for the test with 20% NaCl solution. Figure 4-6 shows a micrograph of an aggregate from this test series. Figure 4-7 gives EDX spectra showing montmorillonite with Mg-substitution by Al and decreased interlayer charge, silica that may have precipitated partly as quartz or cristobalite. The silica may at least partly stem from tetrahedral positions in the montmorillonite where aluminum can have replaced it.

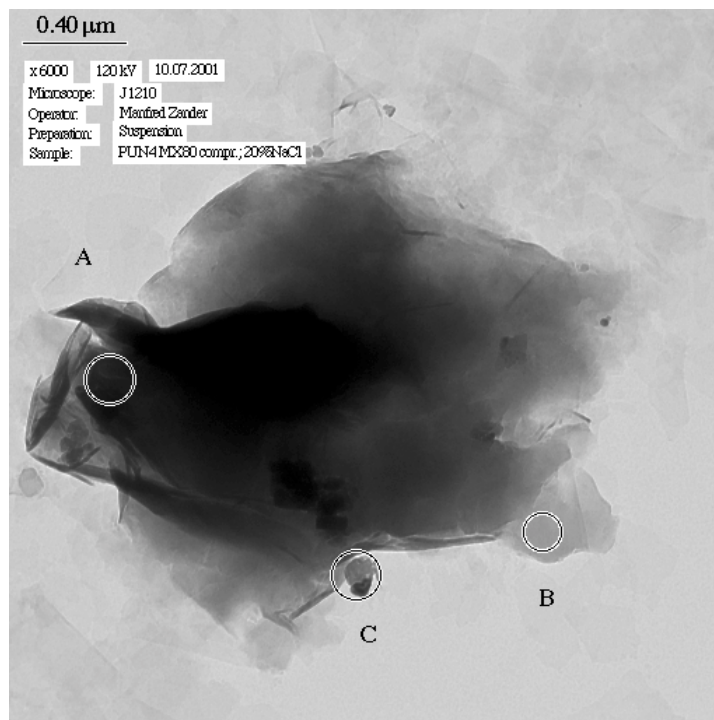


Figure 4-6. Particle aggregate exhibiting crystal lattice changes and precipitation of silicious components (cf. EDX spectra in Figure 4-7).

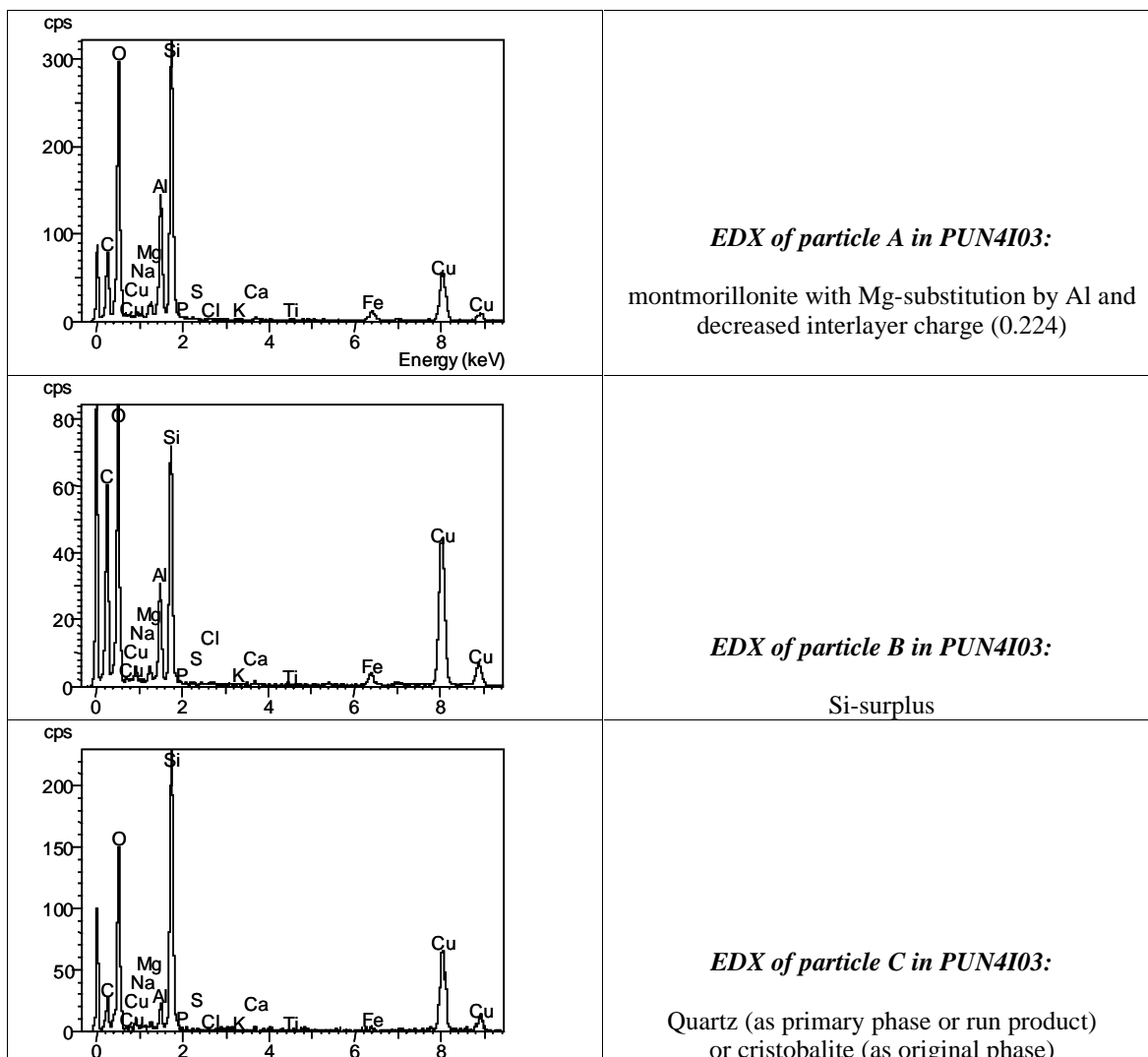


Figure 4-7. Results of EDX analyses of particles forming an aggregate in the hydrothermally treated air-dry clay exposed to 20% NaCl solution.

Figure 4-8 indicates that beidellite may be present as very thin particles. Some of them are lath-formed and may have been neo-formed but some may have been integrated in montmorillonite stacks and released from them in conjunction with the dispersion for specimen preparation. EDX spectra are shown in Figure 4-9.

Electron diffraction analysis was made for examining the orientation of stacks in aggregates and they showed both typical turbostratic arrangement in untreated MX-80 and regular orientation of the thin stacks, representing montmorillonite or beidellite (Figure 4-10).

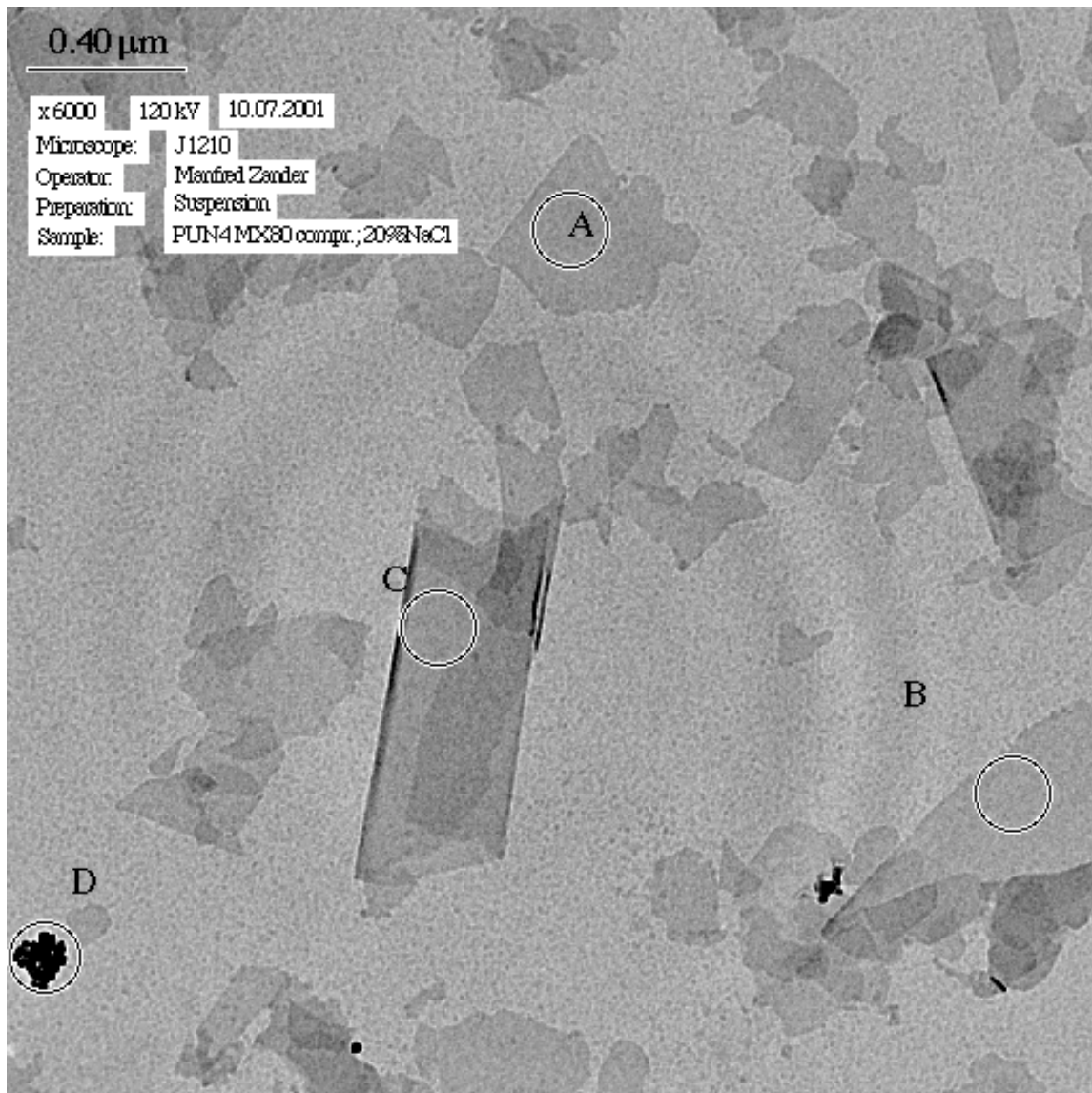


Figure 4-8. Discrete thin stacks, many of which appear to be beidellite. (cf. EDX spectra in Figure 4-9).

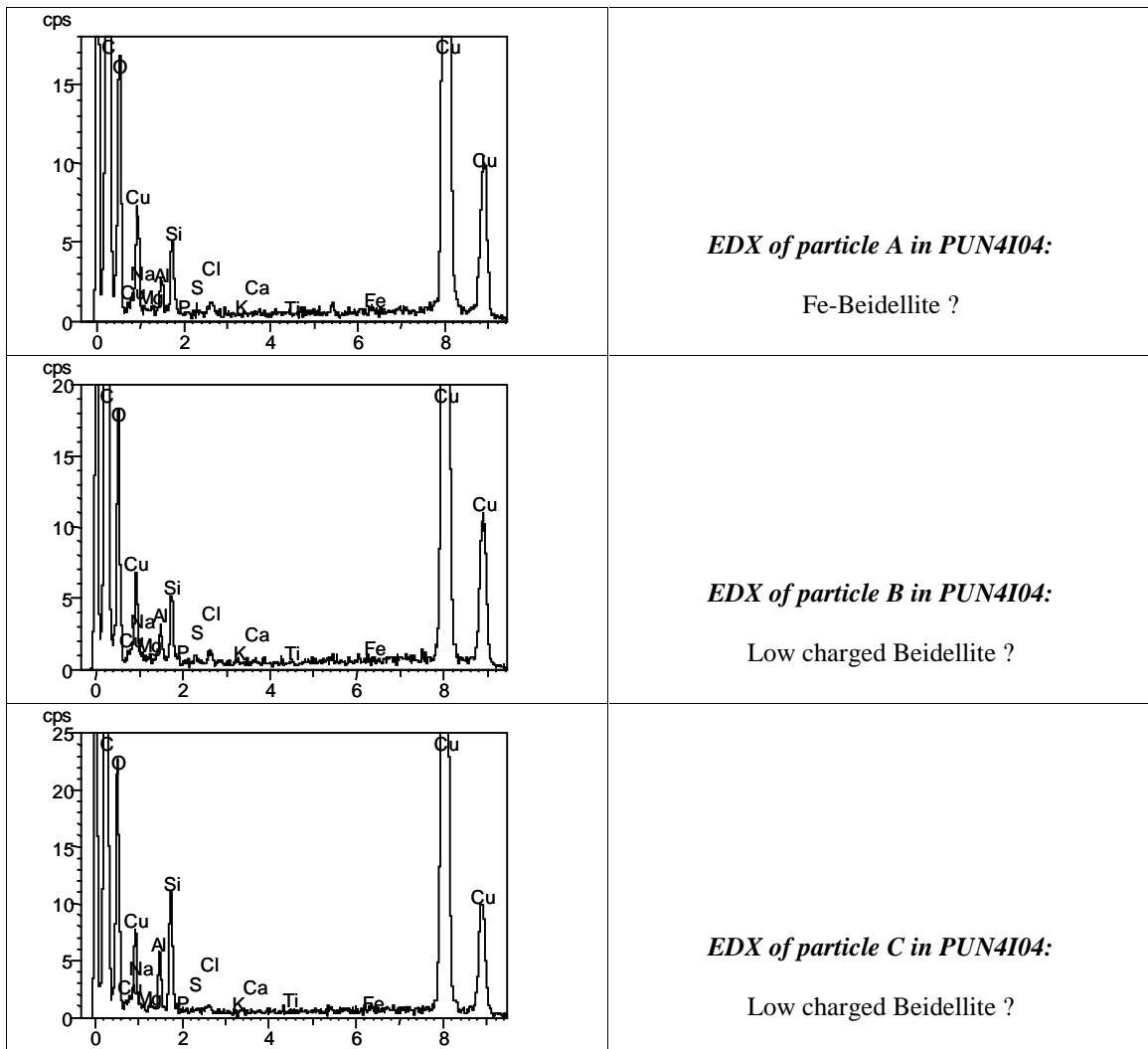


Figure 4-9. Results of EDX analyses of particles in the hydrothermally treated air-dry clay exposed to 20% NaCl solution. Most of them are believed to be beidellite.

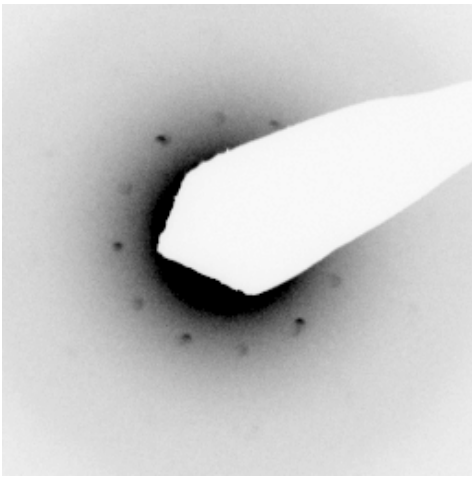
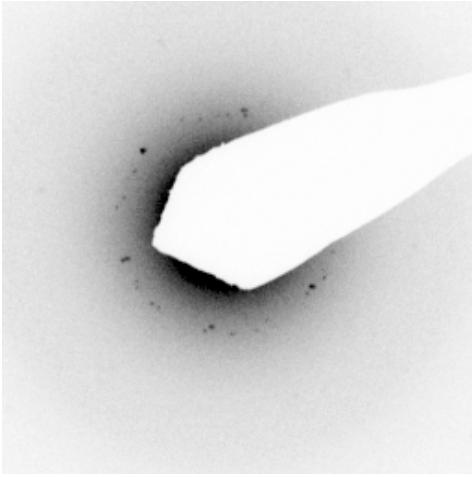


Figure 4-10. Electron diffraction images. Upper: Typical turbostratic stack arrangement in aggregate of montmorillonite. Lower: Regular order aggregate consisting of two stacks with a relative rotation of 60° .

4.4 Scanning microscopy (SEM)

This study was performed at the Geological Department, University of Greifswald, Germany, using undisturbed samples delivered by Geodevelopment AB. The purpose was to find possible significant changes in microstructural arrangement caused by hydrothermal treatment of MX-80 clay. The specimens were broken and the exposed surfaces coated with Pt for subsequent SEM analyses.

The micrographs of specimens from the two different hydrothermal treatments and salt contents were similar and also showed some typical microstructural features of untreated MX-80. Thus, the typical feature of gels formed by coagulation of exfoliated small and thin stacks of lamellae in the hydration phase were found (Figure 4-11). However, a clear difference in size of particle aggregates and voids in the hydrothermally treated clays and untreated MX-80 was observed. Both were significantly larger than in untreated MX-80 with the same bulk density (Figure 4-12).

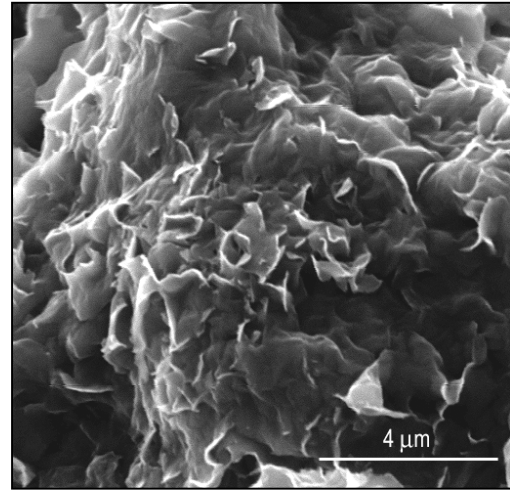
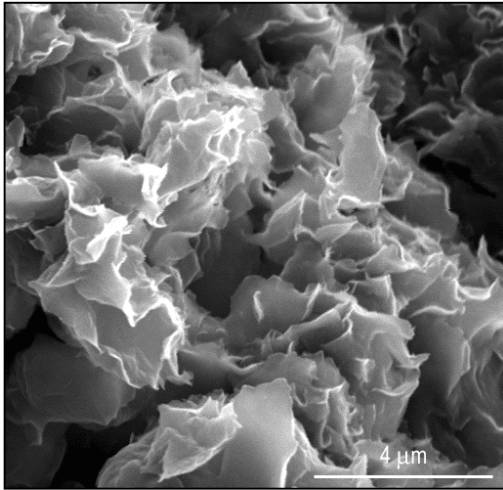


Figure 4-11. Micrographs of the salt hydrothermally treated clays. The microstructure is typical of untreated MX-80 with the same bulk density.

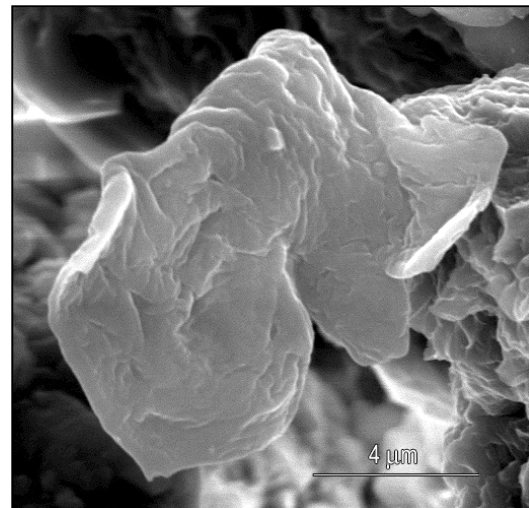
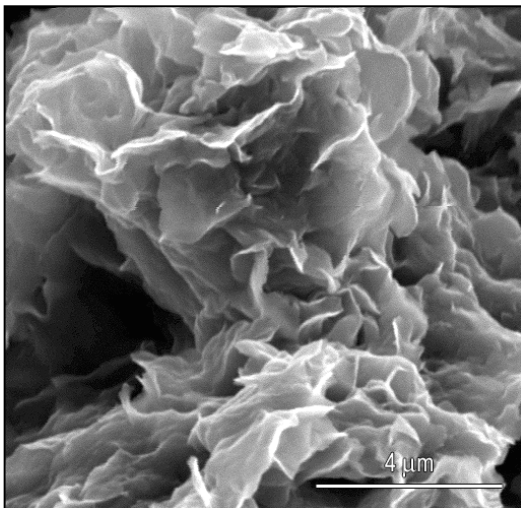


Figure 4-12. Example of large voids (left) and big, dense aggregates (right) in hydrothermally treated salt clay (air-dry powder in contact with 10% salt water while being heated).

The conclusion from the XRD study respecting the size of aggregates is hence supported, and the higher conductivity of the hydrothermally treated, very salt clays is explained by the wider voids. Crystals of halite and gypsum were occasionally found (Figure 4-13). They are estimated to make up less than 1 weight percent in the clays and cannot have affected the hydraulic conductivity of the hydrothermally treated clays.

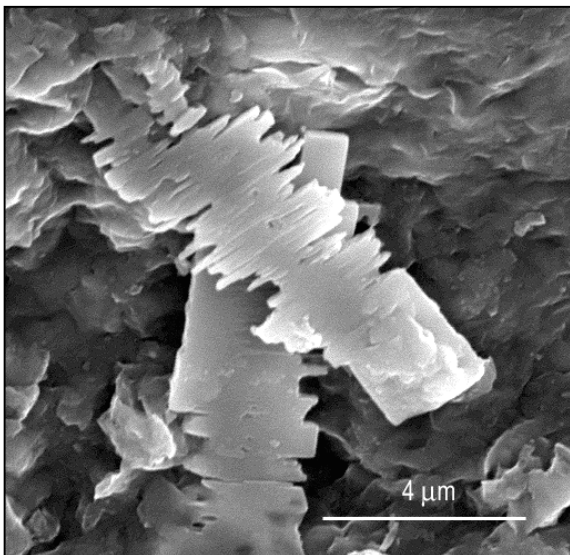
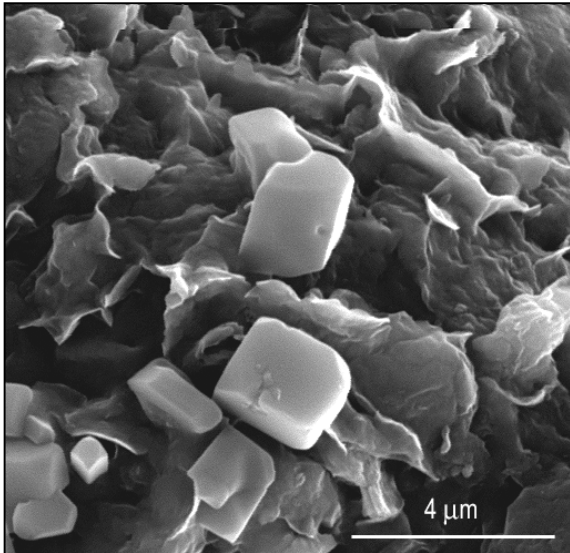


Figure 4-13. Crystals precipitated in the smectite particle matrix of hydrothermally treated salt clay (air-dry powder in contact with salt water while being heated). Upper: Halite. Lower: Gypsum.

5 Discussion and conclusions

5.1 General

The present study comprised laboratory test series with MX-80 clay under conditions that resemble those in a deposition hole in a KBS-3 repository if it is located in rock with very salt, Na-rich groundwater.

5.2 Hydraulic conductivity and swelling pressure

The major outcome of the physical tests is as follows:

- The hydraulic conductivity and swelling pressure of the hydrothermally treated clay samples are on the same order of magnitude as of untreated clay.
- Comparison with illitic clay shows that the latter are much more permeable, i.e. more than a hundred times higher than for the hydrothermally treated salt clays in the present study, which hence indicates that illitization to a practically important extent did not take place. This is obvious also from the fact that while illitic clays exhibit very low swelling pressures the hydrothermally treated clays had swelling pressures on the same order of magnitude as untreated MX-80.

5.3 Mineral changes

XRD

No significant change from the typical mineralogy of untreated MX-80 was found for hydrothermal treatment of clay saturated with 10 and 20% NaCl solution, except for some very slight neoformation/alteration of illite-smectite mixed layers or irreversible partially collapsed phases in the 20% NaCl solution. For dry clay exposed to 20% NaCl solution changes were identified although they were still very limited. Here, formation of Na-illite or fully contracted layers took place and Mg was concluded to have migrated from octahedral lattice positions to interlamellar sites, implying partial dissolution.

Major conclusions from the experiments were:

- The thickness of the montmorillonite particles were comparable to that of untreated MX80 montmorillonite for the hydrothermally treated clay saturated with NaCl solutions, while it was significantly larger for the air-dry clay exposed to such solutions at heating to 110°C. The larger thickness may be an example of Ostwald ripening or aggregation with simultaneous cementation by precipitated silicious matter.

- For the air-dry clay exposed to salt solutions at 110°C followed by percolation with distilled water the interlamellar space was occupied by a mixture of bi- and monovalent cations, of which Mg dominates. The asymmetric second order peak of montmorillonite indicates the presence of neoformed/altered illite-smectite mixed layers or the existence of irreversible partially collapsed phases. Since mixed-layers was not identified in the TEM study, we assume that it is a matter of collapsed phases.
- The ion occupation of the interlamellar space is more complex than in the saturated series. The 20% NaCl solution showed the strongest changes.

TEM EDX

The major conclusions from this study were:

- Replacement of octahedral Mg by Al yielding a drop in interlayer charge was found especially in the air-dry clay powder heated to 110°C under simultaneous exposure to NaCl solutions.
- Silicious matter, partly as quartz or cristobalite may have precipitated. The silica may have originated from tetrahedral positions in the montmorillonite lattice where aluminum can have replaced it, hence forming beidellite. It may also have resulted from dissolution of the smectite, possibly as an effect of exposure to water vapor /13/.
- Beidellite is believed to be present as very thin particles in the air-dry clay powder heated to 110°C under simultaneous exposure to NaCl solutions. They are probably not neo-formed but represent montmorillonite lamellae with the silicons replaced by aluminum.
- Electron diffraction analysis showed both the typical turbostratic arrangement in untreated MX-80 and regular orientation of thin stacks representing montmorillonite or beidellite.

5.4 Microstructure

The SEM study showed that the typical porous gels formed in voids between dense and large aggregates were frequent also in the salt, hydrothermally treated clays. This explains why the hydraulic conductivity of the clays after saturation and percolation with distilled water was not very significantly higher than of untreated MX-80 clay. Still, it exceeded that of untreated clay and this is explained by the SEM study, which showed frequent larger voids and bigger aggregates in the hydrothermally treated clays.

5.5 Final statements

It is concluded that MX-80 clay saturated with or exposed to concentrated NaCl solutions at 110°C, i.e. conditions resembling those of the buffer clay close to the hot canisters in deposition holes, underwent only slight mineralogical changes in the 30 days long hydrothermal period. They had the form of collapse of montmorillonite stacks, conversion to beidellite, and formation of stable aggregates that are larger than in untreated MX-80. The tendency to collapse is believed to be partly caused by neoformation of sodium illite. The mechanical stability of the aggregates is probably due to cementation by precipitation of silicious matter that was set free by the beidellitization or by dissolution of smectite stack edges. In the air-dry clay exposed to NaCl solutions the process may be related to vapor attack.

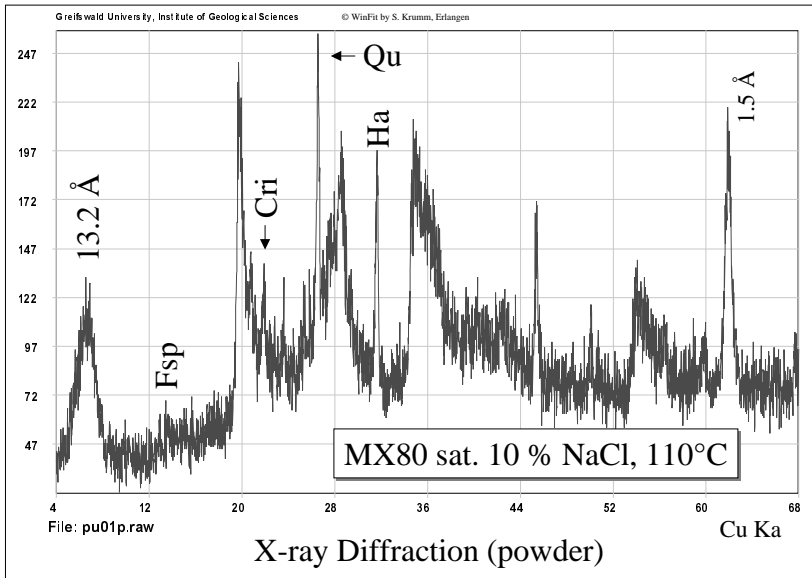
Since the temperature was higher than in a KBS-3 repository and the salt content appreciably higher than what is normally found at 500 m depth in Swedish crystalline rock, these processes may not be significant in the buffer clay. On the other hand, the hydrothermal conditions in the lab study prevailed only for a month while they will last for much longer time in the repository.

6 References

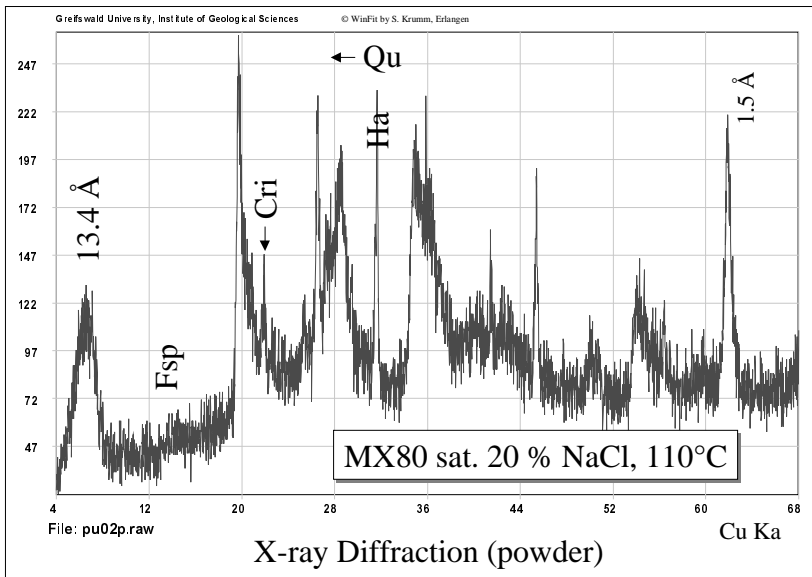
- /1/ **Pusch R, Karnland O, 1988.** Hydrothermal effects on montmorillonite. A preliminary study.
SKB TR 88-15, Swedish Nuclear Fuel and Waste Management Co
- /2/ **Pollastro R M, 1985.** Mineralogical and morphological evidence for the formation of illite at the expense of illite/smectite.
Clays and Clay Minerals, Vol. 33 (pp.265–274)
- /3/ **Nadeau P H, Wilson M J, McHardy W J, Tait J M, 1985.** The conversion of smectite illite during diagenesis: Evidence from some illitic clays from bentonites and sandstones.
Mineral. Mag., Vol. 49 (pp. 393–400)
- /4/ **Inoue A, Kohyama N, Kitagawa R, Watanabe T, 1987.** Chemical and morphological evidence for the conversion of smectite to illite.
Clays and Clay Minerals, Vol. 35 No. 2 (pp. 111–120)
- /5/ **Gueven N, Carney L L., Ridpath B E, 1987.** Evaluation of geothermal drilling fluids using a commercial bentonite and a bentonite/saponite mixture.
Contr. Rep. Sandia 86-7180, SANDIA Nat. Labs. Albuquerque, New Mexico, USA
- /6/ **Tardy Y, Touret O, 1986.** Hydration energies of smectites. A model for glauconite, illite and corrensite formation.
Institut. De Geologie, Univ. Louis Pasteur and Centre de Sedimentologie, Strasbourg
- /7/ **Bannister R A, 1943.** Brammalite (Sodium Illite) a new mineral from Llandebie, South Wales.
Mineralogical Magazine, Vol. 26 (pp. 304–307)
- /8/ **Frey A A, 1969.** A mixed-layer paragonite-phengite of low-grade metamorphic origin.
Contribution of Mineral Petrology, Vol. 24 (pp.63–65)
- /9/ **Kasbohm J, Venz C, Henning K-H, Herbert H-J, 2000.** Zu Aspekten einer Langzeitsstabilität von Bentonit in hochsalinaren Lösungen. In: Hermanns Stengelse R & Plötze M.
Berichte der Deutschen Ton- und Tonmineralgruppe e.V. DTTG2000, Jahrestagung Zuerich, 30.8.–1.9.2000 (pp. 158–170).
- /10/ **Pusch R, Karnland O, Hökmark H, 1990.** GMM – A general microstructural model for qualitative and quantitative studies of smectite clays.
SKB TR 90-43, Swedish Nuclear Fuel and Waste Management Co

- /11/ **Pusch R, 1994.** Waste Disposal in Rock. Developments in Geotechnical Engineering, 76.
Elsevier Publ. Co. ISBN:0-444-89449-7.
- /12/ **Pusch R, 1970.** Use of clays as buffers in radioactive repositories.
SKBF/KBS TR 83-46, Swedish Nuclear Fuel and Waste Management Co
- /13/ **Pusch R, 2000.** On the effect of hot water vapor on MX-80 clay.
SKB TR-00-16, Swedish Nuclear Fuel and Waste Management Co

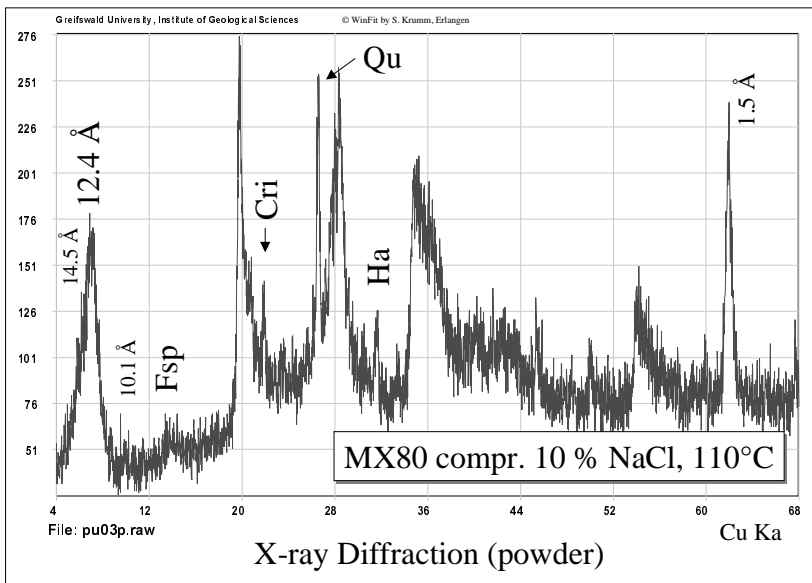
XRD analysis



Legend:
 Fsp – feldspar
 Cri – cristobalite
 Qu – quartz
 Ha – halite



Legend:
 Fsp – feldspar
 Cri – cristobalite
 Qu – quartz
 Ha – halite

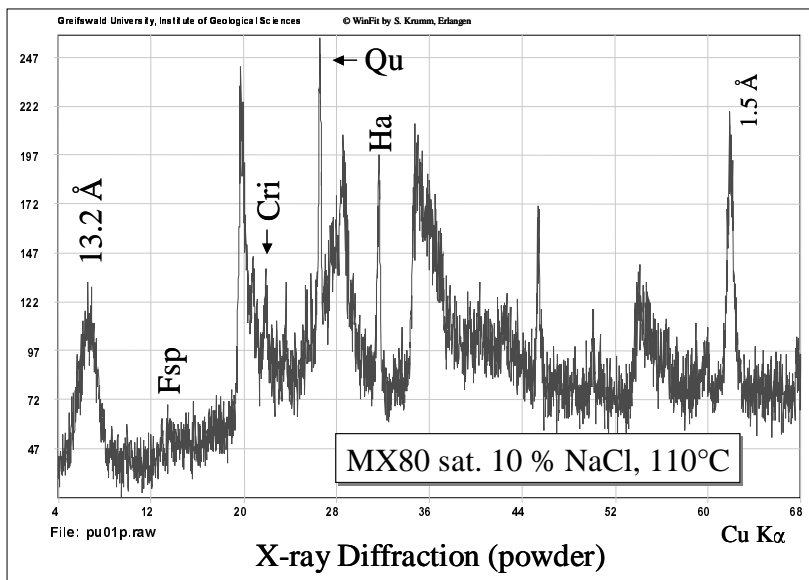


Legend:

- Fsp – feldspar
- Cri – cristobalite
- Qu – quartz
- Ha – halite

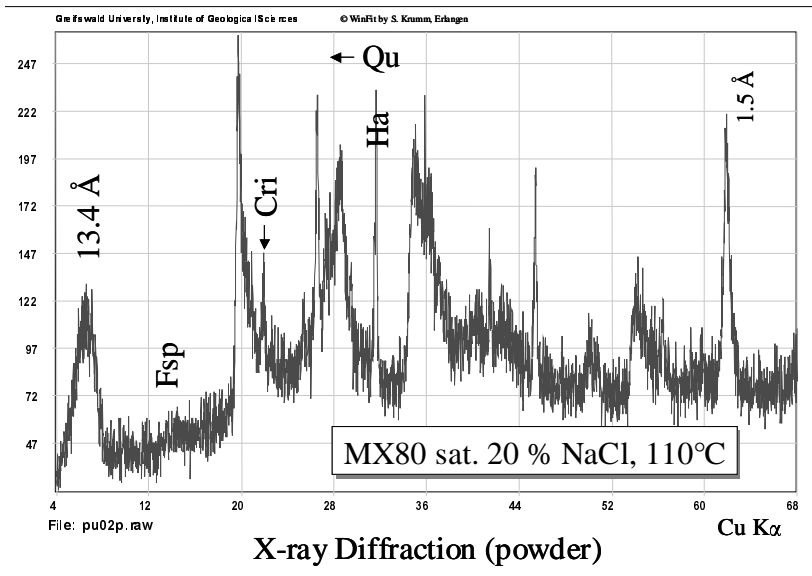
X-ray Diffraction (powder preparation, bulk samples)

MX80 – hydrothermal NaCl-treatment



Legend:

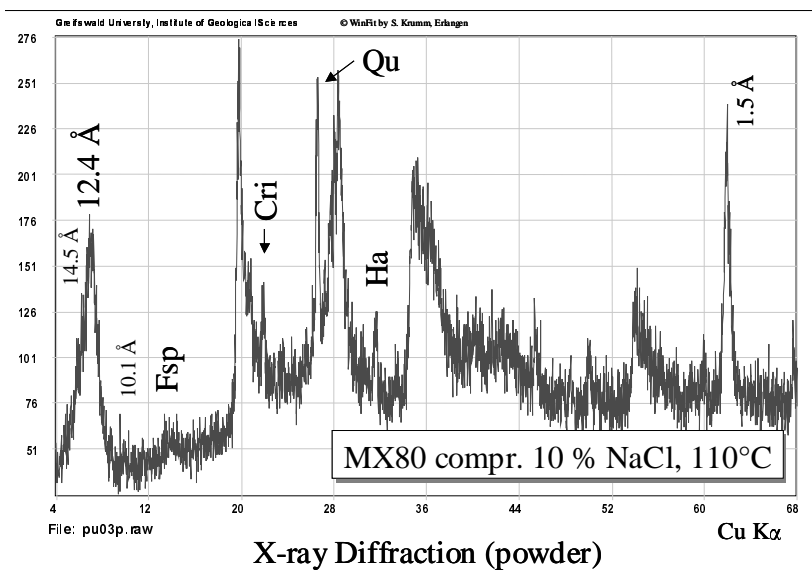
- Fsp – feldspar
- Cri – cristobalite
- Qu – quartz
- Ha – halite



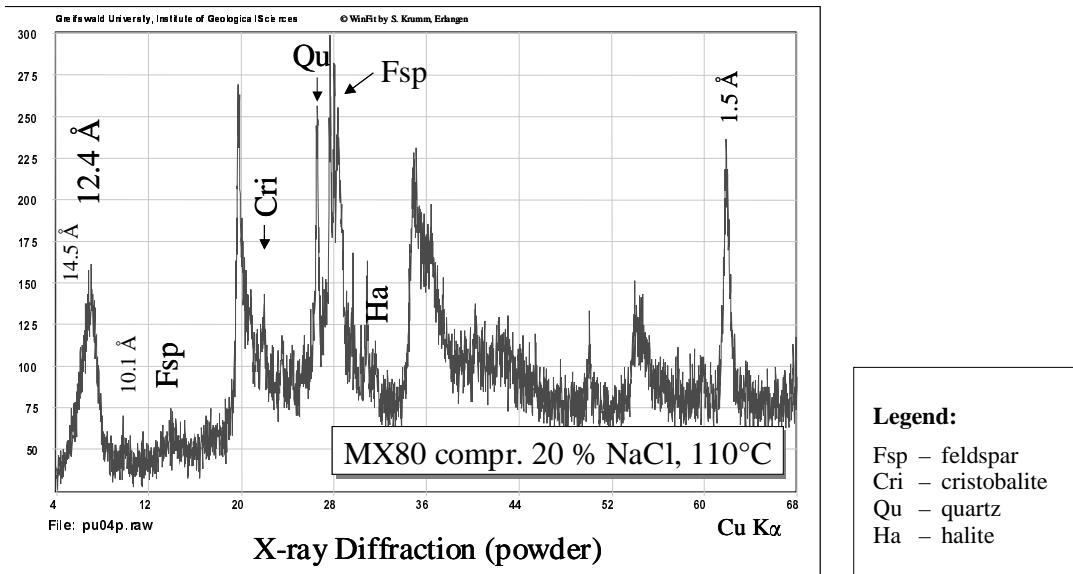
Legend:
 Fsp – feldspar
 Cri – cristobalite
 Qu – quartz
 Ha – halite

Remarks to saturated series:

- no illite or complete contracted layers found,
- symmetric montmorillonite peak at 13.4 Å,
- mineral matter: montmorillonite, quartz, cristobalite, feldspar (comparable to untreated MX80); halite caused by treatment.



Legend:
 Fsp – feldspar
 Cri – cristobalite
 Qu – quartz
 Ha – halite

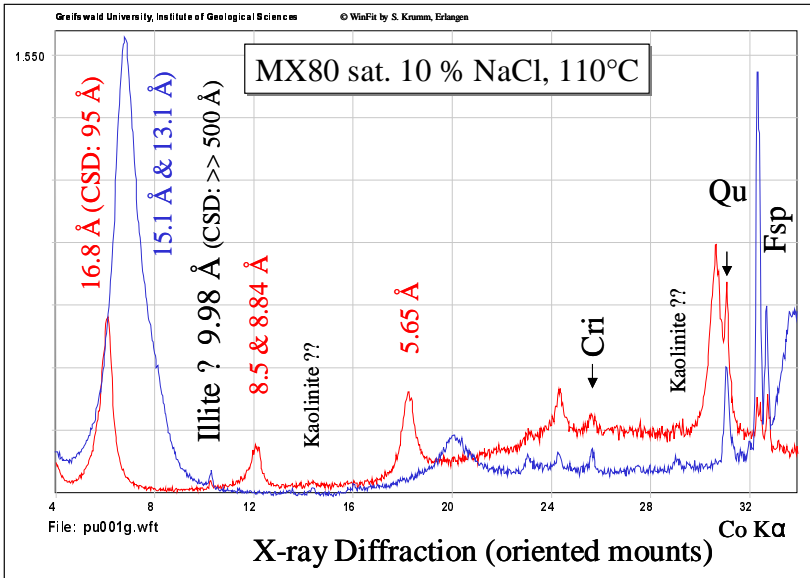


Remarks to compressed series:

- Na-illite or full contracted layers in traces found (10.1 Å),
- asymmetric montmorillonite peak composed by two symmetric peaks at 14.5 Å and 12.4 Å (mixture of mono- and bivalent cations in the interlayers, e.g. Na and Mg),
- origin of Mg in interlayers probably from octahedral layers, that means dissolution processes are present,
- mineral matter: montmorillonite, quartz, cristobalite, feldspar (comparable to untreated MX80); Na-illite or full contracted layers and halite caused by treatment,
- feldspar especially recognizable in the compressed sample treated by 20%NaCl-solution, that could mean in this sample the highest degree of dissolution is present.

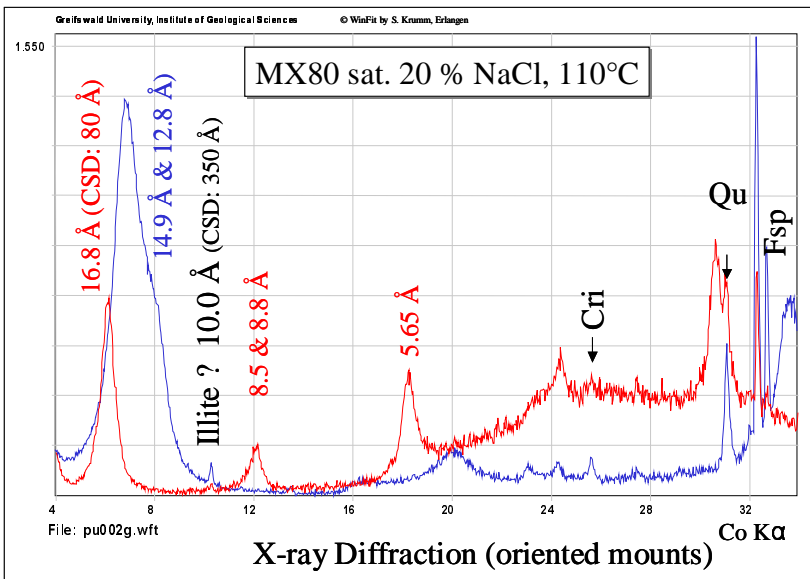
X-ray Diffraction (oriented mounts, < 2 μm)

MX80 – hydrothermal NaCl-treatment



Legend:

Fsp – feldspar
Cri – cristobalite
Qu – quartz
CSD – “Coherent Scattering Domains” comparable with averaged thickness of clay mineral particle



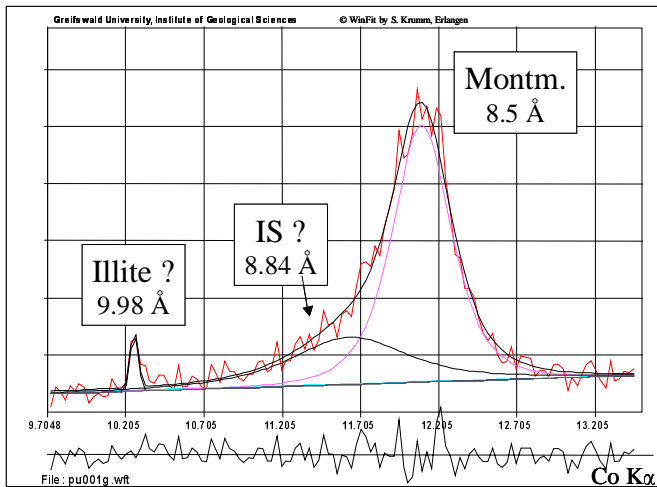
Legend:

Fsp – feldspar
Cri – cristobalite
Qu – quartz
CSD – “Coherent Scattering Domains” comparable with averaged thickness of clay mineral particle

Remarks to saturated series:

- montmorillonite is characterized by complete swelling ability (16.9 Å in glycol-saturated oriented mounts) and the typical positions of the (002)- and (003)-peaks for montmorillonite,

MX80 sat. 10 % NaCl, 110°C



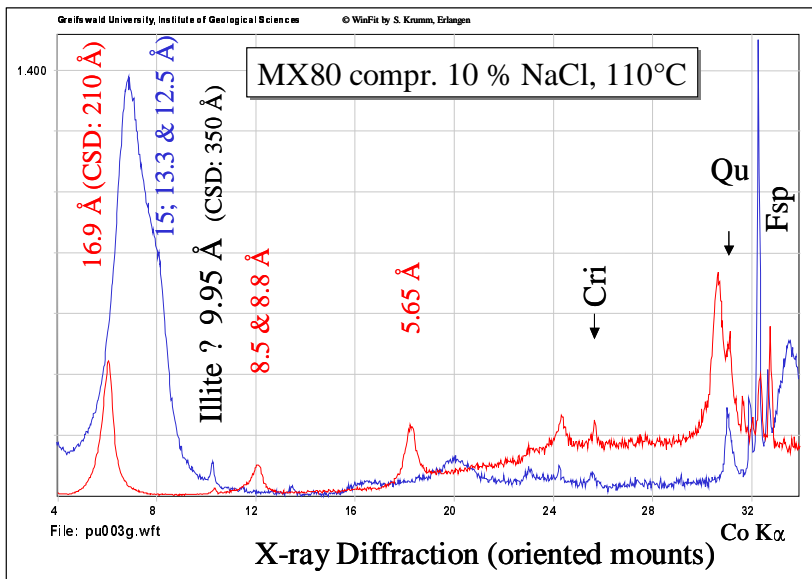
X-ray Diffraction (oriented mounts)
EG-saturated

- non-symmetric montmorillonite peak at 15 Å in air dried preparation, that means:
 - o interlayers of the air dried montmorillonite are occupied by a mixture of bi- and monovalent cations (dominated by bivalent cations),
 - o for bivalent cations e.g. Mg is assumed; this is an indication for dissolution processes, because Mg should cause from the octahedral layer only,
- traces of illite or complete contracted layers found,
- traces of kaolinite (7.17 Å, 3.57 Å) are detected only in the saturated sample by 10% NaCl-solution.

Visualization of the asymmetric second order peak of montmorillonite at 8.5 Å composed by two peaks after deconvolution

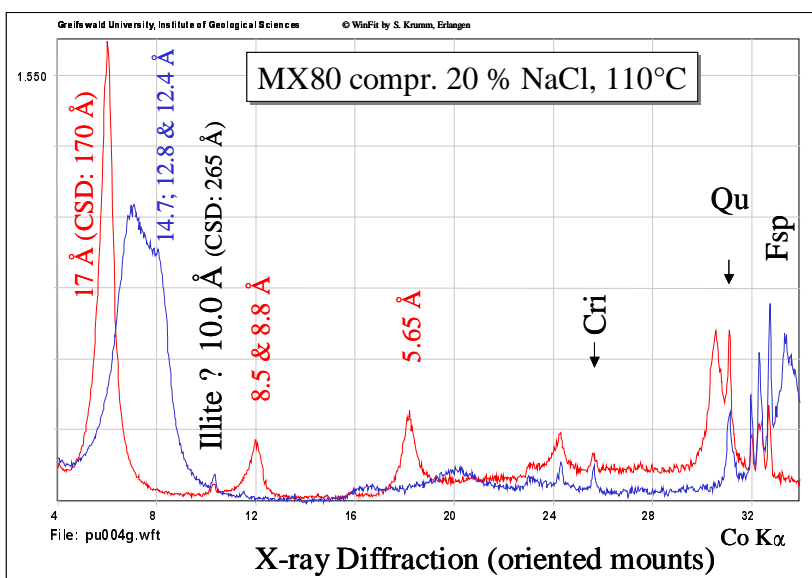
- mineral matter: montmorillonite, illite or complete collapsed phase, quartz, cristobalite, feldspar, IS or partially collapsed phase.

The second order peak of montmorillonite at 8.5 Å (glycol-saturated) shows an asymmetric shape composed by two interferences after WinFit-deconvolution (see figure above). That could indicate the presence of neoformed/alternated illite-smectite mixed layers or the existence of irreversible partially collapsed phases. Because we have not found any mixed layers in this sample by TEM, we assume the last one. This situation is also to observe in the saline saturated sample by 20% NaCl-solution.



Legend:

Fsp – feldspar
 Cri – cristobalite
 Qu – quartz
 CSD – “Coherent Scattering Domains” comparable with averaged thickness of clay mineral particle



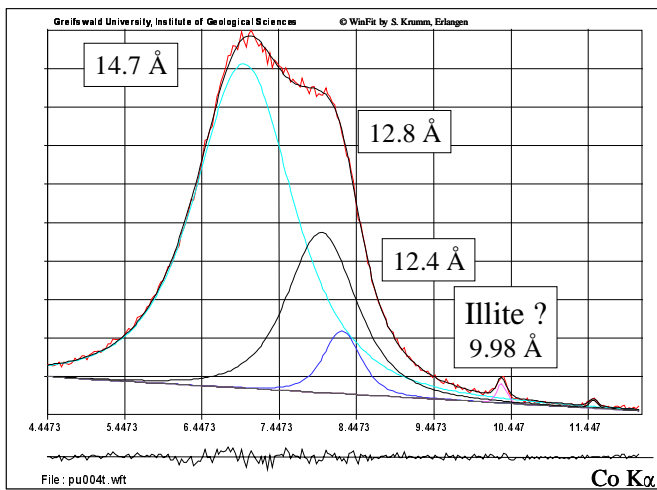
Legend:

Fsp – feldspar
 Cri – cristobalite
 Qu – quartz
 CSD – “Coherent Scattering Domains” comparable with averaged thickness of clay mineral particle

Remarks to compressed series:

- basically comparable to the explanations concerning the saturated samples,
- the occupation of the interlayers in the air dried montmorillonite is more complex in the compressed series than in the saturated series; a sufficient deconvolution is only possible with three peaks (four interferences are also not to exclude); this more complex situation in the interlayers indicates a higher degree of dissolution (because more cations are available); a higher concentrated solution enforced this process.

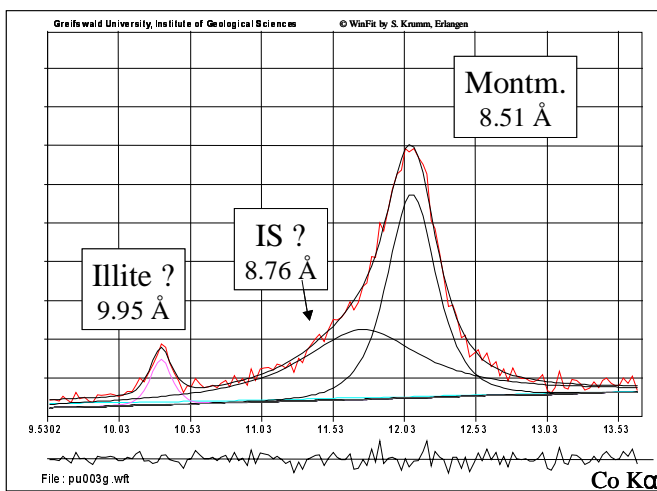
MX80 compr. 20 % NaCl, 110°C



X-ray Diffraction (oriented mounts)
Air dried

Asymmetric shape of the main montmorillonite peak in air dried oriented mounts.

MX80 comp. 10 % NaCl, 110°C



X-ray Diffraction (oriented mounts)
EG-saturated