

**Fe-Bentonite** 

Experiments and Modelling of the Interactions of Bentonites with Iron



Gesellschaft für Anlagenund Reaktorsicherheit (GRS) mbH

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## Kurzfassung

# Eisen-Bentonit – Untersuchung und Modellierung der Wechselwirkung von Bentoniten mit Eisen

Im Rahmen des vom Bundesministerium für Wirtschaft und Technologie (BMWi) geförderten FuE-Projektes 02E10538 wurden von der GRS, der Universität Greifswald und der University of Science, Hanoi, Vietnam, im Zeitraum 2009–2011 modelltheoretische und experimentelle Untersuchungen an Bentoniten durchgeführt.

Zielsetzung dieses Projektes war es, durch Auswertung verfügbarer Informationen und durch gezielte Experimente ein vertiefendes Verständnis über die komplexen Wechselwirkungen zwischen Bentoniten im Kontakt zu Eisen (Abfallbehältern) und salinaren Lösungenzu gewinnen sowie die erzielten Ergebnisse für die Sicherheitsanalyse verwertbar darzustellen.

Bei der Planung der Entsorgung hochradioaktiver Abfälle (HAW) in tiefen geologischen Formationen werden konditionierte Bentonite als Verfüllmaterial im Bereich der Einlagerung und/oder in Schächten als Komponente von Verschlusssystemen in Betracht gezogen. Eine Schlüsselfunktion für den Sicherheitsnachweis haben in diesem Zusammenhang die Prognostizierbarkeit der langfristigen Dichtwirkung der Bentonitbarriere. Gefragt sind die langfristig zu erwartenden rheologischen Eigenschaften der Bentonite, wenn es infolge von Behälterkorrosion zur Bildung von mobilem Eisen kommt und dieses durch geochemische Austauschprozesse die eingesetzten Bentonite verändert.

In die Untersuchungen einbezogen wurden neben MX80 handelsübliche Variationen von klassischen Bentoniten (Friedland-, Geohellas-, Vietnam- und API-Tone) sowie Bentonite, die von der Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) für den Einsatz in Gorleben in Betracht gezogen werden. Als Versuchslösungen wurden gesättigte NaCI- und MgCl<sub>2</sub>-reiche (IP21)-Lösungen sowie artifizielles Formationswasser aus dem Opalinuston-OPWC (Mt. Terri, Schweiz) eingesetzt.

Im Rahmen des Arbeitsprogrammes erfolgte die analytische und mineralogische Typisierung der verschiedenen Bentonite unter besonderer Berücksichtigung der zu diesem speziellen Thema verfügbaren Literatur. Experimentell untersucht wurde die Auswir-

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kung der Oxidation und Ausfällung von gelöstem Eisen auf das Quellvermögen und auf die Permeabilität von kompaktierten Bentoniten ( $\rho = 1,6 \text{ g cm}^{-3}$ ) in Abhängigkeit von der Temperatur (25 °C, 60 °C, 90 °C). Die Zugabe von Eisen zu den Versuchslösungen erfolgte in Form von FeCl<sub>2</sub> in Konzentrationen von 0,1 bis 0,4 mol L<sup>-1</sup>. In einer weiteren Versuchsreihe wurde den Bentoniten metallisches Eisen in Pulverform (10 Gew.%) beigemengt. Aufgrund der Vielzahl möglicher Einflussfaktoren sind die erzielten Ergebnisse der Experimente in die Rubrik qualitativ bzw. semi-quantitativ einzuordnen.

Die Charakterisierung der Bentonite zur Ermittlung geochemischer und morphologischer Veränderungen der Fraktionen erfolgte mittels X-Ray Fluoreszenz (XRF), Röntgendiffraktometrie (XRD), Transmissionselektronenmikroskopie (TEM) und Fourier-Transformations-Infrarotspektroskopie (FT-IR). Für die Analyse der Lösungen und ihrer Komponenten wurden ein Spektrometer mit induktiv gekoppeltem Plasma (ICP) eingesetzt. Für die modellmäßige Betrachtung thermodynamischer und kinetischer Abhängigkeiten beim reaktiven Stofftransport kam das Programm EQ3/6 zur Anwendung.

Bereits in der Literatur spiegelt sich in der Beschreibung der Strukturformeln die heterogene Mineralogie der klassischen Bentonit-Typen z. B. eines MX80 wider. Generalisierte Aussagen zum Einfluss von Eisen auf Bentonite und thermodynamisch induzierte Umwandlungsprozesse, sind daher differenziert zu interpretieren. Dies gilt sowohl für die rheologischen Eigenschaften als auch für Stabilitätsbetrachtungen.

Die ausgewertete Literatur und die vorliegenden experimentellen Ergebnisse bestätigen die These, dass Eisen den mineralogischen-chemischen Umwandlungsprozess von Bentonite beschleunigt. Die Oxidation von Eisen und die daraus resultierenden alkalischen pH-Bedingungen verstärken die Herauslösung von SiO<sub>2</sub> aus dem Kristallgitter und damit die Auflösung der Bentonite. Der Prozess ist umso intensiver je höher die Temperatur und das Konzentrationsverhältnis Eisen/Ton sind. Gleiches gilt für die Salinität der Lösung. Die mineralogischen Veränderungen korrelieren gleichermaßen mit der Entwicklung der Permeabilität und dem Quellvermögen der Bentonite.

Ausschlaggebend für die prognostizierbare Entwicklung der Permeabilität ist die Kenntnis der Thermodynamik bei der Auflösung der Smektitfraktion (z. B. Montmorillonit). Mit der Auflösung dieser Mineralfraktion reichert sich SiO<sub>2</sub> in der Lösung an. Bei der Auflösung zu unterscheiden sind offene (SiO<sub>2</sub>-Defizit) und geschlossene (SiO<sub>2</sub>-Überschuss) aquatische Systeme. Im offenen System wird SiO<sub>2</sub> mit der Lösung aus dem System kontinuierlich ausgetragen, während es sich im geschlossenen System

SiO<sub>2</sub> anreichert. Durch Mineralneubildungen (Smektitisierung/Illitisierung) oder Ausfällung wird der Lösung wiederum SiO<sub>2</sub> entzogen. Voraussetzung für die Smektitisierung ist, dass SiO<sub>2</sub> in der Lösung im Überschuss zur Verfügung steht. In der Natur nachgewiesen wurde dieser Effekt in tropischen Bereichen bei der Verwitterung von Serpentiniten. Der Prozess der Illitisierung der Smektite setzt ein, wenn SiO<sub>2</sub> der Lösung schneller entzogen wird als es durch Mineralauflösung entsteht. Im Versuch mit MX80-, bzw. Friedland Bentonit beschleunigte eine erhöhte Eisen-Konzentration in der Lösung diesen Umwandlungsprozess und die Bildung der weniger quellfähiger Mixed-Layer Minerale Berthierin/Saponit bzw. Chlorit/Saponit. Generell führten die Illitisierung und die Bildung von Mixed-Layern (ML) jeweils zu einer Erhöhung der Permeabilität in den untersuchten Bentoniten. Den gleichen Effekt hätte die, durch die Bildung von amorphem SiO<sub>2</sub> hervorgerufene, Verkieselung bzw. Silifizierung der Bentonite. Solange das Mikrogefüge des Bentonits nicht durch Silifizierung oder anderen Ausfällungen (Fe) beeinträchtigt wird führt eine Erhöhung des Quelldrucks auch zu einer Verbesserung (Reduzierung) der Permeabilität. Mit Auftreten solcher Ausfällungen gilt diese Beziehung nicht mehr, sondern die Permeabilität verbessert sich trotz Verringerung des Quelldruckes und letztendlich erhöht sich die Permeabilität schlagartig, obwohl der Quelldruck im Wesentlichen unverändert hoch ist. Somit ist in Zukunft dem Aspekt Zementation durch Silifizierung verstärkt Aufmerksamkeit zu widmen. Die Effekte treten womöglich schneller und gravierender ein als die häufig diskutierten Aspekte einer möglichen Illitisierung.

FT-IR-Analysen weisen darauf hin, dass Kinetik und Auflösungspotential bzw. die Stabilität von Montmorilloniten vorrangig durch die spezifische Kationenbesetzung in den Oktaeder- und Tetraederschichten bestimmt werden. So zeigten gleichartige Montmorillonite unterschiedliche Auflösungsgeschwindigkeiten bzw. Stresspotentiale, welche u. a. mit den ermittelten Eisen- und Magnesiumgehalten in den Oktaederschichten korrelieren. Ein Indikator für das Stresspotential ist dabei das Verhältnis der Radien der Kationen untereinander und in Bezug auf den Radius von Aluminium, das die Oktaederplätze belegt. Diese sogenannte "Sleeper"- bzw. "Sprinter"-Montmorillonite zeigen eine ausgeprägte Affinität zur Stabilität bzw. Selbstauflösung. Die Ergebnisse legen den Schluss nahe, dass durch eine gezielte Beachtung der Zwischenschicht- und Oktaederschichtbelegung die Stabilität der künftigen Bentonitbarriere gezielt beeinflusst werden kann. Durch die Konditionierung von Bentoniten mit einer solchen "Sleeper"-/"Sprinter"-Fraktion könnten ggf. definierte rheologischen Eigenschaften erzielt werden. Ein "idealer" Bentonit sollte über kinetische Eigenschaften verfügen, die bei thermodynamischer Beanspruchung unerwünschte Umwandlungsprozesse ausschließen.

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Im Hinblick auf ihren Einsatz im Salz sind bevorzugt Bentonite mit einem hohen Anteil an ML-Mineralen (Illit/Smektit ML) zu verwenden, da diese Bentonite über das Potenzial verfügen SiO<sub>2</sub> zu puffern. Die Pufferwirkung, die auf der Neubildung von quellfähigem Smektit beruht, verhindert die Ausfällung von SiO<sub>2</sub>. Die Reduzierung der Auflösung von Smektit und der Ausfällung von SiO<sub>2</sub> wirkt insbesondere der Vergrößerung der Permeabilität entgegen. Abgeleitet aus den Ergebnissen wird der Einsatz von "Sleeper" Bentoniten empfohlen, die über ein geringes Stresspotential verfügen. Mit Blick auf die Dichtwirkung von Verschlusssystemen sind "Sprinter"-Bentonite weniger geeignet.

Ein im Rahmen dieses Projektes entwickeltes Excel-Programm ermöglicht die Charakterisierung von Bentoniten und deren Einordnung in die Kategorien "Sleeper" / "Sprinter". Grundlage des Programmes sind die chemischen Analysedaten vom Bentonit. Dass die Charakterisierung erforderlich ist, verdeutlicht die Wiederholung der Analyse von handelsüblichen MX80. Der von [MAD 1998] beschriebene MX80 weist diesen als "Sleeper" aus, während der MX80 von 2005 über die Eigenschaften eines "Sprinters" verfügt.

Im Projektverlauf hat sich die experimentelle Ermittlung der effektiven Porosität von Bentoniten als problematisch herausgestellt. Die erzielten Ergebnisse waren mehrdeutig und nicht reproduzierbar. Entwicklungsbedarf besteht auch hinsichtlich der gezielten Konditionierung von Bentoniten.

## Abstract

The main objectives of this study were to enhance the understanding of the interactions of bentonites with steel containers in the near field of a repository in salt formations and to determine missing experimental thermo-hydraulical-chemical and mineralogical data needed for the THC modelling of the interactions of bentonites with iron. At the beginning of this project a literature review helped to clarify the state of the art regarding the above mentioned objectives prior to the start of the experimental work. In the following experimental programme the hydraulic changes in the pore space of compacted MX80 bentonites containing metallic iron powder and in contact with three solutions of different ionic strength containing different concentrations of Fe<sup>2+</sup> have been investigated. The alterations of MX80 and several other bentonites have been assessed in contact with the low ionic strength Opalinus Clay Pore Water (OCPW) and the saturated salt solutions NaCl solution and IP21 solution. Under repository relevant boundary conditions we determined on compacted MX80 samples with the raw density of 1.6 g/cm<sup>3</sup> simultaneously interdependent properties like swelling pressures, hydraulic parameters (permeabilities and porosities), mineralogical data (changes of the smectite composition and iron corrosion products), transport parameters (diffusion coefficients) and thermal data (temperature dependent reaction progresses). The information and data resulting from the experiments have been used in geochemical modelling calculations and the existing possibilities and limitations to simulate these very complex near field processes were demonstrated.

The main conclusion of this study is that the alteration of bentonites in contact with iron is accentuated and accelerated. Alterations in contact with solutions of different ionic strength identified by the authors in previous studies were found be much more intensive in contact with metallic iron and at elevated temperatures. The observed chemical and mineralogical changes of the smectites are well understood. Similar changes of the smectites occur in low as well as in high saline solutions with the sole difference that high ionic strength solutions lead to faster and stronger changes. Experimentally observed changes of swelling pressures and permeabilities are well understood and fit onto a coherent picture of mineral evolution. This picture is dependent on the Fe and Si activity in the bentonite-solution system. The observed mineralogical changes could be reproduced by geochemical modelling. The investigation of a large number of different bentonites within the framework of this study showed however that bentonites different wery much from each other and behave differently under similar boundary conditions.

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Favourable and less favourable bentonite compositions were identified. The results of this study have led to the definition of requirements for the bentonites to be used in the near field of a HLW repository.

Summing up all the different findings of this study we conclude that the long term behaviour of the technical barrier bentonite in the near field of a HWA repository is controlled by the fate of Si in the system. Bentonites with mixed layers (%S < 100 %) can take up Si and form new montmorillonite layers. Such bentonites can inhibit or at least slow down the silica precipitation which is responsible for important permeability changes. An ideal bentonite would be a sleeper with %S = 70 %.

## 1 Introduction

Compacted bentonites, pure bentonites as well as clay-sand mixtures are considered to be important technical barriers in all existing concepts for the final disposal of high radioactive wastes in all kind of geological formations. The slow transport of radionuclides through these barriers is a key boundary condition in long term assessment analyses. Changes of the parameters, which control the transport, i. e. porosity, permeability and diffusivity, have an important impact on the results of the long term safety assessment calculations. The interactions of the bentonite barrier with the waste containers may trigger such changes. These must therefore be predictable and quantifiable in the long term. The question of container corrosion and the impact on the long term performance of the bentonite barrier is discussed broadly on international boards of the NEA, the EU and in the national R&D programmes. So far there is no definitive answer to the question of whether the complex processes at the contact bentonite/canister (container corrosion, transport of corrosion products into the pore space of the bentonite, short and long term changes of the mineralogy and chemistry of the expandable smectites etc.) have a decisive or only marginal influence on the long term performance of the bentonite barrier. This project aims at clarifying some of the related open questions.

## 2 Objectives of this study

The main objectives of this study were to determine still missing experimental data and to create a fundamental understanding of the interactions of bentonites with steel containers in the near field of a repository in salt formations. In an experimental programme the hydraulic changes in the pore space of compacted bentonites were investigated and the occurring alterations of MX80 and several other bentonites were assessed. Under repository relevant boundary conditions we have tried to determine simultaneously properties which depend on each other like swelling pressures, hydraulic parameters (porosities and permeabilities), mineralogical data (iron corrosion products and changes of the clay mineralogy), chemical data (diffusion coefficients) and thermal data (temperature dependent reaction progresses). Thus we have collected data for the modelling of these coupled THMC processes. The modelling calculations performed show the existing possibilities and limitations to simulate these very complex near field processes.

### 3 Literature review – state of the art prior to this project

For long term performance assessment analyses of repositories it is important to have reliable information on the influence of the container corrosion on the swelling capacity of bentonites as well as on the influence of the corrosion products on the hydraulic properties of the bentonite barrier.

As one of the results of the EU integrated project *"Understanding and physical and numerical modelling of the key processes in the near-field, and their coupling, for different host rocks and repository strategies*" (NF-PRO) [DEL 2005] published a state of the art report on the chemical processes in the near field of a HAW repository. The main author of this report is also a co-author of the report of [DEL 2005]. The most important conclusions of that report concerning the objectives of this project are repeated below. New results which were published later are also considered here.

# 3.1 Geochemical processes at the HLW-container/bentonite barrier boundary – Container corrosion

The first process which has to be considered in a barrier consisting of compacted bentonite is the saturation of the pore voulme with solution. Container corrosion is accerlerated as soon as the bentonite pore solution comes in direct contact with the container. According to DIN EN ISO 8044 [DIN 8044] corrosion is the physico chemical interaction between a metal and its surroundings which leads to a change of the metal properties and to a substantial damage of its functionality. This interaction is often an electrochemical process and is relatively fast. After failure of the container the interaction between the solution and the waste starts and may lead to a mobilisation and migration of radionuclides through the bentonite barrier and maybe further into the biosphere. Rust is the corrosion product of the iron container which is formed by the iron oxidation with oxygen in the presence of water. Rust is normally a mixture of Fe<sup>2+</sup> oxide and Fe<sup>3+</sup> oxide with the general formula:

$$xFe(II)O \cdot yFe_2(III)O_3 \cdot zH_2O$$
(3.1)

For some metals oxidation leads only to a very thin oxidised film on the uppermost atomic layers at the meltaic surface which protects the material below from further corrosion. Such metals get passivated. However, iron does not form such a protective layers. The corrosion does not stop. The high electric conductivity of the wet rust and its high permeability for oxygen lead to an ongoing corrosion at the rust/iron interface. Rust builds loose structures with low strength. The oxidation leads to a mass and volume increase. Iron corrosion products can migrate into the compacted bentonite and change the hydraulic properties. To measure such effects is one of the objectives of this study.

Under repository conditions the so called hydrogen corrosion will take place. This is a specific corrosion form of metals which leads to the formation of hydrogen in the presence of water at low oxygen contents. The iron surface will be oxidised and iron enters the solution as ions. In an acidic environment protons of the oxonium ions capture electrons and hydrogen is liberated.

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$
 (Oxidation of metal) (3.2)

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$$
 (Reduction of oxonium-ions) (3.3)

The formation of hydrogen may lead to excess pressure and to the development of new water pathways. The first indications of such events which may damage the technical and geological barriers by [NER 1985] have triggered further intensive research. A summary of the results of these studies is given below:

- The rate of hydrogen production is very high until a protective layer has been formed at the iron surface
- The hydrogen production increases with the ionic strength of the solution and with the temperature (but only up to 85 °C; at higher temperatures Fe<sup>2+</sup> hydroxides will be transformed directly into magnetite without hydrogen production)
- The hydrogen production is considerably higher under aerobic conditions and in regions with residual oxygen

Hydrogen can escape by diffusion through the backfill. If the hydrogen transport is slower than the production a pressure increase can occur which may exceed the lithostatic pressure. So far no indication exists that the formation of water pathways induced by gas generation can really seriously damage the bentonite barrier. But there are still no large in-situ investigations to this respect available.

Container corrosion and the chemical conditions in the near field will be influenced by the liberation of  $Fe^{2+}$  from the container surface. The transport of  $Fe^{2+}$  generated by the corrosion is dependent on the hydraulic conditions in the near field. It will be slowed down by the bentonite barrier and the corrosion products.

[SMA 2006a] and [SMA 2006b] are of the opinion that anaerobic steel corrosion is controlled by the formation of a magnetite cover on the steel surface. However such a cover was not observed in several experiments in the presence of bentonite. Iron entered the bentonite during the experiments. The iron surface however stayed blank in spite of intensive corrosion. According to [SMA 2006a] bentonite speeds up iron corrosion because it inhibits the formation of the protective Fe-oxide layer. pH of solution however did not influence Fe-corrosion. Corrosion rates were measured in the pH range between 8.4 and 11. It is assumed the pH of the bentonite pore water in contact with iron is controlled by the buffer capacity of the bentonite.

On the other hand considerably higher corrosion rates were observed at elevated temperatures (50 °C) compared to lower temperatures (30 °C). Fe concentration in the bentonite was highest in the immediate vicinity of the iron/bentonite contact. Two different transport ways through the bentonite are under discussion: 1) through the interlayer space of the smectites and 2) through diffusion in the adherent solution around the mineral grains of the bentonite (montmorillonite, quartz, pyrite). The total amount of iron absorbed by the bentonite in the Swedish experiments was much higher than the concentration decrease of exchangeable cations. This leads to the conclusion that iron liberated from the container by corrosion was directly absorbed by the bentonite. But it was not possible to distinguish by Mössbauer spectroscopy between Fe<sup>2+</sup> and green rust. Possibly Fe<sup>2+</sup> is absorbed on the edges of montmorillonite. This may be clarified by XANES-measurements (X-ray adsorption near edge spectroscopy).

#### 3.2 Transport in compacted bentonites

The transport of solutes is controlled by different processes. A basic transport process is diffusion as a result of molecular motion. This process also takes place in static porewaters and in very small pores. This very slow transport process dominates in argillaceous formations and in compacted bentonites. The intensity of the diffusion controlled transport depends on the porosity and tortuosity of the material. In regions with increased permeability however a flow driven advective transport may dominate. As the intensity of the advection depends not only on porosity and permeability but also on the pressure gradient it is not possible to decide *a priori* if diffusive or advective flow will dominate. In argillaceous rocks which are considered as potential repository host rocks porosities and permeabilities are so low that diffusive transport can be expected. Technically it is feasible (although maybe not desirable) to implement a similar low permeability in the technical barrier bentonite. In a HLW repository compacted bentonites have the function to prevent solutions from getting into contact with the waste or at least to minimise the amount of solution that can reach the waste. Two requirements must be observed. Desirable is a water tight but not entirely gas tight barrier in order to avoid the build-up of gas pressures which may fracture the barrier. Very low permeabilities which impede advective flow and allow only the inevitable diffusive flow can be obtained by the compaction of pure bentonite. In order to avoid critical hydrogen pressures bentonite-sand mixtures are under discussion. Such mixtures may also imply advective flow.

In the literature data can be found for the permeabilities of gas, water and solutions with higher ionic strength. Sometimes pertinent porosities can be found. These data however are not always plausible and sometimes contradictory. Our own measurements on compacted MX80 bentonite with the raw density of 1.6 g/cm<sup>3</sup> revealed a water permeability of  $<10^{-21}$  m<sup>2</sup> and a much higher permeability for NaCl solution,  $10^{-14}$  m<sup>2</sup>. No significant difference between gas permeability ( $1.6 \cdot 10^{-14}$  m<sup>2</sup>) and NaCl-solution permeability ( $6.5 \cdot 10^{-14}$  m<sup>2</sup>) was found. On the other hand [MIE 2003] reported a gas permeability of  $5 \cdot 10^{-13}$  m<sup>2</sup> and a permeability for a Mg-rich IP21 solution of  $< 10^{-21}$  m<sup>2</sup> in a bentonite-sand mixture (50 % MX80 und 50 % sand). Measurements of the pertinent porosities are difficult. Different approaches led to different results [HER 2002].

Several authors have measured diffusion coefficients for iron in bentonites in the range between 10<sup>-14</sup> and 10<sup>-11</sup> m<sup>2</sup>/s [MAD 1991], [IDE 1993], [IDE 2002], [KOZ 1994], [ZHA 2004].

For the modelling of the advective transport permeability and porosity must be known. For diffusive transport the porosity and diffusion coefficients of the interesting ions must be available. Some literature data are available. But no information was found on the changes of these parameters under the influence of the interactions between bentonite and iron. A further objective of this project was therefore to produce such experimental data.

# 3.3 Smectite alteration at the contact between bentonite and iron container

The transport properties of compacted bentonites can change due to porosity changes. Intrusion of corrosion products with their high molar volume reduces the pore space. Changes of the pore space can also be expected by the interactions of the pore solutions with the smectites of the bentonite. Several processes are active. Some like cation exchange are fast. Others like changes in the octahedral layers of the smectites are slower. Even slower are mineralogical changes like dissolution and precipitation of new clay minerals which can change the initial properties of the bentonite barrier drastically.

It is remarkable that only few older publications could be found that describe low temperature iron/bentonites experiments in which no changes of the technicall properties of bentonite like exchangeable cations, CEC, interlayer charge as well as of mineralogical properties were observed [MUL 1991]; [MAD 1998]. Other iron/bentonite experiments have shown a clear loss/decreasing of swelling and CEC, an increasing of hydraulic conductivity and partially clogging processes by Si-precipitation [OSC 1988]; [HER 2004], [BIL 2006]; [CAR 2006], [CAS 2008]; [PER 2010]; [MAR 2010]; [ISH 2008]; [PUS 2010].

A different situation was found when looking at description of mineralogical alterations in iron/bentonite experiments. Many authors have characterised changes in technical properties and also described precipitation of Fe-oxides as well as Fe-oxyhydroxides, but they have denied other mineralogical alterations in the mineral matter ([GUI 2004] – for experiments with magnetite and hematite; [CAR 2006] – with iron/clay = 0.1; [CAR 2006], [CAS 2008]; [ISH 2008]; [STR 2009]; [OSA 2009] – with iron/clay = 0.2). Only few published low temperature experiments with iron/bentonite have shown transformation of smectite into different iron-rich serpentine-type minerals (odonite, berthierine, and cronstedtite), chlorite, trioctahedral smectite, palygorskite, zeolites, and Fe-rich trioctahedral vermiculite ([BIL 2006]; [PER 2008] – with Fe/clay = 0.3; [MOS 2010] – with Fe/clay = 0.5 ... 0.1).

The mineralogical transformation of smectite was modelled by [MON 2005], [WIL 2006a], [WIL 2006b], [MAR 2010] and [SAV 2010a].

[PER 2008] described increasing iron/clay-ratio as a precondition for the neoformation of serpentine-type clay mineral phases. [MOS 2010] underlined the importance of tem-

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perature, initial Fe-amount and the starting pH-value for any mineralogical alteration of smectite.

[BIL 2006] expected alteration of the technical properties and mineralogical composition in less than 10,000 years. [SAV 2010a] have calculated that chlorite growth was not achieved until 5000 years of simulation time and berthierine dominated the solid product assemblage at simulation times greater than 10,000 years. [MON 2005] pronounced that the properties of smectite would be stable up to 10,000 years. [MAR 2010] covered a time frame of 100,000 years in their modelling of compacted MX80 bentonite in Fe<sup>2+</sup>-solutions.

[GUI 2004] investigated the changes of Wyoming bentonite in contact with steel at 80 °C and 300 °C in low ionic strength NaCl and CaCl<sub>2</sub> solutions with and without magnetite and haematite over nine months. No significant chemical changes of the montmorillonite were detected at 80 °C. Obvious was only the rise of the Fe<sup>3+</sup>/Fe<sub>tot</sub> ratio in the clay fraction from 0.55 to 0.9. Analyses of the solutions showed that the system became more oxidising during the experiments. At the end of the experiments montmorillonite contained almost only Fe<sup>2+</sup>. At 300 °C the conditions became reducing. In the presence of Fe-oxides the original montmorillonite was replaced by a trioctahedral Fe<sup>2+</sup> rich saponite like smectite. Simultaneously new feldspars quartz and zeolithes were formed. At 300 °C in the clay fraction of the bentonite the Fe<sup>3+</sup>/Fe<sub>tot</sub> ratio decreased from 0.55 to 0.3 due to the formation of Fe-saponite. At very high temperatures obviously Fe rich clay minerals can be formed which are more stable than the original smectites. The predictability of the long term behaviour of montmorillonite in the presence of steel and corrosion products under the relevant repository temperatures between 25 °C and 90 °C was not enhanced by these experiments.

Detailed mineralogical and chemical investigations of the interactions of smectites and iron were presented by [LAN 2005]. These authors made the following observation. In slightly acidic to medium pH values they observed that at 80 °C significant amounts of iron was corroded and magnetite formed without signs of destabilisation of the smectites. Under alkaline conditions other smectite and iron were destabilised. Beneath magnetite a 1:1 phyllosilicate was formed. A systematic destabilisation of iron and smectites were not affected under the same pH conditions. They observed furthermore that the smectite reactivity rose with rising Fe<sup>3+</sup> content and with rising Na content in the smectite interlayers. [LAN 2005] have developed the following model for the ob-

served processes. The smectite deliberates protons.  $MeFe^{3+}OH$ -groups will be deprotonated preferentially and metallic iron acts as proton catcher. The corrosion of metallic iron is a consequence of the interaction with these protons. The Fe<sup>2+</sup> cations which result from the corrosion will be sorbed at the edges of the smectite particles where they reduce the structural Fe<sup>3+</sup> and migrate into the smectite interlayers in order to compensate the increased interlayer charge. Subsequently Fe<sup>2+</sup> cations migrate from the interlayers into the octahedral layers because of the extreme charge deficiency. At low temperatures this migration will be enhanced by long reaction times and the absence of protons in the di-trigonal void spaces. The destabilisation of smectites is due to the fact that the tetrahedral layers cannot accommodate the newly formed large trioctahedral domains which are built as a consequence of the Fe<sup>2+</sup> migration.

[WIL 2006a] performed theoretical investigations by modelling the system  $AI_2O_3$ -FeO- $H_2O$ -MgO- $Na_2O$ -SiO<sub>2</sub> including Na- und Fe<sup>2+</sup> smectites at 25 °C, 80 °C und 250 °C. They plotted activity diagrams which show the conditions for the transformation of smectites in the presence of iron and discussed two possible reaction pathways under HLW repository conditions:

- 1. transformation of montmorillonite into Fe rich smectites and
- 2. transformation of smectite in non-swelling phyllosilicates like chlorite.

Fe rich smectites (dioctahedral nontronite or Fe-rich saponite) can be encountered in a large variety of geological settings preferably where Fe-rich rocks are decomposed in the air or under water. Fe-rich saponites have been described in weathered tuffs. Fe-rich 1:1 phyllosilicates (berthierine and odonite) are known from laterites and from low metamorphic rocks and hydrothermal systems where they are associated with iron ores. It is supposed that berthierine is a precursor of chlorite. Formation of chlorites is known in sandstones in depth with temperatures of about 90 °C. After the closure of a HLW repository temperatures over 100 °C will be exceeded only at the beginning. Experimental investigations regarding the coexistence of mineral-solution pairs with Fe rich clays like Fe<sup>2+</sup> saponite are not known. Therefore [WIL 2006a] have chosen a theoretical approach and have performed thermodynamical equilibrium calculations. The validity of thermodynamical models with clay minerals has been discussed in the literature on the basis of different hypothesis:

- 1. Clay minerals do not follow the phase rule and should therefore not be integrated in thermodynamical models,
- 2. Clay minerals are no equilibrium phases,

thermodynamic models with illites and smectites do not represent equilibrium conditions.

Further arguments are that clay minerals are metastable compared to homogeneous phyllosilicates like talc, pyrophyllite and the mica family. It cannot be denied that thermodynamic models of mineral-fluid equilibria with clay minerals are uncertain and that kinetic boundary conditions are responsible for the observed mineral paragenesis. Nevertheless the theoretic approach of [WIL 2006a] is justifiable because it is very probable that solute activities have an influence on the type of clay mineral formed at low temperature. Because of these uncertainties it is not yet possible to exactly define the stability limits of the Fe-rich silicates in aqueous solutions. Nevertheless, such calculations are valuable because they render general reference points of the conditions under which Fe rich sheet silicates are probably stable or unstable.

The modelling of [WIL 2006a] allows the assumption that under the oxygen partial pressure in a HLW repository (between H<sub>2</sub>O stability and magnetite haematite equilibrium) montmorillonite may be transformed into Fe<sup>2+</sup> saponite rather than into nontronite. Furthermore, they show that at a higher SiO<sub>2</sub>(aq) activity the formation of Fe<sup>2+</sup> saponite is preferential to the formation of berthierine (under the condition that the solution is saturated with magnetite). That means that the most probable montmorillonite transformation products are Fe<sup>2+</sup>-saponite and berthierine and that their relative stability is controlled by pH, Fe<sup>2+</sup> content and the activity of SiO<sub>2</sub>(aq).

More experimental investigations are needed for the testing of these thermodynmic models and for the determination of the kinetics of the montmorillonite transformation.

# 3.4 Swelling pressure – charge hypothesis – amelioration of bentonite properties

### Swelling pressure – crystalline swelling

Crystalline swelling is a process whereby 0 to 4 discrete layers of water molecules are intercalated between individual 2:1 layers (i. e. in the interlayer positions) within a smectite quasicrystal. Layer hydrates with 0, 1, 2, 3, and 4 layers of water molecules are distinguished by *d*001 (basal) spacing of approximately 10.0, 12.5, 15.0, 17.5 and 20.0 Å, respectively. These physical rearrangements of matter require work, and the

energy needed to effect that work is lost from the chamber to the external universe during both expansion and collapse. In a strict sense, the different layer hydrates of a smectite are separate phases with different thermodynamic properties, and any transition from one layer hydrate to another is a phase change [LAI 1997].

[SLA 1991] quantified decreased crystalline swelling of smectites with increasing layer charge by measuring d-spacing of smectites equilibrated with various NaCl solutions.

Na as dominating cation in interlayer space supports a high swelling pressure. 1 layer of water in interlayer space generates higher swelling pressure than 2 or 3 layers of water [MAD 1988].

### Swelling pressure – double-layer swelling

Double-layer swelling occurs between quasicrystals. An electrostatic repulsion force develops when the positively charged diffuse portions of double layers from two quasicrystals overlap in an aqueous suspension. Layer charge has little or no direct effect on double-layer swelling [LAI 2006]. As layer charge increases, quasicrystals tend to become larger and more stable. The extent of crystalline swelling (d-spacing) is known to decrease with increasing layer charge and this decrease should increase both the size and stability of quasicrystals.

[LAI 2006] described furthermore that, when placed in distilled water or a dilute electrolyte solution, most quasicrystals of low-charge Na-smectites will spontaneously break up such that diffuse double layers form and separate the individual smectite layers. For high-charge, Na-smectite, some quasicrystals will remain intact, but most will at least partially breakup. The addition of kinetic energy by stirring, shaking or sonicating is usually all that is required to disperse a Na- or Li-smectite in distilled water. By contrast, when a Mg- or Ca-saturated smectite is placed in distilled water the d-spacings typically expand from 15 Å (air dry Ca- or Mg-smectite) to 19 Å (Ca- or Mg-smectite in distilled water), but the quasicrystals do not spontaneously delaminate. Stirring, shaking or even sonication will cause some big quasicrystals to break up, forming a suspension of smaller Ca- or Mg-smectite quasicrystals. But most (if not all) Ca-smectites cannot be delaminated even by vigorous sonication.

Na-saturated smectites in dilute aqueous systems can be almost completely delaminated such that diffuse double layers form between all of the individual layers and each layer behaves as a separate colloid. The breakup and formation of quasicrystals is graphically illustrated in Fig. 3.1.



Fig. 3.1 Schematic diagram depicting the breakup and formation of quasicrystals (On the left the layers are grouped together in a single quasicrystal, in the middle the same layers are split into four quasicrystals, and on the right the layers are completely delaminated [LAI 2006])

Summarising, low-charge Na-montmorillonite increases the swelling pressure in contact with water by breakup and delaminating of quasicrystals. High-charged Na montmorillonite will also follow this principle, but before it does it needs an additional impact of kinetic energy (e. g. by stirring or higher activity). Low- or high-charged Ca, Mgmontmorillonite do not have such remarkable influence on swelling pressure.

[LAI 2006] has also described a demixing of interlayer cations when two different types of cations (e. g., Na and Ca) are present in an aqueous smectite system. The smectite may exhibit distinct preference for one cation over the other. In a Na/Ca-smectite system for example, demixing means that Na ions will tend to be segregated in certain interlayers while the competing Ca ions are segregated into other interlayers. When the clay is shaken, the quasicrystals will readily break apart at interlayers dominated by Na (Fig. 3.2). This breaking is to be considered as a further element that affects an increasing swelling pressure or, as summarized by [LAI 2006]: Increasing layer charge tends to inhibit the breakup of quasicrystals and hence to decrease swelling in mixed cation systems.



Fig. 3.2 Schematic diagram depicting the demixing of Ca and Na and the preferential breakup of smectite quasicrystals along interlayers dominated by Na [LAI 2006]

#### Swelling pressure – co-volume swelling

Individual smectite layers are surrounded by a certain volume of diffuse double layer. [LAI 2006] described that furthermore, when two freely rotating smectite layers approach each other, their first interaction will be due to the intersection of the diffuse portions of their double layers, which will result in a repulsive force before the layers actually touch (Fig. 3.3). He assumed that a co-volume of 300 mL is probably realistic for 1 g of fully dispersed smectite imaging the dimension of co-volume swelling. Such large co-volumes mean that, in all but the most dilute suspensions, the rotational freedom of dispersed smectite layers is severely limited. If more water is carefully (without mixing) and isothermally added to the top of such a suspension, the colloidal suspension will expand into the new water volume. The driving force for this expansion is an increase in entropy due to the increased rotational freedom of the smectite colloids. Layer charge will have an indirect effect on co-volume swelling via dynamic formation and breaking of quasicrystals. Theoretically, layer charge will influence the amount of kinetic energy required to both form and break up a quasicrystal [LAI 2006].

Co-volume swelling shows an inverse relation with layer charge.



Fig. 3.3 Schematic diagrams depicting co-volume: A) co-volume is the volume around a particle and the associated diffuse double layer that allows complete rotational freedom. B) when diffuse double layers of two rotating particles intersect a repulsive force develops inhibiting free rotation [LAI 2006]

#### Hydraulic conductivity

Generally, high swelling pressure improves the hydraulic conductivity.

#### Development of interlayer charge and swelling pressure in compacted bentonite

[HER 2008] developed a concept describing the development of swelling pressure in relation to the interlayer charge of smectite in compacted barrier material (Fig. 3.1). This concept was based on Czech mock-up experiments with "RMN" Femontmorillonite analysed by [PUS 2010]. It was detected that there was a dynamic system close to the heater. The run products have shown a partial illitization. Far from the heater, low charged montmorillonite with common Si-surplus (mathematical: Si > 4 per  $(OH)_2 O_{10}$ ) was found. This represented rather more a kaolinitisation accompanied by Si-precipitation (closed reaction system). Run products with lowest interlayer charge were characterised by highest swelling pressure and run products with highest interlayer charge layer charge were linked with the lowest swelling pressure (Fig. 3.6).

In a literature review commissioned by the SKBIn, [SAV 2005] analysed all available publications concerning the topic "Influence of solution salinities on the properties of clay barriers". The conclusions drawn by [SAV 2005] are very similar to those published by [HER 2004] and [HER 2006], which are summarised below:

- A clear correlation exists between the swelling pressures of compacted bentonites and the interlayer spacing of the smectites in the bentonite
- Cations from saline solutions by entering the interlayer space increase the salinity and decrease the water activity in the interlayer solution
- Interactions with saline solutions reduce the swelling capacity of bentonites

[HER 2004] und [SAV 2005] have shown that the emplacement of water and cations in smectites influence the swelling process. The emplacement is dependent on the density of the surface charge (swelling capacity decreases with charge density), on the cations in the interlayers and on the salinity and water activity of the solutions in contact with the bentonites.

[SLA 1991] have shown that charge influences the swelling. The swelling potential decreased with increasing charge. The low charge smectite in the Wyoming MX80 bentonite showed increasing swelling and interlayer spaces (from 15.5 to 18.5 A) with decreasing Na content of the ambient solution. This expansion of the interlayer space corresponds to the transition from one to two water layers in the TOT silicate layers. The concentration of the interlayer cations controls the charge and can rise up to 4 molar. If no other forces than cation hydration were involved only extreme salinities could limit the swelling. But the interlayer forces result from the equilibrium between the cation hydration, electrostatic forces and van der Waals forces. The tendency to hydrate cations and to extend the interlayers is opposed to the electrostatic attraction between the cations and the clay surface. Whereas the tendency to absorb water is linear with the emplacement of cations in the interlayers the corresponding counteracting electrostatic forces increase much faster than the forces leading to the swelling. Correspondingly the swelling capacity is reduced with rising charge. Commercial montmorillonites are normally low charge smectites, which guarantee the desired swelling properties.



(Interlayer charge per half-cell unit = 0 is valid for kaolinite or pyrophyllite as end members of montmorillonite alteration in closed systems; inter-layer charge per half-cell unit = 1 is valid for illite as the end member of montmorillonite alteration in open systems)

# **Fig. 3.4** Hypothetical behaviour of swelling pressure affected by interlayer charge of clay minerals in bentonite

[HER 2004] showed within lab-experiments with mixtures of MX80 and different types of saline solutions that in a closed system, enrichment of aluminium in the octahedral sheet leads to a "low-charge"-modification of the MX80-montmorillonite. Measurements to determine the corresponding change of the swelling capacity were not performed at that time. Nevertheless, experiments with montmorillonite-rich Wyoming bentonite proved this effect and confirmed that a "low-charge" montmorillonite is producing much higher swelling pressure [SAV 2005]. Theoretically, as end member of the complete alteration of montmorillonite in a closed system, clay minerals such as kaolinite and pyrophyllite will appear [HER 2004]. Like muscovite both minerals dispose of no or negligible swelling capacity or these minerals can build up no swelling pressure. According

to this it is self-evident that there is a close dependency between the interlayer charge and the hypothetical swelling pressure (see Fig. 3.4).

Assuming that this hypothesis is appropriate - the selective charging of the interlayer can be used to optimise the swelling pressure and, with respect to the design of engineered barriers, the rheological properties of bentonite.

The application of this hypothetical factor for analysis is limited by the individual specification of bentonite and the experimental conditions. For example, from experimental experiences it is known that solutions of high ionic strength will reduce the swelling pressure of a bentonite MX80 significantly, [XIE 2007].

This measured effect is in good agreement with the theory of "diffuse-double-layer" which is used as the constitutive law to model the behaviour of engineered clay barriers. In practise, according to Fig. 3.3 showing the relation of the interlayer charge to the derived swelling pressure of a Fe-montmorillonit, it can be assumed that a change of the used specific ionic strength will influence directly the range of the swelling pressure.



Fig. 3.5 Experimental and analytical data achieved from measurements with Femontmorillonite confirm the decrease of swelling pressure with the increase of interlayer charge (y-axis, [kPa] with the increase of interlayer XIIcharge (x-axis, [OH)<sub>2</sub> O<sub>10</sub>]), [PUS 2005]

# Indications of the hypothetical constitutive relation of "swelling pressure and interlayer charge"

Experimental and mineralogical investigations of [PUS 2005] within the Czech MOCK-UP were picked up by the authors to formulate a constitutive relation between "swelling pressure and interlayer charge". Results of the MOCK-UP buffer mass experiment (see Fig. 3.6) indicate two significant developments of alteration of the RMN® bentonite, a Fe-rich montmorillonite, induced by the increase of temperature. The beginning of the experiment, at lower temperature (~45 – 55 °C), is accompanied by a reduction of the interlayer charge of the montmorillonite and a reduction of components of mixed-layer.

<u> RMN – Fe-Montmorillonite in MOCK-CZ experiments</u>				
an 6.50 bar 50 d 4.30 bar 3.55 bar 3.10 bar		55°C 45°C 45°C 45°C 45°C	$\frac{smectitization}{(= low charge al}$	t (± closed system) teration) tion (± dynamic) charge alteration) trge (Fe-montm.)
temperature	45°C	55°C	75°C	95°C
Al <sup>VI</sup> Fe <sup>VI</sup> Mg <sup>VI</sup>	1.33 0.40 0.24	1.33 0.40 0.26	1.28 0.42 0.25	1.26 0.41 0.28
interlayer charge swelling pressure (bar)	0.31 4.30	0.27 6.50	0.35 3.55	0.38 3.10
process in sample	smectiti	zation	illitization	

Fig. 3.6 Czech MOCK-UP experiment: Alteration (smectitisation/illitisa-tion) induced by temperature of compacted RMN<sup>®</sup> Fe-montmorillonite was demonstrated [PUS 2005]; the results will be used for the practical application of the constitutive "swelling pressure to interlayer charge" relation with respect to an optimisation

This first stage of alteration is postulated to be a "de facto smectitisation" of the bentonite which is in good agreement with results of measurements on the long-term behaviour of the Wyoming bentonite MX80 in high saline solutions [HER 2004]. An influence of the alteration on the hydraulic conductivity was not measurable at this stage of alter-
ation. Within the second stage of alteration, at higher temperature (~55 - 95 °C), components of mixed-layer occur in higher quantities while the interlayer charge of the remaining montmorillonite is increasing. This stage of alteration is postulated to be the beginning of the "de facto illitisation" of the RMN® bentonite. The latter development leads to an increase of the intrinsic permeability by a factor of 10.

All experiences up to now including the results of the Czech MOCK-UP experiments converge with the hypothesis of the dependency of "swelling pressure to interlayer charge". Nevertheless, it is still a challenge to bring up the objective evidence how the swelling pressure can be controlled by taking credit of the interlayer charge in a closed system that is without considering more complex reactions of an opened thermodynamic system. There is still the necessity to investigate in detail the interaction between, and the influence of the ionic strength of the saline solution on the different types of smectite.

It is the recommendation of the authors to increase the efforts for implementing the postulated constitutive "swelling pressure to interlayer charge" relation with respect to the construction of engineered barriers. The possibility of controlling the swelling properties of bentonite will improve the long-term stability of the buffer material as well as the rheological properties of the barrier. The tests performed indicate that it is possible to reduce the interlayer charge of montmorillonite from 0.4 to 0.2 by technical means and therewith to optimise significantly the swelling properties of montmorillonite. This technical induced "smectitisation" of bentonite buffer material can be adopted on a closed system as given in an underground repository. In contrast "illitisation" is expected for open systems where a continuous exchange of pore fluid is given. "Illitisation", which is accompanied by an increase of the interlayer charge and leads to a reduction of the swelling capacity, is not expected to take place under repository conditions. Within the framework of these investigations the influence of iron-rich solutions on swelling properties is under research.

## 4 Working programme

The programme of work includes experimental and theoretical work, organised in five working packages (AP):

- AP1: Measurements to determine the impact of the oxidation of solved iron on the swelling pressure and the intrinsic permeability of compacted bentonite at different temperatures
- AP2: Determination of the diffusion coefficients in compacted bentonite
- AP3: Kinetics of the interactions of iron and bentonite
- AP4: Impact of iron on the alteration of smectite in closed and open systems
- AP5: Modelling of the interaction iron and bentonite

## 5 Materials used

## 5.1 Bentonites

The following bentonites were applied in the different experiments:

- MX80 (Wyoming-bentonite, trade article from 2005)
- Friedland Clay (Fe-rich IS-ml, Scholle "Burgfeld")
- Vietnam Clay (Fe-rich IS-ml; by-product from chromite exploitation in serpentinised diabase)
- GeoHellas Clay (Fe-rich montmorillonite with palygorskite and saponite)
- Bentonites from API-series (Polkville, Mississippi, API #20; Amory, Mississippi, API #22a; Chambers, Arizona, API #23; Otay, California, API #24; Belle Fourche, South Dakota, API #27; Bayard, New Mexico, API #30; Cameron, Arizona, API #31; Pioche, Nevada, API #32; Garfield Nontronite, Washington, API #33a)
- Bentonite from the BGR collection (04F, 09F, 11F, 12F, 13F)

## 5.1.1 MX80

MX80 bentonite was a commercial product of the Süd-Chemie AG (Moosburg, Germany) bought by GRS mbH in 2005. It originated from latitic or rhyolitic volcanic ash in the sea water in Mowry shale – Wyoming – USA [MOL 2001]. The MX80 starting material was characterised as Na bentonite, which was dominated in XRD of randomly oriented mounts (powder) by 13Å-montmorillonite (monovalent, 1 water layer in interlayer space).

The mineral matter of MX80 starting material was nearly comparable to other published data about MX80 bentonite (Tab. 5.1). On the other hand, it has to be pointed out that the smectite of the applied MX80 starting material has shown remarkable treatment impacts by the seller in the chemical composition in comparison with literature data for MX80 bentonite from [MAD 1988], [KAS 1998], [WOL 2001] and [UFE 2008a]. The applied GRS-MX80 bentonite (trade article from 2005) was more Al-rich smectite and had a lower total charge than in the mentioned analyses published on the former MX80 se-

ries. Detailed analytical data (XRD, TEM-EDX, and FT-IR) are summarised in Appendix A 1.

Phases (wt%)	Own Measurements	Literature Data					
	Mineral composition by BGMN-Rietveld	[LAJ 1996]	[VTT 1996]	[UFE 2008a]	[MAD 1988]		
Smectite	77	75	85 – 95	85.7	75.5		
Cristobalite	3	15 0*	-	1.7	15*		
Quartz	5	15.2	3 – 6	4.5			
Albite	13	5 – 8	1 – 3	5.4	5 – 8		
Calcite	trace	1.4	1 – 3	0.4	1.4		
Muscovite	1	-	-	1.8	-		
Pyrite	-	-	1 – 3	-	0.3		
Gypsum	-	-	-	0.6	-		
Organic matter	-	0.4	-	-	0.4		

Tab. 5.1	Semi-quantitative mineral composition of bulk samples of MX80 bentonite
	by BGMN - Rietveld refinement

Own measurements: bulk sample, random preparation, < 63  $\mu$ m; semi-quantification by BGMN-Rietveld processing of X-ray diffractograms [1-rho = 9.53 %; Rwp = 9.48 %])

\* cristobalite + quartz; structural formula of smectite by BGMN – Rietveld refinement was  $Ca_{0.01} Mg_{0.02} Na_{<0.01} K_{0.02} Al_{1.62} Fe_{0.43} Si_{3.96}Al_{0.04} O_{10}(OH)_2$  and  $Ca_{0.06} Na_{0.02} K_{0.01} Mg_{0.29} Fe_{0.16} Al_{1.55} Si_{3.88}Al_{0.12} O_{10}(OH)_2$ 

The average mineral formula of all TEM-EDX-measured dioctahedral smectitic particles of fraction < 2  $\mu$ m was:

## MX80 (average mineral formula)

 $Ca_{0.04} Mg_{0.04} Na_{0.01} K_{0.02} AI_{1.59} Fe^{3+}_{0.21} Mg_{0.16} Ti_{0.04} (OH)_2 AI_{0.05} Si_{3.95} O_{10}$ (5.1) Interlayer charge XII = 0.19

## 5.1.2 Friedland Clay

The Friedland-Eocene clay was supplied by Mineralische Rohstoffmanagement GmbH, Blautonwerk Friedland in spring 2010. It is sedimentary clay that formed in a shallow marine basin between 57 – 35 million years ago and located in Friedland, Mecklenburg, Western Pomerania, NE Germany. The quarried deposit is very homogeneous and massive, the thickness up to 140 m, the exploitable reserve at approximately 100 million tons clay. The geological background of this area as well as mineralogical composition was reviewed also by [HEN 1998].

The clay material in this thesis was taken in core of the ore body of the "Burgfeld Scholle" quarry. The borehole was located in an open cast mine that is nearby the former exploration and was named TB1/97. It was quarried and drilled at 8 m sea level in summer 2009 by the above company. The clay is grey and blue to dark grey, grain size is very fine and homogenous.

The XRD patterns showed the presence of those minerals: quartz, kaolinite, montmorillonite, illite-smectite mixed layer phases, illite, chlorite, gypsum, kaolinite and feldspars. The weight percent of each phase of bulk sample was calculated by BGMN-Rietveld refinement and evaluated by XRF results: Illite-smectite mixed layer (IS-ml) 36 %, montmorillonite 20 %, quartz 20 %, kaolinite 14 %, feldspars 4 %, chlorite 1 %, and illite 2 %. Pyrite and gypsum occurred in traces. The TB1/97 Friedland clay was characterised by two types of illite-smectite mixed layer: type (i) the main part of mineral matter with 70 % and type (ii) with 10 % smectitic layers. This result was in agreement with the previous publication of [HEN 1998] and [HOA 2006] for a neighbouring location (Siedlungsscholle).

Detailed analytical data (XRD, TEM-EDX, and FT-IR) are summarised in Appendix 1.

The average mineral formula of all TEM-EDX-measured dioctahedral smectitic particles of fraction < 2  $\mu$ m was:

#### Friedland clay TB1/97 (average mineral formula)

 $Ca_{0.01} Mg_{0.11} Na_{0.03} K_{0.23} AI_{1.54} Fe^{3+}{}_{0.31} Mg_{0.12} Ti_{0.02} (OH)_2 AI_{0.38} Si_{3.62} O_{10}$ (5.2) Interlayer charge XII = 0.50

#### 5.1.3 Vietnam Clay

Vietnam clay sample was taken in the Co Dinh valley of Nui Nua massive, Thanh Hoa, Vietnam. Parent rocks were serpentinised diabase. Clay was a by-product of exploiting activities (rock washing for chromite) and was discharged into this valley.

The bulk sample and fraction < 2  $\mu$ m of the sample from the Co Dinh valley were composed mainly of Fe-smectite (70%). Chlorite (8%), quartz (8%), kaolinite (2%), amphibole (2%), talc (9%) and magnetite (traces only) acted as impurity phases.

Detailed analytical data (XRD, TEM-EDX, and FT-IR) are summarised in Appendix 1.

The average mineral formula of all TEM-EDX-measured dioctahedral smectitic particles of fraction < 2  $\mu$ m was:

## Vietnam Clay, Co Dinh valley (average mineral formula)

 $Ca_{0.03} Mg_{0.09} Na_{<0.01} K_{0.03} AI_{0.57} Fe^{3+}{}_{1.19} Cr^{3+}{}_{0.08} Mg_{0.15} Ti_{0.02} (OH)_2 AI_{0.15} Si_{3.85} O_{10}(5.3)$ Interlayer charge XII = 0.27

## 5.1.4 GeoHellas Clay

The soda-activated GeoHellas clay (charge-No.: DA1206) was kindly supplied by GeoHellas S.A. in Athena, Greece. It was material similar to the experiment samples of [PUS 2010]. The semi-quantitative mineral composition was 37 % montmorillonite and related mixed layer phases, 22 % chlorite and chlorite-saponite-vermiculite-mixed layers, 14 % feldspar, 10 % dolomite and Mg-calcite, 8 % quartz, 7 % palygorskite as well as traces of goethite.

Detailed analytical data (XRD, TEM-EDX, and FT-IR) are summarised in Appendix 1.

The average mineral formula of all TEM-EDX-measured dioctahedral smectitic particles of fraction < 2 µm was:

## GeoHellas clay DA1206 soda-activated (average mineral formula)

 $Ca_{0.09} Mg_{0.13} Na_{<0.01} K_{0.12} AI_{1.06} Fe^{3+}{}_{0.55} Mg_{0.36} Ti_{0.02} (OH)_2 AI_{0.23} Si_{3.77} O_{10}$ (5.4) Interlayer charge XII = 0.57

#### 5.1.5 API series

The following bentonites certified by American Petroleum Institute Clay Mineral Standards (API) were used for short-term experiments: Belle Fourche – South Dakota (API #27), Chambers – Arizona (API #23), Bayard – New Mexico (API # 30), Polkville – Mississippi (API # 20), Pioche – Nevada (API #32), Amory – Mississippi (API #22a), Cameron – Arizona (API #31) and Garfield (nontronite) – Washington (API #33a).

The Belle Fourche and Cameron bentonites contained ~13 Å-montmorillonite (monovalent cations in the interlayer space) while XRD patterns of Pioche, Chambers and Bayard, Amory, Polkville bentonite were characterised mostly by 15 Å-montmorillonite (bivalent cations in the interlayer space). Bentonites of this series were composed of a variety of smectite contents between 65 % and 96 %. Bayard and Polkville bentonites were composed nearly completely of montmorillonite. Others also contained remarkable amounts of calcite, quartz, kaolinite, chlorite, illite and feldspar as main impurities. Calcite was detected in Pioche, Polkville and Chambers. Iron oxides phases appeared as traces in Pioche and Cameron bentonite.

Detailed analytical data (XRD, TEM-EDX) are summarised in Appendix 1.

The average mineral formula of all TEM-EDX-measured dioctahedral smectitic particles of fraction < 2  $\mu$ m was:

#### Polkville API #20 (average mineral formula)

 $Ca_{0.01} Mg_{0.10} Na_{0.10} K_{0.02} AI_{1.52} Fe^{3+}{}_{0.25} Mg_{0.22} Ti_{0.01} (OH)_2 AI_{0.08} Si_{3.92} O_{10}$ (5.5) Interlayer charge XII = 0.34

#### Amory API #22a (average mineral formula)

 $Ca_{0.02} Mg_{0.04} Na_{0.18} K_{0.11} AI_{1.42} Fe^{3+}{}_{0.33} Mg_{0.22} Ti_{0.01} (OH)_2 AI_{0.13} Si_{3.87} O_{10}$ (5.6) Interlayer charge XII = 0.40

## Chambers API #23 (average mineral formula)

 $Ca_{0.15} Mg_{0.04} Na_{0.05} K_{0.01} AI_{1.45} Fe^{3+}{}_{0.16} Mg_{0.38} Ti_{0.01} (OH)_2 AI_{0.06} Si_{3.94} O_{10}$ (5.7) Interlayer charge XII = 0.44

#### Otay API #24 (average mineral formula)

 $Ca_{0.03} Mg_{0.02} Na_{0.20} K_{0.06} AI_{1.43} Fe^{3+}{}_{0.32} Mg_{0.19} Ti_{0.02} (OH)_2 AI_{0.07} Si_{3.93} O_{10}$ (5.8) Interlayer charge XII = 0.36

#### Belle Fourche API #27 (average mineral formula)

 $Ca_{0.04} Mg_{0.03} Na_{0.16} K_{0.04} AI_{1.60} Fe^{3+}{}_{0.17} Mg_{0.19} Ti_{0.01} (OH)_2 AI_{0.06} Si_{3.94} O_{10}$ (5.9) Interlayer charge XII = 0.34

#### Bayard API #30 (average mineral formula)

 $Ca_{0.02} Mg_{0.14} Na_{0.11} K_{0.01} AI_{1.49} Fe^{3+}{}_{0.06} Mg_{0.44} Ti_{0.01} (OH)_2 AI_{0.02} Si_{3.98} O_{10}$ (5.10) Interlayer charge XII = 0.44

#### Cameron API #31 (average mineral formula)

 $Ca_{0.02} Mg_{0.07} Na_{0.15} K_{0.26} AI_{1.51} Fe^{3+}_{0.33} Mg_{0.14} Ti_{0.01} (OH)_2 AI_{0.40} Si_{3.60} O_{10}$ (5.11) Interlayer charge XII = 0.59

#### Pioche API #32 (average mineral formula)

 $Ca_{0.01} Mg_{0.12} Na_{0.16} K_{0.06} AI_{1.44} Fe^{3+}_{0.21} Mg_{0.33} Ti_{0.01} (OH)_2 AI_{0.13} Si_{3.87} O_{10}$ (5.12) Interlayer charge XII = 0.48

#### Garfield, Nontronite API #33a (average mineral formula)

 $Ca_{0.02} Mg_{0.03} Fe^{2+}{}_{0.05} Na_{0.07} K_{0.02} AI_{0.20} Fe^{3+}{}_{1.79} Ti_{0.01} (OH)_2 AI_{0.40} Si_{3.60} O_{10}$ (5.13) Interlayer charge XII = 0.29

#### 5.1.6 BGR series

The BGR bentonite series includes 12 bentonite samples that were kindly provided by Dr. Kaufhold of BGR (Bundesanstalt für Geowissenschaften und Rohstoffe, Hanover, Germany). This series was selected from thirty-eight bentonite samples of this research group. They are all raw materials without any prior treatment. The chemical and mineralogical composition of 12 bentonites (04F, 09F, 11F, 12F, 13F, 16F, 22F, 23F, 28F, 31F, 37F, 38F) in the total of 38 bentonite samples was published by [UFE 2008a]. The other properties, such as cation exchange capacity (CEC), pH, and exchangeable cations were investigated by [KAU 2008a], [KAU 2008b], [KAU 2009]), [KAU 2010a], [KAU 2010b]. Smectite was the main phase in all investigated samples with > 70 % (exception: 09F, 16F with > 50 %). Less than 1 % calcite was present in the samples, with the exception of samples 09F and 13F with  $\geq$ 3 %).

Detailed analytical data (XRD, TEM-EDX, and FT-IR) are summarised in Appendix 1.

## 5.2 Solutions

The experiments were performed with three solutions of different ionic strength:

- Opalinus clay pore water (OCPW) with the composition of the pore water of the argillaceous formation Opalinus Clay at the Mont Terry Rock Laboratory in Switzerland [PEA 2003]
- Saturated NaCl solution, a typical brine encounterd in the Zechstein formations in Germany [HER 1991], [HER 2008]
- IP21 solution, a MgCl<sub>2</sub>-rich brine which may be encountered in the Zechstein potash beds in Germany. An IP21 solution is saturated with the salt minerals halite, carnallite, sylvite, kainite and polyhalite [HER 1991], [HER 2008].

The chemical composition of these brines is given in Tab. 5.2.

Tab. 5.2 Chemical composi	ition of brines used in the	e experiments
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Solution	Na	К	Mg	Ca	CI	SO <sub>4</sub>	۳Ц	Density	I
Solution	[mg/l]						рп	[g/cm <sup>3</sup> ]	м
OCPW	5627	62.4	370	906	10668	1184	7.4	1.011	0.377
NaCl	126900	123.5			191050		6.1	1.211	6.686
IP21	9046	14360	87900	< 0.8	268765	24175	5.6	1.317	15.482

Three basic solutions were prepared according to the GRS Standard Operation Procedure (SOP):

- Solution 1; IP21 (SOP-07)
- Solution 2; NaCl saturated (SOP-09)
- Solution 3; Opalinus clay (SOP-10)

Subsequently these basic solutions were spiked with iron-(II)-chloride in concentrations of  $10^{-1}$  to  $10^{-4}$  mol/liter. The used Iron-(II)-chloride (FeCl<sub>2</sub>, anhydrous; 10 mesh 99.99 %) was delivered in glass ampulla, 5 g (10 g) each, by the SIGMAR ALDRICH company.

The NaCl saturated stock solution – spiked with  $10^{-1}$  mol/liter FeCl<sub>2</sub> – contains 394.47 g of NaCl-solution and 5 g of iron-II-chloride. The concentrations  $10^{-2}$ ,  $10^{-3}$  and  $10^{-4}$  mol/liter FeCl<sub>2</sub> were prepared by diluting the stock solution. A small quantity of hydro-chloric acid was added to the IP21 stock solution to solve the FeCl<sub>2</sub> salt.

In preparation of the stock solution the glass ampulla were slit slight with a diamond saw blade. To avoid air contact the mixing of iron-II-chloride salt with the NaCI-solution was handled in an opened box (90 x 90 x 90 cm) completely filled with argon (Fig. 5.1). After cutting the ampulla under inert gas atmosphere the iron-II-chloride was instantaneously mixed and dissolved with the NaCI-solution in a beaker glass, homogenised by shaking and transferred into an air tight steel cylinder. The inner surface of the cylinder (SWAGELOK, Type 304L-HDF4, two gauges, volume 2250 cm<sup>3</sup>, maximum operating pressure 180 bar) is Teflon-coated. Similar to the opened box the air in the steel cylinder was replaced before by filling with argon. For stabilising the iron-II-chloride solution, a piece of metallic palladium – pre-treated with electrons by means of electrolysis – was placed in the steel cylinder.



Fig. 5.1 Lab-Equipment used for the preparation of the stock solutions

- (a) 90 x 90 x 90 cm Plexiglas box, (b) FeCl<sub>2</sub>-ampulla, (c) beaker glass,
- (d) steel cylinder

## 6 Layout of the laboratory experiments

#### 6.1 Swelling pressure measurements

The measurements of the swelling pressure were performed in compact reaction chambers (cells) made primarily of titanium. The specially developed measuring cells were manufactured by INFRASERV, Wiesbaden. To measure the pressure at the bottom of the cells Piezo-pressure transmitters (type pA-8H, KELLER) with a measuring range of 0 to 250 bar were chosen. For pressurising a "High-Performance Liquid Chromatography" pump (HPLC-pump, type BESTA HD 2-400) that is able to create a maximum pressure of 300 bar was connected to the cells. Before starting the measurements the pressure transmitters of the cells and the HPLC-pump pressure transducer were calibrated, filling the device with water and pressurising it. During the calibration test the tightness of the completed test equipment was checked.

During the preparation of samples the loose clay material was compacted by a testing device which is normally used for strength tests (type AMSLER Digicon-2000, WALTER&BAI AG, Switzerland). The device generates a maximum strength of 100 kN and a maximum path length of deformation of 100 mm. The latter was used to set up a defined density of the samples. The process of compaction started when the testing device got into fitting contact (force contact) with the piston of the cell and with the clay material and ended when the piston reached the stipulated value of path length. The exact length of deformation was checked by the control panel of the testing device. (Fig. 6.1)



Fig. 6.1 The reaction chamber fixed in the AMSLER aperture for compaction

Depending on the geometry of the cell (diameter 50 mm) 62.832 g of clay was necessary to generate a sample with a length of 20 mm and a density of 1.6 g/cm<sup>3</sup>. Influenced by the frictional resistance of the piston during compaction the load of strength varied between 9 and 13 kN. After reaching the stipulated length – corresponding with the defined density of the sample – the piston was fixed by the wing nut of the cell.

In the next step the prepared reaction chamber, the HPLC-pump, a balance (type PG503S, Toledo METTLER) and the steel cylinder with an extra pressure transmitter (type PA-33X, range 0 to 250 bar, KELLER) containing the test solution spiked with iron-II-chloride were assembled and connected with the data acquisition system (60-channel device, type 5990, AHLBORN). For hydraulic connections 1/8"-PEEK capillary tubes and ball valves were used.

The measurement started with the pressurisation of the test solution in the steel cylinder with inert gas (nitrogen/argon) up to 50 bar and injection of the iron-II-solution from the bottom of the cell into the reaction chamber. To remove residual gas from the sample and to allow an optimal saturation of the clay particles with the test solution the outlet valve of the cell was opened periodically. One week after the start the injection was stopped and the inlet valve was closed while the outlet valve was opened permanently to assure the relaxation of the sample from hydraulic pressure. The remaining pressure in the reaction chamber is the expected specific swelling pressure of the sample. The test equipment was then used to perform permeability measurements.

#### 6.2 Permeability measurements

#### 6.2.1 Permeability changes in compacted bentonites

In a closed system of an underground repository it is expected that corrosion of steel will release species of  $Fe^{2+}$  into the surrounding buffer (compacted bentonite) only by diffusion – a long-term process. Taking the process of corrosion as already completed the performed time lapse experiments are focused on the petro physical impact caused by iron-II-chloride. To determine the minimal and maximum impact different concentrations ( $10^{-1}$  to  $10^{-4}$  mol/liter) of iron-II-chloride solution are used.

The impact on the permeability was determined directly after finishing the swelling pressure measurements (HASSLER tests). To start the permeability measurement the inlet and the outlet valve of the cell were opened and the test solution was injected into the samples until a constant flow rate was reached (steady state). The mass of solution that was passed through the sample was measured continuously by the balance. The absolute injection pressure had to be varied from 30 to 100 bars depending on the type of solution. IP21 and NaCl solutions require a height of injection pressure of approximately 30 bars while up to 100 bars were necessary to achieve a measurable constant flow rate with the Opalinus clay solution.

#### 6.2.2 Test Procedures

In the first step 30 g of MX80 bentonite is mixed with 1 litre of the specific stock solution. Then the mixture is shaken for at least several weeks to achieve full cation exchange between solid and liquid. During this time the composition of the liquid is analysed periodically to determine the point of equilibrium. When equilibrium is reached the liquid is separated from the solid and spiked with iron-II-chloride in concentrations of  $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$  and  $10^{-4}$ , mol/litre equilibrium solution.

In the second step the conditioned MX80 sample in the reaction chamber (see chapter 6.2) is penetrated with the iron-II-chloride spiked solutions. Due to the cation exchange capacity of the MX80 solved Fe<sup>2+</sup> will be fixed by the solid. The Fe<sup>2+</sup> remaining in the pore solution will be oxidised. To accelerate this process and to determine the impact of oxidation of the hydraulic property of MX80, equilibrium solution without iron-II-chloride is used to perform the permeability measurements.

The test procedure leads to a homogenous optimal distribution of Fe<sup>2+</sup> in the clay samples. The test condition represents the long-term effect of diffuse migration of Fe<sup>2+</sup>solution through the clay which might happen after the corrosion of steel at the waste container/buffer material boundary. The measurements benefit from the homogeneity of the samples and the lack of high gradients in concentration and allow determining directly precipitation effects of iron hydroxide, iron oxide and green rust. A complicated xyz-coordinated qualitative and quantitative determination of phases of iron in the pore space of the sample is not necessary. The determined permeability values are representative of homogenous clay samples and effects caused by chemical-mineralogical alteration of the sample. To determine long-term effects the permeability measurements, performed directly after the swelling pressure test, were repeated after 100, 200 and 300 days.

#### 6.3 Determination of the pore space

The porosity of the compacted clay samples was determined according to the methodology of [HER 2002].

The methodology is following the assumption that the pore volume of the sample is fully filled with solution of a known density and known quantity and that the free water content is equivalent to the difference of total water and interlayer water.

The volume of interlayer water is calculated from balancing masses. The mass of the "void" sample ( $M_{Sa}$ ) is after compaction:

$$M_{Sa} = M_d + M_{PS} + M_{IW} (6.1)$$

 $M_{Sa}$  is the sum of the dry mass of solid  $(M_d)$ , the mass of the pore solution  $(M_{PS})$  and the mass of the interlayer water  $(M_{IW})$ .

The equation implies that the molecular weight of the solid is not significantly influenced by cations exchange. The mass fraction of ad-, absorbed cations related to the mass of the solid is approximately 2%. Cations exchange leads to the substitution of sorbed cations by solved cations in the solution. In the case of a sodium-rich smectite interacting with solutions differing only in parts of magnesium/sodium the molecular weight of the Na-smectite will be changed less than 1% because sodium and magnesium are similar in their molecular weight.

The mass fraction of total water ( $M_{W,tot}$ ), determined by means of Karl-Fischer titration is given by the equation:

$$M_{W,tot} = M_{PW} + M_{IW} (6.2)$$

 $M_{PW}$  is the mass fraction of the pore water. It is assumed that the composition of the pore water ( $M_{PW}$ ) is equal to the composition of the artificial equilibrium solution (test

solution). If the mass of water of the test solution is known,  $M_{PW}$  and  $M_{PS}$  correspond with respect to the water content, *a* [kg water / kg solution] and it can be followed that

$$M_{PW} = a M_{PS} \tag{6.3}$$

The use of eq. (6.3) in eq. (6.2) will lead to:

$$M_{W,tot} = a M_{PS} + M_{IW} \tag{6.4}$$

Now we have two equations eq. (6.1) and eq. (6.4) with two unknown parameters:  $M_{PS}$  and  $M_{IW}$ . The combination of eq. (6.1) and eq. (6.4) results in

$$M_{PS} = \frac{M_{W,tot} - M_{Sa} + M_d}{(a-1)}$$
(6.5)

The application in eq. (6.1) leads to

$$M_{IW} = M_{Sa} - M_d - M_{PS} (6.6)$$

As a result of the porosity and permeability measurements a constitutive law of the porosity/permeability relation was established which can be used for THMC-modelling of a bentonite buffer in a repository for high-level waste.

#### 6.4 Measurements of diffusion coefficients

The experimental procedure to determine the diffusion coefficient in clay was established and is described in the final report of the GRS project 02 E 9541, [ZHA 2004].

The type of cell (cell A) used by [ZHA 2004] differs in its construction from the type of reaction chamber (cell B) used in this project. Technical characteristics of cell A are four valves (two at the bottom of the cell and two at the piston), which are necessary to operate two separate circuits flushing the bottom and the top of the sample. A pressure transmitter was not embedded in cell A.

The procedure of preparation of the samples with cell A and cell B is equal. In both cases the compaction of conditioned clay material with the AMSLER cell leads to samples with a defined density of 1.6 g/cm<sup>3</sup>. Subsequently, for equilibration, the test solution was injected into the sample using a HPLC-pump.

The diffusion measurements started when the peristaltic pump began to pump the "contaminated" solution to the bottom (closed circuit 1) and the test solution to the top (open circuit 2) of the sample at a pumping rate of 55.9  $\mu$ l/min each.

The "contaminated" solution was spiked with  $10^{-3}$  mol/litre zinc, cadmium and lead while the concentration of these species in the test solution was  $10^{-5}$  mol/litre.

Two 5-litre-reservoirs, one with the "contaminated" solution and one with the test solution, were necessary to supply the pump and to assure continuous flow. The "contaminated" solution was recycled to the reservoir and then pumped again to the bottom of the sample. The test solution passed the top of the sample and was collected and balanced outside of the cell. The composition of the solution was analysed.

Already the first results indicated that it is difficult to quantify analytically small changes in concentration of chemical species in higher saline solutions. Realising this fact, the species zinc was replaced by caesium and iron-II-chloride was not added to the solutions. Within the long-term experiments the precipitation of salt in the small pore spaces of the used frit blocked the contact of the solution with the sample.

The diffusion experiments were executed with IP21, NaCl and Opalinus solution. The test with the Opalinus solution had to be stopped after eight months without any result.

Assumptions concerning diffusive transport for determination of diffusion coefficients

- The tracer does not show any interaction with matrix or solution.
- Fick's second law is valid.

The following parameters describe the diffuse mass flow

$$J = -\tau \Theta D_m \rho \nabla c \tag{6.7}$$

- J diffuse mass flow
- au tortuosity

 $\Phi$  porosity

- $\rho$  constrictivity
- $D_m$  coefficient for molecular diffusion
- c concentration of tracer

as well as

$$J = -D_a \rho \nabla c \tag{6.8}$$

#### *D<sub>a</sub>* apparent diffusion coefficient

The two Fick's laws mirror the different processes on microscopic and macroscopic scale. The coefficient  $D_m$  is controlled only by tracer and solution, but Da is also affected by variable pore size.

Precipitation of solid phases from the solution reduces the pore space: reduction of porosity  $\Phi$ . Additionally, the distance is extended for the tracer reducing the coefficient  $\tau$ . In consequence, the apparent diffusion coefficient can only be determined by experiments.

The experimental determination of tortuosity is problematic. Otherwise, the macroscopic diffusion coefficient is easily directly measureable. The penetration of a tracer into a saturated specimen can be measured in one-dimensional experiments.

The specimen is to come in contact with the tracer-bearing solution at the inflow-side. The tracer may not change the properties of the solution. The solution and/or tracer is to be inherent in solid components of the specimen. The equipment has to control a constant concentration of the tracer at the contact side. The opposite area of the specimen is connected with a small reservoir containing tracer-free solution.

The tracer diffuses into the sample, penetrates and leaves the sample after a certain delay. The macroscopic diffusion coefficient is to be determined inversely by analytical equations for the diffusive transport of the tracer after measurement of the time-related change of the tracer concentration in the reservoir.

## 6.5 Experiments for the determination of reaction kinetics during the alteration of bentonites

Short-term overhead-shaking experiments were carried out to understand the kinetics of Fe, Mg-driven alteration processes of bentonite and to identify "sprinters" and "sleepers" under the selected bentonites.

The aim of this research was to focus on alteration processes in buffer material in HLRW repositories in interaction with corroding Fe-canisters. The starting hypothesis for it was: Fe- and Mg-rich bentonite would be expected to be more sensitive to alteration processes than Al-rich smectite. The theoretical background to this hypothesis is the higher diameter of Fe- and Mg-cations in comparison to Al. The larger diameter of Fe- and Mg-cations could cause a higher sheet stress in the octahedral sheets of smectite, which should be the reason for a higher sensitivity of Fe-Mg-rich bentonite to acid attacks, which are called "sprinters" and "sleepers" under the selected bentonites. This hypothesis was already developed by [CIC 1976] on a stochastic formula to calculate the half time of dissolution as a measure of reaction rate.



Fig. 6.2 Hypothesis to understand possible different kinetics of alteration for bentonite as a function of sheet stress in the octahedral layer (caused by higher cation diameter for Fe and Mg in comparison to Al) and cations occupation in the interlayer space

A hypothesis for further experiments was developed (Fig. 6.2). The higher cation diameter of Fe and Mg in comparison to AI and the main interlayer cation are assumed to be the two main driving factors for the kinetics of bentonite. Following the mechanism, described in [CIC 1976] and [KAU 2008b], AI-rich bentonites with Ca in the interlayer space should show the lowest degree of alteration (called "sleepers") in the newly designed experiments and Fe, Mg-rich bentonite with Na as main interlayer cation should be easy to alter (labeled as "sprinters"). Experiments were conducted in which different bentonites were used in overhead shaking systems (parameters: 20 days; room temperature; 1 N NaCI-solution and deionised water; two speeds of overhead shaking: 20 rpm, 60 rpm; "liquid:solid"-ratio like 10:1). Bentonites were chosen from former API-standards, selected bentonites from the BGR-collection, MX80, Friedland Clay, Vietnamese Clay and GeoHellas Clay (Fig. 6.3).

VI: (Fe+Mg)/(Fe+Mg+Al) 10% 30% 60% 80% 90% 100% 0% 20% 40% 50% 70% 0%  $\ominus$ Ca<sub>0.04</sub>Mg<sub>0.04</sub>Na<sub>0.01</sub>K<sub>0.02</sub> Al<sub>1.59</sub>Fe<sub>0.21</sub>Mg<sub>0.16</sub>T<sub>0.04</sub> MX80 04F GeoHellas "SPRINTER? *(*11: Vietnam XII: Can 05 Man 10 Nan 01 Kn 0 Ca<sub>0.09</sub>Mg<sub>0.13</sub>Na<sub>0.00</sub>K<sub>0.12</sub> 10% VI: AI<sub>1.30</sub>Fe<sub>0.45</sub>Mg<sub>0.20</sub>Ti<sub>0.01</sub> XII: Ca<sub>0.01</sub>Mg<sub>0.13</sub>Na<sub>0.03</sub>K<sub>0.23</sub> XII: Ca0.03Mg0.09Na0.00K0.13 Friedland VI: Alo.96Feo.52Mgo.50Tio.02 VI: Al<sub>1.51</sub>Fe<sub>0.31</sub>Mg<sub>0.12</sub>Ti<sub>0.02</sub> VI: Al<sub>0.57</sub>Fe<sub>1.19</sub>Mg<sub>0.15</sub>Ti<sub>0.02</sub> XII\*: Ca<sub>0.15</sub>Mg<sub>0.04</sub>Na<sub>0.05</sub>K<sub>0.01</sub> 20% Chambers VI: Al<sub>1.45</sub>Fe<sub>0.16</sub>Mg<sub>0.39</sub>Ti<sub>0.01</sub> <**∕0**9F XII: Ca<sub>0.04</sub>Mg<sub>0.03</sub>Na<sub>0.02</sub>K<sub>0.01</sub> XII: Na/(Ca+Mg+Na) 30% AI<sub>1.63</sub>Fe<sub>0.20</sub>Mg<sub>0.15</sub>Ti<sub>0.01</sub> XII: Ca<sub>0.02</sub>Mg<sub>0.14</sub>Na<sub>0.11</sub>K<sub>0.01</sub> Bayard VI: Al1.49Fe0.07Mg0.44Ti0.01 40%  $\bigcirc$ XII: Ca<sub>0.01</sub>Mg<sub>0.10</sub>Na<sub>0.10</sub>K<sub>0.02</sub> VI: Al<sub>1.52</sub>Fe<sub>0.25</sub>Mg<sub>0.22</sub>Ti<sub>0.01</sub> XII\*: Ca0.02Mg0.03Na0.07K0.01Fe0.07 50% Al<sub>0.24</sub>Fe<sub>1.74</sub>Mg<sub>0.00</sub>Ti<sub>0.01</sub> VI Ca0 03Mg0 10Na0 18K0 02 Pioche 🚫 >11F Al<sub>1.29</sub>Fe<sub>0.46</sub>Mg<sub>0.16</sub>  $\Diamond$ Belle Fourche 🔿 60% XII: Ca0.02Mg0.05Na0.09K0.02 Amory XII: Ca<sub>0.04</sub>Mg<sub>0.03</sub>Na<sub>0.16</sub>K<sub>0.04</sub> Al1.47Fe0.36Mg0.15Ti0.02 Garfield VI: Al<sub>1.61</sub>Fe<sub>0.17</sub>Mg<sub>0.19</sub>Ti<sub>0.01</sub> 70% Cameron XII: Ca0.02 Mg0.07 Na0.19 K0.19 VI: Al1.49Fe0.32Mg0.16Ti0.01 80% XII\*: Ca<sub>0.04</sub>Mg<sub>0.00</sub>Na<sub>0.20</sub>K<sub>0.05</sub> 🗘 Otay VI: Al<sub>1.43</sub>Fe<sub>0.32</sub>Mg<sub>0.19</sub>Ti<sub>0.02</sub> 90% XII: Ca0 01 Ma0 12 Na0 16K0 0 SLEEPER?" VI: Al<sub>1.44</sub>Fe<sub>0.21</sub>Mg<sub>0.33</sub>Ti<sub>0.01</sub> 100%

XII - interlayer; VI - octahedral layer

Fig. 6.3 Visualisation of applied samples for short-term overhead experiments in the matrix of hypothesis (mineral formulae calculated from TEM-EDX-measurements)

This design of the experiments represented an open system.

# 6.6 Experiments for the determination of the impact of iron on the alteration of smectites

#### 6.6.1 Experimental investigations

GRS mbH (Braunschweig) has carried out experiments with compacted MX80 bentonite and Friedland clay ( $d = 1.6 \text{ g/cm}^3$ ). MX80 bentonite was a trade article of the Südchemie Company. Friedland clay was offered from the Mineralische Rohstoffmanagement GmbH (Blautonwerk Friedland) in spring 2010. This material was originated from the borehole T1/97.

These clays were mixed with 10% of native Fe (grain size  $6-9 \mu m$ ). The compacted material was percolated by different saturated solutions: NaCl and IP21 and Opalinus clay water solution. Additionally, different temperatures (25 °C, 60 °C, and 90 °C) as well as different experiment durations of 1 month and 2 months were considered (Tab. 6.1). This experimental design is to be considered as a dynamic open reaction system.

Greifswald sample lable	Original Material	Solution	Temperature [°C]	Duration of Experiment [months]
FeM01	MX80	IP21	25	1
FeM02	MX80	NaCl	90	1
FeM03	MX80	NaCl	90	2
FeM04	MX80	NaCl	60	2
FeF01	Friedland clay	NaCl	25	2
FeF02	Friedland clay	NaCl	90	2

#### **Tab. 6.1** Series of run products from GRS batch experiments

Density of compacted material: 1.6 g/cm<sup>3</sup>; metallic Fe-powder: 10 %; flow rate of percolation: 3.9 ml/min

The run products of these experimental series were dialysed by QuickStep-system (1 mg material, ~ 2 hours). The samples were measured by XRD and TEM in laboratories of the Institute of Geography and Geology (University of Greifswald). XRF- and AAS-analytics were arranged by the Institute of Mineralogy and Geochemistry (Albert-Ludwig-University of Freiburg). FT-IR was performed at the Department of Chemistry, Pharmacy and Geosciences at Johannes-Gutenberg-University in Mainz.

Run products from temperature series 25 °C and 60 °C have shown a remarkable Ehzoning of Fe-activity (Fig. 6.4). That is why run products of FeM01, FeM04 and FeF01 were sampled in two parts: (a) dark grey or black material (= representing a high Feactivity) and (b) yellow or brown material (= representing a lower Fe-activity).

## Run Products of GRS-experiments



**Fig. 6.4** Zoning (left) and homogeneity (right) of Fe-activity in run products of GRS experiments

#### 6.6.2 Investigations of Natural Analogues

A tropical weathering profile on ultramafic rocks was selected to understand natural processes of smectite alteration as possible natural analogue.

Clay samples were collected from two waste fields of a chromite exploitation process and a cross section of diabas weathered crust in serpentinite mining in Nui Nua Thanh Hoa province, Vietnam (140 km from Hanoi in SW direction). Almost all of them are products of hydrothermal and weathering processes of ultramafic rocks in the Nui Nua complex. This complex belongs to the Song Ma (Black River) satural zone. This zone extends from Tuan Giao – Lai Chau (north east of Vietnam) to Nui Nua (Fig. 5.1a) west of Thanh Hoa town, in the central north of Vietnam. In the upper part of the Song Ma satural zone there are series of small ultramafic massive scattered along the Song Ma fault and related strongly to the metamorphic rocks of the Song Ma formation.

The Nui Nua massive is situated to the West of Thanh Hoa city and this is the largest ultramafic massive in Vietnam. It has an ellipsoid shape and is elongated in NW-SE direction. The total area is approximately 60 km<sup>2</sup>. This massive is divided by NW-SW fracture systems. In NW, this massive is covered by metamorphic rock of sediment that belongs to the Song Ma formation ( $\varepsilon_2$  *sm*) and along its Western boundary; there is a

breccia zone which is composed of ultramafic rocks and schist. Harzburgite, Iherzolite and dunite are identified as parent rocks, which are affected by serpentinisation. The recent rocks are composed by olivine, pyroxene, chromite, chromspinel, magnetite, serpentine, carbonate, talc and tremolite.

There are several kinds of vein rocks such as diabas and gabbrodiabas that penetrated and altered the above ultramafic rocks. Along the edge of the eastern part of the Nui Nua massive, there is a deposit of chromite, where exploitation has been going on as one of the most economically valuable industrial activities of the Thanh Hoa province.

This report focuses on a profile of the Bai Ang area of the Nua Nui complex as an example of a tropical weathering profile. The samples NN 0-1.5 m (bottom), NN 1-2 m (middle part) and NN 3-5 m (top horizon) represent a vertical weathering profile of a serpentinised diabase (appendix 3).

# 7 Methodology for the determination of mineralogical alterations and changes of bentonite

**Alteration of smectite:** X-ray diffraction (XRD), transmission electron microscopy combined with detection of energy-dispersive X-rays (TEM-EDX) and electron diffraction, Fourier transformation-infrared spectroscopy (FT-IR) and X-ray fluorescence spectroscopy (XRF) were applied to identify any mineralogical alteration of smectite in the run products. The analytical methodology was improved in comparison to former investigations published in [HER 2004] and [HER 2008].

#### 7.1 X-Ray Diffraction (XRD)

XRD-investigations were carried out to determine the mineral composition of the samples and their semi-quantitative distribution. The semi-quantitative composition was a result of BGMN-Rietveld refinement, which was based on a XRD diffraction diagram. Additionally, some different parameters were figured out as coherent scatter domains (CSD). The samples were milled to a particle size of < 40 µm before diffraction measurements.

The randomly oriented powder and oriented mounts including air dried (AD) samples, ethylene-glycolated (EG) samples and samples that had been heated up to 550 °C for four hours were measured by a Siemens D5000 X-ray diffractometer (Cu- K $\alpha_{1,2}$  radiation at 30 mA of current and 40 kV of voltage; 0.5/25 soller collimator; step size 0.02 °2Θ with 3 seconds for each measurement step). Some samples with high Feproportions were re-investigated by 0.02 °2Θ for 10 seconds. The XRD-measurement of randomly oriented powder samples were collected from 3 to 65 °2Θ. The identification of the main mineral matter was compared with the ICDD/JCPDS database. The oriented specimens including air dried (AD), ethylene-glycolated (EG) and heated up to 550 °C were recorded from 4 to 34 °2Θ with a step size of 0.02 °2Θ and time of 3 seconds per step for non Fe rich samples and 10 seconds per step for Fe rich samples. The identification of phase was based on the changing behaviour of (00l)-interferences under the three mentioned different environmental conditions minerals according to [STA 1984].

The WinFit-software package, developed by [KRU 1994], was used to fit and analyse the peak profiles of clay mineral structures. This program supported the decomposition

of complex or noisy patterns by Gaussian fitting profile shape functions. Moreover, this program allowed the determination by Fourier transformation of coherent scatter domains (CSD) as indication of the particles thickness distribution.

The NEWMOD-based comparison of positions from the (001)/(002)- and (002)/(003)interferences [MOO 1997] was applied to identify the percentage of smectite layers in illite-smectite mixed layer structures.

The powder diffractograms of bulk samples were processed with the BGMN-Rietveld software package. The BGMN-Rietveld refinement software package was developed by [BER 1998]. This program used fundamental parameters approaching the refinement of the diffraction peak profiles. [UFE 2004], [UFE 2008a], [UFE 2008b]) and [KLE 2010] proved and explained that it is possible to apply the Rietveld methodology not only to ordered but also to turbostratically disordered structure materials like mont-morillonite.

## 7.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) in combination with the detection of energy dispersive X rays (TEM-EDX) was a useful and sensitive method recognising alteration processes in clay minerals (e. g. identifying illitisation, pyrophyllitisation and kaolinitisation by diagenesis or technical processes). The TEM allowed the characterisation of selected particles in clay samples by means of crystal size, morphology, electron diffraction and element distribution. The samples (fraction <  $2 \mu$ m) were diluted in deionised water and dispersed by ultrasonic treatment for approximately 10 to 15 minutes. Eventually, the suspension was dropped on carbon coated Cu-grids and air dried. The contact time between clay and water on the Cu grids was less than 5 hours to avoid any structural alteration of the smectite.

About 100 - 150 particles per sample were investigated by JEOL microscope JEM-1210 (120 kV,  $LaB_6$  cathode) concerning chemical composition, morphology and electron diffraction. This electron microscope was coupled to an OXFORD-LINK EDX system and a GATAN MULTISCAN camera.

Chemical analyses by energy dispersive X-rays (EDX) were carried out on selected particles. The structural formula of each particle was calculated from EDX-spot-like

analyses using an Excel-based toolkit, which was developed by [KAS 2002]. The reproducibility of TEM-EDX data was tested for mica and for montmorillonite by [KAS 2002] and [HER 2008]. A detailed description of the calculation of mineral formulae can be found in Appendix 4.

The particles morphology was described according to [HEN 1986].

The electron diffraction allowed an evaluation of the stack order. Ring-like structures of the electron spots indicated clay minerals with so-called turbostratic orientation of the layers. Phases with  $2M_1$ -polytype and 1M-polytype for 2:1 sheet silicates were characterised by [ZOL 1993]. This author based the methodology on intensities of (110)- and (020)-interferences in convergent beam systems.  $2M_1$ -polytype was present in the case of |110|/|020| > 1 and the opposite behaviour, |110|/|020| < 1, was characteristically of 1M-polytype.

## 7.3 Fourier Transform Infrared Spectrometer (FT-IR)

Nowadays, Fourier Transform Infrared Spectrometer is widely used in researching material. It was discovered by William Herschel in 1800 and has been applied to clay studies since around the 1970s [MAR 1976].

The IR-method was used especially as additional analytical proof for the verification of tetrahedral Si and octahedral Fe in smectite. Typical bands applied were around  $400 \text{ cm}^{-1}$  to  $1200 \text{ cm}^{-1}$  (OH bending region),  $3600 \text{ cm}^{-1}$  to  $3200 \text{ cm}^{-1}$  (H<sub>2</sub>O stretching) and near the  $1630 \text{ cm}^{-1}$  region (bending vibration).

Bentonite was milled to < 40  $\mu$ m and IR spectra of these samples were recorded in the mid-infrared range, which extends from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> using a Nicolet 6700 FT-IR Spectrometer (Johannes Gutenberg-Universität Mainz) with 64 scans and 4 cm<sup>-1</sup> resolution. The IR spectrums were deconvoluted by a peak-fitting program (PeakFit<sup>TM</sup> version 4.12) of Jandel Scientific Software and Origin Pro 8.5 Peak Fitting. Gaussian and Lorentzian distribution functions were applied with the aim to smoothe the spectra and obtain the exact values of position, FWHM, intensity and area.

## H<sub>2</sub>O stretching region

Stretching bands of smectite rise at difference wave length of each phase. Montmorillonite is characterised by 3632 cm<sup>-1</sup>, beidellite ranges between 3660 cm<sup>-1</sup> and 3630 cm<sup>-1</sup> and nontronite rises at 3564 cm<sup>-1</sup> [FAR 1967].

Normally, the band of smectite groups is broad and each of them is raised on a different OH stretching band depending on the chemical composition of the smectite [FAR 1967]. According to [FAR 1974], octahedral layers of smectite are characterised mainly by three stretching bands of Al-OH-Al at  $3620 - 3630 \text{ cm}^{-1}$ , Al-OH-Mg stretching band at  $3687 \text{ cm}^{-1}$  and Al-OH-Fe<sup>3+</sup> at ~ $3597 \text{ cm}^{-1}$ . The OH-stretching bands of kaolinite are sharper than smectite and observed at  $3620 \text{ cm}^{-1}$ ,  $3652 \text{ cm}^{-1}$ ,  $3669 \text{ cm}^{-1}$  and  $3697 \text{ cm}^{-1}$ .

## OH bending region

This region of clay mineral locates at  $950 - 600 \text{ cm}^{-1}$ . Besides, the exact position of bands and molar absorptivity depends on the type of exchangeable cation and the water content [XU 2000]. The Al-OH-Al bending band appears at  $913 - 919 \text{ cm}^{-1}$  for smectite and kaolinite. But the Al-OH-Fe<sup>3+</sup> bending band of smectite locates at  $870 - 890 \text{ cm}^{-1}$ . The wave length position of this band will decrease if the content of Fe increases inversely. The Al-OH-Mg bending bands are characterised by  $840-860 \text{ cm}^{-1}$  for smectite. Additionally, the appearance of bands at  $850 \text{ and } 815 - 850 \text{ cm}^{-1}$  is typical of the Fe<sup>3+</sup>-OH-Fe<sup>3+</sup> bond of nontronite and the band at ~920 cm<sup>-1</sup> will be increased or decreased by the type of interlayer cations, especially in the water content of the smectite.

According to [RUS 1987], beidellite and montmorillonite are distinguished by characteristic of Al-O out of plane and Al-O-Si in plane bands at 818 cm<sup>-1</sup> and 770 cm<sup>-1</sup> even though they have similar spectra.

In general, the FT-IR methodology supports bentonite investigation in addition to X-ray diffraction and TEM-EDX-analyses.

## 7.4 X-Ray Fluorescence (XRF)

The XRF method has been published in detail by [COU 1996]. Samples were milled to  $< 40 \,\mu$ m and dried at 40 °C before XRF measurement. An analysis was carried out at

Albert-Ludwigs-University of Freiburg by using a wavelength dispersive Phillips PW 2404 X-ray spectrometer with 10 mA of current and 20 kV of voltage. 0.8 grams of bulk sample mixed with 2.0 grams of lithium tetraborate ( $Li_2B_4O_7$ ) and 1.932 grams of lithium metaborate ( $LiBO_2$ ) were anhydrously densely molten to guarantee homogeneity. During the measurement, non wetting agent (NWA) or/and oxidiser was used. A loss of ignition (LOI) at about 1000 °C also served as an approximate measure of volatile H<sub>2</sub>O.

The result of XRF-chemical composition was used to verify the results of Rietveldrefinement by BGMN.

## 7.5 pH and Eh measurements

The parameter pH is a tool to measure the hydrogen ion concentration in aqueous solution and Eh is an evaluation of the electrochemical potential or electron availability within these systems. Additionally, the Eh is determined from the concentration of oxidants and reductants in the environment. The pH and Eh values were calculated by the following equation:

$$pH = \frac{1}{log10C}$$
 (7.1)

Parameter C is the concentration of  $H^+$  in solution.

The reduction or redox potential is expressed by the tendency of compounds to accept or donate electrons. They depend on affinity of molecules for electrons and concentration of reductants and oxidants [DEL 2005].

$$Eh = E^{0} - \frac{RT}{nF} ln\left(\frac{reductant}{oxidant}\right) - \frac{mRT}{nF} ln(H^{+})$$
(7.2)

- Eh electrode potential
- E<sup>0</sup> standard half cell potential
- F Faraday constant
- n number of electrons exchanged in the half cell reaction
- m number of protons exchanged

The above equation was simplified by  $R = 8.31 \text{ JK}^{-1} \text{mol}^{-1}$ ;  $F = 9.65 \cdot 10^4 \text{ Cmol}^{-1}$ , T = 298 K and relationship  $\ln(x) = 2.303 \log(x)$ 

$$Eh(mV) = E^{0} - \frac{59}{n} \log\left(\frac{reductant}{oxidant}\right) + 59\frac{m}{n}pH$$
(7.3)

The above two equations reveal that Eh increases with increasing activity of the oxidised component and Eh decreases with increasing activity of the reduced component. It also increases with an increase in H<sup>+</sup> activity or decrease in pH values.

Under saline conditions, the swelling capacity of bentonite will be reduced and the permeability increased [PUS 1991]. The chemical composition of bentonite depends strongly on the pH of the solution that is in contact with the bentonite. Chemical alteration of the bentonite also affects the pH and Eh parameters.

In the case of bentonite suspension in high saline solution, the pH and Eh have to be corrected because their determination will be affected by varying of the diffusion potential between salt solution and referenced electrolyte. In addition, the transformation of cell potentials is unpredictable because of liquid junction potential in potentiometer measurement. The correction can be calculated by the proposal of [MAR 1989], [FAN 1996], [GRA 1990], [ALT 2003], and [FEL 1991]. The calibration of the pH electrode can be expressed by the following equations:

$$pH = -\log a_{H_{+}} = -\log([H^{+}] \cdot \gamma_{H_{+}}$$
(7.4)

$$pH = (pH)exp + \Delta(pH)$$
(7.5)

$$\Delta(\text{pH}) = \log \gamma_{\text{H}+} + \Delta E_{i}(\text{F/RT ln10})$$
(7.6)

The experimental values of  $\Delta$ (pH)correction in NaCl and MgCl<sub>2</sub> solution of  $I > 0.1 \text{ mol kg}^{-1}$  can be expressed by:

$$\Delta(\text{pH})_{\text{NaCl}} = -0.0988 + 0.1715 \text{ m}_{\text{NaCl}} + 0.0013 \text{ (m}_{\text{NaCl}})^2$$
(7.7)

$$\Delta(\text{pH})_{\text{MgCl2}} = -0.0887 + 0.4549 \text{ m}_{\text{MgCl2}} + 0.0172 \text{ (m}_{\text{MgCl2}})^2$$
(7.8)

For the Q solution (Q-brine at room temperature, 25 °C, pH 6.6, Eh –108.9, K<sup>+</sup> = 0.4, Na<sup>+</sup> = 0.43, Mg<sup>2+</sup> = 4.42, SO<sub>4</sub><sup>2-</sup> = 0.4) the correction value was  $\Delta$ (pH) = 1.53 and 1N NaCl-solution  $\Delta$ (pH) = 0.1 [HOF 2004].

The Eh-value will increase when bentonite is in contact with saline solution. It will be highly concentrated by liquid junction potentials that alter the cell potential in an unpredictable way. [VES 2008] mentioned that the apparent Eh decreased in metal chlorite solutions, but increased in salt concentration, and to 30 to 43 mV can be reached near saturation. A contribution by the decreasing concentration of free Fe<sup>3+</sup> due to the formation of Fe<sup>3+</sup>-chloro-complexes was assumed.

The pH- and Eh-values were measured by equipment "inoLab pH 720". This measurement was equipped with the SCHOTT Instruments pH Electrode blueline 14 pH. The electrode was calibrated by buffer solutions of pH = 4; pH = 7 and pH = 10. After the calibration, the equipment automatically evaluates the current status. The asymmetry (mV) and slope (mV/pH) always changed from -15 to + 20 mV and -60.5 to -57 mV/pH respectively.

The development of the pH and Eh value in the reactors was controlled during the overhead shaking experiments nearly daily and at intervals of 5 days in 30 days. The Eh values are affected by pH condition and the oxidative or reductive environment in each reactor was measured as Eh value. That is why the Eh value was converted into the rH parameter by following the equation:

$$rH = \frac{Eh}{28.75} + 2 x pH \tag{7.9}$$

This conversion of Eh data should offer a pH corrected view of the environmental development.

## 8 Experiments – results and discussion

- 8.1 Changes of swelling pressure, permeability and porosity of compacted MX80 bentonite due to oxydation of Fe<sup>2+</sup> and metallic iron in the pore space in the temperature range 25 °C 90 °C
- Tab. 8.1Development of swelling pressure and permeability of compacted MX80<br/>bentonite with NaCl-solution, IP21-solution or Opalinus clay pore water<br/>(OCPW) with different concentrations of Fe (database Fig. 8.1)

			Swellin	g pressu	re [bar]	Permeability [m <sup>2</sup> ]		
			25 °C	60 °C	90 °C	25 °C	60 °C	90 °C
	:(FeCl <sub>2</sub> mol/L]	1.0·10 <sup>-01</sup>	2.4	8.4	13.5	1.88·10 <sup>-16</sup>	6.20 <sup>.</sup> 10 <sup>-14</sup>	3.25·10 <sup>-17</sup>
		1.0 <sup>.</sup> 10 <sup>-02</sup>	3.9	7.8	14.1	3.99 <sup>.</sup> 10 <sup>-16</sup>	2.34·10 <sup>-14</sup>	1.23 <sup>.</sup> 10 <sup>-16</sup>
NaCl sol.		1.0·10 <sup>-03</sup>	4.9	9.1	13.6	6.80 <sup>.</sup> 10 <sup>-16</sup>	2.52·10 <sup>-15</sup>	4.70 <sup>-16</sup>
	0 -	1.0 <sup>.</sup> 10 <sup>-04</sup>	4.5	7.9	12.5	3.20·10 <sup>-14</sup>	8.98·10 <sup>-17</sup>	3.81·10 <sup>-15</sup>
	10% native Fe		4.9	6.8	17.3	1.70 <sup>.</sup> 10 <sup>-16</sup>	8.95 <sup>.</sup> 10 <sup>-14</sup>	2.60 <sup>.</sup> 10 <sup>-14</sup>
	C(FeCl <sub>2</sub> [mol/L]	1.0 <sup>.</sup> 10 <sup>-01</sup>	2.8	4.1		3.47·10 <sup>-15</sup>	2.68 <sup>.</sup> 10 <sup>-12</sup>	
		1.0 <sup>.</sup> 10 <sup>-02</sup>	3.1	3.6		2.20 <sup>.</sup> 10 <sup>-16</sup>	6.61·10 <sup>-12</sup>	
IP21 sol.		1.0 <sup>.</sup> 10 <sup>-03</sup>	2.9	3.6		8.90 <sup>.</sup> 10 <sup>-15</sup>	1.91·10 <sup>-13</sup>	
		1.0 <sup>.</sup> 10 <sup>-04</sup>	4.8	4.9		8.90·10 <sup>-15</sup>	8.05 <sup>.</sup> 10 <sup>-12</sup>	
	10% native Fe		4.8	7.9		9.83·10 <sup>-17</sup>		
Opalinus clay pore sol.	C(FeCl <sub>2</sub> [mol/L]	1.0 <sup>.</sup> 10 <sup>-01</sup>	25.7	16.4	3.5	9.48·10 <sup>-21</sup>	1.92·10 <sup>-17</sup>	3.25 <sup>.</sup> 10 <sup>-14</sup>
		1.0 <sup>.</sup> 10 <sup>-02</sup>	28.5	14.1	4.1	2.20·10 <sup>-20</sup>	3.50 <sup>.</sup> 10 <sup>-17</sup>	6.25·10 <sup>-15</sup>
		1.0 <sup>.</sup> 10 <sup>-03</sup>	19.6		4.9	3.60 <sup>.</sup> 10 <sup>-19</sup>		8.25 <sup>.</sup> 10 <sup>-15</sup>
		1.0 <sup>.</sup> 10 <sup>-04</sup>	35.6	13.9	6.5	6.10 <sup>.</sup> 10 <sup>-20</sup>	2.70 <sup>.</sup> 10 <sup>-18</sup>	7.90 <sup>.</sup> 10 <sup>-13</sup>
	10% native Fe		15.6	12.1	9.2	8.46·10 <sup>-16</sup>	6.85·10 <sup>-15</sup>	1.85·10 <sup>-15</sup>

## 8.1.1 Swelling pressure and permeability – experimental results

The experimental results of the measurement of swelling pressure and permeability are presented in Fig. 8.1 and Tab. 8.1. Temperature and ion strength have shown a clear differentiation in the development of these two parameters (Tab. 8.1). The experiments have shown the impact of the temperature, Fe-concentration and ion strength on swelling pressure and permeability.



empty symbols – FeCl<sub>2</sub> in the pore space; filled symbols – bentonite mixed with 10% Fepowder; experiments performed at 25 °C (diamond); at 60 °C (square) and 90 °C (triangle); size of empty symbols mirror the concentration of FeCl<sub>2</sub>.

Fig. 8.1 Development of swelling pressure and permeability of compacted MX80 bentonite with NaCl-solution (above), IP21-solution (middle), and Opalinus clay pore water (below) with different concentrations of Fe

**NaCl-solution (Fig. 8.1 above; Tab. 8.1):** An increasing temperature of experiments caused a rising swelling pressure (25 °C: < 5 bar; 60 °C: 5 – 10 bar; 90 °C > 10 bar). Otherwise, the temperature has not affected the data intervall of permeability ( $3 \cdot 10^{-17}$  m<sup>2</sup> –  $6 \cdot 10^{-14}$  m<sup>2</sup>). The variability of FeCl<sub>2</sub>-concentration in the experiments caused a different development in permeability. The permeability was reduced with the FeCl<sub>2</sub>-concentration at 25 °C and 90 °C. The experiments at 60 °C have shown an opposite behaviour: Permeability was rising with increased FeCl<sub>2</sub>-amount.

**IP21-solution (Fig. 8.1 middle; Tab. 8.1):** In these experiments, the temperature has differentiated the permeability ( $25 \,^{\circ}$ C: <  $1 \cdot 10^{-14} \,^{m2}$ ;  $60 \,^{\circ}$ C: >  $1 \cdot 10^{-14} \,^{m2}$ ). Here, the swelling pressure was not affected by temperature (nearby constant between 3 – 5 bar). The impact of the variable FeCl<sub>2</sub>-concentration cannot be significantly identified. But it seems that the behaviour of permeability is also following the development of NaCl-solutions: Permeability is reduced with rising FeCl<sub>2</sub>-amount in experiments at 25 °C and it could be increased with rising FeCl<sub>2</sub>-amount in experiments at 60 °C.

**Opalinus clay pore solution (Fig. 8.1 below; Tab. 8.1):** The Opalinus solution represents low ion strength in comparison to the experiments with NaCl- or IP21-solution. Swelling pressure and permeability have covered in Opalinus-experiments a more extended interval than in the two other mentioned experiments with high ion strength. In Opalinus experiments, too, the temperature controlled the swelling pressure like in NaCl-experiments, but in the opposite direction  $(25 \,^{\circ}\text{C}) \ge 20 \,\text{bar}$ ;  $60 \,^{\circ}\text{C}$ :  $10 - 20 \,\text{bar}$ ;  $90 \,^{\circ}\text{C} : < 10 \,\text{bar}$ ). An increasing experimental temperature reduced the resulting swelling pressure. The temperature also affected the permeability  $(25 \,^{\circ}\text{C}) < 1 \cdot 10^{-18} \,\text{m}^2$ ;  $60 \,^{\circ}\text{C} : 1 \cdot 10^{-17} \,\text{m}^2$ ;  $90 \,^{\circ}\text{C} : > 1 \cdot 10^{-16} \,\text{m}^2$ ). The FeCl<sub>2</sub>-concentration has shown a similar impact on swelling pressure or permeability as reported in NaCl- and IP21-solution. The swelling pressure was reduced with increased FeCl<sub>2</sub>-amount at  $60 \,^{\circ}\text{C}$ .

## 8.1.2 Discussion of swelling pressure and permeability results – assumed mechanism

Higher swelling pressure should reduce the permeability for as long as no other parameters influence the system. Following the labelling of data in Fig. 8.2, Fe- and Siprecipitation could also reduce the permeability. Fe precipitates in low temperature experiments (25 °C) and reduces the permeability and the swelling pressure. Breaking

Fe-cemented aggregates form channels and increase in this manner the permeability in experiments at 60 °C. The swelling pressure is maintained. Higher temperatures also increase the chemical activity mirrored by a higher dissolution potential. These conditions lead to an increased uptake and incorporation of Fe in different clay phases, but at 90 °C it also causes precipitation of Si. The higher Si-precipitation results again in a reduction of permeability accompanied by reduced swelling pressure. High Feconcentration could arrange again the formation of channels by breaking Si-cemented aggregates at 90 °C.

**NaCl-solution (Fig. 8.2 above):** In NaCl-solution the behaviour of swelling pressure and permeability show few specifics in comparison to the above described processes. Higher reaction activity by increased temperature leads to rising swelling pressure. It is a closed system. The higher potential of dissolution linked with the higher temperature lets only particles with a low sheet stress "survive", that means only crystals with a low amount of octahedral Fe and Mg. The charge decreases and so does even the thickness of quasicrystals caused by the low charge deficits in tetrahedral and octahedral layers. This process raises the swelling pressure. The decreasing charge with increasing temperature is proved by TEM-measurements from run products of experiments with MX80 bentonite with added 10 % Fe-powder (averaged total charge of all IS-mland diVS-ml-particles from experiments at 25 °C: 0.35; at 60 °C: 0.32; at 90 °C: 0.17; all values per (OH)<sub>2</sub> O<sub>10</sub>). Especially at 90 °C, only a higher concentration FeCl<sub>2</sub>-solution could limit the rising swelling pressure by Si-precipitations. Further increased concentrations of Fe (like in admixture with 10 % Fe-powder) support a channel formation by Si-cementation according to [PUS 1991].

**IP21-solution (Fig. 8.2 middle):** The divalent Mg-cation originated from IP21-solution limits the swelling pressure. Hence only an increasing permeability caused by channel-formation is observed as a response to Fe-cemented aggregates.

**Opalinus clay pore solution (Fig. 8.2 below):** The experiments with Opalinus-solution represent an open reaction system because of the low ion strength of Opalinus-solution in comparison to the NaCl- and IP21-experiments. In consequence of the open system, a higher reaction activity (that means a higher potential of dissolution) is accompanied by a removing of dissolved Si. The higher tetrahedral charge deficit is causing a rise in the total charge and even also the development of thicker quasicrystals. The swelling pressure is decreased with increased temperature. A channel-formation caused by Sicemented aggregates is not observed in these types of experiment.


Fig. 8.2 Assumed mechanism for the development of swelling pressure and permeability of compacted MX80 bentonite with NaCl-solution (above), IP21solution (middle) and Opalinus clay pore water (below) with different concentrations of Fe (legend see Fig. 8.1) Finally, comparing the experiments with three different solutions, ion strength and increasing Fe-amount support the reactivity in the barrier material in the order IP21 > NaCl >> Opalinus.

### 8.1.3 Porosity measurements

The intended porosity measurements were not very successful. Different methods have been applied but no reproducible data have been obtained. We are still working on developing procedures which guarantee better results. The difficulty is not to determine the total porosity but to get reliable figures for the interlayer space of the smectites. The interlayer space must be subtracted from the total porosity in order to obtain the effective porosity which controls the transport through fluid saturated compacted bentonites.

### 8.2 Measurements of diffusion coefficients in bentonites

Originally, it was planned to measure diffusion coefficients in compacted bentonites with and without the influence of iron in the system. However the measurements turned out to be difficult and very time consuming. A new procedure was developed. But so far good diffusion coefficients have been obtained only for systems without iron. The experiments with iron are still going on. First results however indicate that the order of magnitude of diffusion coefficients in systems with and without iron is not changed. These preliminary experimental results were confirmed by the modeling of reactive transport.

The measurement of diffusion coefficients of heavy metals in bentonites is normally very time-consuming. Bentonites are a mixture of different minerals. The more trace components are present in the bentonite, the longer it takes to reach a steady state in the through-diffusion experiments. To overcome this problem, a new method was developed by saturating the sample with target heavy metals at a very low concentration before the start of the through-diffusion experiment (TDE). This method turned out to be very successful.

Through-diffusion experiments were carried out with MX80 bentonite compacted to the raw density of 1.6 g/cm<sup>3</sup>. The solutions used were 50 % and 90 % halite saturated NaCl solution and a 90 % IP21 solution. The diffusion cells were made of titanium. The sam-

ple was flushed with solution containing the target heavy metal at low concentration followed by a through-diffusion experiment.

Through-diffusion experiments were conducted with the traditional and the new methods (Fig. 8.3). The experimental duration with the new TDE is considerably shortened.

Further experiments were conducted for Cd and Cs in 90 % NaCl solutions (Fig. 8.4 and Fig. 8.5) respectively. The boundary conditions of both Cd and Cs were set to the concentrations  $10^{-5}$  M or  $10^{-3}$  M for each end respectively. The samples were flushed with solution including  $10^{-5}$  M Cs and Cd for two days.



# **Fig. 8.3** Diffusion flux of Cs with the traditional (left) and the new through-diffusion experiments (right)



Fig. 8.4 Diffusion experiment with Cd



Fig. 8.5 Diffusion experiment with Cs

As a conclusion it can be said that the newly developed through diffusion method finally works well. It reduces the time needed for the experiments drastically. The results obtained so far for diffusion coefficients in compacted bentonite with NaCl solution are in the same order of magnitude as reported in the literature. The experiments are going on. In the near future results concearning the influence of iron on the diffusion coefficients will be available and published.

### 8.3 Kinetics for alteration of bentonites

### 8.3.1 Indications of different behaviour

Short-term overhead-shaking experiments were carried out to understand the kinetics of Fe, Mg-driven alteration processes of bentonite and to identify "sprinters" and "sleepers" among the bentonites. In addition, the possible effect of interlayer occupation on the alteration rate was also to be considered. A hypothesis was developed by a combination of the above two possible factors affecting alteration of the bentonite (Fig. 6.2 and Fig. 6.3).

A first comparison of TEM-EDX-results between Belle Fourche and Chambers bentonite has shown a remarkably different degree in illitization (Fig. 8.6). The run product of high level energy-experiments (60 rpm) for Belle Fourche bentonite was also characterised by montmorillonite as main phase. In contrast, the run product of Chambers bentonite has shown a remarkable illitisation in this experiment. Illite-smectite mixed layer phases with a %S = 60 % were the main mineral component. A limited degree of illitisation process could be observed for Belle Fourche bentonite, too (%S<sub>orig</sub> = 100 %;  $%S_{60 \text{ rpm}} = 90 \%$ ). The dissolved Si was removed from the tetrahedral space by the shaking procedure. This Si-mitigation process has supported the illitisation of smectite.



Measured using Jeol JEM-1210

Fig. 8.6 Different rates of alteration for different bentonites: Visualisation of TEM-EDX-results for Belle Fourche bentonite (South Dakota, API #27) representing a case of low alteration degree and Chambers bentonite (Arizona, API #23) representing a case of high alteration degree

The two bentonites have also shown a different behaviour in the development of the octahedral layer and the interlayer space during the illitisation process (Tab. 8.2):

- Belle Fourche
  - octahedral layer with a  $\pm$  constant charge (0.28)
  - substitution of AI by Fe in the octahedral sheet
  - ± continuous increasing of divalent cations in the interlayer space
- Chambers
  - octahedral layer with an increasing charge (from 0.37 to 0.43)
  - substitution of AI by Mg in the octahedral sheet
  - continuous decreasing of divalent cations in the interlayer space
  - continuous increasing of monovalent cations in the interlayer space.

Tab. 8.2TEM-EDX-analyses of original Belle Fourche (B. Fourche) (South Dakota,<br/>API #27) and Chambers (Arizona, API #23) bentonites and the run prod-<br/>ucts

	In	terlaye	er Spac	ce	Octahedra				Tetra	hedra	XII	"VI
	Са	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ti	AI	Si	All	n
B.Fourche	0.04	0.03	0.16	0.04	1.60	0.17	0.19	0.01	0.06	3.94	0.34	1.98
20 rpm	0.02	0.05	0.20	0.02	1.57	0.19	0.18	0.01	0.06	3.94	0.35	1.97
60 rpm	0.03	0.08	0.10	0.08	1.56	0.21	0.19	0.01	0.13	3.87	0.40	1.97
Chambers	0.15	0.04	0.05	0.01	1.45	0.16	0.38	0.01	0.06	3.94	0.38	2.00
20 rpm	0.12	0.02	0.13	0.03	1.44	0.16	0.39	0.01	0.06	3.94	0.45	2.00
60 rpm	0.01	0.09	0.32	0.13	1.40	0.17	0.41	0.01	0.24	3.76	0.65	2.00

Measured using Jeol JEM-1210, XII: interlayer charges, n<sup>VI</sup>: number of octahedral cations

Low level energy-overhead shaking (20 rpm) and high level energy-overhead shaking experiments (60 rpm) with remarkable alteration of Chambers from montmorillonite into illite-smectite mixed layer phases with %S ~ 60 % mirrored in tetrahedral Si from 3.94 to 3.87 (data of mineral formulae related to (OH)<sub>2</sub> O<sub>10</sub>)



### IS THERE ANY ALTERATION OF BENTONITE?

Measured using Jeol JEM-1210

diVS-ml structures disappear in Chambers during overhead-shaking experiments (red arrow: position of %Smax), different chemistry and particle thickness of smectite phases could be the possible reason for the different behavior

# Fig. 8.7Different behavior of IS-ml and diVS-ml as the two main smectite groups in<br/>Belle Fourche and Chambers bentonites

Furthermore, the development of smectite was different in the run products of Belle Fourche and Chambers. Smectite can be divided in two groups: (i) illite-smectite mixed layer series (IS-ml) according to [SRO 1992] and (ii) dioctahedral vermiculite-smectite mixed layer series (diVS-ml). According to [KAS 2002], [HER 2004], diVS-ml structures were to be considered as K- and charge deficient variants of IS-ml. diVS-ml particles were dissolved during the overhead-shaking experiment whereas no changes or minor changes in the IS-ml particles could be observed (Fig. 8.7).

# 8.3.2 Low level energy-experiments in 1N NaCl - solution (20 rpm, NaCl)

Seven different bentonites from the API series were used in the low level energyoverhead shaking experiments: Belle Fourche – South Dakota (API #27), Chambers – Arizona (API #23), Bayard – New Mexico (API # 30), Polkville – Mississippi (API # 20), Pioche – Nevada (API #32), Amory – Mississippi (API # 22a), Cameron – Arizona (API #31). Besides, MX80 bentonite in GRS-material series; 04F, 09F and 11F bentonite from selected BGR bentonite series were added in this experiment, too.

The bentonites was saturated by 1N NaCl solution, "solid:liquid"-ratio is 1:4, overhead shaking 20 rpm in 30 days at room temperature. Bentonites of this experiment were characterised by a different degree of smectite layers (from %Smax = 100 % as Belle Fouche and Bayard bentonites to %Smax = 50 % as Cameron bentonite) (Tab. 8.3). The general composition of interlayer space (Na-ratio) and octahedral layer ("Fe+Mg"-ratio) were already visualised in Fig. 6.3.

The related TEM-EDX-results are given in Tab. 8.3. Samples represent a full scale of Na-ratio in the interlayer space, but only in a limited manner the variability of 'Fe+Mg'-ratio for the octahedral layer.

The strength of alteration was described by the parameter  $\Delta$ %S. This parameter shall offer a numeric estimation of the degree of illitisation process in the run products in comparison to the original bentonite,

$$\Delta\%S = \%S_{\text{experiment}} - \%S_{\text{original}} \qquad \Delta\%S < 0: \text{Illitisation}; \Delta\%S > 0: \text{ smectitisation}$$

According to [SRO 1992], different proportions of smectitic layers were listed in Tab. 8.4.

Tab. 8.3 TEM-EDX-analyses of run products<sup>\*</sup> – bentonite in contact NaCl 1N – from low level energy-overhead shaking experiments (20 rpm), data of mineral formulae related to (OH)<sub>2</sub> O<sub>10</sub>

	In	terlaye	er Spa	се		Octahedra				Tetrahedra		
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ti	AI	Si	<b>XII</b>	n
BelleFourche	0.04	0.03	0.16	0.04	1.60	0.17	0.19	0.01	0.06	3.94	0.34	1.98
20 rpm	0.02	0.05	0.20	0.02	1.57	0.19	0.18	0.01	0.06	3.94	0.35	1.97
Chambers	0.15	0.04	0.05	0.01	1.45	0.16	0.38	0.01	0.06	3.94	0.44	2.00
20 rpm	0.12	0.02	0.13	0.03	1.44	0.16	0.39	0.01	0.06	3.94	0.45	2.00
Bayard	0.02	0.14	0.11	0.01	1.49	0.07	0.44	0.01	0.02	3.98	0.44	2.00
20 rpm	0.05	0.10	0.15	0.02	1.46	0.06	0.48	0.01	0.03	3.97	0.48	2.00
Polkville	0.01	0.10	0.10	0.02	1.51	0.25	0.22	0.01	0.08	3.92	0.34	1.98
20 rpm	0.02	0.07	0.20	0.01	1.48	0.25	0.23	0.01	0.12	3.88	0.41	1.97
Pioche	0.01	0.12	0.16	0.06	1.44	0.21	0.33	0.01	0.13	3.87	0.48	2.00
20 rpm	0.12	0.09	0.04	0.06	1.48	0.20	0.31	0.01	0.21	3.79	0.52	2.00
Amory	0.02	0.04	0.09	0.02	1.46	0.36	0.15	0.02	0.09	3.91	0.25	1.99
20 rpm	0.02	0.05	0.18	0.11	1.42	0.33	0.22	0.01	0.13	3.87	0.40	1.98
Cameron	0.02	0.07	0.19	0.19	1.49	0.32	0.16	0.01	0.34	3.66	0.56	1.98
20 rpm	0.02	0.07	0.15	0.26	1.50	0.33	0.14	0.01	0.40	3.60	0.59	1.98
MX80	0.04	0.04	0.01	0.02	1.59	0.21	0.16	0.04	0.05	3.95	0.19	1.99
20 rpm	0.06	0.09	0.00	0.03	1.51	0.17	0.30	0.02	0.05	3.95	0.33	2.00
04F	0.05	0.10	0.01	0.06	1.30	0.45	0.20	0.01	0.08	3.92	0.36	1.97
20 rpm	0.06	0.09	0.00	0.04	1.38	0.38	0.22	0.02	0.12	3.88	0.33	2.00
09F	0.04	0.03	0.02	0.01	1.63	0.20	0.15	0.01	0.01	3.99	0.17	2.00
20 rpm	0.09	0.09	0.00	0.03	1.36	0.30	0.28	0.06	0.16	3.84	0.39	2.00
11F	0.03	0.10	0.18	0.02	1.29	0.46	0.16	0.01	0.13	3.87	0.45	1.92
20 rpm	0.11	0.05	0.00	0.02	1.31	0.43	0.23	0.02	0.09	3.91	0.33	1.99
12F	0.14	0.02	0.00	0.01	1.37	0.29	0.33	0.01	0.01	3.99	0.33	2.00
20 rpm	0.08	0.12	0.00	0.01	1.22	0.38	0.39	0.03	0.03	3.97	0.39	2.01

\* Measured using Jeol JEM-1210; Samples: Belle Fourche – South Dakota (API #27), Chambers – Arizona (API #23), Bayard – New Mexico (API # 30), Polkville – Mississippi (API # 20), Pioche – Nevada (API #32), Amory– Mississippi (API # 22a), Cameron – Arizona (API #31), MX80 – bentpnite from GRSmaterial series, 04F, 09F and 11F from BGR-collection bentonite series. XII: interlayer charge, n<sup>VI</sup>: number of octahedral cations.

	AI_IV	%S <sub>original</sub>	AI_IV	%S <sub>experiment</sub>	<b>Δ%S</b>
	per (OH) <sub>2</sub> O <sub>10</sub>		per (OH) <sub>2</sub> O <sub>10</sub>		
Belle Fourche	0.06	97 %	0.05	97 %	0%
Chambers	0.06	97 %	0.06	97 %	0%
Bayard	0.02	(105 %)	0.03	(103 %)	-2 %
Polkville	0.08	93 %	0.12	85 %	-8 %
Pioche	0.13	83 %	0.21	69 %	-14 %
Amory	0.09	91 %	0.13	83 %	-8 %
Cameron	0.34	49 %	0.40	40 %	-8 %
MX80	0.05	99 %	0.05	99 %	0%
04F	0.08	93 %	0.12	85 %	-8 %
09F	0.01	(107 %)	0.16	(78 %)	-29 %
11F	0.13	83 %	0.09	91 %	+8 %
12F	0.01	(107 %)	0.03	103 %	-4 %

Tab. 8.4Low level energy-overhead shaking experiments (20 rpm) of bentonite in<br/>contact with 1N NaCl

Calculation of  $\Delta$ %S from TEM-EDX-analysed mineral formulae (Measured using Jeol JEM-1210; data presented in Tab. 8.3; calculation visualised in Fig. 6.2 approaching [SRO 1992]);  $\Delta$ %S: degree of alteration ( $\Delta$ %S < 0: illitization;  $\Delta$ %S > 0: smectitisation), %S: smectite layer ratio; Al\_IV: Al<sup>3+</sup> in tetrahedral layer

The transfer of the analytical results to the low level energy experiment's run products in the hypothesis matrix (presented in Fig. 6.2) has shown a conflict with the mentioned hypothesis. The visualisation of parameter  $\Delta$ %S has drawn no clear trend for illitisation with a rising ratio of Na in the interlayer space (Fig. 8.8). Following the hypothesis (Fig. 6.2), Na-bearing smectite has a larger distance of interlayer space and would be more sensitive to breaking stacks than Ca-pronounced smectite. Additionally, an increase of "Mg + Fe" in the octahedral layer has promoted a faster illitisation process. This behaviour could be caused by higher sheet stress due to the higher ion radius of Fe and Mg.

Illitisation was used as main parameter to estimate numerically the different degrees of smectite alteration in the run products. The parameter  $\Delta$ %S was conducted from mineral formulae of the particles basing on TEM-EDX-measurements. For validating these TEM-EDX-data, the positions of (001)/(002)- and (002)/(003)-interferences were used for the estimation of the percentage of smectite in IS-ml (in ethylene-glycol saturated oriented mounts of fraction < 2 µm) according to the NEWMOD-model by [MOO 1997]. This comparison between XRD-methodology and TEM-EDX-measurement has resulted in a general confirmation of the observed illitisation (Fig. 8.9).



Filled circle: illitisation process, open circle: smectitisation process; the size of the circles presents the rate of transformation of the smectite Positions of the samples determined by mineral formulae calculated by TEM-EDX-analyses; alteration  $\Delta$ %S = S%<sub>experiment</sub> - S%<sub>origin</sub> ( $\Delta$ %S > 0: smectitisation;  $\Delta$ %S < 0 illitisation)

Fig. 8.8 Smectitisation and illitisation by low level energy-overhead shaking experiments (20 rpm) of bentonite in contact with 1n NaCl; higher Na-occupation in the interlayer space and higher octahedral Fe, Mg-ratio seemed to increase the alteration process



Dashed line – theoretical baseline for %S by TEM and %S by XRD

**Fig. 8.9** Verification of illitisation basing on TEM-EDX-data by XRD-measurement ("%S by XRD" according to [MOO 1997])

### 8.3.3 High level energy experiments in 1n NaCl - solution (60 rpm, NaCl)

Nine different bentonites were approached in the high level energy overhead shaking experiments (room temperature, 30 days, 1N NaCl-solution, 1:4 "solid:liquid"-ratio; 60 rpm): Belle Fourche – South Dakota (API #27), Chambers – Arizona (API #23), Pio-che – Nevada (API #32), Otay – California (API # 24), Garfield (nontronite) – Washington (API #33a), MX80 bentonite of GRS-material series and 04F, 09F, 11F bentonite from selected BGR bentonite series.

Tab. 8.5 TEM-EDX-analyses of run products – bentonite in contact with NaCl 1n – from high level energy overhead shaking experiments (60 rpm). Data of mineral formulae related to (OH)<sub>2</sub> O<sub>10</sub>

		Inter	layer S	Space		Oc	tahed	ral Spa	ace	Tetrahedra		VII	
	Ca	Mg	Na	к	Fe <sup>3+</sup>	AI	Fe <sup>3+</sup>	Mg	Ti	AI	Si		n
Be. Fourch e	0.04	0.03	0.16	0.04		1.60	0.17	0.19	0.01	0.06	3.94	0.34	1.98
60 rpm	0.03	0.08	0.10	0.08	0.00	1.56	0.21	0.19	0.01	0.13	3.87	0.40	1.97
Pioche	0.01	0.12	0.16	0.06	0.00	1.44	0.21	0.33	0.01	0.13	3.87	0.48	2.00
60 rpm	0.02	0.13	0.14	0.11	0.00	1.43	0.23	0.33	0.01	0.21	3.79	0.55	2.00
Otay	0.03	0.02	0.20	0.06	0.00	1.43	0.32	0.19	0.02	0.07	3.93	0.36	1.96
60 rpm	0.04	0.11	0.09	0.09	0.00	1.40	0.13	0.45	0.02	0.05	3.95	0.49	2.00
Garfield	0.02	0.03	0.07	0.02	0.07	0.24	1.74	0.00	0.01	0.39	3.61	0.39	2.00
60 rpm	0.09	0.12	0.04	0.07	0.02	0.16	1.79	0.03	0.02	*0.56	3.44	0.57	2.00
Chambers	0.15	0.04	0.05	0.01	0.00	1.45	0.16	0.38	0.01	0.06	3.94	0.44	2.00
60 rpm	0.01	0.09	0.32	0.13	0.00	1.40	0.17	0.41	0.01	0.24	3.76	0.65	2.00
MX80	0.04	0.04	0.01	0.02	0.00	1.59	0.21	0.16	0.04	0.05	3.95	0.19	1.99
60 rpm	0.05	0.09	0.00	0.03	0.00	1.52	0.15	0.31	0.02	0.02	3.98	0.31	2.00
04F	0.05	0.10	0.01	0.06	0.00	1.30	0.45	0.20	0.01	0.08	3.92	0.36	1.97
60 rpm	0.04	0.10	0.00	0.03	0.00	1.29	0.45	0.23	0.03	0.10	3.90	0.30	2.00
09F	0.04	0.03	0.02	0.01	0.00	1.63	0.20	0.15	0.01	0.01	3.99	0.17	2.00
60 rpm	0.08	0.10	0.00	0.02	0.00	1.50	0.21	0.24	0.04	0.16	3.84	0.37	2.00
11F	0.03	0.10	0.18	0.02	0.00	1.29	0.46	0.16	0.01	0.13	3.87	0.45	1.92
60 rpm	0.13	0.05	0.00	0.07	0.00	1.29	0.42	0.28	0.01	0.17	3.83	0.43	2.00
12F	0.14	0.02	0.00	0.01	0.00	1.37	0.29	0.33	0.01	0.01	3.99	0.33	2.00
60 rpm	0.06	0.09	0.00	0.10	0.00	1.25	0.35	0.37	0.03	0.03	3.97	0.41	2.00

Measured using Jeol JEM-1210; Samples: Be. Fourche: Belle Fourche – South Dakota (API #27), Chambers – Arizona (API #23), Pioche – Nevada (API #32), Otay – California (API # 24), Garfield (nontronite) – Washington (API #33a); \*0.56 – included also tetrahedral Fe<sup>3+</sup><sub>0.01</sub>, MX80 – bentonite from GRS-material series, 04F, 09F and 11F from BGR-collection bentonite series; XII: interlayer charge, n<sup>VI</sup>: number of octahedral cations.

The related TEM-EDX-results of run products from high level energy overhead shaking experiments in NaCl 1N are summarised in Tab. 8.5. These bentonites were characterised by different values for Si in the tetrahedral layer (from Si = 3.94 (OH)<sub>2</sub>O<sub>10</sub> like Belle Fourche and Chambers to Si =  $3.61 (OH)_2O_{10}$  like Garfield). It was observed that the samples represented a full scale of Na-ratio in the interlayer space and that there was a broad variability of the "Fe+Mg" -ratio for the octahedral layer.

The parameter  $\Delta$ %S was used again to describe the strength of alteration in this experimental series. In accordance with [SRO 1992], the different proportions of smectite layers are listed in Tab. 8.6.

	AI_IV per (OH) <sub>2</sub> O <sub>10</sub>	%S <sub>original</sub>	AI_IV per (OH) <sub>2</sub> O <sub>10</sub>	%S <sub>experiment</sub>	∆%S
Belle Fourche	0.06	97 %	0.13	83 %	-14 %
Pioche	0.13	83 %	0.21	69 %	-14 %
Otay	0.07	95 %	0.05	99%	+4 %
Garfield	0.39	(42 %)	0.56	(22 %)	-20 %
Chambers	0.06	97 %	0.24	64 %	-33 %
MX80	0.05	99 %	0.02	(105 %)	+6 %
04F	0.08	93 %	0.10	89 %	-4 %
09F	0.01	(107 %)	0.16	78 %	-29 %
11F	0.13	83 %	0.17	76 %	-7 %
12F	0.01	(107 %)	0.03	103 %	-4 %

Tab. 8.6High level energy overhead shaking experiments (60 rpm) of bentonite in<br/>contact with 1N NaCl

Calculation of parameter  $\Delta$ %S from TEM-EDX-analysed mineral formulae, measured using Jeol JEM-1210; data presented in Tab. 8.5; calculation visualised in Fig. 6.2 approaching [SRO 1992] $\Delta$ %S: degree of alteration ( $\Delta$ %S < 0: illitisation;  $\Delta$ %S > 0: smectitisation), %S: smectite layer ratio; Al\_IV: Al<sup>3+</sup> in tetrahedral layer

The transfer of the analytical results to the high level energy experiment's run products in the hypothesis-matrix (presented in Fig. 6.2) has shown a conflict with the mentioned hypothesis. The visualisation of  $\Delta$ %S has resulted in an increasing illitisation with a decreasing ratio of Na in the interlayer space (Fig. 8.10). The high level energy experiment's run products have shown the expected behaviour as predicted before in the hypothesis (Fig. 6.2). The decreasing ratio of Na in the interlayer space and increasing "Mg + Fe" in the octahedral layer have promoted a faster illitisation.

Comparing the mineral formulae of the starting material and the high-energy experiment's run products (Tab. 8.5), an increase of interlayer charge could be found. The behaviour of octahedral AI and Fe in the run products was controlled by the Na-ratio in the interlayer space. A high Na-ratio protects octahedral AI and reduces the Fe-value via substitution of Fe by Mg (e. g. Otay). Especially, the start material with low Na-ratio in the interlayer space has shown after the high level energy overhead shaking experiments a high Na-ratio in the interlayer space of run products (e. g., Chambers).



Filled circle: illitizsation process, open circle: smectitisation process; the size of the circles presents the rate of transformation of the smectite Position of the samples determined by mineral formulae calculated by TEM-EDX-analyses; alteration  $\Delta$ %S = S%experiment - S%origin ( $\Delta$ %S > 0: smectitisation;  $\Delta$ %S < 0 illitisation)

Fig. 8.10 Smectitisation and illitisation by high level energy overhead shaking experiments (60 rpm) of bentonite in contact with 1N NaCl; higher "Ca+ Mg"- occupation in the interlayer space and higher octahedral Fe, Mg-ratio seems to increase the alteration process

#### 8.3.4 Low level energy experiments in deionised water (20 rpm, H<sub>2</sub>O)

Two bentonites from the BGR-collection (04F, 09F), two samples from GRS-material (MX80, Friedland clay) and GeoHallas clay, Vietnam clay of HGW-material were used in the low level energy overhead shaking experiment (room temperature, 30 days, de-ionised water, 1:10 "solid:liquid"-ratio, 20 rpm). The bentonites and clays was saturated by deionised water with the ratio of solid:liquid is 1:10.

The starting materials of clay and bentonites are described in chapter 3 and in more detail in Tab. 8.7 by a different content of smectitic layer (from  $S\%_{max} = 100\%$  like 09F bentonite to  $S\%_{max} = 40\%$  like Friedland clay) by TEM-EDX measurement. The general

composition of the Na-ratio in the interlayer space and the Fe+Mg-ratio in the octahedral layer is presented in Tab. 8.8. These present the full scale of the "Fe+Mg" ratio in the octahedral layer but are limited with respect to the variability of the Na-ratio in the interlayer.

Tab. 8.7	Low level energy overhead shaking experiments (20 rpm) of bentonite in
	contact with deionised water

	AI_IV per (OH) <sub>2</sub> O <sub>10</sub>	%S <sub>original</sub>	AI_IV per (OH) <sub>2</sub> O <sub>10</sub>	%S <sub>experiment</sub>	∆%S
04F	0.08	93 %	0.07	95 %	+2 %
09F	0.01	(107 %)	0.12	85 %	-22 %
12F	0.01	(107 %)	0.04	(101 %)	-6 %
MX80	0.05	99%	0.04	(101 %)	+2 %
Friedland clay	0.40	40 %	0.21	69 %	+29 %
GeoHellas	0.27	59%	0.35	47 %	-12 %
Vietnam	0.15	80 %	0.11	87 %	+7 %

Calculation of parameter  $\Delta$ %S from TEM-EDX-analysed mineral formulae (Measured using Jeol JEM-1210 data presented in Tab. 8.8; calculation visualized in Fig. 6.2 approaching [SRO 1992]);  $\Delta$ %S; degree of alteration ( $\Delta$ %S < 0: illitisation;  $\Delta$ %S > 0: smectitisation), %S: smectite layer ratio; Al\_IV: Al<sup>3+</sup> in tetrahedral layer

	Int	terlaye	er Spa	се	Octahedra				Tetrahedra		VII	n <sup>VI</sup>
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ti	AI	Si		n
04F	0.05	0.10	0.01	0.06	1.30	0.45	0.20	0.01	0.08	3.92	0.36	1.97
20 rpm	0.02	0.10	0.00	0.02	1.41	0.37	0.21	0.01	0.07	3.93	0.26	2.00
09F	0.04	0.03	0.02	0.01	1.63	0.20	0.15	0.01	0.01	3.99	0.17	2.00
20 rpm	0.05	0.11	0.00	0.02	1.46	0.24	0.26	0.04	0.12	3.88	0.35	2.00
12F	0.14	0.02	0.00	0.01	1.37	0.29	0.33	0.01	0.01	3.99	0.33	2.00
20 rpm	0.08	0.11	0.00	0.01	1.27	0.31	0.41	0.02	0.04	3.96	0.40	2.01
MX80	0.04	0.04	0.01	0.02	1.59	0.21	0.16	0.04	0.05	3.95	0.19	1.99
20 rpm	0.03	0.07	0.00	0.02	1.63	0.16	0.19	0.02	0.04	3.96	0.22	2.00
Friedland	0.01	0.13	0.03	0.23	1.51	0.31	0.12	0.02	0.40	3.60	0.53	1.96
20 rpm	0.02	0.07	0.00	0.16	1.55	0.30	0.12	0.02	0.21	3.79	0.35	1.99
Geohellas	0.09	0.13	0.00	0.12	0.96	0.52	0.50	0.02	0.27	3.73	0.57	2.00
20 rpm	0.02	0.16	0.00	0.20	1.26	0.46	0.29	0.01	0.35	3.65	0.55	2.03
Vietnam	0.03	0.09	0.00	0.03	0.57	1.19	0.15	0.02	0.15	3.85	0.28	1.93
20 rpm	0.02	0.11	0.00	0.05	0.57	1.20	0.19	0.01	0.11	3.89	0.31	1.97

# **Tab. 8.8**TEM-EDX-analyses of run products – bentonite in contact with deionisedwater – from low level energy overhead shaking experiments (20 rpm)

Data of mineral formulae related to  $(OH)_2 O_{10}$ , measured using Jeol JEM-1210, XII: interlayer charges,  $n^{VI}$ : number of octahedral cations



Filled circle: illitisation process, open circle: smectitisation process; the size of the circles presents the rate of transformation of the smectite

**Fig. 8.11** Smectitisation and illitisation by low level energy-overhead shaking experiments of bentonite in contact with deionised water (20 rpm)

The visualisation of parameter  $\Delta$ %S<sub>max</sub> has shown a cloudy trend and a conflict with the mentioned hypothesis. There are two transformation ways of clay and bentonite in this series. An Illitisation process happened to Geohellas clay, 04F and 09F bentonite in reversible motion to the smectitisation of Vietnam clay, Friedland clay and MX80 bentonite.

### 8.3.5 High level energy experiments in deionised water (60 rpm, H<sub>2</sub>O)

A short-term experiment with six samples (04F bentonite, 09F bentonite, MX80 bentonite, Tab. 8.9 Friedland clay, GeoHellas clay, Vietnam clay) in contact with deionised water and overhead shaking at 60 rpm for 30 days was carried out to analyse mainly the kinetics of Fe, Mg in the octahedral layer and of Na in the interlayer as driven alteration of bentonite.

Position of samples determined by mineral formulae calculated by TEM-EDX-analyses, alteration expressed as  $\Delta$ %S = S%<sub>experiment</sub> - S%<sub>origin</sub> ( $\Delta$ %S > 0: smectitisation;  $\Delta$ %S < 0 illitisation)

Tab. 8.9	High level energy overhead shaking experiments (60 rpm) of bentonite in
	contact with deionised water

	AI_IV per (OH) <sub>2</sub> O <sub>10</sub>	%S <sub>original</sub>	AI_IV per (OH) <sub>2</sub> O <sub>10</sub>	%S <sub>experiment</sub>	∆%S
04F	0.08	93 %	0.13	83 %	-10 %
09F	0.01	(107 %)	0.06	97 %	-10 %
12F	0.01	(107 %)	0.02	(105 %)	-2 %
MX80	0.05	99%	0.06	97 %	-2 %
Friedland clay	0.40	40 %	0.22	67 %	+27 %
Geohellas	0.27	59 %	0.17	76 %	+17 %
Vietnam	0.15	80 %	0.09	91 %	+11%

Calculation of parameter  $\Delta$ %S from TEM-EDX-analysed mineral formulae (data presented in Tab. 8.10; calculation visualised in Fig. 6.2 approaching [SRO 1992]), measured using Jeol JEM-1210;  $\Delta$ %S: degree of alteration ( $\Delta$ %S < 0: illitisation;  $\Delta$ %S > 0: smectitisation), %S: smectite layer ratio; Al\_IV: Al<sup>3+</sup> in tetrahedral layer

**Tab. 8.10** TEM-EDX-analyses of run products – bentonite in contact with deionised water – from high level energy overhead shaking experiments (60 rpm)

	Int	terlaye	er Spa	се		Octahedra				Tetrahedra		, VI
	Ca	Mg	Na	κ	ΑΙ	Fe <sup>3+</sup>	Mg	Ti	AI	Si	ΛII	n
04F	0.05	0.10	0.01	0.06	1.30	0.45	0.20	0.01	0.08	3.92	0.36	1.97
60 rpm	0.02	0.12	0.00	0.03	1.40	0.36	0.21	0.03	0.13	3.87	0.31	2.00
09F	0.04	0.03	0.02	0.01	1.63	0.20	0.15	0.01	0.01	3.99	0.17	2.00
60 rpm	0.04	0.07	0.00	0.02	1.53	0.26	0.18	0.02	0.06	3.94	0.26	1.99
12F	0.14	0.02	0.00	0.01	1.37	0.29	0.33	0.01	0.01	3.99	0.33	2.00
60 rpm	0.02	0.12	0.00	0.01	1.32	0.37	0.29	0.02	0.02	3.98	0.29	2.00
MX80	0.04	0.04	0.01	0.02	1.59	0.21	0.16	0.04	0.05	3.95	0.19	1.99
60 rpm	0.05	0.09	0.00	0.02	1.54	0.16	0.27	0.03	0.06	3.94	0.30	2.00
Friedland	0.01	0.13	0.03	0.23	1.51	0.31	0.12	0.02	0.40	3.60	0.53	1.96
60 rpm	0.01	0.09	0.00	0.18	1.58	0.28	0.10	0.01	0.22	3.78	0.39	1.98
Geohellas	0.09	0.13	0.00	0.12	0.96	0.52	0.50	0.02	0.27	3.73	0.57	2.00
60 rpm	0.04	0.16	0.00	0.10	0.94	0.70	0.33	0.03	0.17	3.83	0.49	2.00
Vietnam	0.03	0.09	0.00	0.03	0.57	1.19	0.15	0.02	0.15	3.85	0.28	1.93
60 rpm	0.03	0.12	0.00	0.01	0.51	1.18	0.24	0.02	0.09	3.91	0.31	1.95

Measured using Jeol JEM-1210; XII: interlayer charges,  $n^{VI}$ : number of octahedral cations, data of mineral formulae related to (OH)<sub>2</sub> O<sub>10</sub>

The general composition of the Na-ratio and Fe+Mg-ratio of the original bentonites was visualised in Fig. 8.12. The run products of them were analysed by TEM-EDX measurement with the aim to identify the transformation of the bentonite. The different proportions of smectite layers were identified by [SRO 1992] and summarised in Tab. 8.9.

Illitisation and smectitisation were detected, alternately. The visualisation of  $\Delta$ %S parameter shows two trends of alteration:

- An increase of illitisation with decreasing ratio of Na/Na+Mg+Ca in the interlayer space and increasing ratio of "Fe+Mg" in the octahedral space for 04F, 09F and MX80 bentonites.
- A higher Na-ratio in the interlayer space and lower "Fe+Mg" in the octahedral layer has prevented an alteration of the bentonite and promoted the smectitisation process like Friedland clay. A decrease of smectitisation happened to the low Na-ratio and high ratio of "Fe+Mg" like Geohellas and Vietnam clay.



Filled circle: illitisation process, open circle: smectitisation process; the size of the circles presents the rate of transformation of the smectite Position of the samples determined by mineral formulae calculated by TEM-EDX-analyses, alteration expressed as  $\Delta$ %S = S%<sub>experiment</sub> – S%<sub>origin</sub> ( $\Delta$ %S > 0: smectitisation;  $\Delta$ %S < 0 illitisation)

**Fig. 8.12** Smectitisation and illitisation by high level energy overhead shaking experiments of bentonite in contact with deionised water (60 rpm)

Concerning the differentiation of mineral formulae between original materials and run product samples, a decrease of the interlayer charge could be detected. The behaviour of Fe and AI in the octahedral layer was driven by the substitution of AI for Si in the tetrahedral and Na-ratio in the interlayer space.

### 8.3.6 Modelling of the driving forces of alteration in smectite

#### Overhead shaking (60 rpm, NaCl)

Overhead shaking experiments at 60 rpm in 1n NaCl-solution have shown that a high Na-amount in the interlayer space seemed to protect smectite against alteration. Otherwise, a high (Fe+Mg)-ratio in the octahedral layer could support the alteration of smectite. Alteration was mainly observed as illitisation (Fig. 8.13). Illitisation was expressed by negative values of the term  $\Delta$ %S (equation (8.2)).



Filled circle: illitisation process, open circle: smectitization process; the size of the circles presents the rate of transformation of the smectite; dashed line – border line between illitisation & smectitisation, which position was mainly caused by the intensity of percolation

Fig. 8.13 Smectitisation and illitisation caused by high energy overhead shaking experiments (OSE), 60 rpm, NaCl

The following procedures were applied to model the measured alteration processes:

 Calculation of smectite layer ratio (%S) using tetrahedral AI from mineral formula according to [SRO 1992]:

$$%S = 100.38 \cdot ({}^{1\vee}AI)^2 - 213 \cdot ({}^{1\vee}AI) + 109.4$$
(8.1)

Calculation of degree of alteration (Δ%S):

$$\Delta \% S = \% Sexperiment - \% Soriginal$$
(8.2)

Illitisation in the case of  $\Delta$ %S < 0 and smectitisation in the case of  $\Delta$ %S > 0

Model of driving forces by interlayer cations (Δ%S<sub>XII</sub>) approaching measured samples (Fig. 8.13):

$$\Delta S_{\rm XII} = 15.09 \cdot \ln(C_{\rm Na}) - 68.26 \tag{8.3}$$

can = Na / (Na + Ca + Mg) in the interlayer space

• Data points (applied in Fig. 8.14A) were empirically determined by:

$$\Delta \% S_{XII\_i} = \Delta \% S_{meas\_i} - \Delta \% S_{VI\_assumed} \qquad \text{for } \Delta \% S_{meas\_i} < 0 \qquad (8.4a)$$

$$\Delta\%S_{XII\_i} = \Delta\%S_{perc} - \Delta\%S_{VI\_assumed} - \Delta\%S_{meas\_i} \quad \text{for } \Delta\%S_{meas\_i} \ge 0 \quad (8.4b)$$

 $\Delta$ %S<sub>VI\_assumed</sub> estimated as -1 %;  $\Delta$ %S<sub>perc</sub> postulated as -35 %

Any dissolution/precipitation process was affected due to the mitigation of dissolved Si and other cations from the interlayer space into the bulk solution by shaking activity. The capacity for this mitigation was defined here as illitisation potential by percolation (shaking) – expressed as  $\Delta$ %S<sub>perc</sub>.  $\Delta$ %S<sub>perc</sub> was assumed empirically in high level energy experiments (60 rpm, NaCl) as -35%. This means that the shaking activity at 60 rpm represented a potential for an illitisation of smectite up to -35% by removing dissolved Si. Consequently, a higher available amount of dissolved Si should cause smectitisation. Additionally, a certain impact of octahedral cations ( $\Delta$ %S<sub>VI\_assumed</sub>) on the measured values also has to be considered.



**Fig. 8.14** Model of the impact of interlayer cations (A) and octahedral cations (B) on illitisation as well as verification of the model with measured data (C)

A similar procedure was applied to model the impact by octahedral cations ( $\Delta$ %S<sub>VI</sub>). The different influence of interlayer cations on each data point was considered by equation (8.3). Finally, the model for driving forces by composition of the octahedral layer ( $\Delta$ %S<sub>VI</sub>) could be described as follows (Fig. 8.14B):

$$\Delta S_{\rm VI} = -4.36 \cdot \ln(C_{\rm FeMg}) + 7.47 \tag{8.5}$$

$$C_{FeMq} = (Fe + Mg) / (Fe + Mg + AI)$$
 in octahedral position

In the end, the total degree of alteration was defined as:

$$\Delta\%S_{\text{total}} = \Delta\%S_{\text{XII}} + \Delta\%S_{\text{VI}}$$
(8.6)

A comparison between the two assumed driving forces  $\Delta$ %S<sub>XII</sub> and  $\Delta$ %S<sub>VI</sub> has shown good agreement (Fig. 8.14C).

An application of this model to the measured results visualised in Fig. 8.13, offeres now the following explanations: A high Na-amount and high amount of octahedral AI stabi-

lises bentonite like Otay against alteration (characterized as "Sleeper"). Higher concentrations of Ca+Mg in the interlayer space and/or octahedral Fe+Mg-cations promote more dissolved Si. Illitisation occurs if this value of dissolved Si is lower than the Simitigation potential by overhead shaking activity ( $\Delta$ %S<sub>perc</sub>) under the applied experimental conditions. However, smectitisation can be detected if the dissolved Si-amount is larger than  $\Delta$ %S<sub>perc</sub>. Intensive dissolution processes can also override the potential of smectitisation (if %S = 100 % would be achieved). Consequently, a clogging by non-mitigated and therefore locally precipitated Si is to be expected (Fig. 8.13).

### Overhead Shaking (20 rpm, NaCl)

The low level energy overhead shaking experiments have shown a more complex data distribution between illitisation and smectitisation than the high energy level experiments (Fig. 8.15). It seems that the multiple switching between illitisation and smectitisation could not only be explained by an approach of the same driving forces as in high level energy experiments. Therefore the samples of this series were divided into two groups. Group A followed the models to  $\Delta\%S_{XII}$  and  $\Delta\%S_{VI}$  tested for high energy level experiments. The model parameters for  $\Delta\%S_{perc}$ ,  $\Delta\%S_{XII}$  and  $\Delta\%S_{VI}$  of this group were adopted as in high level energy experiments (Fig. 8.16). This means that a high Na-amount in the interlayer space and a low octahedral Fe+Mg-ratio would stabilise the smectite. The pressure for illitisation by interlayer cations was lower in low level energy experiments. Otherwise, the forces by octahedral occupation were low and similar for the two types of experiments.

The behaviour of the samples in group B could only be explained by a contrasting behaviour of the interlayer cations: a low Na-amount in the interlayer space now seemed to stabilise the smectite. Additionally, the impact was raised remarkably for illitisation as a result of the occupation of the octahedral layer (Fig. 8.17).



Filled circle: illitisation process, open circle: smectitisation process; the size of the circles presents the rate of transformation of the smectite

Fig. 8.15 Smectitisation and illitisation caused by low level overhead shaking experiments (OSE), 20 rpm, NaCl



Filled circle: illitisation process, open circle: Smectitisation process, crossed symbols: bentonite and clay samples of group B; the size of the circles presents the rate of transformation of the smectite

Dashed line – border line between illitisation & smectitisation, (position was mainly caused by the intensity of percolation)

Fig. 8.16 Modelling of Group A: Smectitisation and illitisation caused by low level energy overhead shaking experiments (OSE), 20 rpm, NaCl



Filled circle: illitisation process, open circle: smectitisation process, crossed symbols: bentonite and clay samples of group A; the size of the circles presents the rate of transformation of the smectite

Dashed line – border line between illitisation & smectitisation, (position was mainly caused by the intensity of percolation)

**Fig. 8.17** Modelling of Group B: Smectitisation and illitisation caused by low level energy overhead shaking experiments (OSE), 20 rpm, NaCl

### Overhead Shaking (20 + 60 rpm, H<sub>2</sub>O)

The alteration in the low and high energy level experiments (20 rpm and 60 rpm) in water was also characterised by the mentioned two types of influence by interlayer cations. The same parameters for modelling were used for 20 rpm in NaCl-solution and in water (Fig. 8.18).

# Explanations regarding to the different $\Delta$ %S<sub>XII</sub>-groups in low level energy experiments (20 rpm, NaCl & H<sub>2</sub>O and 60 rpm in H<sub>2</sub>O)

Interlayer cations have shown in the low level energy-experiments (20 rpm H<sub>2</sub>O, NaCl) two different types of potential for illitisation – group A and group B. Group A (Fig. 8.16) was composed of B09 (BGR-collection), Cameron, Amory, Pioche, Polkville (API-standards) and MX80 samples. Otherwise, samples B04, B11 (from BGR-collection), Belle Fourche, Bayard, Chambers (from API-standards) as well as Vietnam clay and

GeoHellas (Greece) were members of group B (Fig. 8.17). The Friedland clay sample has its own additional driving force concerning illitisation – pyrite. That is why it was not possible to classify this sample into one of the two groups.

In a first discussion it was not clear what could be the significant parameter in the composition to distinguish group A and group B. XRD-, FTIR- and TEM-EDX-results were characterised by large overlapping data intervals for the two groups.



**Fig. 8.18** Overhead shaking experiments: Overview of equations modelling the different impacts by  $\Delta$ %S<sub>XII</sub> and  $\Delta$ %S<sub>VI</sub>

Empirically, a way was found to predict the different behaviours of bentonites in low level energy experiments by chemical parameters of smectite (Fig. 8.19). Following that, smectites with dominating octahedral AI  $[AI_{oct} > 1.4 \text{ per } (OH)_2 O_{10}]$  and a remarkable amount of octahedral Fe  $[Fe^{3+}_{oct} > 0.2 \text{ per } (OH)_2 O_{10}]$  were classified as members of group A. These smectites were protected by high Na in the interlayer space. Otherwise, smectites also with dominating octahedral AI  $[AI_{oct} > 1.4 \text{ per } (OH)_2 O_{10}]$  and low amounts of octahedral Fe  $[Fe^{3+}_{oct} < 0.2 \text{ per } (OH)_2 O_{10}]$  or smectites generally with reduced octahedral AI  $[AI_{oct} < 1.4 \text{ per } (OH)_2 O_{10}]$  or smectites generally with reduced octahedral AI  $[AI_{oct} < 1.4 \text{ per } (OH)_2 O_{10}]$  belonged to group B. Such smectites were protected by Ca and Mg in the interlayer space.



**Fig. 8.19** Chemical parameters classifying bentonites as members of group A or group B concerning their alteration in low energy level experiments



Diagram for pH-related dissolution behaviour according to [SEI 1990]

Fig. 8.20 Different pH-environments during the genesis of bentonites could be responsible for different chemical compositions of octahedral layers of smectites

The combination of TEM-EDX-analyses and the positions of FTIR-bends of  $\delta_{AIFe-OH}$  and  $\delta_{AIAI-OH}$  have shown a strong classification of these two groups (Fig. 8.19).

A discussion of the background of the octahedral composition allows the assumption that there are three classes:

- Class I: Octahedral layer composed by high AI- and remarkable Fe-amounts (AI > 1.4; Fe<sup>3+</sup> > 0.2) belongs to group A. The pH-interval from 5 – 7 represents a region where AI and Fe<sup>3+</sup> have strong preferences to solid states (Fig. 8.20). It is the typical pH-environment for the formation of many bentonites (e. g., Wyoming-type bentonites from Mowry shale).
- Class II: Octahedral layer composed by high Al- but low Fe-amounts (Al > 1.4; Fe<sup>3+</sup> < 0.2) is related to bentonites of group B. A high alcalic pH-interval from 7.5 – 9 meets the borderline of Fe<sup>2+</sup> stability (Fig. 8.20). In such an environment Fe<sup>2+</sup> could be reduced in the clay and Al will maintain its high concentration in the octahedral layer. An environment with low Eh-values and/ or ul-

tramafic parent rocks for the formation of bentonite could represent this development of group B.

Class III: Octahedral layer with low AI- but high Fe-amounts (AI < 1.4; Fe<sup>3+</sup> > 0.2) also belongs to bentonites of group B. The low pH-interval from 2 – 4 (Fig. 8.20) is responsible for AI<sup>3+</sup> preferring a dissolved state (= low AI-amount in octahedral layer) and Fe<sup>3+</sup> still preferring a solid state (= increased portions of Fe3+ in octahedral layer). This region is a typical field for smectite formation under acid hydrothermal conditions or during soil formation supported by organic matter.

This classification gives an indication that the behaviour of bentonite, the type of reaction – Na-stabilized or Ca, Mg-stabilized – is controlled by the genesis of bentonite during its formation process.

The different behaviours of smectite in low energy level experiments and the first analytical differences are summarised in Tab. 8.12. The weakest driving forces were identified in group B with water as percolation agent. The behaviour of bentonite in high energy level experiments is summarised in Tab. 8.11.

		only one group (comparable to group A)
Members		API-standards - Otay, Garfield, Pioche, Polkville, Belle Fourche, ChambersBGR-collection- B04, B09GRS-material- MX80
"Sleeper"	(Δ%S > -10 %)	- Otay
"Sprinter"	(Δ%S < -20 %)	- B04, B09; Chambers; MX80
Result of m Steady beha + effect by i + effect by c	odelling avior, if: nterlayer cations octahedral cations	<ul> <li>high Na-, low Ca+Mg-amount; normal charged smectite &amp; monovalent (impact stronger than in low energy level experiments)</li> <li>low Fe+Mg, high Al (impact comparable to low energy level experiments for group A)</li> </ul>
Assumed m	echanism	

Tab. 8.11	Conditions for a steady behaviour of smectite in high energy level experi-
	ments (60 rpm, NaCl)

Assumed mechanism	
+ effect by interlayer cations	- no reaction - in case of high viscosity of water in diffuse double layer
+ effect by octahedral cations	- no reaction - in case of low sheet stress, because lower ion radius for
	Al than for Fe- & Mg-cations

Tab. 8.12	Conditions for a steady behaviour of smectite in low energy level experi-
	ments (20 rpm, H <sub>2</sub> O & NaCl)

	Group A	Group B
Members	<ul> <li>API-standards</li> <li>Cameron, Amory, Pioche, Polkville</li> <li>BGR-collection</li> <li>B09</li> <li>GRS-material</li> <li>MX80</li> </ul>	API-standards - Belle Fourche, Bayard, Chambers BGR-collection - B04, B11 HGW-material - NN11 (Vietnam), GeoHellas (Greece)
" <b>Sleeper</b> " (Δ%S > -10 %)	- Cameron	- Bayard, Chambers, B04
"Sprinter" (Δ%S < -20 %)	- MX80	- B11
Result of modelling Steady behaviour, if: + effect by interlayer cat- ions	<ul> <li>high Na-, low Ca+Mg-amount</li> <li>normal charged smectite &amp; mon- ovalent</li> </ul>	<ul> <li>low Na-, high Ca+Mg-amount</li> <li>low charged smectite &amp; divalent</li> <li>%S as high as possible</li> </ul>
+ effect by octahedral cations	(impact stronger than in group B) - low Fe+Mg, high Al (impact weaker than in group B)	(impact weaker than in group A) - low Fe+Mg , high Al (impact stronger than in group A)
Assumed mechanism		
+ effect by interlayer cations	<ul> <li>no reaction - in case of high vis- cosity of water in interlayer space</li> <li>no reaction - in case of low sheet</li> </ul>	<ul> <li>no reaction - in case of Ca+Mg can fix the stacks, if opposing charges exist between adjacent layers</li> <li>no reaction - in case of low sheet</li> </ul>
cations	stress, because lower ion radius for Al than for Fe- & Mg-cations	stress, because lower ion radius for Al than for Fe- & Mg-cations
Analytical indications		
for groups + XRD (oriented, air dried)	<ul> <li>dominating IS-ml structures (normal charged, monovalent)</li> <li>total interlayer charge in correla- tion with diVS-ml phases</li> </ul>	<ul> <li>dominating diVS-ml structures (low charged, divalent)</li> <li>total interlayer charge in correla- tion with IS-ml phases</li> </ul>
+ TEM-EDX	<ul> <li>no trend between total interlayer charge and Na-normalised %S of IS-ml phases</li> </ul>	<ul> <li>strong correlation between total in- terlayer charge and Na-normalised %S of IS-ml phases</li> </ul>

### Assumed mechanism for alteration in overhead shaking experiments

The experiments have shown different backgrounds for the transformation of smectite. Therefore, it was classified into group A and group B. These two groups of samples occurred in low energy experiments of bentonite in contact with 1N NaCl as well as low and high energy experiments of bentonite in contact with deionised water. All samples in high energy experiments (60 rpm) with 1n NaCl follow the behaviour of bentonites of group A.

The composition of the octahedral layer has shown the same mechanism in all experiments. A higher "Fe+Mg"-amount supported an alteration. The larger ion diameter of Fe and Mg in comparison to Al caused a higher sheet stress which reduced the resistance of particles against dissolution processes. This assumption followed the concept of "half-life time" for smectite against acid attack by [CIC 1976] and [NOV 1978]. Besides, [KAU 2008b] already expected an influence of interlayer occupation. Indeed, the experiments have shown that the composition of interlayer space affected the degree of illitisation of smectite in different a manner.

In the following, the assumed mechanism for different identified environmental cases will be presented. A fictive smectite with the postulated composition

$$Na_{0.18} Ca_{0.01} Mg_{0.02} AI_{1.20} Fe_{0.60} Mg_{0.20} (OH)_2 AI_{0.04} Si_{3.96} O_{10}$$
(8.7)

with Na-ratio of interlayer cations = 86%FeMg<sub>oct</sub>-ratio = 40%

was applied to demonstrate the different degrees of potential illitisation for the different cases.

### Case "20 rpm NaCl – Sample is member of Group B"

Samples with charges fixed opposite of each other on adjacent layers were protected by high Mg+Ca-cations in the interlayer space. [KAU 2010b] described a similar process in results of drying experiments with different smectites. This mechanism was only valid for low energy level experiments. The description of demixing of interlayer cations (Fig. 3.2 in chapter 3.4) by [LAI 2006] and the preferred breaking of quasicrystals on monovalent occupied interlayers could also explain this behavior.

Modeled Self-Potential of Illitisation (20 rpm):  $\Delta$ %S<sub>total</sub> = -49% (like a "Sprinter")

#### Case "60 rpm NaCl – Sample now reacts like a member of Group A"

[YON 1966] and [LAI 2006] described a high viscosity for water in the diffuse ion layer with increasing Na-amount in the interlayer space. A reduction of the diffuse ion layer by increased electrolyte concentration (or divalent cations) raised the fluid movement in the system. A limited fluid movement also limits reactivity in the system. Therefore, a high Na-environment, like here, stabilises the particles. This mechanism was fully valid for all samples in high energy level experiments with NaCl-solution.

Modeled Self-Potential of Illitisation (60 rpm):  $\Delta$ %S<sub>total</sub> = -10 % (like a "Sleeper")

# 8.4 Alteration of bentonite in interaction with iron

## 8.4.1 Experimental investigations

### 8.4.1.1 Experiments with MX80 as start material

GRS mbH has carried out percolation experiments with compacted MX80 bentonite  $(d = 1.6 \text{ kg/cm}^3)$ . The MX80 bentonite was mixed with 10 % native Fe-powder. Saturated NaCl- or IP21-solution were the two agents for percolation in the different experiment series.

### Mineralogy of bulk samples

The following explanations of the mineralogy of bulk samples were based on XRDmeasurements of occasionally oriented powder specimen. The XRD-traces were processed partially by BGMN-Rietveld refinement [KLE 2008]. Missing structure models for berthierine-saponite- and cronstedtite-vermiculite-mixed layers were the main problems for a successful valid refinement. The mineralogical results are summarised in Tab. 8.14.

	Experiment										
	MX80	MX80 IP21 IP21 NaCl			NaCl	NaCl					
	Starting	1 month	1 month	1 month	2 months	2 months					
	Material	25 °C	25 °C	90 °C	90 °C	60 °C					
	+ 10 % Fe	brown	dark grey			dark grey					
Sample label Greifswald	FeM	FeM01b	FeM01a	FeM02	FeM03	FeM04a					
Maturity Index		0.17	0.25	0.28	0.38						
SiO <sub>2</sub> (%)	57.60	53.20	51.96	52.36	51.93	49.99					
Al <sub>2</sub> O <sub>3</sub> (%)	18.40	17.03	16.55	16.62	16.54	15.92					
Fe <sub>2</sub> O <sub>3</sub> (%)	12.40	14.80	17.69	18.73	14.16	16.52					
TiO <sub>2</sub> (%)	0.10	0.13	0.12	0.13	0.12	0.12					
MnO (%)	< 0.01	0.01	0.01	0.01	0.01	0.01					
MgO (%)	2.10	3.67	3.45	1.87	1.78	1.74					
CaO (%)	1.10	0.45	0.47	0.33	0.33	0.39					
Na <sub>2</sub> O (%)	2.10	0.41	0.40	0.56	6.01	5.80					
K <sub>2</sub> O (%)	0.50	0.52	0.50	0.41	0.38	0.40					
P <sub>2</sub> O <sub>5</sub> (%)	< 0.05	0.04	0.05	0.04	0.06	0.04					
LOI (%)	5.70	9.34	8.73	6.88	8.68	9.07					

 Tab. 8.13
 Main chemical components of MX80-run products (XRF bulk samples)

Smectite was the main phase in all samples (Tab. 8.14; Fig. 8.21). The peak shapes of smectite indicated different processes between run products from 25 °C experiments and experiments with higher reaction temperatures (Fig. 8.21). The run products of experiments at higher temperature than 25 °C were characterised by peak broadening. This peak broadening was considered as result of strong dissolution and precipitation processes during the experiment. The chemical analyses also confirmed the loss of Si and Al caused by percolation (Tab. 8.13).

	Experiment										
	MX80 Starting Material	IP21 1 month 25 °C brown	IP21 1 month 25 °C dark grey	NaCI 1 month 90 °C	NaCl 2 months 60 °C brown	NaCl 2 months 90 °C	NaCl 2 months 60 °C dark grey				
Sample label Greifswald	FeM	FeM01b	FeM01a	FeM02	FeM04b	FeM03	FeM04a				
Maturity Index		0.17	0.25	0.28	0.33	0.38	0.49				
Smectite*	XXX	XXX	XXX	XXX	XXX	XXX	XXX				
Albite	XX	XX	XX	XX	XX	XX	XX				
Quartz	Х	Х	Х	Х	Х	Х	Х				
Cristobalite	traces	traces	traces	traces	traces	traces	traces				
Muscovite	traces	traces	traces	traces	traces	traces	traces				
Calcite	traces	traces	traces	traces	traces	traces	traces				
Akaganeite Goethite		traces X	traces traces	a.p.	traces	traces	traces				
Hematite				•		traces	traces				
Wuestite						traces					
Magnetite					traces	a.p.	traces				
native Fe		traces									
Bertherine-ml		X	Х								
Chlorite-ml				x	a.p.						
Cronstedtite-ml					a.p.	х	х				
Zeolites			a.p.	Х			a.p.				

Tab. 8.14Mineralogical composition of MX80-run products (XRD-results of bulk<br/>samples)

XXX = main phase (> 20 %); XX = minor phase (10 – 20 %); X = low phase (5 – 10 %); traces (< 5 %) PHASES:

Smectite*	full mixed layer series between montmorillonite and illite dominated by smectite layers;
Berthierine-ml	randomly stratified mixed layer series between berthierine and saponite mainly and
	partially also vermiculite;
Chlorite-ml	randomly stratified mixed layer series between chlorite, saponite and vermiculite;
Cronotodtito ml	randomly stratified mixed lover agrice between granted tite and verminulity

Cronstedtite-ml randomly stratified mixed layer series between cronstedtite and vermiculite;

a.p. assumed phase without valid identification;

MATURITY INDEX:

Based on Fe-bearing neoformation identified by TEM in fraction <  $2 \mu m$ : MI = frequency-% of neoformed phases Fe<sup>2+</sup><sub>rel</sub>

BGMN-Rietveld refinement indicated 70 – 80 % smectite, 10 – 15 % albite, ~ 5 % quartz, 2 – 4 % cristobalite.



MX80-bentonite mixed with 10 % native Fe-powder, Fe-grain size:  $6 - 9 \mu m$ ; Musc: muscovite; Goe: goethite; Cri: cristobalite; Q: quartz; Alb: albite; Hem: hematite; Magn: magnetite; ?: no identified phase; the other broad interferences were caused by smectite; traces were sorted upwards from low to high maturity index

# **Fig. 8.21** XRD-traces (randomly oriented powder specimen) of run products from GRS-experiments with compacted MX80-bentonite

### Mineralogy of fraction < 2 µm

The fraction < 2  $\mu$ m of the MX80-bentonite run products were analysed by TEM-EDX and XRD (oriented mounts).

The mineral formula was calculated following [KOS 1977] for each particle measured by TEM-EDX. The results were expressed as frequency-% (Tab. 8.15). Smectite was

also the main phase in fraction < 2  $\mu$ m. A series of mixed layer phases was detected as neoformation in the run products like kaolinite-montmorillonite-dioctahedral vermiculite mixed layers (KSV-mI), berthierine-saponite mixed layers (BS-mI), cronstedtite-trioctahedral vermiculite mixed layers (CroV-mI) and chlorite-saponite-trioctahedral vermiculite mixed layers (CSV-mI). Fe<sup>3+</sup>-rich smectite like nontronite were identified only in run products from sample FeM04a (NaCI, 60 °C, 2 months, black).

	MX80 start	IP21 25 °C	IP21 25 °C	NaCl 90 °C	NaCl 90 °C	NaCl 90 °C	NaCl 60 °C	
		yellow	dark green	black	brown, 2m	black, 2m	black, 2m	
		FeM01b	FeM01a	FeM02	FeM04b	FeM03	FeM04a	
Si-surplus + Quartz	33 %	28 %	23 %	37 %	13%	7 %	19 %	
diVS-ml	61 %	42 %	49 %	41 %	38 %	71 %	59 %	
IS-ml	5%	9%	10 %	0%	26 %	4 %	5%	
KSV-ml		3%	2 %			4 %	1 %	
BS-ml		4%	8 %		1 %		3%	
CroV-ml					9%	11 %	4 %	
CSV-ml		5%	8 %	22 %	12 %	3%	3%	
Nontronite							1 %	
Goethite							3%	
Hematite							3%	

**Tab. 8.15** Mineralogical composition of MX80-run products (fraction < 2 μm) determined by TEM-EDX (in frequency-%)

Si-surplus particles with Si-surplus, a calculation of mineral formula was not possible;

CSV-ml chlorite-saponite-vermiculite mixed layer series;

diVS-ml dioctahedral vermiculite-montmorillonite mixed layer series (= K- and charge deficient phase of IS-ml);

IS-ml illite-montmorillonite mixed layer series;

BS-ml berthierine-saponite mixed layer series;

CroV-ml cronstedtite-vermiculite mixed layer series;

KSV-ml kaolinite-montmorillonite-dioctahedral vermiculite mixed layer series

### Smectite

The first order interference of smectite in run products has shown a different position and peak shape in XRD-traces (oriented mounts, air dried) (Fig. 8.22). It mirrored the impact of different percolation agents (IP21, NaCl) and the reduced capacity of water absorption in the interlayer space. Run products of IP21-series had formed two water layers in the interlayer space, but samples from NaCl-series mainly one water layer. Furthermore, smectite from IP21-run products was characterised by a higher degree of order than run products from NaCl-experimental series.



MX80 bentonite mixed with 10 % native Fe-powder, Fe-grain size: 6 – 9  $\mu m$ ; traces were sorted upwards from low to high maturity index

# Fig. 8.22 XRD-traces (oriented mounts, air dried) of run products from GRSexperiments with compacted MX80 bentonite

Smectite of run products is fully expandable under ethylene-glycol saturation to 17.3 Å (Fig. 8.23).



MX80 bentonite mixed with 10 % native Fe-powder, Fe-grain size:  $6 - 9 \mu m$ ; traces were sorted upwards from low to high maturity index; brown, dashed line - smectite

Fig. 8.23 XRD-traces (oriented mounts, ethylene-glycol saturated) of run products from GRS-experiments with compacted MX80 bentonite

The chemical composition of all IS-/diVS-ml particles was shown in Tab. 8.16. The diversity of montmorillonite sheets (%S) differed from sample to sample. A gradual illitisation was recognised from starting MX80 (Si = 3.95)  $\rightarrow$  IP21, 25 °C, 1 month, brown

 $(Si = 3.85) \rightarrow IP21, 25 \text{ °C}, 1 \text{ month, dark grey (Si = 3.77) as well as generally in the NaCI-series (table 6.11). This illitisation was already described as a typical process in run products of fraction < 2 µm for open reaction system like percolation experiments by [HER 2004].$ 

Tab. 8.16	Average c	omposition	of	smectite	in	fraction	< 2 µm	determined	by	TEM-
	EDX									

		Interlayer				Octahedra				Tetrahedra		
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ті	AI	Si	XII	n <sup>vı</sup>
MX80 Start Material	0.04	0.04	0.01	0.02	1.59	0.21	0.16	0.04	0.05	3.95	0.19	1.99
IP21, 25 °C, 1 month, brown	0.05	0.09	0.01	0.02	1.45	0.35	0.18	0.02	0.15	3.85	0.30	2.00
IP21, 25 °C, 1 month, dark grey	0.04	0.10	0.15	0.04	1.34	0.49	0.14	0.03	0.23	3077	0.35	2.00
NaCl, 90 °C, 1 month	0.02	0.06	0.01	0.01	1.57	0.24	0.16	0.03	0.04	3.96	0.17	2.00
NaCl, 60 °C, 2 months, brown	0.05	0.09	0.00	0.03	1.47	0.25	0.25	0.02	0.09	3.91	0.32	2.00
NaCl, 90 °C, 2 months	0.03	0.05	0.01	0.01	1.63	0.21	0.13	0.03	0.06	3.94	0.17	2.00
NaCl, 60 °C, 2 months, dark grey	0.03	0.06	0.05	0.02	1.45	0.40	0.13	0.02	0.11	3.89	0.24	1.99

Smectite\* - average of all IS-ml and diVS-ml

#### Kaolinite-smectite-dioctahedral vermiculite mixed layer structures (KSV-ml)

KSV-ml structures were identified in four run products (Tab. 8.15) only by TEM-EDX. The ratio of kaolinite layers (%K) from this mixed layer series was lower than 50 % following the chemical composition (Tab. 8.17). The missing indications for KSV-ml in XRD-traces from bulk samples and in fraction < 2  $\mu$ m allowed the assumption that KSV-ml were only in traces available and appeared as thin and highly disordered particles. The high Fe-amount in octahedral position (Tab. 8.17) was a further indication of that.

#### Berthierine-saponite-trioctahedral vermiculite mixed layer structures (BSV-ml)

BSV-ml phases were recognised even in four run products (Tab. 8.15), also only by TEM-EDX. BSV-ml phases were formed mainly as BS-ml structures with berthierine as main component. The BSV-ml structures were shaped as broad laths in TEM-micrographs. This shape is normally typical of phases like goethite (pseudomorph?). The behaviour of the chemical composition (Tab. 8.18) has developed few possible
trends following the order of sample listing (sorted by maturity index): (i) Fe<sup>2+</sup> was the dominating component in octahedral position; (ii) Fe<sup>3+</sup> was increasing in octahedral and tetrahedral sheets and (iii) tetrahedral Si was decreasing in this listing.

Tab. 8.17	Average	composition	of	KSV-ml	in	fraction	< 2 µm	determined	by	TEM-
	EDX									

		Interlayer				Octah	edra		Tet	trahed	Ira		
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>
MX80 Start Material													
IP21, 25 °C, 1 month, brown	0.08	0.06	0.00	0.01	0.72	1.98	0.17	0.02	0.13	0.20	3.67	0.28	2.89
IP21, 25 °C, 1 month, dark grey	0.00	0.17	0.00	0.03	1.41	1.30	0.07	0.00	0.00	0.40	3.60	0.38	2.79
NaCl, 90 °C,													
1 month NaCl. 60 °C.													
2 months, brown													
NaCl, 90 °C, 2 months	0.04	0.01	0.00	0.01	1.29	0.63	0.01	0.01	0.00	0.19	3.81	0.14	2.13
NaCl, 60 °C, 2 months, dark grey	0.02	0.09	0.00	0.00	1.50	1.42	0.04	0.00	0.00	0.17	3.83	0.06	2.96

Sample NaCl, 60 °C, 2 months; dark grey has now statistically sufficient number of particles for valid mineral formula

Tab 818	Average composition of BS-mI in fraction < 2 $\mu$ m determined by TEM-EDX
Tab. 0.10	Average composition of bo-minin naction < 2 µm determined by TEM-EDA

		Interlayer				Oc	tahedr	a		Tet	rahed	lra		
	Са	Mg	Na	κ	AI	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vi</sup>
MX80 Start Material														
IP21, 25 °C,	0.01	0.08	0.00	0.01	0.14	0.86	3.79	0.32	0.00	0.20	0.95	2.85	0.18	5.12
1 month, brown										••				
1 month dark arev	0.03	0.00	0.00	0.00	0.04	1.10	4.08	0.23	0.03	0.26	0.97	2.80	0.06	5.48
NaCl, 90 °C,														
1 month														
NaCl, 60 °C,	0.05	0.02	0.00	0.02	0.00	1.38	3.66	0.19	0.00	0.64	0.82	2.54	0.16	5.23
2 months, brown	0.00	0.0_	0.00	0.01	0.00		0.00	00	0.00	0.0.	0.02		00	0.20
2 months														
NaCl, 60 °C,	0.00	0.00	0.00			4.04	0.00	0.40	0.00	4.04			0.40	- 07
2 months, dark grey	0.00	0.06	0.00	0.06	0.00	1.34	3.80	0.13	0.00	1.01	0.60	2.39	0.18	5.27

Sample NaCl, 60 °C, 2 months, brown has now statistically sufficient number of particles for valid mineral formula

#### Chlorite-saponite- trioctahedral vermiculite mixed layer structures (CSV-ml)

CSV-ml phases were identified in all run products by TEM-EDX (Tab. 8.15, Tab. 8.19). Proof for chlorite was also possible by FTIR (Tab. 8.18) for the sample FeM02 (NaCl,

90 °C, 1 month) with the highest CSV-ratio. Fe<sup>2+</sup> was the dominating cation in the octahedral layer (Tab. 8.19). Mg occurred only in traces there.

		Interlayer				00	tahedr	a		Tet	rahed	lra		
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>
MX80 Start Material														
IP21, 25 °C, 1 month, brown	0.06	0.12	0.00	0.04	0.54	0.00	2.94	0.16	0.03	0.00	0.78	3.22	0.40	3.68
IP21, 25 °C, 1 month, dark grey	0.04	0.11	0.08	0.04	0.62	0.00	2.69	0.17	0.03	0.00	0.85	3.15	0.41	3.51
NaCl, 90 °C, 1 month	0.03	0.11	0.00	0.00	0.15	0.75	3.10	0.05	0.02	0.18	0.85	2.97	0.28	
NaCl, 60 °C, 2 months, brown	0.07	0.08	0.00	0.02	0.32	0.22	3.25	0.20	0.01	0.11	0.71	3.19	0.32	4.00
NaCl, 90 °C, 2 month	0.01	0.12	0.00	0.01	0.59	0.00	2.69	0.00	0.00	0.00	0.64	3.36	0.28	3.29
NaCl, 60 °C, 2 months, dark grey	0.02	0.17	0.02	0.00	0.19	0.39	2.89	0.01	0.07	0.22	0.96	2.82	0.51	3.56

Tab. 8.19 Average composition of CSV-ml in fraction < 2  $\mu m$  determined by TEM-EDX

### Cronstedtite-saponite-trioctahedral vermiculite mixed layer structures

#### (CroSV-ml)

CroSV-ml phases were recognised only in the last three run products (Tab. 8.15, Tab. 8.20), also only by TEM-EDX. CroSV-ml phases were formed mainly as CroV-ml structures with cronstedtite as main component. The  $Fe^{3+}$ -ratio is higher than  $Fe^{2+}$ -proportion and  $Fe^{3+}$  is located in the octahedral and tetrahedral layers (Tab. 8.20). The Si-value for CroSV-ml was remarkably lower than in BSV-ml structures.

**Tab. 8.20** Average composition of CroV-mI in fraction < 2 μm determined by TEM-EDX

		Inter	layer			Oc	tahedr	a		Tet	rahed			
	Са	Mg	Na	к	AI	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>
NaCl, 60 °C, 2 months, brown	0.04	0.02	0.00	0.04	0.05	2.10	3.08	0.20	0.03	2.09	0.42	1.49	0.18	5.46
NaCl, 90 °C, 2 months	0.04	0.00	0.00	0.00	0.00	2.03	3.78	0.06	0.01	2.21	0.35	1.43	0.08	5.35
NaCl, 60 °C, 2 months, dark grey	0.03	0.01	0.02	0.00	0.00	2.57	2.88	0.15	0.01	1.93	0.62	1.45	0.10	5.57

#### 8.4.1.2 Experiments with Friedland clay as start material

The applied Friedland clay originated from "Scholle Burgfeld" of the marine Eocene clay close to Friedland town (Mecklenburg-Western Pomerania, Germany; kindly provided by Mineralische Rohstoffmanagement GmbH, Blautonwerk Friedland).

The following explanations of mineralogy of bulk samples were based on XRDmeasurements of occasionally oriented powder specimens. Missing structure models for IS-mixed layer phases were the main problem for an approach of BGMN-Rietveld refinement. The mineralogical results were summarised in Tab. 8.21 (left). The Friedland clay from "Scholle Burgfeld" was characterised by 17 % montmorillonite, 12 % ISml, 28 % illite/muscovite, 13 % kaolinite (determined as fireclay), 2 % chlorite, 25 % quartz, 1 % K-feldspar, 1 % albite, and 1 % pyrite (MRG-datasheet). The chemical composition of the Friedland starting material was comparable to the "Scholle Burgfeld" Friedland clay published by Mineralische Rohstoffmanagement GmbH.

Smectite occurred in the run products as montmorillonite (15 - 16 Å) and diVS-mixed layer phases (11 - 13 Å). It was in all samples a main or minor phase (Tab. 8.21; Fig. 8.24). The intensity ratio between mica (10 Å) and diVS-ml and its peak shapes indicated different processes between run products from 25 °C experiments and experiments with higher reaction temperature (Fig. 8.24). The run products of experiments at 25 °C were characterised by peak broadening and decreasing of intensity. This was considered to be the result of strong dissolution processes during the experiment. The chemical analyses confirmed again the loss of Si and Al caused by percolation (Tab. 8.21 right).

Pyrite from the original material was identified in all run products. Lepidocrocite (both experiments at  $25 \,^{\circ}\text{C}$  – FeF01a, FeF01b), goethite (only in dark grey run products from  $25 \,^{\circ}\text{C}$  – FeF01a) and magnetite (in dark grey run products of  $25 \,^{\circ}\text{C}$  and  $90 \,^{\circ}\text{C}$  – FeF01a, FeF02) were neoformation originated from native Fe. The dark grey run products from  $25 \,^{\circ}\text{C}$  experiments (FeF01a) have also shown the occurrence of native Fe. It indicated incomplete flooding of the sample during this experiment.

The chemical composition of samples FeF01a (dark-grey, 25 °C) and FeF02 (90 °C) were very similar (Tab. 8.21 right). But the two samples have shown a different mineralogical composition concerning Fe-phases (lepidocrocite + goethite vs. magnetite) and diVS-ml structures (compare peak shape of diVS-ml and intensity ratio between mica 10 Å and first order interference of diVS-ml (Fig. 8.24). Tab. 8.21Mineralogical and chemical composition of Friedland clay-run products<br/>(from bulk samples by XRD + XRF)

	Experiment			
	Friedland	NaCl	NaCl	NaCl
Mineralogical	Starting	2 months	2 months	2 months
composition	Material	25 °C	25 °C	90 °C
		brown	dark grey	
Sample label Greifswald	FeF	FeF01b	FeF01a	FeF02
Maturity Index		0.20	0.38	0.37
Smectit*	XXX	XX	XX	XX
Musc./Illite	XXX	XXX	XXX	XXX
Quartz	XXX	XXX	XXX	XXX
Kaolinite	XX	XX	XX	XX
Chlorite	traces	traces	traces	traces
K-Feldspar	traces	traces	traces	traces
Albite	traces	traces	traces	traces
Pytite	traces	traces	traces	traces
Gypsum	traces			
Lepodocrocoite		Х	Х	
Goethite			Х	
Magnetite			traces	traces
??? (3.29 Å)				Х

		Expe	riment	
	Friedland	NaCl	NaCl	NaCl
Chemical	Starting	2 months	2 months	2 months
composition	Material	25 °C	25 °C	90 °C
	+ 10 %Fe	brown	dark grey	
Sample label Greifswald	FeF	FeF01b	FeF01a	FeF02
Maturity Index		0.20	0.38	0.37
SiO <sub>2</sub> (%)	57.10	52.21	48.59	48.87
Al <sub>2</sub> O <sub>3</sub> (%)	16.50	15.22	14.20	14.31
Fe <sub>2</sub> O <sub>3</sub> (%)	14.20	19.51	16.45	16.01
TiO <sub>2</sub> (%)	0.90	0.83	0.75	0.76
MnO (%)	< 0.01	0.01	0.01	0.01
MgO (%)	1.50	1.36	1.26	1.28
CaO (%)	0.20	0.12	0.12	0.10
Na <sub>2</sub> O (%)	0.90	0.86	5.18	4.91
K <sub>2</sub> O (%)	2.70	2.42	2.18	2.20
P <sub>2</sub> O <sub>5</sub> (%)	< 0.05	0.09	0.07	0.06
LOI (%)	6.00	7.24	11.19	11.50



Friedland clay mixed with 10 % native Fe-powder, Fe-grain size: 6 – 9 µm; Musc – muscovite+ illite; diVS-ml – randomly interstratified dioctahedral vermiculite-montmorillonite mixed layer structure (= K- and/or charge-deficient IS-ml); kaol + chl – kaolinite + chlorite; Lepidocr. – Lepidocrocite; Goe – goethite; Magn – magnetite; ? – no identified phase; traces were sorted upwards from low to high maturity index

Fig. 8.24 XRD-traces (randomly oriented powder specimens) of run products from GRS experiments with compacted Friedland clay

#### Mineralogy of fraction < 2 µm

The fraction < 2  $\mu$ m of the Friedland clay run products were analysed by TEM-EDX and XRD (oriented mounts).

It was calculated the mineral formula following [KOS 1977] for each particle measured by TEM-EDX. The results were expressed as frequency-% (Tab. 8.22). Smectite (IS-mI + diVS-mI) was also the main phase in fraction < 2 µm. Additionally, a series of mIphases like kaolinite-montmorillonite-dioctahedral vermiculite mixed layers (KSV-mI), and chlorite-saponite-trioctahedral vermiculite mixed layers (CSV-mI) was detected in the start material already. Other mixed layer structures like berthierine-saponite mixed layers (BS-ml) and cronstedtite-trioctahedral vermiculite mixed layers (CroV-ml) were detect in the run products only. Fe<sup>3+</sup>-rich smectite like nontronite were identified only in run products from sample FeF02 (NaCl, 90 °C, 2 months). Remarkable numbers of native iron particles were also measured in the run products.

	Friedland	NaCl 25 °C	NaCl 25 °C	NaCl 25 °C
	start	brown, 2m	grey, 2m	2 months
		FeF01b	FeF01a	FeF02
Si-surplus + Quartz	3%		4 %	
CSV-ml	3%	11 %	6 %	15 %
diVS-ml	37 %	39 %	42 %	44 %
IS-ml	11 %	8 %	21 %	7 %
BS-ml		1 %		
CroV-ml			4 %	3%
KSV-ml	38 %	17 %	17 %	15 %
Fe-oxides			2 %	
native Fe in alteration		23 %	4 %	15 %
Nontronite				2 %

Tab. 8.22	Mineralogical composition of Friedland clay-run products (fraction < 2 $\mu$ m)
	determined by TEM-EDX (in frequency-%)

Si-surplus – particles with Si-surplus, a calculation of mineral formula was not possible; CSV-ml – chloritesaponite-vermiculite mixed layer series; diVS-ml – dioctahedral vermiculite-montmorillonite mixed layer series (= K- and charge deficient phase of IS-ml); IS-ml – illite-montmorillonite mixed layer series; BS-ml – berthierine-saponite mixed layer series; CroV-ml – cronstedtite-vermiculite mixed layer series; KSV-ml – kaolinite-montmorillonite-dioctahedral vermiculite mixed layer series

#### Smectite

The first order interference of smectite in run products has shown a different position and intensity ratio ("10 Å:12 Å") between mica and IS-mI in XRD-traces (oriented mounts, air dried) (Fig. 8.25). The different positions mirrored the impact of NaCI-percolation agents. An increasing "10 Å:12 Å"-intensity ratio (Fig. 8.25) represented rising dissolution processes of smectite phases.

Smectite of run products was only partially fully expandable under ethylene-glycol saturation to 17.0 - 17.3 Å (Fig. 8.26).



Friedland clay mixed with 10 % native Fe-powder, Fe-grain size:  $6 - 9 \mu m$ ; traces were sorted upwards from low to high maturity index; Musc./Illite – muscovite+ illite; kaol + chl – kaolinite + chlorite

Fig. 8.25 XRD-traces (oriented mounts, air dried) of run products from GRS experiments with compacted Friedland clay



Friedland clay mixed with 10 % native Fe-powder, Fe-grain size:  $6 - 9 \mu m$ ; traces were sorted upwards from low to high maturity index; Musc./Illite – muscovite+ illite; kaol + chl – kaolinite + chlorite

Fig. 8.26 XRD-traces (oriented mounts, ethylene-glycol saturated) of run products from GRS experiments with compacted Friedland clay

The chemical composition of all IS-/diVS-ml particles was shown in Tab. 8.22. The diversity of montmorillonite sheets (%S) differed from sample to sample. A gradual illitisation was recognised from starting Friedland clay (Si = 3.62)  $\rightarrow$  NaCl, 90 °C, 2

months (Si = 3.48) (Tab. 8.22). This illitisation was already described as typical process in run products of fraction < 2  $\mu$ m for open reaction systems like percolation experiments by [HER 2004]. IS-ml phases have shown a higher proportion for %S in those mixed layer structures than diVS-ml (Tab. 8.23a, b). Both types of mixed layer phases have altered only the charge in the tetrahedral layer (illitisation). The octahedral charge was constant. An AI-Fe-substitution could only slightly be recognised.

**Tab. 8.23** Average composition of smectite\* in fraction < 2 μm determined by TEM-EDX

		Interlayer				Octah	edra		Tet	rahed	ra			
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>	
Friedland Start Material	0.01	0.11	0.03	0.23	1.54	0.31	0.12	0.02	0.00	0.38	3.62	0.50	1.99	
NaCl, 25 °C, 2 months, brown	0.01	0.12	0.00	0.33	1.10	0.77	0.11	0.01	0.00	0.49	3.51	0.50	1.99	
NaCl, 25 °C, 2 months, dark grey	0.01	0.12	0.00	0.21	1.45	0.39	0.14	0.01	0.00	0.29	3.71	0.47	1.98	
NaCl, 90 °C, 2 months	0.07	0.13	0.00	0.18	1.16	0.69	0.11	0.03	0.02	0.50	3.48	0.50	1.99	

Smectite\* - average of all IS-ml and diVS-ml

### **Tab. 8.23a** Average composition of smectite in fraction < 2 µm determined by TEM-EDX: sub-group "IS-mI

		Interlayer				Octa	nedra		Те	trahed	dra			
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>	%S
Friedland Start Material	0.00	0.08	0.01	0.36	1.30	0.41	0.25	0.01	0.00	0.20	3.80	0.52	1.97	71
NaCl, 25 °C, 2 months, brown	0.03	0.10	0.00	0.35	1.08	0.66	0.20	0.01	0.00	0.30	3.70	0.62	1.96	55
NaCl, 25 °C, 2 months, dark grey	0.01	0.09	0.00	0.47	1.05	0.67	0.24	0.02	0.00	0.37	3.63	0.67	1.98	44
NaCl, 90 °C, 2 months	0.03	0.10	0.00	0.35	1.08	0.66	0.20	0.01	0.00	0.30	3.70	0.62	1.96	55

# **Tab. 8.23b** Average smectite composition in fraction < 2 μm determined by TEM-EDX: sub-group "diVS-ml"

		Interlayer				Octal	nedra		Tetrahedra					
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>	%S
Friedland Start Material	0.01	0.12	0.04	0.19	1.61	0.28	0.09	0.02	0.00	0.43	3.57	0.48	2.00	36
NaCl, 25 °C, 2 months, brown	0.01	0.12	0.00	0.30	1.12	0.79	0.08	0.01	0.00	0.52	3.48	0.57	2.00	26
NaCl, 25 °C, 2 months, dark grey	0.01	0.12	0.00	0.19	1.50	0.39	0.10	0.01	0.00	0.36	3.64	0.46	2.00	46
NaCl, 90 °C, 2 months	0.07	0.13	0.00	0.15	1.18	0.69	0.10	0.03	0.02	0.53	3.45	0.59	2.00	23

#### Kaolinite-smectite-dioctahedral vermiculite mixed layer structures (KSV-ml)

KSV-ml structures were identified by TEM in the starting material and hence also in all run products Tab. 8.22, Tab. 8.24). The XRD-traces have also shown (bulk samples and fraction < 2  $\mu$ m) strong interferences at 7.2Å and 3.56Å in all samples (Fig. 8.24 to Fig. 8.26). The kaolinite proportion in the samples was reduced with the higher maturity of the run products. The ratio of kaolinite layers (%K) from this mixed layer series was estimated between 20 – 60% following the chemical composition (Tab. 8.24). The missing indications for swelling components of KSV-ml in XRD-traces from bulk samples and in fraction < 2  $\mu$ m allowed the assumption that KSV-ml were only present in traces and appeared as thin and highly disordered particles. The remarkable Fe-amount in octahedral position (Tab. 8.24) was a further indication for that. The ratio "Al:Si" has drawn an decreasing trend with rising maturity of run products (Tab. 8.24).

Tab. 8.24	Average	composition	of	KSV-ml	in	fraction	< 2 µm	determined	by	TEM-
	EDX									

	Interlayer				Octah	edra		Tetrahedra					
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ті	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>
Friedland Start Material	0.03	0.03	0.04	0.04	2.69	0.14	0.05	0.01	0.00	0.16	3.84	0.21	2.89
NaCl, 25 °C, 2 months, brown	0.02	0.04	0.00	0.06	2.51	0.52	0.07	0.01	0.00	0.14	3.86	0.16	3.12
NaCl, 25 °C, 2 months, dark grey	0.02	0.05	0.00	0.04	2.32	0.32	0.08	0.00	0.00	0.14	3.86	0.17	2.75
NaCl, 90 °C, 2 months	0.05	0.03	0.00	0.03	2.24	0.71	0.11	0.02	0.02	0.13	3.87	0.19	3.08

Tab. 8.25	Average composition of BS-mI in fraction < 2	µm determined by	y TEM-EDX
			,

	Interlayer				Oc	taheo	dra		Tetrahedra					
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>
Friedland Start Material NaCl, 25 °C, 2 months, brown NaCl, 25 °C, 2 months, dark grey NaCl, 90 °C, 2 months	0.00	0.07	0.00	0.09	0.01	1.67	3.14	0.13	0.02	0.93	0.91	2.16	0.24	4.96

#### Chlorite-saponite-trioctahedral vermiculite mixed layer structures (CSV-ml)

CSV-ml phases were identified in all samples by TEM-EDX (Tab. 8.22), XRD (Fig. 8.23) and FTIR. (Fig. 8.27)  $Fe^{2+}$  was commonly the dominating cation in the octa-

hedral layer. The ratio "AI : Si" has also drawn in CSV-mI at a decreasing trend with rising maturity of run products (Tab. 8.26).

		Interlayer				Oc	tahed	dra		Tetrahedra				
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>
Friedland Start Material	0.04	0.00	0.05	0.15	1.20	0.00	1.05	0.58	0.03	0.00	0.76	3.24	0.29	2.86
NaCl, 25 °C, 2 months, brown	0.02	0.03	0.00	0.23	0.64	0.27	2.91	0.15	0.01	0.02	0.87	3.11	0.34	3.99
NaCl, 25 °C, 2 months, dark grey	0.01	0.14	0.00	0.02	0.43	0.39	2.32	1.14	0.00	0.11	0.93	2.96	0.31	4.29
NaCl, 90 °C, 2 months	0.08	0.08	0.00	0.05	0.46	0.12	2.53	0.20	0.03	0.00	0.69	3.31	0.39	3.35

Tab. 8.26Average composition of CSV-ml in fraction < 2  $\mu$ m determined by TEM-<br/>EDX



Fig. 8.27 Decomposition of FTIR spectrum from sample FeM0<sub>2</sub> (NaCl, 90 °C, 1 month) also including chlorite phases

# Cronstedtite-saponite-trioctahedral vermiculite mixed layer structures (CroSV-ml)

CroSV-ml phases were recognized only in the last two run products (Fig. 3.1, Tab. 8.27) detected only by TEM-EDX. CroSV-ml phases were formed mainly as CroV-ml structures with cronstedtite as main component. The total  $Fe^{3+}$ -ratio is higher than the  $Fe^{2+}$ -proportion and  $Fe^{3+}$  is located in the octahedral and tetrahedral layers (Tab. 8.27). The Si-value for CroSV-ml was remarkably lower than in BSV-ml structures (compare Tab. 8.25 and Tab. 8.27).

Tab. 8.27Average composition of CroV-ml in fraction < 2  $\mu$ m determined by TEM-<br/>EDX

		Interlayer				Oc	Octahedra				Tetrahedra			
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mg	Ti	Fe <sup>3+</sup>	AI	Si	XII	n <sup>vı</sup>
Friedland Start Material NaCl, 25 °C, 2 months, brown														
NaCl, 25 °C, 2 months, dark grey	0.02	0.06	0.05	0.00	0.00	1.84	3.25	0.24	0.01	1.68	0.66	1.66	0.21	5.34
NaCl, 90 °C, 2 months	0.05	0.04	0.00	0.02	0.00	1.85	3.36	0.02	0.01	2.05	0.16	1.78	0.23	5.25

#### 8.4.1.3 Proof of mineralogical alteration in run products

#### Smectite

The different percolation agents (IP21, NaCl) have affected the occupation of interlayer space mirrored by the position of 1st order interference for smectite (Fig. 8.22: MX80-series, oriented mount, air dried). The same XRD-traces also indicated a variable concentration and degree of order for smectite by the different peak shape.

Few elements in the MX80-series would be removed out of the reaction system like  $SiO_2$ ,  $Al_2O_3$ , MgO and with higher maturity also  $Fe_2O_3$  (Tab. 8.13). Otherwise,  $Na_2O$  was incorporated in the phases. Additionally,  $K_2O$  was also reduced in the Friedland clay-series (Tab. 8.21 right).

FTIR-measurements of the bulk samples have shown variable positions and intensities for typical smectite bands (Fig. 8.28), e. g. for Si-O-signals at 990-1000 cm<sup>-1</sup> as well as at 1033-1044 cm<sup>-1</sup> and for Al-OH-Mg (844-855 cm<sup>-1</sup>), Al-OH-Fe (875-883 cm<sup>-1</sup>) and Al-

OH-AI (912-916 cm<sup>-1</sup>). The stable adjustment of measurement is documented by the position of the quartz band at 795-798 cm<sup>-1</sup> and 777 cm<sup>-1</sup>.



Differences e. g. in intensity and position of Si-O-signals at  $990 - 1000 \text{ cm}^{-1}$  as well as at  $1033 - 1044 \text{ cm}^{-1}$  and for Al-OH-Mg (844 - 855 cm<sup>-1</sup>), Al-OH-Fe (875 - 883 cm<sup>-1</sup>) and Al-OH-Al (912 - 916 cm<sup>-1</sup>)

**Fig. 8.28** FTIR-spectra (400 – 1150 cm<sup>-1</sup>) of MX80 bentonite start material and run products (bulk samples)

The smectite in run products was characterised by different Fe-contents in the octahedral position. This information based on TEM-EDX-measurements (Tab. 8.16 for MX80-series; Tab. 8.23 for Friedland clay-series). A comparison of the TEM-EDX-data with XRD- and FTIR-measurements was performed, verifying these data. The XRD-intensity quotient "3rd order : 2nd order" described the variable octahedral Fe-ratio in smectite in ethylene-glycol saturated oriented mounts of fraction < 2 µm. Otherwise, the FTIR-wave number of the AI-OH-Fe-band is also linked with the octahedral Feconcentration in the smectite. Higher octahedral Fe-content causes lower wave numbers of the  $\delta_{AIFe-OH}$  band for cis-vacant smectite [CRA 1984]; [RUS 1994]; [VAN 2001a]; [GAT 2005]. The FTIR-measurement was carried out on bulk samples.



Differences e. g. mainly in intensity of Si-O-signal at 987 – 994 cm<sup>-1</sup> and for Si-O-Si-signals lower than 550 cm<sup>-1</sup>

**Fig. 8.29** FTIR-spectra (400 – 1150 cm<sup>-1</sup>) of Friedland start material and run products (bulk samples)

The XRD-indicator has shown a correlated trend with the TEM-EDX-results (Fig. 8.30). This observation is also valid for the XRD-indicator and the FTIR-measurement (Fig. 8.30) as well as the TEM-EDX- and FTIR-data (Fig. 8.30). The FTIR-fit quality was controlled by the  $r^2$  value (> 0.999). This comparison visualised that all particle size classes of smectite (TEM-EDX: thinnest particles of fraction < 2 µm; XRD: fraction < 2 µm; FTIR: bulk sample) followed the described alteration of the octahedral Feamount.



ed mounts, ethylene-glycol saturation) with TEM-EDX-measurement (fraction  $< 2 \, \mu m$ )





a Comparison of XRD-data (fraction < 2 µm, orient- b Comparison of XRD-data (fraction < 2 µm, oriented mounts, ethylene-glycol saturation) with FTIRmeasurement (bulk sample)

	MX80	TEM-EDX	XRD	FTIR
Friedland		<< 2 µm	< 2 µm	bulk
TEM-EDX	<2 μm		0.985	0.992
XRD	<2 µm	0.995		0.975
FTIR	bulk	0.959	0.963	

d Overview of correlation coefficients from a-c

circles - MX80-series diamond - Friedland clay series grey filled label - start material

Fig. 8.30 Proof of alteration of octahedral Fe-content in smectite

The smectite in run products was also characterised by different Si-content in the tetrahedral position. This information was based on TEM-EDX-measurements (Tab. 8.16 for MX80-series; Tab. 8.23 for Friedland clay-series). Again, a comparison of the TEM-EDX-data with XRD- and FTIR-measurements was performed, verifying these data. The NEWMOD-based calculation of the distance (001)/(002)- and (002)/(003)interferences in according to [MOO 1997] described the variable ratios of illite and smectite layers in IS-ml & diVS-ml phases in ethylene-glycol saturated oriented mounts of fraction < 2 µm. Otherwise, the FTIR-wave number of Si-O-band is also linked with tetrahedral Si-concentration in smectite. The FTIR-measurement was carried out on bulk samples.

The XRD-indicator has shown a correlated trend with the TEM-EDX-results, but certain limitations for the MX80-series and the Friedland clay-series had to be considered (Fig. 8.30). The run products of the MX80-series percolated by NaCl-solution have shown a different scale of correlation than percolated by IP21-solution. An exception of the XRD-indicator has to be considered in the run products of the Friedland clay-series sample FeF01b (NaCl, 2 months, 25 °C). The intensities of the (001)/(002)- and (002)/(003)-interferences of this sample were very weak. This is limiting the success of the fitting procedure.



smectite by comparison of XRD-data (fraction < 2 µm, oriented mounts, ethylene-glycol saturation) with TEM-EDX-measurement





a Proof of alteration of tetrahedral Si-content in b Proof of alteration of tetrahedral Si-content in smectite by comparison of XRD-data (fraction < 2 µm, oriented mounts, ethylene-glycol saturation) with FTIR-measurement (bulk sample)

	MX80	TEM-EDX	XRD	FTIR
Friedland		<< 2 µm	< 2 μm	bulk
TEM-EDX	<< 2 µm		0.734	0.860
XRD	< 2 µm	0.863		0.877
FTIR	bulk	0.935	0.938	

d Overview of correlation coefficients from a-c

circles - MX80-series in NaCI-solution triangle - MX80-series in IP21-solution diamond - Friedland clay series grey filled label - start material

#### Fig. 8.31 Proof of alteration of tetrahedral Si-content in smectite

The XRD-indicator has shown a correlated trend with the TEM-EDX-results, but certain limitations for the MX80-series and the Friedland clay-series had to be considered

(Fig. 8.31). The run products of the MX80-series percolated by NaCI-solution have shown a different scale of correlation than percolated by IP21-solution. An exception of the XRD-indicator has to be considered in the run products of the Friedland clay-series – the sample FeF01b (NaCI, 2 months, 25 °C). The intensities of the (001)/(002)- and (002)/(003)-interferences of this sample were very weak. This is limiting the success of the fitting procedure.

This observation is also valid for the XRD-indicator and the FTIR-measurement b). TEM-EDX- and FTIR-data (c) have also shown such correlation, this time including all samples from the Friedland clay-series. This comparison illustratesagain that all particle size classes of smectite (TEM-EDX: thinnest particles of fraction < 2  $\mu$ m; XRD: fraction < 2  $\mu$ m; FTIR: bulk sample) followed the described alteration of tetrahedral Si-amount.

#### 8.4.1.4 Mineralogy of run products in the context of thermodynamics

Especially, the mineral matter of fraction < 2  $\mu$ m has shown temporary Fe-bearing neoformed sheet silicates like berthierine-saponite mixed layer phases (BS-ml), chlorite-saponite-trioctahedral vermiculite mixed layer structures (CSV-ml) and cronstedtite-trioctahedral vermiculite mixed layer phases labeled as CroV-ml (Tab. 8.15, Tab. 8.22). The occurrence of these phases was partially limited to certain experimental conditions (Fig. 8.32). BS-ml phases were identified in experiments with IP21-solution at 25 °C (Fig. 8.32d) and CroV-ml structures were more common in experiments with a duration of 2 months (Fig. 8.32b). CSV-ml phases filled the gap between BS-ml and CroV-ml (Fig. 8.32c). This figure was based on the distribution of Fe-bearing neoformed phases (in frequency-%) and the ratio "Fe<sup>2+</sup>/Fe<sub>total</sub>", both parameters identified by TEM in fraction < 2  $\mu$ m.

This mineral distribution offered an interpretation of possible stability fields for the mentioned neoformed phases (Fig. 8.32f). This interpretation confirmed results of [BIL 2006], [WIL 2006a], [PER 2008]), and [SAV 2010a]. All these authors described in their experiments or simulations serpentine-like phases and chlorite as solid minerals in the run products as alterations of montmorillonite. [BIL 2006] already mentioned the occurrence of cronstedtite and berthierine. Together with [WIL 2006a], these authors estimated that those phases could be detrimental to the performance of HLW repositories. [SAV 2010a] described a sequence of solid alteration products: magnetite  $\rightarrow$ cronstedtite  $\rightarrow$  berthierine  $\rightarrow$  chlorite.



based on frequency-% of these phases and Fe<sup>2+</sup>/Fe<sub>total</sub>-ratio (both parameters determined by TEM-EDX in fraction < 2 µm); the size of balls represents the frequency-% of a phase in a certain run product a: Fe-oxyhydroxides; b: Cronstedtite-trioctahedral vermiculite mixed layer phases; c: Chlorite-saponite-trioctahedral vermiculite mixed layer phases; c: Chlorite-saponite-trioctahedral vermiculite mixed layer phases; e: berthierine-saponite mixed layer phases; f: Interpretation of stability fields considering the recognised mineral matter distribution

### **Fig. 8.32** Distribution of neoformed Fe-bearing phases in run products of the MX80and Friedland clay series

The "Neoformation of Fe-bearing phases :  $Fe^{2+}/Fe_{total}$ "-ratio was applied to introduce a so-called maturity indicator (Fig. 8.33). This maturity indicator could describe a pathway of alteration through the different experimental set-ups.

The sequence of alteration "Fe-oxyhydroxide, Fe-smectite  $\rightarrow$  KSV-ml  $\rightarrow$  BS-ml  $\rightarrow$  CSV-ml  $\rightarrow$  CroV-ml  $\rightarrow$  BS-ml, KSV-ml  $\rightarrow$  Fe-oxyhydroxide, Fe-smectite" would generalise this maturity indicator (Fig. 8.34). The presented pathway (Fig. 8.34) has shown a hysteresis from Fe-oxyhydroxide & Fe-smectite to chlorite-bearing phases via berthier-ine-structures and again back to Fe-oxyhydroxide and Fe-smectite via cronstedtite-structures.



0.20 – value of maturity indicator; filled diamond – experimental series with MX80 bentonite as starting material; open circle – experimental series with Friedland clay as starting material; IP21, NaCl – percolation agents; 30d, 60d – duration of experiments in days; 25 °C, 60 °C, 90 °C – temperature of experiments in days

**Fig. 8.33** Maturity Indicator ('neoformation' divided by 'Fe<sup>2+</sup>/Fe<sub>total</sub>'): Methodology to describe numerically the degree of alteration and to illustrate a pathway of alteration

The Si-behavior in the run products was assumed as the main reason for the different reverse pathways in Fig. 8.34. Si-loss in relation to AI was observed in the first part of this pathway of alteration ("KSV-mI  $\rightarrow$  BS-mI  $\rightarrow$  CSV-mI"). The Si/AI-ratio (Fig. 8.34a right footnotes) was reduced from KSV-mI (average: 2.7) in the direction of the stability field for CSV-mI (average: 2.3). CroV-mI phases had shown again a rising Si-ratio (average: 4.5) in the second part of alteration. The development of smectite (%S) has mainly shownan illitisation (compare Si<sub>tet</sub>-development in smectite of fraction < 2 µm: Tab. 8.16, Tab. 8.22). This illitisation process was disrupted in two regions of the pathway: (i) at the point of highest values for neoformed Fe-bearing clay minerals and "Fe<sup>2+</sup>/Fe<sub>total</sub>" ratio as well as and close to the end of alteration pathway (Fig. 8.35b).



Activity Si/H<sup>+</sup>

Solid line – alteration in the case of increasing Fe-activity (mainly mirrored by increasing  $Fe^{2+}$ -ratio); dashed line – alteration in the case of reducing Fe-activity (mainly mirrored by increasing  $Fe^{3+}$ -ratio)

**Fig. 8.34** Generalized illustration of the sequence alteration following the introduced maturity index from Fig. 8.33



a Si/Al-ratio (footnote, right) and Fe<sub>i</sub>/Fe<sub>total</sub>-ratio (headnote, left) in neoformed clay minerals; b  $\Delta$ Si<sub>tet</sub> in smectite (calculated by Si<sub>i</sub> – Si<sub>start material</sub>);

c Fe-content of smectite in comparison to total Fe from all clay minerals

Fig. 8.35 Si- and Fe-behaviour in neoformed clay minerals and smectite of run products from the MX80- and Friedland clay-series (fraction < 2 μm; TEM-EDXbased)

These two regions were recognised as smectitisation (labeled as blue spheres in Fig. 8.35b) or reduced degree of illitisation (labeled as small red spheres in Fig. 8.35b) in comparison to the starting material. Smectite has shown a low octahedral Fe-concentration in the same two regions (Fig. 8.35c). The described synchronous development of  $Si_{tet}$  and  $Fe_{oct}$  could indicate a high pressure by dissolution. Montmorillonite

with a high amount of Fe and Mg (higher ion radius than for AI) has shown a lower resistance than AI-rich montmorillonite. This means that the parameter "Fe<sup>2+</sup>/Fe<sub>total</sub>" (Fig. 8.35) could mirror effects by Si-activity caused by rising values for Eh and pH as a result of Fe-oxidation.

# 8.4.1.5 Assumed mechanism for the alteration of smectite in contact with iron

#### **Development of Smectite**

The observed illitisation of the smectitic run products was changing in two areas in a Smectitisation (Fig. 8.35b). The two areas were located in the stability field of CSV-ml and CroV-ml phases (Fig. 8.35a). Smectite in start material and run products was characterised in TEM-micrographs by two different types of morphology: (i) dark (= thick) xenomorphous flakes with swelling items like rolled edges and (ii) light grev (= thin) hypidio- or xenomorphous plate with discrete margins mainly without swelling items (Fig. 8.36c). These two morphological types were also recognised by XRD. The composing of (00I)-peaks of smectite by two interferences was an expression of that (Fig. 8.36a). These two groups of smectite particles also underwent an alteration of the stack order. The starting material has shown a typically turbostratic stack order. This ordering means each sheet was independently oriented towards the neighbored sheets in the same stack. A higher maturity of run products was accompanied by an increasing ordering into a 1M polytypes (Fig. 8.37a). This development was interrupted in the same regions like mentioned before for smectitisation (Fig. 8.35b). The run products from these phases of maturity have shown again a turbostratic ordering of the stacks (Fig. 8.37a).

The development of "Coherent Scattering Domains" (CSD) for 'thick' particles was also characterised by a specific situation in these two regions (Fig. 8.37b). The CSD-values were determined at (001)-interference of smectite by XRD of ethylene-glycol saturated oriented mounts. The lower CSD-values in regions with a low maturity could be explained by a disaggregation of stacks. Oswald ripening (dissolution of small crystals and the redeposition of the dissolved substances on the surfaces of larger crystals) could be discussed as a reason for the rising CSD-values in run products located in the stability field for CSV-ml and CroV-ml. This means that the dissolution rate in this area was higher than removable by percolation. The rising CSD-values (240 Å) in the region

of highest maturity mirrored the dissolution of the smallest particles. The dissolved cations were removed by percolation and not redeposited in the sample.



A: XRD: oriented mounts, ethylene-glycol saturated B: Zoom from image A - 2. order interference of smectite composed by two peaks of smectite: (i) 8.69 Åpeak represented thin particles with a CSD-value 65 Å and (ii) 8.59 Å-peak mirrored thick particles with a CSD-value 225Å;

C: TEM-micrograph characterised by large particles (dark) and xenomorphous thin particles (grey)

**Fig. 8.36** Two groups of smectite in starting material and run products – example: sample FeM0<sub>2</sub> (NaCl, 30 days, 90 °C)

The CSD-values of "thin" particles indicate a continous growth of particles by Oswald ripening (Fig. 8.37c).

The comparison of the frequency-ratio between "thick" (7 - 35 sheets per stack) and 'thin' (3 - 5 sheets per stack) particles has shown for the lowest maturity a temporary rising portion of 'thick' particles. The further development was characterised by a continuous reduction of these 'thick' particles (Fig. 8.37d).



a Stack order (by TEM - electron diffraction)



b CSD of 'thick' smectite particles (by XRD)



**Fig. 8.37** Different behaviour of smectite particles in the run products analysed by TEM-EDX (A) and XRD (B-D)

Finally, the changing development in smectite of run products between illitisation and smectitisation was assessed as a system which was controlled by three driving forces (Fig. 8.38): (i) "flow rate of percolation" determines the maximum of the removing capacity of dissolved cations; (ii) "rate of dissolution by  $Fe^0 \rightarrow Fe^2$ -oxidation" and also (iii) "rate of dissolution by  $Fe^{2+} \rightarrow Fe^{3+}$  oxidation" can excite the removing capacity by percolation in the case of high Fe-activities (smectitisation). Percolation was responsible for illitisation, which occurred in the case of low Fe-activities. The dissolved Si and the other cations were liberated in lower concentrations than the possible removable capacity by percolation.



system controlled by "flow rate of percolation" [solid line], "rate of dissolution by "Fe<sup>0</sup>  $\rightarrow$  Fe<sup>2+</sup>"-oxidation" [dashed line] and "rate of dissolution by "Fe<sup>2+</sup>  $\rightarrow$  Fe<sup>3+</sup>"-oxidation" [spotted line]; smectitisation if rate of dissolution is higher than flow rate of percolation, otherwise illitisation

**Fig. 8.38** Illustration of the changing development in smectite of run products between illitisation and smectitisation

#### Fe in Smectite

Different authors [CRA 1984]; [RUS 1994]; [VAN 2001a]; [GAT 2005] described that higher octahedral Fe-contents cause lower wave numbers of the  $\delta_{AIFe-OH}$  band for cisvacant smectite. This description is also valid for all investigated starting materials of bentonite (Fig. 8.39). Two groups were identified: (a) lower Fe-level for samples MX80, Friedland clay (from GRS-material) and B09 (from BGR-collection) as well as (b) higher Fe-level for samples B04, B11, B12, B13 (from BGR-collection). The different Fe-levels mean: Fe has entered the trans-octahedral position in natural smectite in group A earlier than in group B.

The percolation experiments have also shown a strong trend between octahedral Feamount and FTIR-wave number, but in opposite directions. Higher octahedral Fecontents caused higher (and not lower) the wave numbers of  $\delta_{AIFe-OH}$  band (Fig. 8.30). This means that the additional Fe has occupied the cis-octahedral position in the smectite of run products.

The opposite development for the incorporation of Fe indicated a metastable behaviour only for the run products.



Fig. 8.39 Comparison of octahedral Fe-amount (TEM-EDX-based) and FTIRmeasurement for the different starting bentonites

#### 8.4.2 Investigations of Natural Analogues

A tropical weathering profile on ultramafic rocks was selected to understand natural processes of smectite alteration in contact with a possible natural analogue.

This report focused on a profile of the Bai Ang-area of the Nua Nui-complex. The samples NN 0 – 1.5 m (bottom), NN 1 – 2 m (middle part) and NN 3 – 5 m (top horizon) represent a vertical weathering profile of serpentinised diabase (Fig. A.10).

**Bulk sample – XRD:** The bottom sample is composed of talc, serpentine antigorite  $((Mg, Fe^{++})_6 Si_4 O_{10} (OH)_8)$ , chlorite and CSV-mI as well as smectites (saponite, stevensite) and IS-mI. In the sample of the middle part, the former talc and serpentine antigorite were substituted by ferro-actinolite (a Fe-Mg-hornblende: Ca<sub>2</sub>(Mg,Fe<sup>++</sup>)<sub>5</sub>Si<sub>8</sub>O<sub>22</sub> (OH)<sub>2</sub>). Feldspar albite and Fe-poor actinolite were further phases in the sample of the upper horizon (Tab. 8.28; Fig. 8.40).

**Fraction < 2 µm – XRD:** The general mineral matter of fraction < 2 µm was comparable mainly with the bulk sample. Talc was not to identify in fraction < 2 µm. Probably, talc occurred in a grain spectrum larger 2 µm. Antigorite (or trioctahedral vermiculite) and ferro-actinolite were also available in the fine fraction, but not the Fe-poor version of actinolite in the upper sample. This sample has also shown a clear 10 Å-interference, but the type of mica (biotite or muscovite) in the fraction < 2 µm of the bottom sample could not be identified.

 
 Tab. 8.28
 Mineral matter in weathering profile of serpentinised diabase (Bai Angarea) analysed by XRD

Powder Specimen	[bulk sa	ample)	I	Oriented Mounts [f	B Ifraction < 2 µm multiple for the second					
	NN 0 <sup>-</sup> 1.5 m bottom	NN 1 <sup>-</sup> 2 m	NN 3 <sup>-</sup> 5m top		NN 0 <sup>-</sup> 1.5 m bottom	NN 1 <sup>-</sup> 2m	NN 3 <sup>-</sup> 5m top			
Quartz				Quartz						
Lepidocrocite				Cronstedtite 17-0470						
Kaolinit 14-0164				Mica	Х					
Albite 09-0466			XX	Ferro-Actinolite 23-0118	XX	XX	XX			
Actinolite 25- 0157			XX	Smectit + IS-ml	XXX	XXX	XXX			
Ferro-Actinolite 23-0118		XXX	XX	CSV-ml	Х	XX	XX			
Smectit + IS-ml	XX	XX	XXX	trioct. Vermiculite	XX					
Chlorite + CSV	XX	XXX	XX	Talc 29-1493						
unnown 20A-phase	XX									
Antigorite 21-0963	XXX									
Talc 29-1493	Х									

**Fraction < 2 µm – TEM:** TEM-investigations (Tab. 8.29) have shown saponite as main phase as well as CSV-mI, TSV-mI, IS-mI and diVS-mI as minor phases in the NN 0 – 1.5 m (bottom). In the middle part, diVS-mI and KSV-mI were the main phases (minor phases: cronstedtite and CSV-mI; traces: saponite, actinolite, TSV-mI, and IS-mI). The clay mineral matter of sample NN 3 – 5 m (top horizon) is similar to the middle part: diVS-mI and KSV-mI were again identified as main phases, but extended by CSV-mI (minor phases: beidellite/Fe-beidellite, actinolite and a further unkown phase; traces: saponite and IS-mI).

**Alteration – Minerals:** Tab. 8.29 illustrates the substitution of trioctahedral sheet silicates by dioctahedral clay minerals in progress of the weathering process (from saponite in the bottom sample to diVS-ml in the middle and upper sample).

Saponite and talc are to be considered as hydrothermal products of serpentinite during serpentinisation. These two trioctahedral phases altered during weathering processes partially into CSV-ml and actionlite (a Fe, Mg-member of hornblende-group), but mainly into diVS-ml and KSV-ml as well as beidellite/nontronite as minor phases (Tab. 8.29). Iron was highly concentrated in cronstedtite in the middle sample.



 Fig. 8.40 XRD-traces of bulk sample (left; powder, randomly orientation) and fraction
 < 2 µm (right; oriented mount, air dried) of weathering profile of serpentinised diabase (Bai Ang-area)

Alteration – Fe-pathway (Fig. 8.41): Iron was mainly concentrated in clay mineral matter in divalent bounding (60%) and only occurred in traces (5%) as 3-valent cation. The middle horizon has shown the highest amount of Fe in clay mineral matter. The divalent Fe-part was reduced to 40% in trioctahedral clay minerals, but the 3-valent Fe-amount was raised to 40% in dioctahedral phases and 5% also in trioctahedral sheet silicates. This high amount in dioctahedral phases was caused by mitigation of Fe from the upper horizon downward into the middle part of the profile. A small amount of divalent Fe (5%) originated in trioctahedral clay minerals and was transferred after oxidation into dioctahedral clay minerals. All clay mineral phases in the upper horizon have shown increased values for octahedral AI and decreased amounts of octahedral Fe mirroring the Fe-mitigation downwards into the middle horizon.

Tab. 8.29	Mineral matter of fraction < $2 \mu m$ in weathering profile of serpentinised dia-
	base (Bai Ang-area) identified by TEM-analysis (in frequency-%)

Phase		Profile Bai Ang	
FlidSe	bottom	middle	top
Unkown Fe,Mg-silicate			12 %
Cronstedtite		100 %	
Actinolite		5%	9%
Beidellite/Nontronite		13 %	11 %
Kaolinite + KSV-mI		26 %	21 %
diVS-ml	9%	30 %	28 %
Chlorite + CSV-ml	4%	10 %	16 %
IS-ml	13%	2 %	2 %
Talc + TSV-ml	20 %	1 %	
Saponite	55 %	2 %	2 %



orange values –  $Fe^{2+}$  in relation of max.  $Fe_{total}$ ; green values –  $Fe^{3+}$  in relation of max.  $Fe_{total}$ ; VI – composition of octahedral sheet

## **Fig. 8.41** Illustration of Fe-flow in Bai Ang-profile based on the frequency of minerals identified by TEM

# 8.4.3 How to apply the knowledge about the self-potential of smectites for illitisation?

The overhead shaking experiments have shown the self-potential of smectites for dissolution. This self-potential is driven by cation's occupation in the interlayer space and in the octahedral layer. Each bentonite has its unique geological background and so its unique chemical composition. This means that each bentonite has its own unique self-potential.

This knowledge now offers the opportunity to reprocess the results also from former experiments, especially in order to be able to understand what conditions are to be expected in final repositiories.

[PUS 2007] have carried out short-term corrosion experiments with Cu-plates (Fig. 8.42) in contact with three different bentonites (MX80, Friedland Clay, GeoHellas Clay). All three clays were also used in this project, but the MX80 in experiments from Pusch was comperable to [MAD 1998]. Cu has penetrated the MX80 bentonite at 100 °C at a depth of 1.5 mm. The shape of distribution of Cu in the bentonite indicated a channel-like pathway of Cu. The Fe-rich Friedland Clay was contaminated only in the direct contact region between bentonite and Cu-plate. No Cu was detected anwhere in the GeoHellas Clay. This was a suprising result, because the expectation was: no contamination in MX80 (Na-montmorillonite = high swelling pressure) and remarkable interaction for the other two bentonites (Fe-rich in the octahedral layer, hence easier to attack for dissolution processes).

8 weeks, from 100°C (hot Cu-plate) to 35°C (outside), 1% CaCl<sub>2</sub> solution





Friedland clay

GeoHellas clay

Red circle – Cu detected by SEM-EDX; Blue circle – Cu under the detection limit by SEM-EDX.

# Fig. 8.42 Experiments with heated Cu-plate and three different smectite-bearing and compacted clays by [PUS 2007]

An approach to the knowledge concerning driving forces for self-potential for the dissolution of bentonites will be given in following explanation (in the case of a close reaction system  $\Delta$ %S<sub>perc</sub> = 0 and a low energy-level): The specific potential for the dissolution of bentonite ( $\Delta$ %S<sub>prec</sub>) of MX80 was the lowest among these three bentonites. MX80 bentonite was like a "Sleeper". It was followed by GeoHellas Clay. Friedland clay has shown a "Sprinter"-like specific potential.

**MX80**: The small amount of dissolved Si from MX80 bentonite cannot form new montmorillonitic layers in existing quasicrystals. MX80 smectite is already fully developed. This dissolved Si is precipitating. Following the model for Si-precipitation by [PUS 1991], it will glue and collaps quasicrystalls and broaden the pores. As a result, Cu could penetrate channel-like deeply in MX80-bentonite.

**Friedland Clay**: The low Na-amount in the interlayer space and the high Fe+Mg-ratio give this clay a remarkable specific dissolution potential. Only 70 % of layers are mont-morillonite in the mixed layers of Friedland clays. This means that Friedland is undergoing a smectitisation. The Si-buffer, offered by the mixed layer, is sufficient to consume all dissolved Si of the "Sprinter" Friedland clay before Si is precipitating the compacted material. As a result, Cu could penetrate Friedland Clay only in the direct interface between clay and Cu-plate.

**GeoHellas Clay**: The octahedral composition of GeoHellas Clay determines this clay as type B (Ca+Mg is stabilising the smectite). That is the reason why the high Ca- and Mg-amount are responsible for its limited specific dissolution potential. GeoHellas Clayis is also composed of mixed layer phases, which offer a high Si-consumption potential. That is why Si-precipitation is underpressed by Si-buffering as additional montmorillonite layers in the mixed layer phases (smectitisation).

This example illustrates that the Si-buffer capacity of bentonites would be much more important in a closed system than the specific dissolution potential.

In another experiments concerning contact of Fe-rich bentonite with Fe-canister (Czech Mock Up-experiments in [PUS 2005]), the Czech RMN-bentonite developed a hydraulic conductivity increased by two magnitudes close to the hot canister. The bentonite has shown an illitisation. This situation represents more an open reaction system. Far removed from the hot canister, the run products of this bentonite were characzterised by smectitisation. The composition of RNM-bentonite determines this clay as "Sprinter". The amount of dissolved Si is precipated and has broadened the pores. This development changed the reaction system from close to open. In concequence, further dis-

solved Si could be transported away from the canister causing an illitisation of the bentonite close to the canister.

It seems that the direct contact with Fe increased the reaction activity. An open system could be possible close to the Fe-source.

### 9 Modeling of the interactions of iron – bentonite

#### 9.1 Introduction

The geochemical reaction simulation of three different solutions (e. g. IP21, saturated NaCl solution and Opalinus-clay pore water) with iron bentonite for a HLW repository was undertaken with the aid of ChemApp. The calculations presented in this report are aimed to provide a preliminary evaluation of the geochemical stability of MX80 bentonite through the influence of iron powder as well as Fe<sup>2+</sup> in the ground water with varying salinity. The long term stability of these materials is a key issue for the sealing function of bentonite. This is governed by many factors such as geotechnical, hydraulic and geochemical processes. In order to better understand the potential effect of geochemical processes on the long term properties of the bentonite, geochemical simulations of the potential interactions between groundwater and iron bentonite were undertaken.

#### 9.2 Geochemical composition of solid phases and solution

The solid materials considered in the geochemical simulation are MX80 bentonite and a mixture of MX80 with 10 wt% zero valent iron powder (Fe(cr)). The chemical composition of the MX80 is composed mainly of smectite with 77 wt%, which is a mixture of different montmorillonites (Tab. 9.1). Additionally, there are also albite (13 wt%), quartz (5 wt%), cristobalite (alpha) (3 wt%) and muscovite (1 wt%).

Minerals	Mass fraction	Mass amount in sample	Mol weight	Mol amount in sample
	[wt%]	[g]	[g/mol]	[mol]
Montmorillonite-Na	4.62	2.610	367.017	7.11·10 <sup>-03</sup>
Montmorillonite-K	7.70	4.350	372.333	1.17·10 <sup>-02</sup>
Montmorillonite-Ca	32.34	18.269	366.043	4.99 <sup>.</sup> 10 <sup>-02</sup>
Montmorillonite-Mg	32.34	18.269	363.441	5.03·10 <sup>-02</sup>
Cristobalite(alpha)	3.00	1.695	60.084	2.82·10 <sup>-02</sup>
Quartz	5.00	2.825	60.084	4.70 <sup>.</sup> 10 <sup>-02</sup>
Albite	13.00	7.344	262.223	2.80 <sup>.</sup> 10 <sup>-02</sup>
Muscovite	1.00	0.565	398.308	1.42 <sup>.</sup> 10 <sup>-03</sup>
Total	99.00	55.925		

Tab. 9.1	The mineral com	position of MX80	and mol am	nounts in the	samples
140.0.1			una mor un		oumpieo

For the mixture of MX80 bentonite and Fe(cr), the mineral composition is calculated as follows: Taking the size of the sample (5 cm in diameter and 2 cm in height) and the dry density of  $1600 \text{ kg/m}^3$ , the mass amount of a sample is 62.773 g. The 10 wt% Fe(cr) is 6.27 g, which is equivalent to 0.1125 mol. The rest of the solid material is MX80 and the amounts of each mineral are calculated as shown in Tab. 9.1.

#### 9.3 Geochemical composition of solutions

The chemical compositions of three different solutions (i. e. saturated NaCl-solution, IP21 and Opalinus-clay water (OPC)) are listed in Tab. 9.2.

Species	Concentration [molal]		
	NaCl	IP21	OPC
Na+	6.1722	0.4804	0.1284
K+		0.5684	0.0008
Mg2+		4.2113	0.0049
Ca2+		0.0006	0.0069
Sr2+			0.0003
Ba2+			0.0000
CI-	6.1722	8.8402	0.1301
HCO3-			0.0005
SO42-		0.3162	0.0148

Tab. 9.2	Chemical com	position of NaCl-	IP21- and OPC	solutions (	(CHEMOTOX)
1 a.b. J.Z	Onernical comp			3010110113	

### 9.4 Geochemical database

The applied geochemical database is based on the EQ3/6 data0.ypf and transformed into ChemApp format. This database includes Pitzer parameters and is thus valid for the highly saline solution cases. However, the temperature dependent Gibbs free energy of formation for several minerals (e. g. Berthierine, Nontronite and Vermiculite) is not available yet, in which berthierine plays an important role in the geochemical interactions of Fe(cr), bentonite and solutions. Therefore, the geochemical simulation is restricted to 25 °C.

#### 9.5 General assumptions of geochemical reaction calculation

The general assumptions of the geochemical batch reaction calculation are:

- The temperature and pressure conditions were assumed to be constant (25 °C and 1 bar) for all geochemical simulations;
- 2. All geochemical calculations refer to a state of thermodynamic equilibrium, kinetic reactions are not considered;
- 3. The solution is prepared without air isolation. After the injection of solution, the experimental cell is closed which prevents the solution from further air contact thereafter. Therefore, for the calculation, solution is firstly equilibrated with air and then reacts with MX80 bentonite/Fe(cr) mixtures. In this case only the dissolved amount of O<sub>2</sub>(aq) in the solutions is considered for the calculation.
- 4. The amount of solution for the calculation includes the solution in the bentonite pore spaces of bentonite and both filters (5 mm thickness each with 80 % porosity) adjacent to the bentonite sample. When the solution was consumed, the system was reopened and solution was re-injected.

#### 9.6 Simulated results

The geochemical calculation is undertaken with a ChemApp based program by adding three different solutions, i. e. saturated NaCl-solution, IP21 and Opalinus-clay water (OPC) into the sample with Fe(cr) and MX80 bentonite.

#### 9.6.1 Saturated NaCl case

In this case, saturated NaCI-solution reacts with Fe(cr)/Bentonite mixture.

**Tab. 9.3**The input amounts of substances (NaCl case)

STREAM CONSTITUENTS	AMOUNT/mol
O2(g)/GAS/	1.8521E-06
H2O/AQUEOUS/	1.6657E+00
Muscovite_KAI3Si3O10(OH)	1.4182E-03
Albite_NaAlSi3O8	2.8006E-02
Cristobalite(alpha)_SiO2	2.8206E-02
Montmorillonite-Na	7.1109E-03
Montmorillonite-K	1.1682E-02
Montmorillonite-Ca	4.9909E-02
Montmorillonite-Mg	5.0266E-02
Quartz_SiO2	4.7009E-02
Fe(cr)	1.1251E-01
Na	1.8521E-01
CI	1.8521E-01

### Tab. 9.4The generated gases (NaCl case)

	EQUIL AMOUNT	MOLE FRACTION	FUGACITY
PHASE: GAS	mol		Pa
H2	1.0894E-01	9.9987E-01	1.7470E+07
H2O(g)	1.4507E-05	1.3316E-04	2.3265E+03
O2(g)	0.0	0.0	

In which H2(g) is the dominated gas.

Tab. 9.5	The mineral	composition after	reactions	(NaCl case)
				\ ····/

	Mol	ACTIVITY
Quartz_SiO2	2.8480E-01	1.0000E+00
Berthierine	5.6254E-02	1.0000E+00
Montmorillonite-Na	4.1915E-02	1.0000E+00
NaCI_Halite	1.4273E-02	1.0000E+00
Albite_low_NaAlSi3O8	1.3638E-02	1.0000E+00
Saponite-Na	1.0980E-02	1.0000E+00
Laumontite	4.5661E-03	1.0000E+00
Muscovite_KAl3Si3O10(OH)	4.3024E-03	1.0000E+00
Albite_NaAlSi3O8	0.0000E+00	9.9500E-01
# 9.6.2 IP21 case

In this case, IP21-solution reacts with Fe(cr)/Bentonite mixture.

Tab. 9.6	The amount of each reactant is listed (	IP21 ca	ase)
	The amean of each reactant is noted (		200,

STREAM CONSTITUENTS	AMOUNT/mol
O2(g)/GAS/	1.8521E-06
H2O/AQUEOUS/	1.2852E+00
Muscovite_KAI3Si3O10(OH)	1.4182E-03
Albite_NaAlSi3O8	2.8006E-02
Cristobalite(alpha)_SiO2	2.8206E-02
Montmorillonite-N	7.1109E-03
Montmorillonite-K	1.1682E-02
Montmorillonite-Ca	4.9909E-02
Montmorillonite-Mg	5.0266E-02
Quartz_SiO2	4.7009E-02
Fe(cr)	1.1251E-01
Na	1.1122E-02
К	1.3160E-02
Mg	9.7507E-02
Са	1.4711E-05
S	7.3213E-03

# Tab. 9.7The generated gases (IP21 case)

	EQUIL AMOUNT	MOLE FRACTION	FUGACITY
PHASE: GAS	mol		Ра
H2	2.3912E-01	9.9992E-01	3.8872E+07
H2O(g)	1.9074E-05	7.9760E-05	3.1007E+03
O2(g)	NOT CALCD.	NOT CALCD.	< 1.0000E-75
TOTAL:	2.3914E-01	1.0000E+00	1.0000E+00

# Tab. 9.8The solid phases after the reaction (IP21 case)

	Mol	ACTIVITY
Quartz_SiO2	2.4776E-01	1.0000E+00
Berthierine	5.6254E-02	1.0000E+00
Saponite-Na	4.6506E-02	1.0000E+00
Muscovite_KAI3Si3O10(OH)	1.7512E-02	1.0000E+00
Montmorillonite-Na	1.5522E-02	1.0000E+00
Analcime	6.5563E-03	1.0000E+00
Laumontite	4.5830E-03	1.0000E+00
Phillipsite	0.0000E+00	9.8232E-01

# 9.6.3 OPC case

In this case, IP21-solution reacts with Fe(cr)/Bentonite mixture.

Tab. 9.9	The amount of each reactant is listed (OPC case)
----------	--

STREAM CONSTITUENTS	AMOUNT/mol
O2(g)/GAS	1.8521E-06
H2O/AQUEOUS	1.8578E+00
Muscovite_KAl3Si3O10(OH)	1.4182E-03
Albite_NaAlSi3O8	2.8006E-02
Cristobalite(alpha)_SiO2	2.8206E-02
Montmorillonite-Na	7.1109E-03
Montmorillonite-K	1.1682E-02
Montmorillonite-Ca	4.9909E-02
Montmorillonite-Mg	5.0266E-02
Quartz_SiO2	4.7009E-02
Fe(cr)	1.1251E-01
Na	4.2986E-03
К	2.6942E-05
Mg	1.6520E-04
Са	2.3221E-04
S	4.9372E-04
С	1.7724E-05

	EQUIL AMOUNT	MOLE FRACTION	FUGACITY
PHASE: GAS	mol		Ра
H2	1.1266E-01	9.9982E-01	1.7752E+07
H2O(g)	2.0043E-05	1.7787E-04	3.1581E+03
CO2(g	2.1199E-08	1.8813E-07	3.3402E+00
O2(g)	NOT CALCD	NOT CALCD.	< 1.0000E-75
TOTAL:	1.1268E-01	1.0000E+00	1.0000E+00

**Tab. 9.10**The generated gases (OPC case)

Tab. 9.11The solid phases (OPC case)

	mol	ACTIVITY
Quartz_SiO2	2.4205E-01	1.0000E+00
Berthierine I	5.6254E-02	1.0000E+00
Montmorillonite-Na	4.6681E-02	1.0000E+00
Saponite-Na	1.0771E-02	1.0000E+00
Analcime	9.7739E-03	1.0000E+00
Phillipsite	7.5719E-03	1.0000E+00
Stellerite	6.9030E-05	1.0000E+00
Laumontite	0.0000E+00	9.1739E-01
Albite_low_NaAlSi3O8	0.0000E+00	7.5467E-01
Albite_NaAlSi3O8	0.0000E+00	7.5088E-01

Based on the batch geochemical simulation mentioned above, new minerals berthierine and saponite-Na formed in all three calculations. Montmorillonite dissolves and quartz precipitates. When the geochemical reactions reach equilibrium state in a closed system, the main mineral phases are quartz, berthierine and montmorillonite or saponite-Na. Other minerals like albite, Laumontite, Analcime etc. depend on the chemical composition of the solutions.

#### 9.7 Reactive transport

The corrosion of HLW-canisters made of carbon steel and steel in concrete under HLW repository conditions can be distinguished as aerobic corrosion at the beginning after closure and as anaerobic corrosion thereafter. In the saline solution (e. g. saturated NaCl solution, IP21) the corrosion process might be enhanced. From a long-term point of view, the corrosion products, for instance FeCl2 under anaerobic condition, can be transported and migrate into the buffering material like MX80. Therefore, it is important

to investigate the interaction between MX80 bentonite and the solutions including Fe<sup>2+</sup>. This is realised by conducting reactive transport modelling.

## 9.7.1 Theoretical background

Reactive transport modelling is an important tool to investigate geochemical processes in the underground especially to analyse the interaction of solution with solid phases. The reactive transport model applied for the current work is OpenGeoSys, which has been developed for fully saturated porous media where the aqueous and/or gaseous phases are considered mobile, while the solid phases are considered immobile. The general equations for liquid flow and mass transport can be found in [KOL 1995]; [BEA 1988]. The equation for mass transport with geochemical reaction in saturated porous media is:

$$\frac{\partial C_i}{\partial t} = -v_a \nabla C_i + \nabla \cdot (D \nabla C_i) + Q_{C_i} + Reakt(C_i, \dots, C_n)$$
(9.1)

- C<sub>i</sub> concentration of the chemical component or element i
- $v_a$  flow velocity (advection),  $v_a = permeability \cdot hydraulic gradient$
- *D* diffusion coefficient
- Q<sub>ci</sub> source term of the chemical component or element *i*

 $Reakt(C_1, ..., C_n)$  concentration change owing to chemical reactions

In the simulation, conservative mass transport and geochemical reaction processes are calculated separately. The geochemical reaction is executed by integrating the ChemApp based geochemical module with OpenGeoSys. Details of the model can be found in [XIE 2011].

## 9.7.2 Model description

A one dimensional reactive transport model was set up to simulate the related laboratory tests for the injection of solution containing  $\text{FeCl}_2$  (in different concentrations) into the compacted bentonite from one side (Fig. 9.1). The height of the sample is 2 cm (or 0.02 m).



Fig. 9.1 Model set-up

The material properties of the sample are listed in Tab. 9.12. The diffusion coefficient of all solutes (e. g.  $Fe^{2+}$ ) is set to be  $2 \cdot 10^{-11}$  m<sup>2</sup>/s, which is an averaged diffusion coefficient of diffusion experiments. This data is also similar as in the literature [WER 2007].

 Tab. 9.12
 Input data used for the reactive transport modelling

Parameter	Unit	Test case A	Test case B
Diffusion coefficient	m²/s	2·10 <sup>-11</sup>	2·10 <sup>-11</sup>
Porosity	%	45.66	45.66
Dry density	Mg/m <sup>3</sup>	1.60	1.60
Fe <sup>2+</sup> source concentration	М	0.1	1.0·10 <sup>-4</sup>
Background solution	-	Saturated NaCl solution	Saturated NaCl solution

The simulated cases A and B differ only in the boundary condition – the Fe<sup>2+</sup> source concentration. The aim of the simulations is to investigate the influence of Fe<sup>+</sup> concentration on the bentonite alteration processes. All other parameters and concentrations are almost identical (Tab. 9.12). The background solutions for both cases are saturated NaCl solution. The boundary condition includes only 0.1 M NaCl (Case A) or 0.0001 M NaCl (Case B) and 6.28 M NaCl. The initial conditions are set with the measured composition of MX80 bentonite equilibriated with saturated bentonite. Such an equilibrium geochemical calculation for initialisation results in the variation of mineral compositions of the sample. The smectite as a mixture of various montmorillonites, for instance, remains only montmorillonite-Na.

It is important to note that some general assumptions as follows:

- mass transport is diffusion only; diffusion coefficient is constant;
- no sorption is applied;
- equilibrium geochemical reaction without kinetic reaction;

- temperature is constant at 25 °C;
- anaerobic condition.

#### 9.7.3 Simulated results of Case A (NaCl + 0.1 M FeCl<sub>2</sub>)

The calculation of Case A simulates the reactive transport process with the  $0.1 \text{ FeCl}_2$  dissolved in saturated NaCl solution and its migration and interaction with bentonite. Simulated results showed that with the intrusion of the solution, montmorillonite dissolves, berthierine and quartz precipitate (Fig. 9.2 – Fig. 9.5). Such processes are progressing with the further intrusion of the solution and additionally saponite-Na precipitates.

#### 9.7.4 Simulated results of Case B (NaCl + 0.0001 M FeCl<sub>2</sub>)

Similiar calculations were undertaken to simulate the influence of the source  $\text{FeCl}_2$  concentration change on the mineral/solution interaction. The initial mineral composition is the same as shown in Fig. 9.2. As the concentration of  $\text{Fe}^{2+}$  is now with  $1.0 \cdot 10^{-4}$  M, which is much lower than that in case 1 with 0.1 M, the concentration gradient of  $\text{Fe}^{2+}$  is thus much lower. Consequently, the amount of  $\text{Fe}^{2+}$  into the sample will correspondingly be much less. This caused much less berthierine precipitation (compare Fig. 9.3 to Fig. 9.6 for the mineral composition profiles at one day, or Fig. 9.4 to Fig. 9.7 at 10 days).

This indicates that berthierine formation is largely dependent on the  $Fe^{2+}$  availability. Other minerals showed at the beginning almost the same behaviour (compare Fig. 9.3 to Fig. 9.6). However, such similiarity is disturbed with the further migration of  $Fe^{2+}$  in distinct quantity (compare Fig. 9.5 to Fig. 9.8). This is because the formation of berthierine consumes Fe as well as AI, Si, Mg, O and H, which accelerates the dissolution of montmorillonite and thus the related reactions.

The numerical simulations mentioned above are all based on the assumption of equilibrium geochemical reaction. Therefore, such results are difficult to be applied to the comparison with laboratory experiments which are highly kinetically controlled. Nevertheless, the fact that main model minerals were detected in the relatively short laboratory experiments indicates the reliability of the thermodynamic database for the simulation as well as the high reactivity of Fe(cr) and Fe<sup>2+</sup>.



Fig. 9.2 Profile of the initial mineral composition



Fig. 9.3 Profile of the mineral composition at 1 day (case A)



Fig. 9.4 Profile of the mineral composition at 10 days (case A)



Fig. 9.5 Profile of the mineral composition at 100 days (case A)



Fig. 9.6 Profile of the mineral composition at 1 day (case B)



Fig. 9.7 Profile of the mineral composition at 10 days (case B)



Fig. 9.8 Profile of the mineral composition at 100 days (case B)

# 10 Relevance for Final Repositories

## 10.1 Preselection of suitable bentonite as future barrier material

#### **10.1.1** Specific dissolution potential of bentonite - Set of driving parameters

The experiments have proved that bentonites are characterised by a specific dissolution potential. Stable bentonites have a low specific dissolution potential and are called "Sleeper" here. Fast reacting bentonites show high specific dissolution potential and are labelled here as "Sprinter". A preselection of suitable bentonites can apply the chemical composition of smectite and the FT-IR spectrum of montmorillonite as indicators to estimate the specific dissolution potential of bentonite (Fig. 8.19). Admixtures like pyrite or calcite could increase the specific dissolution potential determined by the above mentioned chemical composition and FT-IR measurement.

In detail, following parameters were identified to affect the composition of smectite in the run products:

#### Main parameters:

•	Im	pact by composition of interlayer space	(Δ%S <sub>×II</sub> )		
	_	and low activity environment:	Ca + Mg can stabilise smectite. (fixing adjacent layers, if opposite locat- ed charge sites would be available)		
	_	and low and high activity environ-	high Na-amount can stabilize smectite		
		ment:	(High viscosity of water in the diffuse ion layer limits fluid movement and thus also the reactivity of smectite)		
•	Im	pact by composition of octahedral layer	(Δ%SVI)		
	_	And low & high activity environment:	high octahedral Al-amount can stabilise smectite		
			(Al has a low ion radius, that is why re- sulting low sheet stresses offer an addi- tional resistance against any agents)		

#### Additional specific parameters:

Impact by specific minerals in bentonite (Δ%Sspec)
 e. g. oxidation of native Fe or Fe<sup>2+</sup>; occurrence of pyrite, partially calcite

#### Alteration limiting parameters:

- Impact by fluid movement (e. g. flow rate of percolation)  $(\Delta\%S_{perc})$
- Impact by amount of smectite layers in IS-ml and diVS-ml series (%S)

The degree of alteration was expressed as a reduction or raising of the amount of smectite layers ( $\Delta$ %S<sub>total</sub>). The measured alteration was a summarised effect like

$$\Delta \% S_{\text{total}} = f(\Delta \% S_{\text{XII}} + \Delta \% S_{\text{VI}} + \Delta \% S_{\text{spec}}, \Delta \% S_{\text{perc}}, \% S)$$
(10.1)

Negative values for  $\Delta$ %S<sub>total</sub> describe alteration in the direction of illitisation and positive values of  $\Delta$ %S<sub>total</sub> mean smectitisation. The impact of flow rate ( $\Delta$ %S<sub>perc</sub>) determines the direction of alteration (illitisation or smectitisation). A case like  $\Delta$ %S<sub>XII</sub> +  $\Delta$ %S<sub>vI</sub> +  $\Delta$ %S<sub>spec</sub> >  $\Delta$ %S<sub>spec</sub> causes an illitisation. Smectitisation would be a consequence of the opposite case. In this case the original amount of smectite layers is responsible for precipitation of Si, if  $\Delta$ %S<sub>XII</sub> +  $\Delta$ %S<sub>vI</sub> +  $\Delta$ %S<sub>spec</sub> -  $\Delta$ %S<sub>spec</sub> + %S > 100%.

A special Excel-based software tool was developed on this basis supporting this new option to preselect optimal bentonites from the viewpoint of specific dissolution potential.

# 10.1.2 Specific dissolution potential of bentonite – Mirroring in experiments with compacted bentonites

The "Rate of Alteration" experiments indicated that each bentonite should have its own specific degree of alteration (see chapter 10.1.1). It should possible now to select optimal bentonites as barrier material for the different conditions. Furthermore, it should possible now to predict much better the expected impact on hydraulic conductivity and swelling pressure and such processes like clogging of aggregates by Fe- or Siprecipitation and formation of channels in the sense of [PUS 1992].

The "Clay/Iron-Interaction"-experiments were performed mainly on compacted MX80 bentonite with different "clay/iron"-ratio. It is now the question how to transfer the results from the "Rate of Alteration" experiments (pure bentonite, suspended particles, different energy levels, no additional Fe-admixtures) to compacted material like in the "Clay/Iron-Interaction" experiments.

For further discussions, the investigated bentonites were classified into a "Sleeper"group, a medium group and a "Sprinter"-group. The following limits were postulated to divide these three groups: (i) "Sleeper" as slow reacting bentonites with a specific dissolution potential  $\Delta$ %S<sub>total</sub> not stronger than - 5; (ii) medium class with a specific dissolution potential  $\Delta$ %S<sub>total</sub> between - 5 and - 20, and "Sprinter" as fast reacting bentonites with a specific dissolution potential  $\Delta$ %S<sub>total</sub> stronger than - 20. Symbols in Fig. 10.1 and Fig. 10.2 are labelled in this manner: "Sleepers" as blue triangles, "medium" class as yellow squares and "Sprinters" as red diamonds.

#### Experiments with compacted MX80 bentonite in open reaction systems

The behaviour of compacted MX80 bentonite has shown an open reaction system in experiments with Opalinus clay pore water-solution (Fig. 8.2 below) and IP21-solution at 25 °C. This was caused by the high flow rate of percolation. The percolation is removing dissolved Si. "Illitisation" in the run products is then a result of this Si-mitigation. The main driving force for this process would be not the additional impact of Fe-activity. It is assumed that the high flow rate of percolation would be responsible to maintain continuously a high gradient of concentration between solution and quasicrystals. This gradient also promotes a continuous dissolution of particles. In this case, this type of experiment can directly be compared with the "Rate of Alteration" experiments on non-compacted material.

It is not possible to verify the transferability of the specific dissolution potential of MX80 bentonite to experiments with compacted bentonite in Opalinus clay pore watersolution because of missing mineralogical investigations to the amount of smectite layers (%S) per quasicrystal. Otherwise, these data are available from IP21-experiments at 25 °C. The colouring of the compacted material after the experiments has shown yellow and dark brown zoned areas (Fig. 6.3 left). The run products are characterised by a strong "illitisation". The tetrahedral Si in smectites from yellow zones was reduced from 3.95 to 3.77 per (OH)<sub>2</sub> O<sub>10</sub> representing an alteration of  $\Delta$ %S<sub>meas</sub> = - 33. The theoretical total specific dissolution potential of MX80 bentonite at high energy level was determined with  $\Delta$ %S<sub>total</sub> = - 37 (Tab. 10.1 right). A similarly good agreement was measured for the smectites in the dark brown zones with  $\Delta$  %S<sub>meas</sub> = - 19 and the theoretical specific dissolution potential at low energy level  $\Delta$ %S<sub>total</sub> = -21 (Tab. 10.1 left).



x-axis – specific dissolution potential ( $\Delta$ %S<sub>total</sub> = 0 means "no change" – montmorillonite with %S = 100 % will be stable;  $\Delta$ %S<sub>total</sub> = -50 means "strong alteration is expected" – former montmorillonite with %S = 100 % will alter into mixed layer phases with %S = 50 %); y-axis – ratio of smectite layers in illite-smectite mixed layer phases (%S = 100 % means montmorillonite, %S = 0 % means illite); blue triangle – bentonite is defined as sleeper if  $\Delta$ %S<sub>total</sub> between 0 and -5; yellow squares – bentonites with a specific dissolution potential between sleeper and sprinter; red diamond – bentonite is defined as sprinter if  $\Delta$ %S<sub>total</sub> exceedes values like -20; indices like (14, 10) – in case of closed reaction system these indices describe the impact by mixed layer phases as potential reservoir for dissolved Si prior to Si-precipitation (e. g.,  $\Delta$ %S<sub>total</sub> = -24, where %S = 14% would be the value for smectitisation and equivalents of %S = 10% would be finally the scale of Si-precipation)

**Fig. 10.1** Bentonites classified by "Rate of Alteration" experiments (H<sub>2</sub>O, open system) representing experiments with lowest energy level



Fig. 10.2 Bentonites classified by "Rate of Alteration" experiments (NaCl, open system) representing experiments with highest energy level (legend see Fig. 10.1)

H2O low and high					NaCl high								
		group	∆%SXII	∆%SVI	Σ	%S			group	∆%SXII	∆%SVI	Σ	%S
	Garfield	В	-18	-76	-94	42		GeoHellas	В	-54	-9	-63	66
Ľ,	Vietnam	В	2	-62	-60	80		Vietnam	В	-45	-11	-56	80
nte	11F	В	-18	-8	-26	83		12F	В	-42	-8	-49	107
bri	GeoHellas	В	7	-32	-25	66		13F	В	-42	-7	-49	64
ŝ	16F	Α	-18	-6	-24	95		04F	В	-41	-8	-48	93
	MX80, 2005	В	-16	-5	-21	99	-	28F	В	-41	-6	-47	109
	09F	Α	-11	-4	-16	107	ter	31F	В	-36	-7	-44	107
	Polkville	Α	-6	-6	-11	93	rin	38F	В	-37	-6	-43	99
	Pioche	Α	-5	-6	-11	83	'Sp	16F	Α	-36	-6	-43	95
E	Amory	Α	-4	-6	-10	91	•	23F	В	-37	-5	-42	107
e di	04F	В	0	-10	-10	93		37F	В	-35	-4	-39	107
Ň	Cameron	Α	-3	-6	-9	49		MX80, 2005	Α	-32	-5	-37	99
	Otay	Α	-2	-6	-8	95		22F	В	-30	-5	-35	109
	31F	В	-2	-5	-7	107		Chambers	В	-22	-7	-29	97
	Bayard	В	-15	9	-6	105		09F	Α	-21	-5	-27	107
	Chambers	В	-9	4	-5	97		Bayard	В	-12	-7	-19	105
	12F	В	1	-5	-5	107		Garfield	В	-7	-12	-19	42
	13F	В	1	-5	-4	64		Polkville	Α	-10	-6	-16	93
er'	28F	В	0	11	0	109	ш	Pioche	Α	-8	-7	-15	83
eeo	38F	В	-2	25	0	99	ŝdit	11F	В	-7	-8	-15	83
Į.	22F	В	-5	29	0	109	M	Amory	Α	-6	-7	-13	91
	23F	В	-2	40	0	107		Cameron	Α	-5	-6	-11	49
	37F	В	-3	43	0	107		Belle Fourche	В	-4	-5	-9	97
	Belle Fourche	В	-19	31	0	97		Otay	Α	-2	-7	-2	95

Tab. 10.1Database on specific dissolution potential of bentonite classified by "Rate<br/>of Alteration" experiments (Fig. 10.1, Fig. 10.2)

The different coloured zones in Tab. 10.1 mirror a different degree of percolation. The percolation was stronger in yellow zones and has thinned the Fe-concentration in the pores that caused a preferred precipitation of Fe-hydroxides (verified also by XRD & TEM). The percolation was reduced in the dark brown zones. As a result, Fe was preferentially incorporated in clay mineral phases (verified by XRD & TEM). That is why run products from dark brown areas show by the identified mineral matter a low energy impact by percolation, but also a higher reaction impact by higher Fe-activity. Otherwise, the run products from yellow zones mirror a higher impact of percolation and a lower degree of alteration by Fe-activity.

#### Experiments with compacted MX80 bentonite in closed reaction systems

Especially the experiments with saturated solutions (NaCl, IP21) at 60° and 90 °C represent closed reaction systems (see chapter 8.1). In closed reaction systems, dissolved

Si forms new smectite layers or precipitates cementing quasicrystals in the sense of [PUS 1992]. Bentonites composed by illite-smectite mixed layers could absorb a certain amount of dissolved Si as new smectite layers. This process can be identified as smectitisation. The data symbols in the following diagrams (Fig. 10.1, Fig. 10.2) contain an additional index. The first value in this index means the amount of smectite layer ( $\Delta$ %S), which could be absorbed by illite-smectite mixed layers. The second value of this index represents the amount of precipitated Si ( $\Delta$ %S<sub>prec</sub>) as rest between the total specific dissolution potential and the absorbed amount of dissolved Si. The experiments with compacted MX80 bentonite have shown a remarkable influence of Siprecipitation only at high temperatures like 90 °C (Fig. 8.2, above). This behaviour would be more comparable with data of specific dissolution potential at low energy level (Fig. 10.1, red, bold lined symbol; Tab. 10.1). An increased Fe-concentration raises the Si-precipitation.

	closed	reaction	system	open r	eaction s	system	
	e	nergy lev	vel	er	hergy lev	el	
	all	low	high	all	low	high	
	H <sub>2</sub> O	NaCl	NaCl	H <sub>2</sub> O	NaCl	NaCl	
Vietnam							
MX80, 2005							
16F							
Garfield							
Geo Hellas							
09F							
04F							Logond
12F							Legena
31F							Closed reaction system
11F							amount of precipitated Si:
22F							high;
23F							with Δ%Sp <sub>rec</sub> < - 20
28F							With Z $\Delta$ %S <sub>max</sub>
37F							between $-20$ and $-5$
38F							low;
Chambers							$\Delta$ %S <sub>prec</sub> > - 5
13F							Open reaction system
Bayard							specific dissolution potential:
Pioche							high;
Cameron							with ∆%Sp <sub>rec</sub> <- 20
Amory							medium;
Polkville							with $Z \Delta \% S_{prec}$
Otay							low:
Belle Fourche							$\Delta\%S_{\rm prec} > -5$

Tab. 10.2 Visualisation of optimal bentonites for "all cases" view

# Conclusions from the comparison of experiments with non-compacted and compacted bentonites

The effective clay/iron-ratio, the reduction potential of Fe (Fe<sup>0</sup> or Fe<sup>2+</sup> as starting material), the reaction temperature and the ion strength of pore solution are typical determinants of chemical reaction activity in the system. A lower total chemical reaction activity (mainly at 25 °C) allows an open reaction system, where the percolation could cause an "illitisation" at a high energy level of specific dissolution potential. The "illitisation" is accompanied by reduced swelling pressure and increased permeability. Fe is preferred to precipitate as oxyhydroxides. This process reduces additionally swelling pressure and permeability.

A higher chemical reaction activity (e. g., at 90 °C) is acting as a closed system. The Fe-activity and missing percolation cause a smectitisation with a specific dissolution potential at low energy level. The smectitisation is accompanied by increased swelling pressure and permeability. Illite-smectite mixed layer could uptake dissolved Si as new-ly formed smectite layer up to %S = 100 %. A further Si-amount is precipitated and reduces swelling pressure and increases permeability again.

In both cases, a rising Fe- or Si-precipitation could form channels in the sense of [PUS 1992]. This strongly increases permeability.

#### Mirroring of specific dissolution potential of bentonite in other experiments

The experiments with three different compacted bentonites and heated basic Cu-plates by [PUS 2007] were already described in chapter 8.4.3. After two months, MX80 bentonite already showed a channel-like distribution of Cu a few millimetres from the basic Cu-plate. GeoHellas clay was really dense under the same experimental conditions (Fig. 8.42). The two different bentonites have a similar specific dissolution potential at low energy level (Tab. 10.1) and can be considered as "Sprinters" (Tab. 10.1). Responsible for this positive behaviour of GeoHellas clay was the ability to absorb dissolved Si caused by the illite-smectite mixed layer as main mineral phase with %S = 66 %. The MX80 bentonite is composed of smectite with %S = 90 %. This surplus of Si-precipitation in MX80 bentonite causes increased permeability.

Fe-rich RMN-bentonite was used in the Czech-Mock-up experiments. [PUS 2010] reported a strongly increasing permeability linked with a slight smectitisation of run prod-

ucts. The RMN-bentonite is characterised as "Sprinter" with a specific dissolution potential  $\Delta$ %S<sub>total</sub> = -34 at low energy level. RMN-bentonite is composed of smectite with %S = 92%. This means that the identified lesser suitability as a barrier would be caused by high Si-precipitation.

#### What would be the optimal bentonite?

The classification of all investigated bentonites concerning their specific dissolution potential in low and high energy level and the %S-impact in closed reaction systems is summarised in Tab. 10.2. Such bentonites like Bayard, Pioche, Cameron, Amory, Polkville, Otay and Belle Fourche are characterised in all discussed cases as suitable bentonite.

## 11 Summary and conclusions

The main objectives of this study were to enhance the understanding of the interactions of bentonites with steel containers in the near field of a repository in salt formations and to determine missing experimental thermo-hydraulical-chemical and mineralogical data needed for the THC modeling of the interactions of bentonites with iron. At the beginning of this project a literature review helped to clarify the state of the art regarding the above mentioned objectives prior to the start of the experimental work. In the experimental program the hydraulic changes in the pore space of compacted MX80 bentonites containing metallic iron powder and in contact with three solutions of different ionic strength containing different concentrations of Fe<sup>2+</sup> have been investigated. The alterations of MX80 and several other bentonites in contact with the low ionic strength Opalinus Clay Pore Water (OCPW) and the saturated salt solutions NaCl solution and IP21 solution have been assessed. Under repository relevant boundary conditions we determined simultaneously interdependant properties on compacted MX80 samples like swelling pressures, hydraulic parameters (permeabilities and porosities), mineralogical data (changes of the smectite composition and iron corrosion products), transport parameters (diffusion coefficients) and thermal data (temperature dependent reaction progresses). The information and data resulting from the experiments have been used in geochemical modelling calculations and the existing possibilities and limitations to simulate these very complex near field processes were demonstrated.

The main results can be summarised as follows:

#### Evolution of swelling pressure, permeability and porosity

Swelling pressures and permeabilities were determined in different settings. In one set of experiments the pore space of compacted MX80 bentonite with a raw density of 1.6 g/cm<sup>3</sup> was flooded with OPCW, with NaCl and Mg rich IP21 solution. The solutions were spiked with different amounts of FeCl<sub>2</sub> (0.1, 0.2 0.3 and 0.4 mol/L). In a second group of experiments 10 wt.-% of metallic iron powder was added to the bentonite. The mixture was compacted to a raw density of 1.6 g/cm<sup>3</sup> and the pore space was flooded with the three solutions, but this time without FeCl<sub>2</sub>. For both types of experiments swelling pressure and permeability were measured at 25 °C, 60 °C and 90 °C. The mineralogical and chemical changes of the smectites of MX80 bentonite observed in previous studies could be observed in these experiments again. However an important difference was noted. Iron in the system accentuated and accelerated these changes.

The observed chemical and mineralogical changes of the smectites in contact with iron were fast and very intensive. The intensity of the interactions increased with increasing temperature, with increasing ionic strength and with the amount of iron in the system. The observed changes of swelling pressure and permeability are also correlated with hydraulic properties of the system. During the reaction smectite is dissolved and  $SiO_2(aq)$  liberated into the solution. With increasing  $Fe^{2+}$  in the system the original smectites were transformed in berthierine-saponite mixed-layers (ml) and further into chlorite-saponite ml. These mineralogical changes are controlled by the velocity of dissolution of the original smectite and the removal of SiO<sub>2</sub>(aq) from the solution. If removal of  $SiO_2(aq)$  is faster than the increase of  $SiO_2(aq)$  in solution by smectite dissolution an illitisation process is favoured. Consequently the swelling pressure is reduced and permeability increases. If more  $SiO_2(aq)$  enters the solution than is removed no more illites but new smectites can be formed leading to an increase of swelling pressure and a decrease of permeability. Swelling pressure and permeability however are not dependent only on the total amount of swelling smectite in the bentonite. These properties also depend on the associated mineralogical changes in the bentonite. The described direct relations between swelling pressure and permeability were additional affected by Fe- and Si-precipiation. Such precipitations reduce the swelling pressure and permeability with increasing Fe- or dissolved Si-amount. Otherwise, a further increasing Fe- or Si-cementation of particles leads to a foramtion of channels, which strongly increases permeability. The swelling pressure is constant in this phase of reaction.

Whereas very good results were obtained regarding swelling pressures and permeabilities the experimental determination of corresponding porosities was not successful. Different experimental approaches led to different results. This is a field which still needs more work.

# Interpretation of the observed mineralogical changes in different types of bentonites

#### Thermodynamic approach

MX80 bentonite and Friedland Clay showed significant signs of chemical and mineralogical alteration in the run products with the neoformation of serpentine and chlorite in different mixed layer phases. Also, the smectite in run products was altered in terms of the composition of the octahedral and tetrahedral layers as well as the interlayer sheet. The observed changes reach from illitisation to smectitisation depending on the activity of iron in the system and on the hydraulic conditions. In open systems SiO<sub>2</sub>(aq) is removed faster than smectite dissolution increases the Si content of the solution. The reverse is true if the Si content of the solution increases faster the system is considered to be closed and under these conditions smectitisation takes place. The degree of alteration was controlled by the degree of chemical activities (ion strength, Fe- and Siactivity, concentration). Higher reactivities lead to higher rates of Si dissolution from clay minerals. The oxidation of native iron (Fe<sup>0</sup>  $\rightarrow$  Fe<sup>2+</sup>) is recognised as the main driving force for dissolution, but also the oxidation of Fe<sup>2+</sup> (Fe<sup>2+</sup>  $\rightarrow$  Fe<sup>3+</sup>) can change an open into a closed reaction system by increased Si-pre-cipitation. The observed mineralogical changes were well understood from the point of view point of thermodynamics. The mineralogical changes observed in the experiments have also been observed in nature where tropical weathering if serpentinites occures.

#### **Kinetic approach**

Montmorillonites react with different velocities. They have specific potentials for dissolution. These dissolution potentials are controlled by the composition of the octahedral layers and the interlayer space. Rising amounts of Fe and Mg in the octahedral layer increase the dissolution potential (the higher ion radiuses of Fe and Mg compared to Al lead to an increased stress in the octahedral layer). The composition of the octahedral layer results primarily from the pH conditions during the formation of the bentonites (a geologic fingerprint). Stable bentonites (with a low specific dissolution potential) were called "Sleepers" here and fast reacting bentonites (with a high specific dissolution potential) "Sprinters".

The composition of the octahedral layer controls the stability of the interlayer:

- A) Al<sub>oct</sub> > 1.4 and Fe<sub>oct</sub> > 0.2 (per (OH)<sub>2</sub> O<sub>10</sub>) leads to delamination of quasicrystals. The swelling pressure increases by co-volume process between the delaminated layers (higher numbers of quasicrystals), in the case of Na-dominated by occupation of the interlayer sheet [LAI 2006]. In this situation, the layers are limited for its free rotation. Such Na-montmorillonites can be considered as stable phases and have only a low specific dissolution potential (so-called "Sleeper").
- B) Al<sub>oct</sub> > 1.4 and Fe<sub>oct</sub> < 0.2 or Al<sub>oct</sub> < 1.4 and Fe<sub>oct</sub> > 0.2 (per (OH)<sub>2</sub> O<sub>10</sub>) promote demixing between monovalent and divalent interlayer cations [LAI 2006]. Ca, Mg-

dominated interlayers tend to be more stable than Na-bearing interlayers and help maintain a quasicrystal structure. Such Ca, Mg montmorillonites also show a low specific dissolution potential at low energy level experiments. They can also be considered as "Sleepers".

Depending on the octahedral composition, certain cations in the interlayer can stabilise bentonites against mineralogical changes. Montmorillonites stabilised by high Nacations were classified in category A. Montmorillonites stabilised by high Ca, Mg cations in the interlayer sheet were grouped in category B. The classification of a smectite into the categories A or B defined above can be best achieved by IR analyses that yield useful chemical information concerning the composition of the octahedral sheets.

#### Means of controlling the thermodynamical and kinitic processes

Having in mind the above mentioned effects, best suited bentonites can be defined for their use in the near field of HLW repositories:

An ideal bentonite has kinetic properties which reduce the velocity of the thermodnamical changes towards zero. In general we propose:

Preferentially, bentonites with illite-smectite mixed layers (IS mI) should be used. Such bentonites have a high buffer potential for incorporating  $SiO_2(aq)$ . This process leads to the formation of new expandable smectite and prevents the precipitation of  $SiO_2$ . The less  $SiO_2$  is precipitated due to smectite dissolution the less permeability increase must be expected. We recommend the use of "Sleepers" with a low dissolution potential of the original smectites. "Sprinters" should be avoided. MX80 sold in 2005 is a "Sprinter" whereas the MX80 described by [MAD 1988] is a "Sleeper". This illustrates that each bentonite must be carefully and individually characterised. It is easily possible to determine if a bentonite belongs to one or the other categors by determining its chemical composition. For this task a Microsoft Excel-based software tool was developed.

## Impact of iron on the changes in bentonites

The contact with metallic iron leads to a strong increase of the dissolution potential. The reason for this is the reducing potential of the iron oxidation, which leads to alkaline pH and to an increased dissolution of Si from the clay particles.

### Impact of the ionic strength of the pore solutions in compacted bentonites

The higher the ionic strength of the pore solutions, the faster and stronger are the chemical, mineralogical and hydraulical changes in the bentonites.

#### Conclusive remarks

The main conclusion of this study is that the alteration of bentonites in contact with iron is accentuated and accelerated. Alterations in contact with solutions of different ionic strength identified by the authors in previous studies were found to be much more intensive in contact with metallic iron and at elevated temperatures. The observed chemical and mineralogical changes of the smectites are guite well understood. Similar changes of the smectites occur in low as well as in high saline solutions with the sole difference that high ionic strength solutions lead to faster and stronger changes. Experimentally observed changes of swelling pressures and permeabilities are well understood as well and fit onto a coherent picture of mineral evolution. This picture is dependent on the Fe and Si activity in the bentonite-solution system. The observed mineralogical changes could be reproduced by geochemical modelling. The investigation of a large number of different bentonites within the framework of this study showed however that bentonites differ very much from each other and behave differently under similar boundary conditions. Favorable and less favorable bentonite compositions were identified. The results of this study can lead to the definition of requirements for the bentonites to be used in the near field of a HLW repository.

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# Glossary

# Abbreviation

API	American Petroleum Institute Clay Mineral Standards
BGMN	BERGMANN: Rietveld software package for refinement of powder XRD- pattern
BGR	Bundesanstalt für Geowissenschaften und Rohstoffe (Federal Institute for Geosciences and Natural Resources)
СМ	Clay mineral
CMs	Clay minerals
CMS	The Clay Mineral Society
CSD	Coherent Scatter Domain
diCM	dioctahedral clay mineral
EBS	Engineered barrier system
EDX	Energy dispersive X-ray
FT-IR/IR	Fourier Transform Infrared Spectroscopy (Infrared Spectroscopy)
FWHM	Full Width at Half Maximum
GeoHellas	Technical Clays, Natural Solution company, Athena, Greece
GRS	Gesellschaft für Anlagen und Reaktorsicherheit mbH
HLW	High level radioactive waste
KBS	Kärnbränslesäkerhet (Nuclear Fuel Safety in Sweden)
LOI	Loss of ignition
MBS	Mössbauer spectroscopy
OSE	Overhead shaking experiments
rpm	rounds per minute
SKB	Svensk Kärnbränslehangereing AB (Swedish Nuclear Fuel and Waste Management Company)
TEM	Transmission electron microscopy
THMC- experment	Thermal-Hydraulic-Mechanical-Chemical experiment
XRD	X-ray diffraction
XRF	X-ray fluorescence

## Abbreviation

%S <sub>MAX</sub> or %S	Proportion of smectitic layer in illite-smectite or dioctahedral vermiculite- smectite mixed layer particles
Δ%S	degree of alteration measured by altered %S from smectite in original ben- tonite and run product like $\Delta$ %S = %S <sub>run product</sub> - %S <sub>original</sub> (smectitisation in case of $\Delta$ %S > 0; illitisation in case of $\Delta$ %S < 0)
∆%S <sub>∨I</sub>	Part of self-potential for illitisation, which is driven by octahedral cations
$\Delta\%S_{XII}$	Part of self-potential for illitisation, which is driven by cations in interlayer space
$\Delta\%S_{perc}$	Flow rate (= potential for Si-mitigation, e. g. by percolation) expressed as equivalent degree of alteration
BS-ml	Berthierine – saponite mixed layer
CroSV-ml	Cronstedtite – saponite – trioctahedral vermiculite mixed layer
CSV-ml	Chlorite – saponite – trioctahedral vermiculite mixed layer
diVerm	dioctahedral vermiculite
diVS-ml	dioctahedral vermiculite – smectite mixed layer
IS-ml	Illite – smectite mixed layer
KSV-ml	Kaolinite – montmorillonite – dioctahedral vermiculite mixed layer
Montm.	Montmorillonite

Mineral	Group	Formula
Beidellite	Smectite group	$(Ca_{0.5}, Na)_{0.3} AI_2 Si_{3.5} AI_{0.5} O_{10} (OH)_2 \cdot nH_2O$
Berthierine	Serpentine group	$(Fe^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+})_{4-6} (Si, Al)_4 O_{10} (OH)_8$
Chlorite (Chamosite)	Chlorite group	$(Fe^{2+}, Fe^{3+}, Mg^{2+})_5 AI (Si_3 AI) O_{10} (OH)_8$
Cronstedtite	Serpentine group	Fe <sub>4</sub> <sup>2+</sup> Fe <sub>2</sub> <sup>3+</sup> (Si Fe <sup>3+</sup> ) <sub>2</sub> O <sub>10</sub> (OH) <sub>8</sub>
Illite	Illite series	K <sub>0.65</sub> Al <sub>2.0</sub> (Si <sub>3.35</sub> Al <sub>0.65</sub> ) O <sub>10</sub> (OH) <sub>2</sub>
Kaolinite	Kaolinite group	Al <sub>4</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>4</sub>
Montmorillonite	Smectite group	(Ca, Na) <sub>0.3</sub> (Al, Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> · nH <sub>2</sub> O
Nontronite	Smectite group	(Ca <sub>0.5</sub> , Na) <sub>0.3</sub> Fe <sub>2</sub> <sup>3+</sup> Si <sub>3.5</sub> Al <sub>0.5</sub> O <sub>10</sub> (OH) <sub>2</sub> · nH <sub>2</sub> O
Odinite	Serpentine group	$(Fe^{2+}, Fe^{3+}, AI^{3+}, Mg^{2+})_5$ (Si, AI) <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>
Palygorskite	Palygorskite group	(Mg, Al) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) $\cdot$ 4H <sub>2</sub> O
Saponite	Smectite group	(Ca_{0.5}, Na)_{0.3} (Mg, Fe^{2+})_3 (Si, Al)_4 O_{10} (OH)_2 \cdot nH_2O
Talc	Talc group	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
Vermiculite (dioct.)	Illite series	= interlayer-deficient mica
Vermiculite (trioct.)	Vermiculite group	$(Fe^{3+},Al^{3+},Mg^{2+})_3~(Si,Al)_4~O_{10}~(OH)_2\cdot 4H_2O$

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# Attachments

# A Appendix 1: Detailed description of samples

The following bentonites were applied in the different experiments:

MX80 (Wyoming bentonite, trade article of 2005) Friedland Clay (Fe-rich IS-ml, Scholle "Burgfeld") Vietnam Clay (Fe-rich IS-ml; by-product of chromite exploitation in serpentinised diabase) GeoHellas Clay (Fe-rich montmorillonite with palygorskite and saponite)

## **API-series**

Polkville (Mississippi, API #20) Chambers (Arizona, API #23) Belle Fourche (South Dakota, API #27) Cameron (Arizona, API #31) Garfield Nontronite (Washington, API #33a) Amory (Mississippi, API #22a) Bayard (New Mexico, API #22a) Pioche (Nevada, API #32) Otay (California, API #24)

## **BGR-series**

04F, 09F, 11F, 12F, 13F, 16F, 22F, 23F, 28F, 31F, 37F, 38F

## A.1 MX80 – Starting Material

#### Source and approach

MX80 bentonite was a commercial product of the Süd-Chemie AG (Moosburg, Germany). It was originated from latitic or rhyolitic volcanic ash in the sea water in the Mowry shale – Wyoming – USA [MOL 2001]. This product was used widely for research related to buffer materials for high level nuclear waste repositories. This MX80 bentonite was applied by GRS in 2009 within the framework of project "Fe-bentonite" and also became the starting material of experiments with compacted MX80 bentonite  $(d = 1.6 \text{ g/cm}^3)$ .

#### Mineralogy – bulk sample and fraction < 2 $\mu$ m (by XRD)

Na-montmorillonite was the main phase of applied MX80 bentonite used as starting material (Fig. A.1, Tab. A.1). The following minerals were identified as further minor phases: quartz, cristobalite, albite and calcite. Muscovite was recognised in traces only.



Sample milled and sieved to < 63 µm before measuring

**Fig. A.1** XRD patterns of MX80 bentonite from powder mount, °2Θ CuKα position

The MX80 bentonite was characterised as Na bentonite, which was dominated by 13 Åmontmorillonite (monovalent, 1 water layer in interlayer space). In the XRD air dried specimen profile, there were fitted overlapping peaks of different occupation in interlayers at 12.9, 14.3 and 15.3 Å. After ethylene-glycol saturation, the interlayer sheets of the three mentioned types of occupation were expandable to 17.2 Å peak (Fig. A.1, Fig. A.2). The (001)/(002)-interference at 8.6 Å and (002)/(003)-peak at 5.7 Å, which was fitted from the ethylene-glycol saturated specimen profile, presented a pure montmorillonite composition. The other identified phases were semi-quantified by the BGMN-Rietveld methodology and evaluated by XRF-chemistry results (Tab. A.1, Tab. A.2). In general, there was good agreement between the chemical model by BGMN-Rietveld refinement and the measured XRF-data (chemical error was 1.5%). The mineral matter of the MX80 starting material was similar to other published data about MX80 bentonite (Fig. A.1). Otherwise, it has to be stressed that the smectite of the applied MX80 starting material has shown remarkable treatment impacts by the seller in the chemical composition in comparison with the literature data relating to MX80-bentonite of [MAD 1988], [HOA 2006], [UFE 2008a]. GRS-MX80 smectite (trade article of 2005) was a more AI rich smectite than in former the MX80-series (Tab. A.2).



XRD patterns including air-dried (AD), ethylene-glycol saturated (EG) and 550 °C heated (550) specimen patterns

Fig. A.2 XRD patterns of MX80 bentonite from oriented specimens

Tab. A.1 Semi-quantitative mineral composition of bulk samples of MX80 bentonite by BGMN - Rietveld refinement (own measurements: bulk sample, randomly oriented preparation, < 63 μm; semi-quantification by BGMN-Rietveld processing of X-ray diffractograms [1-rho = 9.53 %; Rwp = 9.48 %])

Phases	Own Measurements	Literature Data								
(wt%)	Mineral composition by BGMN-Rietveld	[LAJ 1996]	[VTT 1996]	[UFE 2008a]	[MAD 1988]					
Smectite	77	75	85- 95	85.7	75.5					
Cristobalite	3	15.0*	-	1.7	15*					
Quartz	5	15.2	3-6	4.5	15					
Albite	13	5-8	1-3	5.4	5-8					
Calcite	trace	1.4	1-3	0.4	1.4					
Muscovite	1	-	-	1.8	-					
Pyrite	-	-	1-3	-	0.3					
Gypsum	-	-	-	0.6	-					
Organic matter	-	0.4	-	-	0.4					

\* cristobalite + quartz; structural formula of smectite by BGMN – Rietveld refinement was  $Ca_{0.01} Mg_{0.02} Na_{<0..01} K_{0.02} AI_{1.62} Fe_{0.43} Si_{3.96} AI_{0.04} O_{10}(OH)_2$  and  $Ca_{0.06} Na_{0.02} K_{0.01} Mg_{0.29} Fe_{0.16} AI_{1.55} Si_{3.88} AI_{0.12} O_{10}(OH)_2$ 

Tab. A.2	Verification of mineral composition (Tab. A.1) by chemistry (bulk samples
	< 63 $\mu$ m) and referenced chemistry (XRF data) of MX80 bentonite.

Floment	Ow	n M	easurements	Literature Data						
(wt%)	Chemistry XRF data	by	Chemistry by BGMN- Rietveld model	[MAD 1988]	[HOA 2006]	[UFE 2008a]				
SiO <sub>2</sub>	63.4		65.7	60.25	58.13	60.8				
$AI_2O_3$	20.2		21.7	19.61	16.71	19.0				
$Fe_2O_3^*$	3.6		3.0	3.88	3.30	3.6				
MnO	0.0		0.0	0.001	0.02	0.0				
MgO	2.3		2.6	2.38	2.08	2.3				
CaO	1.2		1.4	1.83	1.58	1.2				
Na <sub>2</sub> O	2.3		1.7	0.03	1.69	2.0				
K <sub>2</sub> O	0.6		0.2	0.1	0.39	0.5				
TiO <sub>2</sub>	0.2		0.0	-	0.14	0.1				
$P_2O_5$	0.1		0.0	-	0.05	-				
LOI	6.2		6.2 3.8		5.44	9.9				
Total	100.1		100.1	88.1	89.53	99.4				

LOI: loss of ignition; \*: FeO + Fe<sub>2</sub>O<sub>3</sub>

Tab. A.3	Mineral formulae [per O <sub>10</sub> (OH) <sub>2</sub> ] of MX80 montmorillonite, based on TEM-
	EDX analyses

	lr	nterlaye	er Spac	e		Octal	hedra		Tetra	hedra	VII	
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ті	AI	Si	XII	n
				٥١	wn mea	sureme	ent					
Ø	0.04	0.04	0.01	0.02	1.59	0.21	0.16	0.04	0.05	3.95	0.19	1.99
di.phases												
Ø IS-ml	0.08	0.09	0.03	0.06	1.46	0.12	0.19	0.05	0.09	3.91	0.44	1.82
Ø diVS-ml	0.04	0.05	0.01	0.02	1.57	0.19	0.14	0.04	0.05	3.95	0.21	1.94
					Literatu	ire data	l					
(1)	0.02	0.05	0.02	0.01	1.61	0.21	0.16	0.01	0.03	3.97	0.17	1.99
(2)	0.07	0.00	0.22	0.04	1.54	0.17	0.26	0.00	0.05	3.95	0.40	1.97
(3)	0.00	0.00	0.30	0.00	1.55	0.20	0.24	0.00	0.04	3.96	0.30	1.99
(4)	0.03	0.01	0.21	0.01	1.55	0.19	0.26	0.00	0.04	3.96	0.30	2.00

di. Phases: dioctahedral phases, XII: interlayer charge, n<sup>VI</sup>: octahedral occupation; (1) referenced from [HOA 2006] and measured by TEM measurement; (2) referenced from [KAS 1998] and measured by TEM; (3) referenced from [MAD 1988]; (4) referenced from [WOL 2001] and measured by ICP, CEC.

#### A.1.1 Mineralogy of fraction < 2 µm (by TEM)

MX80 bentonite could be classified into two groups of sizes for particles for the TEM investigations: Large particles with a diameter of about  $1 - 2 \mu m$  and very small particles like a film-like matrix. The morphology of the large ones was mainly xenomorphic or curved edges. They were very typical of MX80 bentonite. The turbostratic orientation demonstrated by electron diffraction in a ring-like structure of montmorillonite particles. The chemical formulae of them are presented in Tab. A.3.

The TEM-EDX investigation (<  $2 \mu$ m) has shown low charge montmorillonite (diVS-ml series) was the main phase with 61 frequency-%. Other common phases were normal charge montmorillonite (IS-ml series) with 5 frequency-% and quartz + Si-surplus with 33 frequency-%. There were some differences in octahedral occupation, interlayer space and total charge in comparison with the referenced literature regarding MX80. It may be caused by the alteration of montmorillonite during the treatment procedures by Süd-Chemie Company. This caused the substitution of Al for Mg in the octahedral sheet and loss of Na in the interlayer and partial substitution by Mg. Substitution of Al for Mg in the octahedral sheet was a reason for reducing the layer charge of the montmorillonite from high charge and normal charge to low charge (Tab. A.3).

In general, the MX80 bentonite before 2006 was dominated by Na (monovalent cation) in the interlayer sheet and AI in the octahedral sheet. The octahedral composition was

also confirmed by FTIR results (Fig. A.3). Especially the domination of low charge montmorillonite in the sample reflected the transformation of starting MX80 montmorillonite in material purchased from Süd-Chemie after 2005.

#### A.1.2 Mineralogy – bulk sample (by FT-IR measurement)

The FT-IR spectroscopic measurement of MX80 bentonite from GRS is shown in Fig. A.3. It indicated that montmorillonite was the dominant phase in this bentonite. The broad absorption band at 3626 cm<sup>-1</sup> (AI-OH-AI) represented the high AI-amount of montmorillonite [GAT 2005]; [ZVI 2004]. The 3420 cm<sup>-1</sup> band was due to the O-H stretching vibaration of the silanol (Si-OH) groups. They originated from the solid and H-O-H stretching of the water molecules which were absorbed on the solid surface. Moreover, the band at 1634 cm<sup>-1</sup> was typical of an overtone of the bending vibration of water, which was retained in the matrix.

The broad band at 987 – 1040 cm<sup>-1</sup> represented the stretching vibrations of Si-O-Si groups in the tetrahedral sheet. The spectral bands at 916 cm<sup>-1</sup> indicated the stretching vibration of AI-OH-AI and 875 cm<sup>-1</sup>, 846 cm<sup>-1</sup> corresponding to AI-OH-Fe and AI-OH-Mg respectively while the band at 515, 416 cm<sup>-1</sup> was related to AI-O-Si and Si-O-Si in the tetrahedral sheet, respectively. The coupled AI-O and Si-O out of plane vibration was assigned to the band at 622 cm<sup>-1</sup>. There was a sharp band at 779 and 796 cm<sup>-1</sup>, which confirms the appearance of quartz as impurity phase.

Besides, the bands at 3420 and 3240 cm<sup>-1</sup> indicated cristobalite, which were overlapped by Si-O groups. These results were in agreement with previous XRD data.



**Fig. A.3** Infrared spectrum of starting MX80 bentonite sample, small box in upper right corner shows details of OH bending region

#### A.2 Friedland Clay

#### Source and Approach

The Friedland-Eocene clay was supplied by Mineralische Rohstoffmanagement GmbH, Blautonwerk Friedland, in spring 2010. It is sedimentary clay that formed in a shallow marine basin between 57 – 35 million years ago and is located in Friedland, Mecklenburg Western Pomerania, NE Germany. The quarried deposit is very homogeneous and massive, the thickness up to 140 m, the exploitable reserve approximately 100 million tons of clay. The geological background of this area as well as its mineralogical composition was also reviewed by [HEN 1998].



**Fig. A.4** XRD patterns of Friedland clay from powder mount, °2Θ CuKα position



XRD patterns including air-dried (AD), ethylene-glycol saturated (EG) and 550 °C heated (550) specimen patterns

**Fig. A.5** XRD patterns of Friedland clay from oriented specimens (< 2 µm)

Clay samples	Friedland clay <sup>1</sup>	[HOA 2006] <sup>2</sup>	[KAS 2003] <sup>3</sup>	[KAR 2007] <sup>4</sup>
Clay samples	(Burgfeld Scholle)	(Siedlungsscholle)	(Siedlungsscholle)	
SiO <sub>2</sub> (%)	62.0	56.7	58.6	60.9
TiO <sub>2</sub> (%)	0.97	0.94	0.1	0.9
Al <sub>2</sub> O <sub>3</sub> (%)	17.96	18.1	18.2	17.3
Fe <sub>2</sub> O <sub>3</sub> * (%)	5.42	7.3	11.5	6.4
MnO (%)	0.01	0.04	-	-
MgO (%)	1.68	2.01	2.7	1.9
CaO (%)	0.23	0.54	0.7	0.4
Na₂O (%)	0.98	0.96	0.2	1.1
K <sub>2</sub> O (%)	2.94	3.01	3.4	3.1
P <sub>2</sub> O <sub>5</sub> (%)	0.07	0.11	-	0.1
LOI (%)	6.48	7.24	-	7.6
H <sub>2</sub> O (%)	-	2.65	4.6	-
Total (%)	98.74	99.6	100	99.7

Tab. A.4Chemical composition of Friedland by XRF (%) by own measurement<sup>1</sup> and<br/>referenced data by XRF<sup>2,3</sup> and AAS<sup>4</sup>

LOI: loss of ignition; \*: FeO + Fe<sub>2</sub>O<sub>3</sub>

The clay material in this thesis was taken in core from the ore body of the "Burgfeld Scholle" quarry. The borehole was located in the open cast mine that is nearby the former exploration and was named TB1/97. It was quarried and drilled at 8m above sea level in the summer of 2009 by the above company. The clay is grey and blue to dark grey, the grain size is very fine and homogenous. The grain size distribution of the sample was analysed by Atterberg sedimentation. The results figured out as following:  $> 63 \,\mu\text{m}$ :  $8 \,\%$ ;  $20 - 63 \,\mu\text{m}$ :  $8 \,\%$ ;  $6.3 - 20 \,\mu\text{m}$ :  $15 \,\%$ ;  $2 - 6.3 \,\mu\text{m}$ :  $24 \,\%$  and  $< 2 \,\mu\text{m}$ :  $45 \,\%$ . Friedland clay contained mainly a fine grain size of  $< 2 \,\mu\text{m}$ , which occupied about a half of the whole sample. It presented appropriate result to previously published data [HEN 1998]; [HOA 2006].

#### A.2.1 Mineralogy (by XRD)

The visual XRD patterns of randomly oriented samples showed the presence of the following minerals: quartz, kaolinite, montmorillonite, illite-smectite mixed layer phases, illite, chlorite, gypsum, kaolinite and feldspars (Fig. A.4). The weight percent of each phases of grain size < 63  $\mu$ m was calculated by BGMN-Rietveld refinement and evaluated by XRF results (Tab. A.4): Illite-smectite mixed layer (IS-ml) 36 %, montmorillonite 20 %, quartz 20 %, kaolinite 14 %, feldspars 4 %, chlorite 1 %, and illite 2 %. Pyrite and gypsum occurred in traces. This method also allowed modelling the quantitative structural formulae of each phase:

Illite - Smectite mixed layer (IS-ml) phase:

$$Ca_{0.02} K_{0.62} AI_{1.24} Fe^{3+}{}_{0.49} Mg_{0.27} Si_{3.6} AI_{0.4} O_{10} (OH)_2$$
(A.1)

Dioctahedral vermiculite - smectite mixed layer (diVS-ml) series:

$$Na_{0.2} Mg_{0.08} AI_{1.41} Fe^{3+}{}_{0.46} Mg_{0.13} Si_{3.84} AI_{0.16} O_{10} (OH)_2$$
(A.2)

XRD measurement with oriented samples, including air dried, ethylene glycol saturated and 550°C heated samples, was used to characterise the expandable layers (Fig. A.5). The smectite group that included montmorillonite and illite-smectite mixed layer (IS-mI) presented clearly in this sample that 14.8 Å increased up to 17 Å peak after ethylene glycol saturation. Illite was identified at a 10.2 Å peak and chlorite at 14.3 Å which have a slightly larger spacing than typical 10 Å and 14 Å, respectively. The chlorite and kao-linite are demonstrated at 11.92 and 12.29° 2Θ CuKα which is proportional to the peak of chlorite and kaolinite respectively. After heating, the 7 Å peak of kaolinite disappeared, but there is still remaining a peak at 14 Å mirroring the occurrence of chlorite.

Proportions of illitic layers in IS-ml were calculated by [MOO 1997]. This calculation is based on the relationship between the positions of (001)/(002) interference and (002)/(003) interference taken from a ethylene-glycolated specimen. The TB1/97 Fried-land clay was characterised by two types of illite-smectite mixed layer: type (i) with 30 % and type (ii) with 90 % illitic layers. This result is in agreement with previous publication of [HEN 1998] and [HOA 2006] for a neighbouring location (Siedlungsscholle).

#### A.2.2 TEM – EDX measurement

The clay mineral distribution of TB1/97 Friedland clay was also investigated in detail by TEM – EDX measurement. The sample was dominated by mixed layer phases of the IS-mI and diVS-mI series. Most frequent were particles of kaolinite-smectite-vermiculite mixed layer (KSV-mI) structures.

The frequency of mixed layer series including IS-ml, diVS-ml (three categories distinguished by charge deficiency) and KSV-ml are presented in Fig. A.6. It is clear to see that KSV-mI is the dominant group, followed by the diVS-mI-mI and IS-mI phase. The KSV-mI particles showed a high content of kaolinite and a low content of dioctahedral vermiculite in the sample. Besides that, the detailed diversity of IS-mI and diVS-mI particles is shown detail in Fig. A.7. The ratio between IS-mI and diVS-mI was calculated to be 30:70 (30% IS-mI and 70% diVS-mI). This ratio is in good agreement with [HOA 2006].

The morphology of the mixed layer particles was described mainly as being slat, lath or xenomorphic flake-shaped. These morphologies were described by [HEN 1986] as "muscovite-montmorillonite" mixed layer from Tertiary marine clay, near Friedland. Some kaolinite-smectite-vermiculite mixed layer particles were identified in pseudohex-agonal shape. The appearance of the shape of the edges will depend on the proportion of the kaolinitic layer in the mixed layer, higher kaolinitic particles having sharper a edge. There is no significant difference in the morphology of the illite-smectite mixed layer and dioctahedral vermiculite-smectite mixed layer series, but the latter are more in xenomorphic flakes. In Friedland clay, the morphology of the diVS-ml phases, dioctahedral vermiculite and montmorillonite was similar for small xenomorphic particles. Electron diffraction patterns have shown a 1M-polytype for the xenomorphic morphology of diVS-ml structures and flake-like IS-ml phases with a higher percentage of smectitic layer > 50 %.

The mixed layer particles were also presented in a ternary diagram (Fig. A.8) that is based on TEM – EDX results. In general, the attended particles are close to the pyrophyllite corner and some particles are close to the muscovite corner. This may be due to a reduction in the tetrahedral charge and yielded octahedral charge. In addition, the octahedral ternary plot of the sample was made. Two groups were classified, one group was rich in octahedral AI and Mg, the other was enriched in Fe and Mg.

The structure formulae of different mixed layer series are given in Tab. A.5. The calculation is based on TEM-measurements of individual particles.



Fig. A.6 TEM-EDX measurement: Diversity of illite-smectite mixed layer phases (ISml), different classes of dioctahedral vermiculite-smectite mixed layer structures (diVS-ml) and kaolinite-smectite-vermiculite mixed layer phases (KSV-ml) in Friedland clay (Burgfeld Scholle)



Fig. A.7 Tendency of IS-ml/diVS-ml ratio TB1/97, Friedland Clay samples (Burgfeld Scholle), based on TEM-EDX analyses

Montm. - montmorillonite; diVerm. - dioctahedral vermiculite



C - position of Celadonite KAl<sub>2</sub>(OH)<sub>2</sub> Si<sub>4</sub> O<sub>10</sub>; P - position of pyrophyllite Al<sub>2</sub>(OH)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>; M - position of muscovite KAl<sub>2</sub>(OH)<sub>2</sub> Si<sub>3</sub>Al O<sub>10</sub>; b) Ternary diagram representing octahedral Al-Fe-Mg distribution of endmember and mixed-layer particles from TB1/97 – Friedland clay, based on TEM-EDX analyses. Montm.: montmorillonite; diVerm.: dioctahedral vermiculite; diVS-ml : dioctahedral vermiculite - smectite mixedlayer; IS-ml: illite - smectite mixed layer

- Fig. A.8 Ternary diagrams representing the charge of end-member particles (in according to [KOS 1977]) and mixed-layer particles (left) and ternary diagram of octahedral occupation (right) from TB1/97 - Friedland Clay, based on TEM-EDX analyses
- Tab. A.5Mineral formulae  $[O_{10}(OH)_2]$  for di.Phases, IS-ml, diVS-ml and  $[O_{10}(OH)_5]$ for KSV-ml of Friedland clay, based on TEM-EDX analyses

	In Ca	terlaye Mg	er Spa Na	ce K	AI	Octah Fe3+	edra Mg	Ti	Tetra Al	hedra Si	XII	nVI
	•	•		ТВ	1/97 – F	riedland	l clay		•		•	
Ødi.phases	0.01	0.11	0.03	0.23	1.54	0.31	0.12	0.02	0.38	3.62	0.50	1.99
Ø IS-ml	0.01	0.09	0.02	0.34	1.37	0.39	0.18	0.02	0.27	3.73	0.57	1.96
Ø diVS-ml	0.01	0.14	0.03	0.20	1.58	0.29	0.10	0.02	0.48	3.52	0.50	1.87
			Mine	eral for	mula of	special	IS-ml g	roups				
		Illite	– Smec	ctite mi	xed lay	er (50 %	Illite; 5	0 % Srr	nectite)			
Average	0.01	0.09	0.01	0.44	1.24	0.51	0.19	0.01	0.31	3.69	0.65	1.95
STDV	0.01	0.06	0.01	0.10	0.59	0.45	0.16	0.01	0.01	0.01		
Min	0.00	0.05	0.00	0.32	0.56	0.13	0.04	0.00	0.30	3.67		
Max	0.02	0.15	0.02	0.51	1.71	1.01	0.35	0.02	0.33	3.70		
		Illite	– Smec	tite mi	xed lay	er (60 %	Illite; 4	0 % Sm	nectite)			
Average	0.00	0.10	0.02	0.34	1.31	0.44	0.18	0.03	0.26	3.74	0.56	1.96
STDV	0.01	0.03	0.02	0.03	0.09	0.13	0.18	0.05	0.02	0.02		
Min	0.00	0.07	0.00	0.30	1.19	0.34	0.02	0.00	0.24	3.72		
Max	0.01	0.14	0.05	0.37	1.36	0.59	0.37	0.08	0.28	3.76		

# Tab. A.5 [Continued] Mineral formulae [O10(OH)2] for di.Phases, IS-ml, diVS-ml and [O10(OH)5] for KSV-ml of Friedland clay, based on TEM-EDX analyses

			Min	eral F	ormul	ae of	spo	ecial	l diV	S-m	nl gro	ups						
Dioctahe	Dioctahedral vermiculite – smectite mixed layer (30 % smectite; 70 % dioctahedral vermiculite)																	
Average	0.00	0.10	0.0	02 0	).12 1	1.63	0.2	25	0.10	) (	0.02	0.25	,	3	.75	0.3	34	2.00
STDV	0.00	0.03	0.0	02 0	.08 0	).22	0.1	14	0.07	' C	0.02	0.02		0	.02			
Min	0.00	0.06	0.0	00 0	).02 ·	1.26	0.	12	0.01	1 0	0.00	0.23	}	3	.73			
Max	0.01	0.15	0.	04 0	).19 ·	1.81	0.	47	0.20		0.05	0.27	7	3	.77			
Dioctahe	dral ver	miculit	e – sr	nectit	e mixe	ed lay	yer (	(40 %	∕₀ sm	ecti	ite; 60	) % d	ioct	aheo	dral	vern	nicu	ulite)
Average	0.01	0.0	09	0.03	0.19	1.7	2	0.19	0.	.09	0.00	0.3	31	3.6	9	0.41	2	.00
STDV	0.01	0.	04	0.04	0.10	0.1	2	0.06	S 0.	.07	0.00	0.0	03	0.0	3			
Min	0.00	0.	05	0.00	0.12	1.5	7	0.13	3 0.	.05	0.00	0.2	28	3.6	7			
Max	0.02	0.	12	0.08	0.31	1.8	2	0.25	5 0.	.17	0.00	0.	33	3.7	2			
Dioctahe	dral ver	miculit	e – sr	nectit	e mixe	ed lay	yer (	(50 %	∕₀ sm	ecti	ite; 50	) % d	ioct	aheo	dral	vern	nicu	ulite)
Average	0.01	0.0	08	0.03	0.23	1.6	9	0.17	0.	10	0.04	0.3	38	3.6	2	0.44	2	.00
STDV	0.01	0.	03	0.04	0.04	0.1	7	0.13	8 0.	.08	0.02	2 0.	01	0.0	1			
Min	0.00	0.	05	0.00	0.17	1.4	4	0.06	s 0.	.00	0.01	0.	36	3.6	0			
Max	0.04	0.	13	0.10	0.28	1.9	2	0.36	0	.22	0.05	5 0.4	40	3.6	4			
Dioctahe	dral ver	miculit	e – sr	nectit	e mixe	ed lay	yer (	(60 %	∕₀ sm	ecti	ite; 40	) % d	ioct	aheo	dral	vern	nicu	ulite)
Average	0.00	0.1	16	0.05	0.19	1.4	8	0.36	0.	.13	0.03	3 0.4	45	3.5	5	0.56	2	.00
STDV	0.00	0.	03	0.06	0.08	0.2	0	0.15	5 0.	.11	0.02	2 0.0	02	0.0	2			
Min	0.00	0.	12	0.00	0.05	1.2	3	0.20	0	.00	0.00	0.	42	3.5	2			
Max	0.00	0.	18	0.14	0.29	1.7	<b>'</b> 5	0.63	8 0.	.35	0.06	6 O	48	3.5	8			
Dioctahe	dral ver	miculit	e – sr	nectit	e mixe	ed lay	yer (	(70 %	∕₀ sm	ecti	ite; 30	) % d	ioct	aheo	dral	vern	nicu	ulite)
Average	0.01	0.1	12	0.02	0.25	1.7	6	0.21	0.	.02	0.01	0.	52	3.4	8	0.52	2	.00
STDV	0.02	0.	04	0.03	0.07	0.1	1	0.12	0	.04	0.01	0.0	02	0.0	2			
Min	0.00	0.	08	0.00	0.13	1.5	6	0.11	0.	.00	0.00	0.	49	3.4	5			
Max	0.05	0.	18	0.05	0.33	1.8	5	0.40	0	.09	0.03	3 0.	55	3.5	1			
					Dioct	ahed	ral	verm	nicul	ite								
Average	0.03	0.32	0.01	0.1	2 1.3	5 (	).52	0.	12	0.0	1 0	.86	3.1	7	0.8	33 2	2.0	)
STDV	0.03	0.03	0.03	0.0	9 0.5	6 0	).52	0.	23	0.0	01 0	.11	0.1	13				
Min	0.00	0.30	0.00	0.0	2 0.7	5 (	0.11	0.	00	0.0	0 0	.77	2.9	99				
Max	0.07	0.37	0.06	0.2	2 1.8	85	1.23	0.	46	0.0	)2 1	.01	3.3	30				
			Min	eral F	Formul	ae o	f sp	ecia	ΙΚν	S-m	l gro	ups						
Kaolinite	– verm	iculite	– sme	ectite	mixed	laye	r (50	0%	kaoli	nite	e; 25 %	% ver	micı	ulite	; 25	% sr	nec	ctite)
Average	0.03	0.03	0.04	0.0	5 2.7	3 (	).16	0.	06	0.0	2 0	.19	3.8	31	0.2	21	2.96	6
STDV	0.03	0.04	0.06	0.0	7 0.3	8 0	0.09	0.	06	0.0	3 0	.16	0.1	6				
Min	0.00	0.00	0.00	0.0	0 2.0	0 0	0.00	0.	00	0.0	0 0	.00	3.3	36				
Max	0.09	0.13	0.20	0.3	3 3.3	0 0	).33	0.	24	0.1	1 0	.64	4.0	)1				

di. Phases: dioctahedral phases, XII: interlayer charge,  $n^{VI}$ : octahedral occupation; IS-mI: illite – smectite mixed layer, diVS-mI: dioctahedral vermiculite – smectite mixed layer, KSV-mI: kaolinite – vermiculite – smecite mixed layer. Average: average index, Min: minimal index, Max: maximal index, STDV: standard deviation



**Fig. A.9** Infrared spectrum of Friedland clay (Burgfeld Scholle). Note small box in upper right corner showing a detail of OH bending region

The cation exchange capacity (CEC) of Friedland clay was mentioned in some previous works. [AMM 2003] used the copper complex exchange method to identify 37 meq/100 g CEC and 280 m<sup>2</sup>/g of specific surface area of Friedland clay. [HEN 1998] published 54 meq/100 g, [MEI 1999] identified 75 meq/100 g and [KAR 2006] measured CEC by exchange against Cu(II) – trien of 21 meq/100 g CEC.

#### A.2.3 Mineralogy – Bulk sample (by FT-IR)

A FTIR scan of Friedland clay (Fig. A.9) presented strongly distinct OH-stretching bands at 3620 cm<sup>-1</sup>, ~ 3670 cm<sup>-1</sup> and a Si-O-deformation band at 687 cm<sup>-1</sup>, which indicated the presence of kaolinite and a possible absorption band of smectite at ~3600 cm<sup>-1</sup> region [FAR 1974]. The tetrahedral silica and quartz was assigned by Si-O stretching and Si-O vibration at 1100 cm<sup>-1</sup> and 994 cm<sup>-1</sup> respectively. Especially, the intensity of Si-O vibration was proportional to the intensity of kaolinite bands. In FTIR spectra, the AI-OH-AI bending band assigned clearly at 915 cm<sup>-1</sup> a typical smectite and kaolinite [FAR 1974]. The AI-OH-Fe<sup>3+</sup> band at 876 cm<sup>-1</sup> was presented by a lower intensity that reflected the high Fe content in Friedland clay [CRA 1984]; [RUS 1994]; [VAN 2001b]; [GAT 2005]. Moreover, bending at 828 cm<sup>-1</sup> due to AI-OH-Mg and AI-O vibrations of illite arise to 753 cm<sup>-1</sup>. A AI-O-Si band also appeared [FAR 1974];

[RUS 1987]. Besides, the FTIR patterns of Friedland clay show distinct Si-O stretching bands at double peaks of 778 cm<sup>-1</sup> and 797 cm<sup>-1</sup> indicate the presence of quartz [CRA 1984].

#### A.3 Vietnam Clay

#### Source and Approach

A Vietnam clay sample was taken in the Co Dinh valley of Nui Nua massive, Thanh Hoa, Vietnam. Clay was a by-product of exploiting activities (rock washing for chromite) and was discharged into this valley. Vietnam clay was used as starting material for short-term overhead shaking experiments.

#### XRD measurement

The bulk sample (Fig. A.10) and fraction <  $2 \mu m$  samples (Fig. A.11) from the Co Dinh valley were composed mainly of Fe-smectite (Tab. A.6). Chlorite, quartz, kaolinite, amphibole, talc and magnetite acted as impurity phases. The content of smectite increased significantly from bulk sample to fraction <  $2 \mu m$ .

The XRD patterns of air dried and ethylene glycol solvated (Fig. A.11) showed the typical characteristics of smectite. The  $d_{001}$  value of smectite at 14.4 Å expanded to 17.5 Å after being saturated by ethylene glycol and collapsed to 9.7 Å under heating at 550 °C. Moreover, the sample from oriented specimens showed that smectite contained a 10 % illitic layer. The position of the  $d_{060}$  peaks at 1.51 Å indicates an Fe-bearing dioctahedral smectite and is in agreement with [KOE 1999].



Sample was milled by hand and sieved to < 63 µm before measuring

**Fig. A.10** XRD patterns of Co Dinh clay sample from powder mount, <sup>°</sup>2Θ CuKα position



XRD-patterns with air-dried specimen patterns (AD), ethylene-glycol saturated specimen patterns (EG), 550 °C heated specimen patterns (550); ML10: illite - smectite mixed-layer series with 10 % of illitic layer

**Fig. A.11** XRD patterns from the Co Dinh valley sample from oriented specimens, °2Θ CuKα position

# Tab. A.6Mineral matter in bulk and oriented samples from the Co Dinh valley (Vi-<br/>etnam Clay) analysed by XRD

Phases (wt %)	Bulk sample	Fraction < 2 µm
Fe-Smectite	70	87
Kaolinite	2	4
Quartz	8	2
Chlorite	8	4
Talc	9	3
Amphibole	2	
Antigorite	trace	trace
Feldspars	trace	
Magnetite	trace	trace

Modeled by BGMN-Rietveld refinement; Fe-Smectite - are mainly Fe-montmorillonite and mixed layer series between Fe-montmorillonite and illite dominated by smectite layers.

#### A.3.1 Mineralogy – Fraction < 2 µm (by TEM – EDX measurement)

The TEM observation showed that almost all smectite particles of this series presented a particle-oriented (= no film-like) suspension of  $< 2 \mu m$  fraction. In total, size particles could be classified by 3 categories. The largest one was about 2.2 to 3 µm in length and 1.2 to 1.7 µm in width. These particles were characterised by sharp and more curled edges of the particles. They were typical of montmorillonite that is rich in iron and their morphology was xenomorphic, isometric or an aggregation of nepheloid, and the edges of some particles were strongly curled. The middle one changes from 2.0 to 3.2 µm in length and 1.0 to 1.7 µm in width, was medium sharp with curled edges of the particles, these particles being characterised by being nepheloid, xenomorphic or slightly elongated. The smallest one appeared as thin and xenomorphic aggregated particle, sometimes of lath shape or platy xenomorphic with shaped edges or an aggregation of xenomorphic particles. The morphology of Fe-smectite in this valley was in agreement with [PET 2002], but the size of them is smaller. Electron diffraction patterns presented a ring-like polytype structure of the electron spots for platy xenomorphic and lath particles. This was the structure of dioctahedral vermiculite-smectite mixed layer and montmorillonite particles.

Fe-rich montmorillonite and its member of diVS-ml were the most frequently determined mineral group (35-40%). The mixed layer phases have shown a high proportion of montmorillonite layers (mostly 70-95%).

More than 36 % of all measured and calculated particles of clay sample in the Co Dinh valley have been identified as phases of the illite-smectite mixed layer series, including normal charge montmorillonite as end-member. Montmorillonite dominates. The IS-mI series was recognised with 60-95 % of smectitic layers.

According to TEM-EDX measurements, smectites in the Co Dinh valley (Tab. A.7) belonged to low charge group. The octahedral layer was composed mainly of Fe and traces of  $Cr^{3+}$ .

Moreover, the trioctahedral phases including the CSV-ml, TSV-ml, CrSV-ml phases were identified, too. Their structure formulae are presented in Tab. A.7.

Tab. A.7	Average min	eral	formulae of c	lay mineral	phases < 2 µr	m of Co Dinh va	alley,
	determined	by	TEM-EDX	analyses,	[O <sub>10</sub> (OH) <sub>2</sub> ],	<sup>1</sup> [O <sub>10</sub> (OH) <sub>6</sub> ],	and
	<sup>2</sup> [O <sub>10</sub> (OH) <sub>8</sub> ]						

Dhaaaa		Interlayer					Octahedral					trahe	dral	VII	VI
Phases	Са	Mg	Na	Κ	Cr <sup>3+</sup>	AI	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mg	Ti	AI	Si	Fe <sup>3+</sup>	XII	n
di.phases	0.03	0.09	0.00	0.03	0.08	0.57	1.19	0.00	0.15	0.02	0.15	3.85	0.00	0.28	2.01
IS-ml	0.04	0.06	0.00	0.02	0.06	0.47	1.22	0.00	0.21	0.03	0.03	3.97	0.00	0.22	1.99
Fe-diVS-ML	0.03	0.11	0.00	0.03	0.09	0.46	1.25	0.00	0.16	0.04	0.19	3.81	0.00	0.32	2.00
Al-diVS-ml	0.08	0.14	0.00	0.05	0.03	1.48	0.39	0.00	0.09	0.01	0.40	3.60	0.00	0.50	2.00
CSV-ml <sup>1</sup>	0.01	0.05	0.00	0.00	0.11	0.60	0.00	0.22	3.84	0.01	1.28	2.94	0.00	0.12	4.78
TSV-ml	0.00	0.02	0.00	0.08	0.03	0.44	0.00	0.33	2.02	0.00	0.21	3.79	0.00	0.12	2.82
tri-Verm	0.01	0.29	0.00	0.02	0.17	0.08	0.44	0.00	2.35	0.01	1.24	2.76	0.00	0.62	3.05
CrSV-ml <sup>2</sup>	0.02	0.00	0.00	0.02	0.03	0.00	0.87	2.07	0.06	0.00	0.14	1.06	0.80	0.06	3.03

Fe-Montm: Fe-montmorillonite, IS-ml: illite – smectite mixed layer, Fe-diVS-ml: Fe-bearing dioctahedral vermiculite – smectite mixed layer, Al-diVS-ml: Al-bearing dioctahedral vermiculite – smectite mixed layer, CSV-ml: chlorite – saponite – trioctahedral vermiculite mixed layer, TSV-ml: talc – saponite – trioctahedral vermiculite, CrSV-ml: cronstedtite – saponite – tri

#### A.4 Geohellas Clay

#### Source and Approach

GeoHellas clay was kindly supported by GeoHellas S.A. in Athena, Greece. It was similar to samples involved in experiment conducted by [PUS 2010] and has been used as a possible tool to identify so called "Sprinters" or "Sleepers" concerning mineralogical alteration processes in buffer material of HLW-repositories.

A semi-quantitative composition of GeoHellas clay is presented in Tab. A.8. It was a result of BGMN-Rietveld refinement and was verified by chemistry.

The XRD investigation has shown that GeoHellas clay was characterised by different kinds of smectite: montmorillonite including dioctahedral vermiculite – smectite mixed layer (K and charge deficient of illite – smectite mixed layer) and saponite. Additionally, palygorskite, chlorite, quartz, dolomite, Mg-bearing calcite, K- and Na-feldspar occurred as minor phases. Goethite was only found in traces.

Mineralogical composition (wt%)		Chemical composition by XRF (wt%)	
Phase	Weight %	Element	XRF (wt%)
Chlo-Sapo-Verm-ml (CSV-ml)	18	SiO <sub>2</sub>	54.0
Montmorillonite & IS-ml	24	$AI_2O_3$	9.1
Montmorillonite & diVS-ml	13	Fe <sub>2</sub> O <sub>3</sub>	10.0
Palygorskite	7	MnO	0.1
Quartz	8	MgO	9.6
Chlorite	4	CaO	3.7
Dolomite	6	Na₂O	1.3
K-Feldspar	8	K <sub>2</sub> O	0.7
Na-Feldspar	6	TiO <sub>2</sub>	0.5
Goethite	< 1	$P_2O_5$	0.0
Mg-Calcite	4	LOI	10.2

Tab. A.8Chemical and mineral composition of GeoHellas clay (soda-activated) by<br/>XRF and BGMN-Rietveld refinement

## A.4.1 Mineralogy (by XRD measurement)

**Montmorillonite & diVS-ml:** This diVS-ml-series was in this sample fully expandable from 14.5 Å to 17.7 Å. The difference of peak positions between (002)/(001)- and (003)/ (002)-interferences of 9.06 Å and 5.46 Å characterises this phase as diVS-ml-series with 60 % of smectite layers for crude material and with 50 % of smectite layers (Fig. A.12). The dioctahedral character of these mineral structures is proved by (060)-interference in the powder specimen at 1.50 Å (Fig. A.13). The BGMN-Rietveld refinement has identified this phase as Al-dominated smectite (100 % trans-vacancy) with a high amount of Fe and Mg.
**Montmorillonite & IS-mI:** The second dioctahedral smectite was also fully expandable after ethylene-glycol saturation. This phase can only be recognised in remarkable amounts in the sample as air dried 13 Å-Phase (monovalent cations and only one water layer in the interlayer space) (Fig. A.12).



Measured using Siemens D5000 XRD patterns including air dried (AD), ethylene glycol saturated (EG), heated at 550 °C in 4 hours (550); Montm: montmorillonite, CSV-ml: chloritesaponite-vermiculite mixed layer, diVS-ml: dioctahedral vermiculite-smectite mixed layer

## **Fig. A.12** XRD patterns of GeoHellas clay (soda-activated) from oriented specimens, °2Θ CuKα position

**CSV-mI:** Furthermore, the samples also contained trioctahedral smectite. This structure was characterised by a broad 11 Å-peak overlapping the main peak of palygorskite at 10.7 Å. This 11 Å-peak indicated a high ratio of K-bearing trioctahedral vermiculite in this assumed mixed layering between trioctahedral vermiculite, saponite and chlorite.

**Palygorskite:** The following peaks 10.8 Å (100), 6.46 Å (10), 4.5 Å (45), 5.51 Å (55), 3.67 Å (50) and 2.20 Å (30) were identified in powder specimens as main interferences for palygorskite.

**Chlorite:** The double peaks at ~ 7 Å and 3.55 Å as well as the heated oriented specimens were proof of the occurrence of chlorite together with the CSV-ml in the samples (Fig. A.12). Chlorite seemed to be formed as Fe-rich (di, tri)-chlorite.



Measured using Siemens D5000 for grain sized < 63  $\mu$ m. The patterns present the montmorillonite (Montm.), illite-smectite mixed layer (IS-mI), palygorskite, chlorite, albite, dolomite, dioctahedral clay mineral (diCM)

**Fig. A.13** XRD-patterns of GeoHellas clay (soda-activated) from randomly oriented powder mounts, °2Θ CuKα position

#### A.4.2 Mineralogy of fraction < 2 µm (by TEM – EDX measurement)

The TEM-micrographs of the GeoHellas clay were characterised by needle-like particles in mixture with small xenomorphous plates (Fig. A.14). The fibres had an average length of 400 - 800 nm and their width may vary between 50 - 150 nm (aspect ratio  $\sim 6 - 8$ ).

In the fraction < 2 µm palygorskite, normal charged montmorillonite, members of the Kdeficient mixed layer series between montmorillonite and dioctahedral vermiculite and members of a trioctahedral mixed layer series between chlorite, saponite and vermiculite were identified.

**Palygorskite:** In comparison to the theoretical composition, palygorskite in GeoHellas clay was not really Mg-rich (Tab. A.9). This structure has a tetrahedral charge, which was compensated by Ca- and K-cations mainly. It was expected that palygorskite from GeoHellas should be characterised by a high swelling charge because of the available low interlayer charge of 0.18 per (OH)O<sub>10</sub>.



Measured using Jeol JEM-1210; magnification: 4,000 x

- Fig. A.14 TEM images of GeoHellas clay (soda-activated)with needle-like morphology of palygorskite and small xenomorphous plates of saponite, montmorillonite, dioctahedral vermiculite – smectite mixed layer, illite – smectite mixed layer phases
- **Tab. A.9** TEM-EDX-analyses of GeoHellas clay (soda activated). Data of mineral formulae related to (OH)<sub>2</sub>O<sub>10</sub> and (OH)O<sub>10</sub> for palygorskite and (OH)<sub>2.93</sub>O<sub>10</sub> for average of CSV-ml

	Interlayer Space				Octah	edral	Space	Tetra	hedra	VII	n VI		
	Ca	Mg	Na	к	AI	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Mg	Ti	AI	Si		
Palygor.	0.08	0.00	0.00	0.03	0.56	0.00	0.49	0.90	0.02	0.18	3.82	0.19	1.97
Saponite	0.09	0.00	0.00	0.03	0.98	0.45	0.00	0.95	0.01	0.42	3.58	0.21	2.39
diVS-ml	0.10	0.14	0.00	0.11	0.97	0.00	0.52	0.49	0.02	0.32	3.68	0.59	2.00
IS-ml	0.08	0.08	0.00	0.13	0.93	0.00	0.51	0.54	0.01	0.08	3.92	0.45	1.99
di.phases	0.09	0.13	0.00	0.12	1.06	0.00	0.55	0.36	0.02	0.23	3.77	0.57	1.99
CSV-ml	0.04	0.10	0.00	0.09	1.03	1.22	0.00	1.37	0.01	0.90	3.10	0.37	3.63
Palygor.	0.08	0.00	0.00	0.03	0.56	0.00	0.49	0.90	0.02	0.18	3.82	0.19	1.97

Measured using Jeol JEM-1210; Palygor.: palygorskite, Montm.: montmorillonite, diVS-ml: dioctahedral vermiculite – smectite mixed layer, IS-ml: illite – smectite mixed layer, di. phases: mean of dioctahedral phases; CSV-ml: chlorite – saponite – vermiculite mixed layer.

**Montmorillonite & IS-mI:** The samples contained mainly montmorillonite as end member of this mI-series. The octahedral sheets have shown a high amount of Mg, low amount of Fe, but AI is the dominating cation there (Tab. A.9).

**Montmorillonite & diVS-ml:** diVS-ml structures with 60% smectite layers are very common in the GeoHellas clay. The octahedral composition is comparable to montmorillonite of the above mentioned IS-ml-series. The higher tetrahedral charge of the diVS-ml is compensated by Mg-cations in the interlayer space (Tab. A.9). The total charge is comparable theoretically to IS-ml with 60% smectite layers, but the K-ratio is lower in the diVS-ml than in IS-ml. The expected contribution of diVS-ml to the swelling pressure should be comparable to normal IS-ml.

**Saponite & CSV-mI:** A mixed layer series between chlorite, saponite and trioctahedral vermiculite was also identified as minor structure. It also included the identification of pure saponite as one of the end members of this mixed layer series. Saponite is Aland Fe<sup>2+</sup>-rich in the octahedral sheet. The CSV-mI phases have shown a similar octahedral composition, but the Mg-ratio was dominating. Pure chlorite as the other end member of CSV-mI was not identified by TEM.

#### A.5 API-Series

The following bentonites certified by American Petroleum Institute Clay Mineral Standards (API) were used for short-term experiments: Belle Fourche – South Dakota (API #27), Chambers – Arizona (API #23), Bayard – New Mexico (API # 30), Polkville – Mississippi (API # 20), Pioche – Nevada (API #32), Amory – Mississippi (API #22a), Cameron – Arizona (API #31) and Garfield (nontronite) – Washington (API #33a).

The Belle Fourche and Cameron bentonites contained ~13 Å -montmorillonite (monovalent cations in the interlayer space) while XRD patterns of Pioche, Chambers and Bayard, Amory, Polkville bentonite were characterised mostly by 15 Å-mont-morillonite (bivalent cations in the interlayer space). Bentonites of this series were composed of a variety of smectite contents between 65 % and 96 %. Bayard and Polkville bentonites were composed nearly completely of montmorillonite. Otherwise, they also contained remarkable amounts of calcite, quartz, kaolinite, chlorite, illite and feldspar as main impurities (Tab. A.10).

#### Polkville-bentonite (API #20), Mississippi

The association of peaks at 15.5, 5.02, 4.51, 2.56, 1.70 and 1.50 Å in the randomly oriented powder mount specimens of XRD-patterns of Polkville bentonite indicated nearly homogenous bivalent in interlayer montmorillonite (95 wt%) (Fig. A.1, Tab. A.10). There is a small amount of quartz and calcite impurities. Montmorillonite was fully expanded by ethylene-glycol saturation at 17.01 Å. The double peak at 8.52 Å and 5.61 Å decomposed from ethylene-glycol saturated specimens reflected the presence of not only montmorillonite but also illite-smectite mixed layer series with 10 % of illitic layer [MOO 1997]. Relating to the structural formulae composition calculated by TEM-EDX, the Polkville smectite has 10 % of illitic layer (Si<sup>4+</sup> = 3.92 per O<sub>10</sub>(OH)<sub>2</sub>). The octahedral layer was indicated by the domination of Al<sup>3+</sup> and medium content of Fe<sup>3+</sup> and Mg<sup>3+</sup> (Tab. A.11). The interlayer space contains mainly Na<sup>+</sup> and Mg<sup>2+</sup> and is very poor in Ca<sup>2+</sup>. It indicated that Mg<sup>2+</sup> decided (001)-spacing at 15 Å instead of Ca<sup>2+</sup>. The cation exchange capacity of Polkville is about 121 meq/g [OST 1952].

#### Amory-bentonite (API #22a), Mississippi

Amory bentonite contained mainly montmorillonite and impurities of kaolinite, quartz and microcline (Tab. A.10). The oriented mounts and randomly oriented powder XRDpatterns are presented in Fig. A.15 and Fig. A.17. This bentonite was composed mainly of 15 Å-montmorillonite (bivalent cations in the interlayer space) in randomly oriented powder XRD-pattern. The oriented mounts XRD-patterns showed the (001)-peak as double peak at 13 Å and 14 Å. They have full expandability to 16.9 Å after saturation with ethylene glycol. Moreover, the (001)/(002) peak at 8.60 Å and (002)/(003) peak at 5.61 Å in ethylene glycol staturated specimen shows the presence of illite-smectite mixed layer with 10 % illitic layer. The presence of 12 % microcline (main peak at 3.26 Å) as impurity in bentonite is in good agreement with chemical data (0.66 wt% K<sub>2</sub>O). Besides, quartz was detected in randomly oriented powder and oriented amounts XRD-patterns. Kaolinite was identified in traces only in oriented amounts XRD-patterns at 7.11 Å. Presence of 7 Å peak with very low intensity survived after heating at 550 °C in 4 hours where it is assumed as traces of chlorite (Fig. A.17)

TEM-EDX measurement and calculated average chemical formulae of Amory smectite presented domination of Na<sup>+</sup> and accompanied Mg<sup>2+</sup> in the interlayer space. Al<sup>3+</sup> dominated in the octahedral layer. Octahedral Fe<sup>3+</sup> exceeded with 0.33 (OH)<sub>2</sub>O<sub>10</sub>, the

amount of  $Mg^{2+}$  is 0.22 (OH)<sub>2</sub>O<sub>10</sub> (Tab. A.11). The exchange capacity of clay dried at 85 °C was 84.7 meq/100 g [OST 1952].

#### Chambers-bentonite (API #23), Arizona

Chambers bentonite originated from the Chambers area located in Apache County (Arizona, USA). Under XRD investigation, this bentonite was composed mainly of 15 Åmontmorillonite (bivalent cations in the interlayer space), confirmed by oriented mounts and randomly oriented powder XRD-patterns (Fig. A.17). The (001)- peak at 15 Å was composed of a double peak - 15.6 Å and 14.8 Å for randomly oriented powder (Fig. A.15). These peaks have shown a full swelling ability to 17 Å and 18.6 Å after saturation with ethylene glycol. Besides, the double peak at 8.53 Å and 5.61 Å identified by decomposition of ethylene glycol saturated specimen pointed out the presence of illitesmectite mixed layer, with the proportion of illitic layer being about 10% [MOO 1997]. The impurities of Chambers bentonite were calcite and guartz. The presence of calcite in the sample caused a high content of CaO (8%) as well as higher (001)-spacing at 15 Å. TEM-EDX investigation and calculated average chemical formula of Chambers montmorillonite have shown a domination of Ca<sup>2+</sup> in the interlayer space and Al<sup>3+</sup> in the octahedral layer. However, the coefficient of Mg<sup>2+</sup> is guite higher and the amount of Fe is less than in the other bentonite in this series (Tab. A.11). The ratio of (Mg+Fe)/(Mg+Fe+AI) in the octahedral sheet was ~ 27 % and Na/(Ca+Mg+Na) in the inter-layer sheet was 20%. Chambers montmorillonite has shown a morphology characterised by xenomorphic plates with thick curved edges in turbostratic orientation [HOA 2006]. [SRO 2006] determined of the total surface area with about 805  $m^2/g$ .

#### Otay-bentonite (API #24), California

Otay bentonite is characterised in oriented mounts (air-dried) by a composition of two kinds of montmorillonite: bivalent cations (~15 Å) and monovalent cations in the interlayer space (13.1 Å). These 001-spacing peaks shifted to 16.9 Å after saturation with ethylene-glycol (Fig. A.15 and Fig. A.17). Besides, the couple of 8.61 and 5.59 Å peaks were decomposed from the ethylene-glycol saturated specimen pattern. According to [MOO 1997], this couple indicated the presence of IS-ml series with illitic layer proportion of about 10 % in the sample. Otay bentonite contains albite and quartz as minor phases. The morphology and electron diffraction characteristics of Otay smectite were recorded by TEM experiment. The sample was characterised by small xenomorphic particles with curved edges with an indication of swelling ability. The particles have shown a turbostratic orientation of disorder structure. The calculated chemical formulae of Otay montmorillonite by TEM-EDX is shown in Tab. A.11.

The cations-anions exchange capacity of Otay bentonite was 122.47 meq/100 g ([OST 1952]).

#### Belle Fourche-bentonite (API #27), South Dakota

The deposit of Belle Fourche-bentonite is located in the east and northeast of Black Hills, South Dakota, USA. It was in interbedded Graneros and Pierre shales formations in the age of Cretaceous. The sample is characterised by (001)-spacing at 12.7 Å and other typical peaks at 6.55 Å, 4.51 Å, 2.57 Å and 1.50 Å of Na-montmorillonite in randomly oriented powder XRD-pattern (Fig. A.15). The XRD-traces of oriented mounts indicated a composition of two types of montmorillonite: 13.6 Å and 12.6 Å, which were decomposed by fitting from an asymmetric peak. The (001)-peaks were fully expandable (shifted to 17.7 Å and 17 Å after saturation with ethylene glycol). This characteristic proved the full expandability of smectite. Moreover, a couple of peaks at 8.55 and 5.67 Å which were decomposed and identified from the ethylene glycol saturation specimen pattern confirmed the high content of montmorillonite without any illitic layer proportion (Fig. A.17)

The calculated structural formulae of Belle Fourche bentonite by TEM-EDX is presented in Tab. A.11. The ratio of (Mg+Fe)/(Mg+Fe+Al) was 19.07 % and Na/-(Ca+Mg+Na) was about 60.73 %. The cation exchange capacity of this bentonite differed from about 85 meq/100 g [RAV 1972] to 78.86 meq/100 g [OST 1952].

#### Bayard-bentonite (API #30), New Mexico

Bayard bentonite was characterised as bentonite admixed by bivalent and monovalent cations in the interlayer space of montmorillonite (Fig. A.15). The XRD-pattern from oriented mounts has shown (001)-in-terferences of montmorillonite at 12.8 and 13.8 Å (Fig. A.17). The area ratio between the two (001)-spacings indicated a dominance of 14 Å-mont-morillonite. Montmorillonite was fully expanded by ethylene-glycol saturation. The double peaks at 8.53 and 5.61 Å decomposed from ethylene-glycol saturated

specimen mirrored the presence of 10 % illititic layers in IS-ml series [MOO 1997]. Bayard bentonite was quite homogenous, contains only montmorillonite. The d(060)peak at 1.50 Å proved the domination of dioctahedral smectite in the sample.

Concerning the structural formulae composition resulting from TEM-EDX, the Bayard smectite has a main composition of pure montmorillonite (Si<sup>4+</sup> = 3.98 per O<sub>10</sub>(OH)<sub>2</sub>). The octahedral layer showed Fe-poor montmorillonite but quite high Mg<sup>2+</sup> and Al<sup>3+</sup> (Tab. A.11). This montmorillonite is characterised by a domination of Na in the interlayer. It is confirmed by the presence of a 6.45 Å peak in random powder which is due to a Na-montmorillonite phase. Besides, the content of Na (0.11 (OH)<sub>2</sub>O<sub>10</sub>) in Tab. A.11 has confirmed that the main element in the interlayer space of Bayard bentonite is Na. The octahedral (Mg+Fe)/(Mg+Fe+Al)-ratio and Na/(Ca+Mg+Na)-ratio in the interlayer is 25 % and 40 % respectively. Bayard bentonite has a cation exchange capacity of about 127 meq/100 g [RAV 1972].

#### Cameron-bentonite (API #31), Arizona

Cameron bentonite has shown in randomly oriented powder 13 Å-montmorillonite and in air-dried oriented mounts 12.6 Å and 14 Å peaks. By ethylene glycol saturation, the interlayer sheet of montmorillonite was fully expandable at 17 Å (Fig. A.17). A couple of 8.89 and 5.49 Å peaks in ethylene-glycol saturated pattern indicated the presence of illite-smectite mixed layer series with an illitic layer proportion of 40 % (~60 % by TEM-EDX measurement). Cameron bentonite also contains 20 % quartz and signs of quartz, kaolinite and hematite.

Under TEM investigation, the Cameron bentonite highlighted a very high content of Na<sup>+</sup> and K<sup>+</sup> and traces of Mg<sup>2+</sup> in the interlayer space. The dominant element in the octahedral layer is Al<sup>3+</sup> while Fe<sup>3+</sup> and Mg<sup>2+</sup> occur in a content similar to Amory montmorillonite. Al<sup>3+</sup> substituted strongly to Si<sup>4+</sup> in the tetrahedral layer (Tab. A.11), it caused a negative charge of montmorillonite and the result is in agreement with XRD data.

#### Pioche-bentonite (API #32), Nevada

The clear peaks at 15.4, 5.02, 4.5, 2.58, 1.7 Å in the randomly oriented powder mount specimen of XRD-patterns of Pioche bentonite pointed out the enrichment of the montmorillonite phase (Fig. A.15). The (001)-spacing of montmorillonite (15.4 Å) in the random powder pattern was shaped by an asymmetric peak decomposed to peaks of

13.3 Å, 14.8 Å, 15.2 Å (in orientd mount, air dried). These peaks scattered from monoto bivalent cations, but dominated by bivalent cations in the interlayer space (15 Å). The full expandability of all above mentioned peaks at 16.8 Å after ethylene glycol saturation is shown in Fig. A.17. The spacing values at 8.52 and 5.60 Å obtained from the EG sample confirmed the true montmorillonite of Pioche bentonite. The (060)-spacing peak at 1.50 Å indicated the dioctahedral character of smectite in Pioche sample. Additionally, the sample contained impurities like mica, quartz, kaolinite and calcite.

The mineral formula of smectite is presented in Tab. A.11. It was in agreement with XRD by a high content of  $Mg^{2+}$  in the interlayer space. Moreover, this was reflected by a high ratio of Na/(Ca+Mg+Na) with 56 % as well as a quite high  $Mg^{2+}$  ratio in the interlayer space. The octahedral (Mg+Fe)/(Mg+Fe+Al)-ratio is 28 %.

#### Garfield-nontronite (API #33a), Washington

Garfield nontronite was a weathering product of the basalt zone in the Garfield area, Washington/USA. The clear peaks of nontronite were presented at about 15.8, 4.57, 4.33, 2.30, 1.73 and 1.53 Å in a XRD pattern of randomly oriented powder mount [HOA 2006]. Montmorillonite was also detected in a XRD air-dried specimen pattern at ~13 Å (Fig. A.17). The 001-spacing peak of nontronite and montmorillonite have expandibility to ~17 Å after saturation with ethylene-glycol. The smectite phases collapsed to 9.66 Å after heating at 550 °C in 4 hours. The double peak at 8.49 Å and 5.64 Å obtained from the ethylene-glycol-saturated pattern confirmed that montmorillonite contains 100 % of montmorillonitic layer. The peaks at 3.34 Å and 4.26 Å indicated the presence of quartz as impurity besides traces of illite at 10.0 and 4.47 Å (Fig. A.10 and Fig. A.11).

TEM-EDX measurement allowed calculating structural formulae of nontronite and montmorillonite and is presented in Tab. A.11. Montmorillonite in this sample contains a high content of  $Ca^{2+}$  in the interlayer sheet and is  $Al^{3+}$  dominated in octahedral instead of Fe<sup>3+</sup> in nontronite. The morphology of nontronite particles showed as lath-shaped and platy xenomorphic plats. The total surface area of Garfield nontronite was 656 m<sup>2</sup>/g [SRO 2006].

In summary, the bentonite samples from Belle Fourche, Amory and Otay were characterised by a domination of sodium in the interlayer space, those from Chamber bentonite were largely dominated by calcium clay; while the Polkville, Pioche, Bayard and Cameron, bentonite contained more nearly equal amounts of exchangeable calcium, magnesium and sodium. The program BGMN [BER 1998] and model for the turbostratic disorder of smectite [UFE 2004] are used for the Rietveld refinement. The mineralogical composition of the API bentonite series is presented in Tab. A.10. Smectite is the most abundant minerals in all bentonite samples, while Garfield nontronite contained mainly nontronite phase. Calcite was detected in Pioche, Polkville and Chambers. Iron oxide phases appeared as traces in Pioche and Cameron bentonite. Quartz is presented in almost all samples in this series.

Sample (wt%)	Polk- ville	Amory	Cham- bers	Belle Fourche	Bayard	Cameron	Pioche	Garfield
Smectite	95	84	89	86	96	79	65	38
Illite		1					6	
Chlorite		trace					4	
Quartz	3	3	3	8		20	3	2
Hematite						trace		
Magnetite							trace	
Calcite	2		8				16	
Kaolinite						1	5	
Microcline		12						
Albite				6	4			
Nontronite								60

 Tab. A.10
 Mineral composition of API series bentonite by BGMN software - Rietveld method (wt%)



Measured using Siemens D5000 for grain sized <  $63\,\mu$ m; the patterns present the montmorillonite (Montm), dioctahedral clay mineral (diCM) and quartz, calcite, feldspar

**Fig. A.15** XRD-patterns of applied API-bentonites from randomly oriented powder mounts, °2Θ CuKα position



Measured using Siemens D5000 for grain sized  $< 63 \mu m$ ; the patterns present the montmorillonite (Montm), dioctahedral clay mineral (diCM) and quartz, calcite, feldspar, kaolinite, hematite

**Fig. A.16** (continued) XRD-patterns of applied API-bentonites from randomly oriented powder mounts, °2Θ CuKα position



**Fig. A.17** XRD patterns of API collection bentonites from oriented specimens, °2Θ CuKα position



From above left to bottom right: patterns of Polkville, Amory, Chambers, Otay, Belle Fourche, Bayard, Cameron, Pioche and Garfield nontronite

Measured using HZG4/Seifert C3000; XRD patterns including air dried (AD), ethylene glycol saturated (EG), heated at 550°C in 4 hours (550)



#### A.6 BGR-Series

The BGR bentonite series includes 12 bentonite samples that were kindly provided by Dr. Kaufhold in BGR (Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany). This series was selected from thirty eight bentonite sample of this research group. They are all raw materials without any prior treatment. The chemical and mineralogical composition of 12 bentonites (04F, 09F, 11F, 12F, 13F, 16F, 22F, 23F, 28F, 31F, 37F, 38F) in the total of 38 bentonite samples was published by [UFE 2008a]. The other properties, such as cation exchange capacity (CEC), pH, and exchangeable cations was investigated by [KAU 2008a], [KAU 2008b], [KAU 2009]), and [KAU 2010a], [KAU 2010b]). Therefore, samples will mainly be characterised by TEM-EDX only with suspension < 2µm particles and FT-IR for bulk samples with the aim to recognise the sensitive material for further experiments in this research.

	Interlayer Space					Octal	hedra		Tetra	hedra	VII	VI		
	Ca	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ti	AI	Si	XII	n		
Polkville-Mississippi (API #20)														
Ø di.phases	0.01	0.10	0.10	0.02	1.52	0.25	0.22	0.01	0.08	3.92	0.34	1.99		
Ø IS-ml	0.01	0.13	0.11	0.02	1.50	0.23	0.24	0.00	0.07	3.93	0.39	1.97		
Ø diVS-ml	0.01	0.08	0.10	0.01	1.53	0.28	0.20	0.01	0.09	3.91	0.28	2.01		
Amory - Mississippi (API #22a)														
Ø di.phases	0.02	0.04	0.18	0.11	1.42	0.33	0.22	0.01	0.13	3.87	0.40	1.98		
Ø IS-ml	0.02	0.05	0.21	0.12	1.40	0.32	0.24	0.02	0.13	3.87	0.46	1.98		
Ø diVS-ml	0.02	0.02	0.14	0.08	1.46	0.36	0.17	0.01	0.13	3.87	0.30	1.99		
Chambers – Arizona (API #23)														
Ø di.phases	0.15	0.04	0.05	0.01	1.45	0.16	0.38	0.01	0.06	3.94	0.44	2.00		
Ø IS-ml	0.14	0.03	0.04	0.01	1.47	0.16	0.36	0.01	0.05	3.95	0.40	2.00		
Ø diVS-ml	0.18	0.09	0.09	0.01	1.34	0.15	0.50	0.01	0.16	3.84	0.65	2.01		
Otay - California (API #24)														
Ø di.phases	0.03	0.02	0.20	0.06	1.43	0.32	0.19	0.02	0.07	3.93	0.36	1.96		
			Belle	Fourch	e - Sou	th Dako	ota (AP	l #27)						
Ø di.phases	0.04	0.03	0.16	0.04	1.60	0.17	0.19	0.01	0.06	3.94	0.34	1.97		
Ø IS-ml	0.04	0.03	0.23	0.05	1.56	0.17	0.21	0.01	0.09	3.91	0.44	1.95		
Ø diVS-ml	0.03	0.02	0.04	0.03	1.67	0.17	0.15	0.00	0.01	3.99	0.18	2.00		
				Baya	rd Mexi	co (API	#30)					-		
Ø di.phases	0.02	0.14	0.11	0.01	1.49	0.06	0.44	0.01	0.02	3.98	0.44	2.01		
	1		(	Camero	on - Ariz	zona (A	PI #31)	1			1			
Ø di.phases	0.02	0.07	0.15	0.26	1.51	0.33	0.14	0.01	0.40	3.60	0.59	1.99		
Ø IS-ml	0.02	0.06	0.24	0.25	1.46	0.33	0.15	0.01	0.32	3.68	0.64	1.95		
Ø diVS-ml	0.02	0.07	0.11	0.27	1.54	0.33	0.13	0.01	0.43	3.57	0.56	2.01		
				Pioch	e - Neva	ada (AP	l #32)							
Ø di.phases	0.01	0.12	0.16	0.06	1.44	0.21	0.33	0.01	0.13	3.87	0.48	1.99		
Ø IS-ml	0.01	0.10	0.16	0.06	1.46	0.20	0.32	0.01	0.09	3.91	0.43	1.99		
Ø diVS-ml	0.01	0.20	0.16	0.06	1.38	0.25	0.36	0.01	0.27	3.73	0.63	2.00		
		G	arfield	(nontro	nite) - V	Nashin	gton (A	PI #33a	ı)					
Ø Montm.	0.05	0.03	0.03	0.01	1.56	0.09	0.32	0.04	0.00	4.00	0.33	2.00		
Ø Nontro.	0.02	0.08*	0.07	0.02	0.20	1.79	0.00	0.01	0.40	3.60	0.29	2.00		

Tab. A.11TEM-EDX-analyses of API collection bentonite by TEM-EDX. Data of min-<br/>eral formulae related to  $(OH)_2 O_{10}$ .

Measured using Jeol JEM-1210; diVS-ml: dioctahedral vermiculite – smectite mixed layer, IS-ml: illite – smectite mixed layer, di.phases: dioctahedral phases, nontro.: nontronite, \* including 0.05 of Fe<sup>2+</sup>.

The particles of the investigated BGR-samples were characterised mainly by xenomorphous platey particles with swelling remarks at the edges. According to the morphology of finest particles, the BGR bentonite series was grouped into 3 classes by using TEM measurement.

These samples could be distinguished in the morphology of finest particles in the matrix. They could be grouped in three classes using the morphology of particles in TEMmicrographs (Fig. A.18). Samples like 09F, 12F, 13F and 16F were characterised by few large xenomorphous and non-discrete plates with swelling remarks. The finest xenomorphous particles in the matrix were mostly film-like or partially lath-like. The opposite view of the matrix could be recognised in samples like 04F, 11F, 22F, 28F, 31F, 37F, and 38F.





Finest particles were missed mostly in the matrix (blank areas between larger particles). Sample 23F was characterised by intermediate shaped particles between the two mentioned groups of samples.

The classification into three groups has not shown a clear trend of mineralogical properties of the samples. Each of the two largest groups was represented by high, normal or low charged smectites as well as different cation's composition in the interlayer space and octahedral layer. Furthermore, turbostratic ordered stacks also dominated in the two largest groups. Probably, a weak trend could be described that low charged smectite with mainly divalent cations in the interlayer space would dominate in the group with strong matrix-like particles. The matrix-poor group is characterised by a weak trend for more normal or high charged smectites, which have partially a remarkable amount of monovalent cations in the interlayer space.

The mineral formulae of all smectite particles were calculated following the methodology described in chapter 8.2 and appendix 4. Tab. A.12 summarises the calculated mineral formulae. Larger ratios of illitic layers of smectite were identified in samples 11F (%S = 80 %) and 13F (%S = 70 %).

The mineralogy of the bulk BGR-samples were published by [UFE 2008a]. Smectite was the main phase in all investigated samples with > 70 % (exception: 09F, 16F with > 50 %). Calcite was present in the samples lower than 1 %, but only in samples 09F and 13F with  $\ge$  3 %).

The FT-IR measurement supported enrichment of montmorillonite in all bentonites of the BGR series.

The IR spectra in the OH-stretching region  $(3500 - 3800 \text{ cm}^{-1})$  are plotted in appendix 10. All spectra exhibit broad features with maxima position at  $3621 - 3628 \text{ cm}^{-1}$  except for 09F smectite at  $3633 \text{ cm}^{-1}$ . Such a position can be ascribed to Al-OH-Al stretching vibrations.

The spectra of montmorillonite with relatively high Mg low Fe content such as 23F bentonite, in addition to AI-OH-Fe and Fe-OH-Fe vibration of 04F, 11F, 13F and 31F bentonite, were detected in the positions of 3587 cm<sup>-1</sup> and 3560 cm<sup>-1</sup>, 3569 cm<sup>-1</sup>, respectively. These positions indicated that these sample contain a high content of Fe (> 0.3  $O_{10}(OH)_2$ ) and a low content of AI (< 1.4  $O_{10}(OH)_2$ ). They are all in agreement with structural formulae of smectite calculated by TEM-EDX.

# Tab. A.12Mineral formulae of smectite from selected BGR bentonites calculated by<br/>TEM-EDX $(O_{10}(OH)_2)$

Sample and	Interlayer				Octahedral layer				Tetral	nedral				IS-ml/
phases	Са	Mg	Na	к	AI	Fe <sup>3+</sup>	Mg	Ti	AI	Si	XII	n <sup>vi</sup>	S%	diVS-ml
04F													90	59/41
ø montmorillonite	0,05	0,06	0,01	0,04	1,36	0,40	0,23	0,01	0,04	3,96	0,26	2,00		[
ø dioct. phases	0,05	0,10	0,01	0,06	1,30	0,45	0,20	0,01	0,08	3,92	0,36	1,97		
ø IS-ml	0,06	0,10	0,01	0,06	1,28	0,47	0,20	0,01	0,08	3,92	0,39	1,96		
ø diVS-ml	0,03	0,09	0,01	0,05	1,38	0,40	0,21	0,01	0,09	3,91	0,29	2,00		
09F	-								-				100	7/93
ø montmorillonite	0,04	0,03	0,02	0,01	1,64	0,20	0,15	0,01	0,00	4,00	0,16	1,99		
ø dioct. phases	0,04	0,03	0,02	0,01	1,63	0,20	0,15	0,01	0,01	3,99	0,17	2,00		
ø IS-ml	0,09	0,01	0,14	0,02	1,59	0,14	0,22	0,00	0,00	4,00	0,36	1,95		
ø diVS-ml	0,04	0,03	0,01	0,01	1,64	0,21	0,15	0,01	0,01	3,99	0,16	2,00		a= (a
11F	0.00	0.00	0.40	0.00	1.00	0.00	0.00	0.04	0.00	0.07	0.04	4.00	80	97/3
ø montmorilionite	0,03	0,06	0,12	0,02	1,36	0,33	0,28	0,01	0,03	3,97	0,31	1,98		
ø dioct. pnases	0,03	0,10	0,18	0,02	1,29	0,46	0,16	0,01	0,13	3,87	0,45	1,92		
Ø 15-mi	0,03	0,10	0,19	0,02	1,30	0,46	0,15	0,01	0,13	3,87	0,46	1,92		
0 01V S-MI	0,03	0,06	0,14	0,02	1,20	0,52	0,18	0,03	0,21	3,79	0,34	1,99	100	94/16
12F	0.14	0.02	0.00	0.01	1 27	0.20	0.22	0.01	0.00	4.00	0.22	2.00	100	04/10
g dioct phases	0,14	0,02	0,00	0,01	1,37	0,29	0,33	0,01	0,00	3 00	0,33	2,00		
ø ligent	0,14	0,02	0,00	0,01	1,37	0,29	0,33	0,01	0,01	3,99	0,33	2,00		
ø di\/S-ml	0,14	0,02	0,00	0,01	1,37	0,29	0,33	0,01	0,00	3.08	0,35	2,00		
13F	0,14	0,05	0,00	0,01	1,55	0,50	0,52	0,02	0,02	5,50	0,55	1,33	70	17/83
a montmorillonite	0.09	0.00	0.00	0.03	1 36	0.44	0.18	0.01	0.02	3 08	0.22	1 00	10	17/03
g dioct phases	0,03	0,00	0,00	0.05	1,30	0,44	0,10	0.02	0,02	3.76	0,22	1 00		
ø IS-ml	0,10	0,00	0,00	0,03	1 33	0,43	0,12	0,02	0,24	3.04	0,30	1 03		
ø diVS-ml	0,11	0,03	0,01	0.05	1 37	0,40	0,12	0.02	0,00	3 72	0,37	2.00		
16F	0,10	0,07	0,00	0,00	1,57	0,40	0,12	0,02	0,20	5,72	0,00	2,00	92	21/79
ø montmorillonite	0.04	0.06	0.01	0.02	1.51	0.26	0.22	0.01	0.01	3 99	0.22	2 00	02	21,10
ø dioct phases	0.03	0.08	0.01	0.04	1,51	0.28	0.20	0.01	0.07	3.93	0.28	1.99		
ø IS-ml	0.05	0.09	0.03	0.04	1.44	0.31	0.22	0.01	0.06	3.94	0.35	1.97		
ø diVS-ml	0.03	0.08	0.01	0.04	1.53	0.27	0.20	0.01	0.08	3.92	0.26	2.00		
22F	-,	-,	0,01	-,	.,	0,=:	-,	-,	-,	0,01		_,	100	75/25
ø montmorillonite	0,07	0,07	0,02	0,03	1,59	0,06	0,34	0,01	0,00	4,00	0.25	2.00		
ø dioct. phases	0,08	0,06	0,02	0,03	1,60	0,06	0,31	0,01	0,00	4,00	0.33	1,99		[
ø IS-ml	0,09	0,06	0,03	0,03	1,58	0,07	0,34	0,01	0,00	4,00	0.36	1,99		
ø diVS-ml	0,04	0,07	0,00	0,02	1,68	0,06	0,25	0,01	0,00	4,00	0,24	2,00		
23F													99	38/62
ø montmorillonite	0,04	0,08	0,00	0,01	1,67	0,06	0,25	0,01	0,00	4,00	0,25	2,00		
ø dioct. phases	0,04	0,08	0,00	0,02	1,67	0,07	0,25	0,01	0,01	3,99	0,25	2,00		
ø IS-ml	0,05	0,09	0,00	0,03	1,64	0,07	0,28	0,01	0,01	3,99	0,30	1,99		
ø diVS-ml	0,03	0,07	0,00	0,01	1,69	0,07	0,23	0,02	0,01	3,99	0,23	2,00		
28F					-				-				100	86/14
ø montmorillonite	0,06	0,09	0,00	0,01	1,50	0,16	0,33	0,02	0,00	4,00	0,31	2,00		
ø dioct. phases	0,06	0,09	0,00	0,01	1,50	0,16	0,33	0,02	0,00	4,00	0,31	2,00		
ø IS-ml	0,06	0,09	0,00	0,01	1,49	0,16	0,33	0,02	0,00	4,00	0,32	2,00		
ø diVS-ml	0,06	0,06	0,00	0,01	1,52	0,18	0,27	0,02	0,01	3,99	0,26	2,00		
31F													99	71/29
ø montmorillonite	0,04	0,08	0,00	0,05	1,38	0,29	0,30	0,02	0,00	4,00	0,29	2,00		
ø dioct. phases	0,04	0,07	0,00	0,06	1,36	0,30	0,31	0,03	0,01	3,99	0,30	2,00		
ø IS-ml	0,05	0,08	0,00	0,08	1,32	0,32	0,33	0,02	0,01	3,99	0,32	2,00		
ø diVS-ml	0,04	0,07	0,00	0,02	1,47	0,24	0,26	0,03	0,01	3,99	0,24	2,00		
37F													99	18/82
ø montmorillonite	0,02	0,08	0,00	0,03	1,67	0,09	0,22	0,01	0,00	4,00	0,22	2,00		
ø dioct. phases	0,02	0,08	0,00	0,02	1,69	0,09	0,21	0,01	0,01	3,99	0,21	2,00		
ø IS-ml	0,03	0,09	0,00	0,03	1,61	0,10	0,29	0,01	0,00	4,00	0,28	2,00		
ø diVS-ml	0,02	0,07	0,00	0,02	1,71	0,09	0,19	0,01	0,02	3,98	0,20	2,00		aa (= -
38F	0.00				4				0.01	0.00	0.00		96	22/79
ø montmorillonite	0,08	0,02	0,00	0,03	1,61	0,16	0,22	0,01	0,01	3,99	0,23	2,00		
ø dioct. phases	0,09	0,03	0,01	0,03	1,59	0,17	0,23	0,01	0,05	3,95	0,27	2,00		
Ø 15-mi	0,13	0,01	0,01	0,03	1,54	0,16	0,28	0,02	0,02	3,98	0,32	1,99		
ø aivs-mi	0,08	0,03	0,01	0,03	1,61	0,17	0,21	0,01	0,05	3,95	0,25	2,00		l

IS-ml: illite – smectite mixed layer. diVS-ml: dioctahedral vermiculite – smectite mixed layer. n<sup>VI</sup>: number of octahedral occupation. XII: interlayer charge. S%: smectitic layer proportion in mixed layer

In the OH-bending region at 400 – 1000 cm<sup>-1</sup>, three major bands, AI-OH-AI at 908 – 913 cm<sup>-1</sup>, Al-OH-Fe at 872 – 891 cm<sup>-1</sup> and Al-OH-Mg at 833 – 844 cm<sup>-1</sup> were detected in all the spectra. For the 22F and 23F bentonites, the position of AI-OH-Fe is very high (891 cm<sup>-1</sup>) which showed the low content of Fe in the octahedral layer relative to 04F, 11F, 13F and 31F. These samples with a higher content of Fe have shown also a lower wave number position [CRA 1984]; [RUS 1994]; [VAN 2001b]; [GAT 2005]. All the IR spectra exhibit a couple of bands at 779 cm<sup>-1</sup> and 799 cm<sup>-1</sup> which can be assigned to the Si-O bending vibration of quartz or cristobalite. Especially, the presence of the significant position of cristobalite at 618 cm<sup>-1</sup> is very clear. Moreover, the bulk sample of 09F, 22F and 23F bentonites contains a high content of guartz and cristobalite, which was published by [UFE 2008a], confirmed by strong bands with a high intensity of that position in IR spectra, too. No signs of MgMg and FeFe pair were detected in any of the selected BGR bentonites. This is in agreement with TEM-EDX results since the Mg<sup>2+</sup> and Fe<sup>3+</sup> content was not high enough to assume detectable peaks [FAR 1974]; [MAD 1994]; [CUA 1998]. In general, the results of IR spectra of all selected BGR bentonites have been supported the results of not only TEM-EDX measurement but also XRD of mineralogical composition.

Sample	04F	09F	11F	12F	13F	16F	22F	23F	28F	31F
SiO <sub>2</sub> (%)	49.4	59.6	46.1	47.9	44.6	51.5	62.4	58.7	58.8	52.1
TiO <sub>2</sub> (%)	0.7	0.1	2.4	0.6	2.0	0.4	0.2	0.2	0.2	0.4
Al <sub>2</sub> O <sub>3</sub> (%)	15.6	14.7	14.4	13.6	16.2	20.1	15.0	17.5	13.5	12.8
Fe <sub>2</sub> O <sub>3</sub> (%)	8.0	3.0	15.7	9.8	10.1	5.9	1.1	1.1	2.1	8.4
MnO (%)	0.0	0.3	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0
MgO (%)	3.1	1.4	2.5	3.9	2.1	2.9	3.3	3.1	3.1	2.7
CaO (%)	0.9	5.4	0.9	3.1	3.1	1.4	1.0	1.2	2.7	1.9
Na <sub>2</sub> O (%)	0.6	2.2	1.8	1.6	0.1	0.1	2.3	2.5	0.1	0.4
K <sub>2</sub> O (%)	0.4	0.4	0.1	0.1	0.6	1.7	0.4	0.5	0.5	0.5
LOI (%)	19.5	12.2	15.9	17.7	20.4	15.5	13.9	14.8	18.4	20.1
Total (%)	98.3	99.3	99.8	98.3	99.3	99.4	99.7	99.6	99.6	99.4

 Tab. A.13
 Chemical composition (wt%) of selected BGR bentonites by XRF

 [UFE 2008a]

Sample (wt%)	04F	09F	11F	12F	13F	16F	22F	23F	28F	31F
Smectite	91.6	58.8	89.2	91.0	86.8	57.8	76.0	79.9	69.0	92.4
Muscovite (1M)		3.0								
Muscovite (1M <sub>2</sub> )						34.2				
Kaolinite					2.7	3.1				
Quartz	1.7	8.5	1.3	1.4	5.5	4.6	4.0	9.8	2.0	0.2
Cristobalite		11.4					11.7		8.0	0.1
Hematite			0.1	2.4						
Ilmenite			0.1							
Rutile			0.3		0.2					
Anatase			2.5		1.4					
Goethite			5.6							
Calcite		8.0	0.8	0.9	2.9	0.5	0.3			
Dolomite										0.5
Siderite										0.2
Barite	1.5									
Gypsum		0.3				0.4				
Orthoclase	1.6	4.7					3.4	3.2	2.3	
Albite	3.6	3.8								
Plagioclase (An <sub>50</sub> )					0.6		4.7	7.1	2.1	1.9
Heulandite		0.8								
Analcime		0.6								
Clinooptilolite									16.7	4.6
Fluorapatite				4.3						

Tab. A.14Mineral composition (wt%) of selected BGR bentonites by Rietveld method[UFE 2008a]



Fig. A.19 XRD powder bulk samples



Fig. A.20 XRD (Oriented mounts, fraction < 2 µm, air dried



**Fig. A.21** XRD (Oriented mounts, fraction < 2 µm, ethylene-glycol saturation)

#### TEM and electron diffraction images of selected BGR bentonites



Measured using Jeol JEM-1210; the images show the particles of smectite as dominating particles

TEM-micrographs from 04F bentonite sample

top left: Overview of 04F (1,000x)

top right: Zoom of image (3,000x) – xenomorphous plates with swelling remarks; mostly non-discretes plates; no film-like particles in the matrix

bottom left: Zoom of image (3,000x) – circle represents measurement point for electron diffraction (right) bottom right: turbostratic electron diffractions of 04F montmorillonite

### Fig. A.22 TEM – SAMPLE 04F



TEM images of 09F bentonite sample top left: Overview of 09F (1,000x)

top right: Zoom of image (3,000x) - few large xenomorphous and non-discretes plates with swelling re-

marks; mostly film-like xenomorphous particles in the matrix (partially lath-like) bottom left: Zoom of image (3,000x) - circle represents measurement point for electron diffraction (right) bottom right: turbostratic electron diffractions of 09F montmorillonite

Fig. A.23 TEM - SAMPLE 09F



TEM images of 11F bentonite sample top left: Overview of 11F (1,000x) top right: Zoom of image (3,000x); - large xenomorphous and non-discretes plates with swelling remarks; mostly film-like xenomorphous particles in the matrix

bottom left: Zoom of image (3,000x) - circle represents measurement point for electron diffraction (right) bottom right: turbostratic electron diffractions of 11F montmorillonite

Fig. A.24 TEM – SAMPLE 11F



TEM images of 12F bentonite sample top left: Overview of 12F (1,000x) top right: Zoom of image (3,000x); xenomorphic and isometric morphology and some large xenomorphic ones

bottom left: Zoom of image (3.000x) - circle represents measurement point for electron diffraction (right) bottom right: Turbostratic electron diffractions of 12F montmorillonite

Fig. A.25 TEM – SAMPLE 12F



TEM images of 13F bentonite sample top left: Overview of 13F (1,000x) top right: Zoom of image (4,000x)

bottom left: Zoom of image (3,000x) - circle represents measurement point for electron diffraction (right) bottom right: large image = ED of circle No. 2 = diVS-ml with %S = 30 %; small image = ED of circle No. 3 with turbostratic stack order of 13F montmorillonite

Fig. A.26 TEM – SAMPLE 13F



TEM images of 16F bentonite sample top left: Overview of 16F (1,000x) top right: Zoom of image (3,000x)

bottom left: Zoom of image (3,000x) - circle represents measurement point for electron diffraction (right) bottom right: large image = ED of circle with turbostratic stack order of 16F montmorillonite (with beginning weak 1M-ordering)

Fig. A.27 TEM – SAMPLE 16F



TEM images of 22F bentonite sample top left: Overview of 22F (1,000x) top right: Zoom of image (3,000x) bottom left: Zoom of image (3,000x) - circle represents measurement point for electron diffraction (right) bottom right: large image = ED of circle with turbostratic stack order of 22F montmorillonite

Fig. A.28 TEM – SAMPLE 22F



TEM images of 23F bentonite sample top left: Overview of 23F (1,000x) top right: Zoom of image (3,000x) bottom left: Zoom of image (3,000x) - circle represents measurement point for electron diffraction (right) bottom right: large image = ED of circle with turbostratic stack order of 23F montmorillonite

Fig. A.29 TEM – SAMPLE 23F



TEM images of 28F bentonite sample left: Zoom of image (4,000x) right: turbostratic electron diffractions of 28F montmorillonite

## Fig. A.30 TEM – SAMPLE 28F



Measured using Jeol JEM-1210; the images show the particles of smectite as dominating particles

TEM images of 31F bentonite sample left: Zoom of image (3,000x) right: turbostratic electron diffractions of 31F montmorillonite

# Fig. A.31 TEM – SAMPLE 31F



TEM images of 37F bentonite sample left: Zoom of image (3,000x) right: turbostratic electron diffractions of 37F montmorillonite

## Fig. A.32 TEM – SAMPLE 37F



TEM images of 38F bentonite sample top left: Overview of 38F (1,200x); top right: Zoom of image (5,000x);

bottom left: Zoom of image (4,000x) - circle represents measurement point for electron diffraction (right); bottom right: large image = ED of circle with turbostratic stack order of 38F montmorillonite

TEM – Sample 38F Fig. A.33









Fig. A.34 TEM – diversity of IS-ml and diVS-ml series





Fig. A.34 (continued) TEM – diversity of IS-ml and diVS-ml series








Fig. A.35 TEM – composition of octahedral layer for IS-ml and diVS-ml series





Fig. A.35 (continued) TEM – composition of octahedral layer for IS-ml and diVS-ml series



Position of AI-OH-AI is average of 10 bentonites, position of AI-OH-Fe is average of 04F, 28F, and 31F bentonites, AI-OH-Mg is average of 09F, 13F, 16F, 23F

**Fig. A.36** FT-IR spectra (3500 – 3800 cm<sup>-1</sup>) of collected BGR bentonites



Number of wave number show in the figure is average position of all ten bentonites; Crist: cristobalite

**Fig. A.37** FT-IR spectra (400 – 1100 cm<sup>-1</sup>) of collected BGR bentonites

### A.7 API-Bentonites

Samples (wt%)	Chambers (API #23)	Garfield (API #33a)	Polkville (API #20)	Belle Fourche (API #27)	Amory (API #22a)	Otay (API #24)
	[HOA	2006]		[OST 1	952]	
SiO <sub>2</sub>	43.26	40.14	63.42	61.12	59.30	63.04
$AI_2O_3$	14.54	5.54	19.44	23.10	30.40	18.44
Fe <sub>2</sub> O <sub>3</sub>	2.81	31.79	1.87	4.37	7.74	1.20
TiO <sub>2</sub>	0.29	0.07	0.32	0.09	0.76	0.14
MnO	0.04	0.01	0.00	trace	0.07	0.01
MgO	3.29	0.69	5.00	2.50	2.40	7.30
CaO	8.18	2.07	0.11	0.24	0.03	0.08
Na <sub>2</sub> O	0.12	0.23	3.46	2.90	2.52	3.40
K <sub>2</sub> O	0.06	0.17	0.08	0.04	0.66	0.02
$P_2O_5$	0.03	0.05	0.04	0.05	0.14	0.05
LOI	11.69	6.50				
H <sub>2</sub> O	13.54	13.86	6.15	5.85	6.25	6.47
Total	98.93	101.10	99.89	100.25	100.27	100.15

Tab. A.15 Chemical composition by XRF of selected bentonites in API series (wt%)

### TEM and Electron Diffraction images of API bentonite series



Measured using Jeol JEM-1210; the images show the platelets and nepheloid morphology of smectite and smectite as dominating particles

Zoom of image (8,000x) – circle represents measurement point for electron diffraction (left top); top left: ED of circle with block-wise order of Pioche smectite

Fig. A.38 TEM – Sample Pioche (API #32)



Measured using Jeol JEM-1210; the images show big xenomophic morphology with sign of swelling particles from Chambers smectite, smectite as dominating particles

Zoom of image (3,000x) – circle represents measurement point for electron diffraction (right bottom); bottom right: ED of circle with turbostratic stack order of Chambers montmorillonite

Fig. A.39 TEM – Sample Chambers (API #23)



Measured using Jeol JEM-1210; the images show big particles of xenomophic morphology with full sign of swelling ability from Belle Fourche smectite, smectite as dominating particles Zoom of image (5,000x) – circle represents measurement point for electron diffraction (right); top left: ED of circle with turbostratic stack order of Belle Fourche smectite

Fig. A.40 TEM – Sample Belle Fourche (API #27)



Measured using Jeol JEM-1210; the images show big particles of xenomophic morphology with full sign of swelling ability from Otay smectite, smectite as dominating particles

Zoom of image (8,000x) – circle represent measurement point for electron diffraction (bottom left); bottom left: ED of circle with turbostratic stack order of Otay smectite

Fig. A.41 TEM – Sample Otay (API #24)



Measured using Jeol JEM-1210; the images show lath-shaped xenomophic and platy xenomorphic morphology from Garfield nontronite; Zoom of image (6,000x).

**Fig. A.42** TEM – Sample Garfield (Nontronite) (API #33a)

## B Appendix 2: Microsoft Excel-based Guideline for Calculation of Specific Potential of Bentonites concerning Illitization and Smectitization

It was developed an Excel-based software tool "Checklist for specific dissolution potential of bentonites.xlsx" to calculate the specific dissolution potential of bentonites.

Following input data are requested for this tool:

- amount of Na, Ca and Mg in the interlayer space per (OH)<sub>2</sub> O<sub>10</sub> for calculation of dissolution caused by the interlayer composition (Δ%S<sub>XII</sub>).
- amount of AI, Fe<sub>total</sub> and Mg in octahedral layer for the determination of type of stabilization (group A or group B) and for calculation of dissolution caused by the octahedral layer composition (Δ%S<sub>VI</sub>).
- amount of tetrahedral Si to calculate the Si-buffer capacity.
- limits for octahedral AI and Fe to distinguish between groups A and B (group A is characterized typically by Al<sub>oct</sub> > 1.39 and Fe<sub>oct</sub> > 0.19 per (OH)<sub>2</sub>O<sub>10</sub>).

The software tool is calculating the results for three basic scenarios:

- scenario A: high energy level (60 rpm) in 1n NaCl solution.
- scenario B: low energy level (20 rpm) in 1n NaCl solution.
- scenario C: high & low energy level (60 rpm. 20 rpm) in deionized water.

It would be calculated for these three scenarios as output data the total specific dissolution potential and for one close and five different open reaction systems the amount of Si-precipitation. All values would be expressed as reduced percentage of smectitic layers. A  $\Delta$ %S<sub>total calc</sub>-value = -33 means that a bentonite with %S = 100% (a real montmorillonite) has a specific dissolution potential equivalent to a lost of 33%-points of smectitic layers. It will have in a full open system at the end still %S = 67%. Following procedures were applied to model the measured alteration processes:

 Calculation of smectite layer-ratio (%S) using tetrahedral AI from mineral formula (in according to [SRO 1992]):

$$\%S = 100.38 \cdot (^{V}AI)^2 - 213 \cdot (^{V}AI) + 109.4$$
(B.1)

- Model of driven forces by interlayer cations ( $\Delta$ %S<sub>XII</sub>):

Scenario A: 
$$\Delta \% S_{XII} = 15.09 \cdot \ln(C_{Na}) - 68.26$$
 (B.2)  
 $C_{Na} = Na / (Na + Ca + Mg)$  in interlayer space  
Scenario B:  $\Delta \% SXII = 6.94 \cdot \ln(CNa) - 32.62$  group A (B.3)

$$\Delta$$
%SXII = -9.51 · ln(CNa) + 16.83 group B (B.4)

Scenario C: 
$$\Delta$$
%SXII = 6.94 · ln(CNa) - 32.62 group A (B.5)

$$\Delta$$
%SXII = -7.91 · ln(CNa) + 14.53 group B (B.6)

### - Model of driven forces by octahedral cations ( $\Delta$ %S<sub>VI</sub>):

Scenario A: 
$$\Delta$$
%SVI = -4.36 · In(CFeMg) – 68.26 (B.7)

CFeMg = (Fe + Mg) / (Fe + Mg + AI) in octahedral position

Scenario B:	$\Delta\%\text{SVI} = -4.3$	In(CFeMg) + 7.94	group A	(B.8)
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$$\Delta$$
%SVI = -76.5 · ln(CFeMg) + 258.6 group B (B.9)

Scenario C: 
$$\Delta$$
%SVI = -4.3 · In(CFeMg) + 7.94 group A (B.10)

$$\Delta$$
%SVI = -68.5 · ln(CFeMg) + 230.4 group B (B.11)

Following limiting rules were introduced calculating the effective or total specific dissolution potential:

• a low special potential by interlayer forces is reducing the impact of negative octahedral forces (if  $|\Delta\%S_{XII}| < 2$  than  $\Delta\%S_{VI\_effective} = \Delta\%S_{VI} : 4$ ). • a positive  $\Delta \% S_{VI}$ -value is to set to zero if this value is higher than the negative  $\Delta \% S_{XII}$ -value (if  $\Delta \% S_{VI} > | \Delta \% S_{XII} |$  for  $\Delta \% S_{XII} < 0$  than  $\Delta \% S_{VI} = 0$ ).

Finally, the Si-precipitation ( $\Delta$ %S<sub>precip</sub>) is calculated as function of total  $\Delta$ %S, the percolation or flow rate ( $\Delta$ %S<sub>perc</sub>) and the Si-buffer of bentonite (%S):

$$\Delta \% S_{\text{precip}} = 0. \quad \text{if } \Delta \% S_{\text{total}} - \Delta \% S_{\text{perc}} < 0 \tag{B.12}$$

 $\Delta\%S_{\text{precip}} = \Delta\%S_{\text{perc}} - \Delta\%S_{\text{total}} - (100\% - \%S). \quad \text{if } \Delta\%S_{\text{total}} - \Delta\%S_{\text{perc}} > 0 \quad (B.13)$ 

### Appendix 3: Description of Tropical Weathering Profile as Natural Analoga

С



**Fig. C.1** Geological map of the Song Ma satural zone (a - above) and detailed map of Nui Nua massive (b - below) adapted from [LED 1995]



**Fig. C.2** Selected tropical weathering profile of serpentinized diabase in Bai Angarea of the Nua Nui-complex (Vietnam, Thanh Hoa province) with position for samples NN 0 - 1.5 m (A: bottom), NN 1 – 2 m (B: middle part) and NN 3 – 5 m (C: top horizon)

# D Appendix 4: Methodology for the evaluation of TEM-EDX analyses

### D.1 Calculation of mineral formulae for clay minerals by TEM-EDXanalysis

The mineral formulae for the measured particles were calculated following the international classification for theoretical formula. Additionally, a matrix of specific coefficients was developed with a certain empirical formula range based on different published references (Tab. D.1).

### D.1.1 Smectite

According to [GUV 1988] and [NEW 1987] montmorillonite and beidellite series are presented by dioctahedral aluminous smectite according to the ideal structure formula:

$$(AI_{2-y}Mg^{2+}_{y}) (Si_{4-x}AI_{x})O_{10}(OH)_{2}M^{+}_{x+y} nH_{2}O.$$
(D.1)

 $M^+$  represents the interlayer cations. octahedral and tetrahedral substitutions are presented by x and y respectively. Smectite with y > x are called montmorillonite and those with y < x are beidellite. Trivalent Fe often occurs in octahedral layers.

Nontronite is the ferric end-member of dioctahedral smectite and a counterpart of beidellite, whose layer charge arises mainly by isomorphous substitution in the tetrahedral sheet [BRI 1980]. Fe-rich montmorillonite is a non-ideal smectite and has *trans*-vacant structures with structural formulae similar to Al-montmorillonite, but Al is substituted by Fe in the octahedral layer. Those minerals are distinguished by the substitution of the tetrahedral layer even though both are dominated by Fe in the octahedral layer.

Saponite can be defined as trioctahedral smectite with Mg and Fe<sup>2+</sup> as predominant cations. The average chemical composition of this mineral was given by [KOS 1981]

$$M_{0.48}^{+} (Mg_{2.92} Fe^{3+}{}_{0.02} AI_{0.03}) (Si_{3.53} AI_{0.47}) O_{10} (OH)_{2}.$$
(D.2)

### D.1.2 Dioctahedral Mica

In publications of [MEU 2004], [ROS 2002] muscovite is defined as end-member of the illite series. But following IMA [RIE 1998], illite is by definition a series name of nomenclature of mica with potassium in the interlayer of 0.6 - 0.85. Muscovite is another series name in the mica group with potassium in the interlayer from 0.7 - 1.0 per  $O_{10}$  (OH)<sub>2</sub> (interlayer  $\ge 0.85$ ). Substitution caused by interlayer charge leads to changes in octahedral and tetrahedral layer charges. In fact, the structural formulae of illite in this research (see Tab. D.1) was combined by several authors such as [WAR 1989], [VIN 1997], [JOH 1998], [SRO 1992] and is described as following:

 $M_{0.85-1.00}^{+} (AI_{1.85}Fe_{0.05}Mg_{0.10}) (Si_{2.80-3.22}AI_{1.2-0.78}) O_{10} (OH)_{2}.$ (D.3)

### D.1.3 Palygorskite

Palygorskite is a fibrous clay mineral. The structure consists of ribbons of a 2:1 silicate and the approximate structural formulae were first published by [BRA1940]

$$Mg_{2.5} Si_4 O_{10} (OH)_1 (OH_2)_2 \cdot 4H_2 O$$
(D.4)

and modified by proposal of [DRI 1971] as follows:

$$(Mg_{5-y-x}Ry^{3+}\Pi_z)(Si_{8-x}R_x^{3+})O_{20}(OH)_2(OH_2)_4R^{2+}_{(x-y+2z)/2}.(H_2O)_4.$$
 (D.5)

# D.2 Calculation of mineral formulae for 2-member mixed layer series (IS-ml and diVS-ml)

"IS-ml" and "diVS-ml" are named for clay series formed of illite-smectite mixed layer and dioctahedral vermiculite-smectite mixed layer phases, respectively.

The total charge of half unit cell is the basis for the calculation of the mineral formula considering [KOS 1977]. [SRO 1992] offering a further tool. They have established a set of equations allowing quantifying the ratio of illite and smectite in mixed layers (IS-ml). The main principle of that is the relationship of "fixed" cations in the interlayer with the expandability ( $\%S_{MAX}$ ) of particles (D.6). The end members are postulated by interlayer charge for smectite with 0.4 and for illite with 0.89 per O<sub>10</sub> (OH)<sub>2</sub> (D.7). Based on IS-ml data published by these authors,  $\%S_{MAX}$  can also be calculated by tetrahedral Al

(D.8). Finally, the calculation of the mineral formula has to consider the principle of total charge according to [KOS 1977].

%S <sub>MAX</sub>	= (95.6 - 105.75 · FIX)	(D.6)
Interlayer charge	= [0.89 · (100 - %S) + 0.4 ·%S] / 100	(D.7)
%S <sub>MAX</sub>	= 100.38 · ( <sup>IV</sup> AI) <sup>2</sup> - 213 · ( <sup>IV</sup> AI) + 109.4	(D.8)
%I	= 100 - %S	(D.9)

1:1 sheet silicates						2:"	1 sheet	silicat	es					
		Kaolinite	Cronstedtite	Berthierine	Talc	Illite	Dioctahedral vermiculite	Trioctahedral vermiculite	Montmorillonite	Beidellite <sup>1)</sup>	Nontronite <sup>2)</sup>	Saponite	Chlorite <sup>3)</sup>	Palygorskite <sup>4)</sup>
tc		28	28	28	22	22	22	22	22	22	22	22	28	21
VII	Max	0.05	0.05	0.05	0.05	1.00	1.00	0.90	0.45	0.50	0.50	0.50	0.05	0.40
	Min	0.00	0.00	0.00	0.00	0.85	0.60	0.60	0.15	0.30	0.30	0.30	0.00	0.00
	Max	4.05	6.05	6.05	3.00	2.00	2.03	3.05	2.02	2.10	2.10	3.05	6.05	2.15
n	Min	3.95	5.80	4.00	2.90	1.90	1.95	2.90	1.90	1.98	1.98	2.65	3.95	1.95
c; <sup>4+</sup>	Max	4.10	2.40	3.20	4.00	3.22	3.30	2.95	4.00	3.60	3.60	3.75	3.20	4.00
31	Min	3.95	1.00	2.00	3.90	2.80	2.80	2.70	3.93	3.40	3.40	3.40	2.30	3.70
K+	Max	0.05	0.02	0.02	0.02	1.00	0.80	0.90		0.10	0.10		0.05	0.15
	Min	0.00	0.00	0.00	0.00	0.85	0.00	0.30		0.00	0.00		0.00	0.00

 Tab. D.1
 Matrix of coefficients in structural formulae of selected clay minerals.

tc: total charge, XII: interlayer charge;  $n^{VI}$ : octahedral occupation;, <sup>1</sup> VI: Al<sup>3+</sup> > 1.85; <sup>2</sup> VI: Me<sup>3+</sup> > 1.85 VI: Fe<sup>3+</sup> > Al; <sup>3</sup> chlorite can be 1:2:1 sheet silicate; <sup>4</sup> VI: Me<sup>2</sup> > Me<sup>3+</sup>. Based on structural formula for **palygor-skite** of [GAR 2004], [GAL 1999], [TOR 1994]; **dioctahedral vermiculite** of [GRA 1997], [VIN 1997], [DEL 1988]; **Illite** of [WAR 1989], [VIN 1997], [JOH 1998] ; **Beidellite** of [WEI 1965], [JOH 1998], [VIN 1997], montmorillonite of [MAD 1998], [JOH 1998], [EMM 1998]; **kaolinite** of [EGG 1998]; **chlorite** of [JOS 1989], [KOG 1998], [SHI 1965]; **saponite** of [NAD 1998], [KOS 1981]; **nontronite** of [EGG 1977], [HEN 1967], **talc** of [BAD 1992]; **cronsteditie** of [KOG 2001]; **trioctahedral vermiculite** of [GRA 1997].

Experience with TEM-EDX analyses has shown that one has to distinguish between ISml in senso of [SRO 1992], but also IS-ml phases, which are characterised by K- and charge-deficiency. This group is called by authors dioctahedral vermiculite-smectite mixed layer phases (diVS-ml). Additionally, diVS-ml was classified into three classes:

- High diVS-ml: Interlayer charge of 0.9 for dioctahedral vermiculite and 0.3 for smectite
- Medium diVS-ml: Interlayer charge of 0.75 for dioctahedral vermiculite and 0.3 for smectite

 Low diVS-ml: Interlayer charge of 0.65 for dioctahedral vermiculite and 0.15 for smectite

In general, a IS-mI series in senso of [SRO 1992] is characterised by interlayer charge for illite with 0.89 and smectite with 0.4 per  $O_{10}$  (OH)<sub>2</sub>. Otherwise, diVS-mI represented a K- and charge deficient variety of IS-mI. This developed indicative system to identify and calculate structural formulae of IS-mI and diVS-mI particles was applied to Fried-land clay by [NGU 2010b] and visualised also in Fig. D.1.



Measured by Jeol JEM-1210; XII = total or interlayer charge; FIX = K in illite;  $AI_VI =$  tetrahedral AI example: Friedland clay with structural formula Mg<sub>0.07</sub> Ca<sub>0.05</sub> Na<sub>0.03</sub> K<sub>0.28</sub> Al<sub>1.19</sub> Fe<sup>3+</sup><sub>0.56</sub> Mg<sub>0.19</sub> Ti<sub><0.01</sub> [(OH)<sub>2</sub> Si<sub>3.80</sub> Al<sub>0.02</sub> O<sub>10</sub>; S<sub>max</sub> = 70 % (70 % smectite and 30 % illite)

Fig. D.1 Graphical guidance for verification of IS-ml in senso of [SRO 1992] by mineral formula; the morphology of diVS-ml and IS-ml is similar to montmorillonite under TEM images. They are mainly in the shape of xenomorphic plates or laths.

### D.3 Calculation of mineral formulae for 3-member mixed layer series

The methodology to calculate the mineral formula of non-mixed layer clay mineral phases and for dioctahedral mixed layer phases with 2 members were described in [KAS 2002], [NGU 2010a], and [NGU 2010b] according to the standard formulae structure of each phase like in Tab. D.1.

Furthermore, a methodology was developed to apply TEM-EDX measurements for the calculation of mineral formulae also for mixed layer phases with three members. e. g. mixed layers like CSV-ml (chlorite-saponite-vermiculite mixed layer). KSV-ml (kaolinite-montmorillonite-vermiculite mixed layer) and CrSV-ml (cronstedtite-saponite-trioctahedral vermiculite mixed layer).

### D.3.1 CSV-ml

TEM-EDX measurements for the calculation of mineral formulae also for mixed layer phases with three members. e. g. mixed layers composed of a ratio of 1:2:1 sheet silicates like chlorite (%C) with ratios of 2:1 sheet silicates like saponite (%S) and vermiculite (%V).

# Tab. D.2Main setting of start coefficients for the calculation of mineral formulae for<br/>mixed layer phases with three members

		KSV-ml			CSV-m	nl	CrSV-ml		
	Kao.	Montm.	diVerm	Chl.	Sap.	triVerm	Cron.	Sap.	triVerm
Total charge	28	22	22	28	22	22	28	22	22
Interlayer charge	0	0.15	0.7	0	0.35	0.9	0	0.35	0.9
Si <sup>IV</sup>	4	4	3.3	2.75	3.7	2.9	1.3	3.7	2.9
Octahedral occupation	4	2	2	5 or 5.6	2.7	3	6	2.7	3
(OH) <sub>n</sub>	8	2	2	8	2	2	8	2	2

KSV-ml: kaolinite-smectite-vermiculite mixed layer; CSV-ml: chlorite-saponite-trioctahedral Vermiculite mixed layer; CrSV-ml: cronstedtite-saponite-trioctahedral vermiculite mixed layer; Kao.: kaolinite, Montm.: montmorillonite, diVerm: dioctahedral vermiculite, Chl.: chlorite, Sap.: saponite, Cron.: cronstedtite; XII: interlayer charge, SiIV: number of Si in tetrahedral layer (formulae unit); nIV: number of octahedral cations

This means that the equation %C + %S + %V = 1 describes the distribution of the three different members in the modelled mixed layer phase (CSV-ml).

In general, the calculation of such mineral formulae has considered four coefficients for each member of this mixed layer series (Tab. D.2): the total charge (tc), the interlayer charge, the numbers of cations in octahedral position, and the amount of tetrahedral Si<sup>4+</sup> and the number of hydroxyl-groups.

The starting point for the modelling of mineral formulae of 3-member mixed layer phases is the approach to a mineral formula by the mentioned standard procedure related to

a total charge of 22 per (OH)<sub>2</sub> O<sub>10</sub>. The parameters Si in the tetrahedral layer (<sup>IV</sup>Si<sub>meas 22</sub>), the numbers of atoms in the octahedral layer (<sup>VI</sup>n<sub>meas 22</sub>), and the interlayer charge (XII<sub>meas 22</sub>) from this first mineral formula were used for further data processing. These first values of the mineral formula related to the total charge 22 were compared with the start setting of the coefficients for the three assumed end-members of the mixed layers also presented in Tab. D.2 (e. g. chlorite: <sup>IV</sup>Si<sub>mod C</sub> = 2.75. <sup>VI</sup>n<sub>mod C</sub> = 5.6 and XII<sub>mod\_C</sub> = 0; saponite:  $^{IV}Si_{mod_S} = 3.7$ ,  $^{VI}n_{mod_S} = 2.7$ , and XII<sub>mod\_S</sub> = 0.35; vermiculite: <sup>IV</sup>Si<sub>mod V</sub> = 2.9, <sup>VI</sup>n<sub>mod V</sub> = 4, and XII<sub>mod V</sub> = 0.75). In relation to the ratio of chloritic layers (%C) in the mixed layer phase the total charge of the modelled phase differs between 22 ... 28. Additionally to the total charge, the interlayer charge is also caused by the composition and amount of vermiculite and saponite (interlayer charge of chlorite = 0). A comparison of the modelled and the measured interlayer charge calculated only from ratio "saponite: vermiculite" allows the determination of the valid data for the relative number of vermiculite layers (% $V_{rel}$ ) in the mixed layers for % $V_{rel}$  = %V / (%S+ %V). Mg can be located in the octahedral layer, but also in the interlayer space. An Excel-based tool offered an iterative shifting of available Mg between the two layers to calculate the expected value of %Vrel.

With the knowledge of the ratio "saponite layers : vermiculite layers" (%Vrel) all three parameters (%C, %S, %V) can now be determined for each total charge. That is why the mentioned two sets of parameter (from EDX-analysis and from the model of the three members of mixed layers) may be used to normalise the tetrahedral Si. Then tc or %C is valid if the request <sup>IV</sup>Si<sub>meas</sub> = <sup>IV</sup>Si<sub>mod</sub> is true.

#### Parameters of data model

- 1 = %C + %V + %S(D.10)
- $V_{rel} = V / (S + V)$  (D.11)

 $tc_{mod} = 28 \cdot \%C + 22 \cdot \%S + 22 \cdot \%V$ (D.12)

$$^{VI}\mathbf{n}_{mod} = 6 \cdot \% C + 2.7 \cdot \% S + 3 \cdot \% V = {}^{VI}\mathbf{n}_{meas \ 22} / 22 \cdot tc_{mod}$$
 (D.13)

$$XII_{mod} = 0.35 \cdot \%S + 0.75 \cdot \%V = XII_{meas_{22}} / 22 \cdot tc_{mod}$$
(D.14)

$${}^{\text{IV}}\mathbf{Si}_{\text{mod}} = 2.75 \cdot \% \text{C} + 3.7 \cdot \% \text{S} + 2.9 \cdot \% \text{V} = {}^{\text{IV}}\text{Si}_{\text{meas}_{22}} / 22 \cdot \text{tc}_{\text{mod}}$$
(D.15)

#### Calculation of SV-ratio in mixed layers using parameter %Vrel for

$$%V_{rel} = %V / (%S + %V)$$

modelled data in SV-system for tc = 22

in SV-system 
$$^{VI}\mathbf{n}_{mod} = (^{VI}\mathbf{n}_{mod V} - ^{VI}\mathbf{n}_{mod S}) \cdot \% V_{rel} + {}^{VI}\mathbf{n}_{mod S}$$
 (D.16)

in SV-system 
$$XII_{mod} = (XII_{mod_V} - XII_{mod_S}) \cdot \%Vrel + XII_{mod_S}$$
 (D.17)

measured data in SV-system for tc = 22 via expected XII (valid  $V_{rel}$  if XII<sub>mod</sub> = XII<sub>exp</sub>)

in SV-system	<sup>VI</sup> Mq <sub>surplus</sub>	$= ^{VI}n_{mea}$	$h_{\rm N} = 22 - V_{\rm N} n_{\rm mod V}$	(D.18)
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in SV-system 
$$XII_{meas\_exp} = XII_{meas\_22} + 2 \cdot {}^{VI}Mg_{surplus}$$
 (D.19)

in SV-system: 
$$%V_{rel}$$
 is valid for XII<sub>mod</sub> = XII<sub>meas exp</sub> (D.20)

#### Calculation of %C, %S and %V for each tc-value

for each tc-value

% <b>C</b>	= $(tc_{mod} - 22) / 6$ as result of (1) into (3)	(D.21)
%V	= (1 - %C) · %V <sub>rel</sub>	(D.22)
% <b>S</b>	= 1 - %C - %V	(D.23)

for valid %C-value

%C is valid for  $Si_{meas_{tc}} = Si_{mod_{CSV}}$  (D.24)

### D.3.2 KSV-ml

Similar to CSV-ml. a methodology was developed to apply TEM-EDX measurements for the calculation of mineral formulae also for mixed layer phases with 3 members. e. g. mixed layers composed of a ratio of 1:1 sheet silicates like kaolinite (%K) with ratios of 2:1 sheet silicates like montmorillonite (%S) and vermiculite (%V). This means that the equation %K+ %S + %V = 1 described the distribution of the three different members in the modelled mixed layer phase (KSV-ml).

The start of the calculation procedure is comparable to the one described before for the CSV-ml series. The start setup for the assumed end-member of the KSV-ml series was adopted here (kaolinite:  $^{IV}Si = 4$ ,  $^{VI}n = 4$  and XII = 0; montmorillonite:  $^{IV}Si = 4$ ,  $^{VI}n = 2$  and XII = 0.15; dioctahedral vermiculite:  $^{IV}Si = 3.3$ ,  $^{VI}n = 2$  and XII = 0.7). The iterative

shifting of available Mg between the octahedral layer and the interlayer space has given the valid value of the total charge, if the following request was fulfilled:  $|XII_{meas} - XII_{mod}| = |^{VI}n_{meas} - {}^{VI}n_{mod}|$ . A graphical description of this calculation is shown in Fig. D.2.



**Fig. D.2** Graphical guidance for modeling of the ratio for %K, %S and %V in KSVml series by mineral formula from TEM-EDX-analysis; Example: Friedland clay

1 = % K + % V + % S(D.25)

 $tc_{mod} = 28 \cdot \% K + 22 \cdot \% S + 22 \cdot \% V$ (D.26)

$$^{VI}\mathbf{n}_{mod} = 4 \cdot \% \mathbf{K} + 2 \cdot \% \mathbf{S} + 2 \cdot \% \mathbf{V}$$
 (D.27)

$$XII_{mod} = 0.15 \cdot \% S + 0.7 \cdot \% V$$
 (D.28)

 $^{V}\mathbf{Si}_{mod} = 4 \cdot \% K + 4 \cdot \% S + 3.3 \cdot \% V$  (D.29)

 $^{VI}\mathbf{n}_{meas} = tc_{mod}/22 \cdot (^{VI}\mathbf{n}_{meas}_{22} + 4) - 4$  considering different AI-amount in tetrahedral layer (D.30)

$$XII_{meas} = XII_{meas_{22}} / 22 \cdot tc_{mod}$$
(D.31)

<sup>VI</sup> Si <sub>meas</sub>	$=$ <sup>IV</sup> Si <sub>meas_22</sub> /2	2 ⋅ tc <sub>mod</sub>	(D.32)

(D.25) into (D.26):  $%K = (tc_{mod} - 22) / 6$  (D.33)

(D.25), (D.32)) into ((D.29)):  $\% V = (4 - {}^{IV}Si_{meas_{22}}/22 \cdot tc_{mod})/(4-3.3)$  (D.34)

applying (D.25): 
$$\$S = 1 - \%K - \%V$$
 (D.35)

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