Doctoral Thesis

Influence of physical factors on properties of clays in the radioactive waste disposal

Author(s):
Valter, Martin

Publication Date:
2015

Permanent Link:
https://doi.org/10.3929/ethz-a-010560704

Rights / License:
In Copyright - Non-Commercial Use Permitted
INFLUENCE OF PHYSICAL FACTORS ON PROPERTIES OF CLAYS IN THE RADIOACTIVE WASTE DISPOSAL

MARTIN VALTER
INFLUENCE OF PHYSICAL FACTORS ON PROPERTIES OF CLAYS IN THE RADIOACTIVE WASTE DISPOSAL

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

(Dr. sc. ETH Zurich)

presented by

MARTIN VALTER

Mgr., Comenius University Bratislava

born on 08.06.1983

citizen of Slovakia

accepted on the recommendation of

Prof. Dr. Alexander Puzrin

Prof. Dr. Laurence Warr

Dr. Michael Plötze

2015
# Table of contents

Summary .................................................................................................................................................... vii

Zusammenfassung ...................................................................................................................................... ix

1 Introduction ............................................................................................................................................ 11
   1.1 Motivation of the thesis ............................................................................................................... 11
   1.2 Objectives of the thesis ................................................................................................................ 12
   1.3 Structure of the thesis .................................................................................................................. 13

2 Outline and state of the art .................................................................................................................... 15
   2.1 Temperature ................................................................................................................................. 15
   2.2 Compressive stress ...................................................................................................................... 17

3 Characteristics of variably saturated granular bentonite after long-term storage at near-field relevant temperature ................................................................................................................................. 23
   3.1 Introduction ................................................................................................................................. 24
   3.2 Materials and description of the experiment ............................................................................... 26
      3.2.1 Bentonite ............................................................................................................................... 26
      3.2.2 Artificial pore water ................................................................................................................ 28
      3.2.3 Thermal treatment ................................................................................................................ 29
   3.3 Analytical methods ...................................................................................................................... 29
      3.3.1 Mineralogical characterization ............................................................................................. 29
      3.3.2 Physical and physicochemical properties ............................................................................. 31
   3.4 Results ......................................................................................................................................... 32
      3.4.1 Mineralogical characterization ............................................................................................. 32
      3.4.2 Physical and physicochemical properties ............................................................................. 38
3.5 Discussion ................................................................................................................ ................... 42

3.6 Conclusions ................................................................................................................................. 45

4 Discrete geometry model of heat in granular bentonite barriers ...................................................... 51

4.1 Introduction ................................................................................................................................. 52

4.2 Physics ......................................................................................................................................... 54

4.2.1 Constitutive relations ............................................................................................................ 54

4.2.2 The simulation software ....................................................................................................... 56

4.3 The model .................................................................................................................................... 56

4.3.1 Geometry of the model ......................................................................................................... 56

4.3.2 Parameters of subdomains .................................................................................................... 60

4.3.3 Boundary conditions ............................................................................................................. 63

4.3.4 Meshing and study settings .................................................................................................. 64

4.3.5 Post-processing ..................................................................................................................... 64

4.4 Laboratory measurements ........................................................................................................... 65

4.5 Results ......................................................................................................................................... 66

4.5.1 The model ............................................................................................................................. 66

4.5.2 Comparison with laboratory measurements ......................................................................... 68

4.6 Discussion ................................................................................................................................... 70

4.6.1 Spatial geometry .................................................................................................................... 70

4.6.2 Circle packing ....................................................................................................................... 71

4.6.3 Geometric complexity .......................................................................................................... 71

4.6.4 Water content ......................................................................................................................... 71

4.6.5 Heat capacity ........................................................................................................................ 72

4.6.6 Modelled and experimental ETC .......................................................................................... 72
5 Response of kaolin, bentonite and illite to cold isostatic pressing ...................................................... 79

5.1 Introduction ........................................................................................................................................ 80

5.2 Materials and experimental setup ................................................................................................ 84

5.2.1 Clay materials ................................................................................................................................ 84

5.2.2 High pressure apparatus ................................................................................................................. 85

5.3 Analytical methods ............................................................................................................................ 86

5.4 Results ............................................................................................................................................... 88

5.4.1 Specific surface area ....................................................................................................................... 88

5.4.2 Microporosity ................................................................................................................................. 89

5.4.3 Clay fabrics ................................................................................................................................... 91

5.4.4 Mean layer charge, cation exchange capacity and the amount of leachable cations .............. 92

5.4.5 Crystalline order of clay minerals ............................................................................................... 92

5.4.6 Thermal behaviour ....................................................................................................................... 93

5.5 Discussion .......................................................................................................................................... 96

5.6 Conclusions ....................................................................................................................................... 103

6 Conclusions and outlook ....................................................................................................................... 111

6.1 Main findings ................................................................................................................................... 111

6.2 Research outlook ............................................................................................................................. 113

Acknowledgments .................................................................................................................................... 115
Summary

Clays are products of weathering stable under conditions on the Earth’s surface. Either utilized in industrial applications or taking part in the rock cycle, clays are exposed to various physical and chemical alteration factors. The focus of the present work were the physical factors, high temperature and pressure being the most common and prominent ones. Clays react on them when the factors’ intensity reaches a critical threshold and their properties are subjected to alteration of their properties, e.g. a decreased specific surface area or a reduced cation exchange capacity. The aim of this thesis was to quantitatively determine alteration of thermally treated clay for an improved understanding of their behavior in a future repository for radioactive waste. The second aim was to obtain new fundamental scientific knowledge about the compressive-stress-induced alterations of different clays and to broaden it further.

Two experiments were conducted under laboratory conditions to simulate extensive temperatures and compressive stresses. The temperature experiment allowed approximating temperature and saturation conditions awaited in the engineered barrier of a planned radioactive waste repository. The conception of the heat transfer non-linearity emerging from the character of the barrier was underlined in a finite element model delivering outcomes for an improvement of the current knowledge about heat transfer in a granular bentonite barrier. An application of high compressive stresses on clays provided an insight into the alteration of structural and physicochemical properties of several clays which includes a pioneering section of the microporosity mapping of compressed clays.

The temperature studies were focused on the material for the engineered barrier in the future repository for radioactive waste in Switzerland – granular sodium bentonite MX-80. Different portions of bentonite having an identical dry density were stored in a closed system at specific temperatures for several years. The water contents at specific temperatures corresponded to awaited conditions in the near-field of a repository. The alteration of various properties of bentonite, which are important for its utilization in a repository, was analyzed as a function of the storage temperature and time. The experiment helped to determine a threshold temperature between 105-120 °C inducing unfavorable alterations of the bentonite; e.g. a drastic decrease of the specific surface area and of the water uptake capacity was recognized. After an initial reduction, the cation exchange capacity, one of the most valued properties of bentonite, showed a recovery in time at temperatures below 120 °C.

The Swiss concept utilizes a granular mixture of pre-compressed bentonite pellets encapsulating canisters with radioactive waste. To describe the non-linear character of the heat transfer in the granular body, a discrete geometry considering the space arrangement and the amount of different grain size classes was applied. This option was utilized in modelling of the bentonite barrier for the
first time. The purpose of the model was to develop fundamentals for a determination of the resaturation time scale after which the canister corrosion will start. The outcomes of the model are related to the geometry of the granular system and to the water content. Heat transfer is managed by tortuosity of the system which is directly determined by the pellet packing and pellet size variability. Differences between various structural geometries fade out with increasing water content and they become practically insignificant in fully saturated systems. The model also enables calculation of the temperature equilibrium periods what is an essential tool towards the final solution of the resaturation period problem.

Kaolin, illite and bentonite were included in the high compressive stress experiments. The study of the stress-induced alteration contained one-of-its-kind evaluation of the clay microporosity. A possible decrease of the clay mineral interlayer accessibility leads for instance in case of compressed montmorillonite to a reduction of its cation exchange capacity. Compressive stress was translated into the structural integrity of clay minerals. Alteration of the kaolinite crystalline order was predominantly time-dependent. On the other hand, the crystalline order of illite appears to possess a potential to be improved under certain compression conditions even at room temperature.

Studies confirmed an overall stability of clays to described physical factors. The alteration effects often bordered line of the analytical resolution. The alteration was, however, clearly detectable outside specific limits which enabled to identify critical conditions under which clay properties start to change. The influence of physical factors not surprisingly intensified in time. On the other hand, some altered properties were able to recover or even to improve during long term presence of physical factors what is an important contribution especially for the radioactive waste disposal.
Zusammenfassung


interessanterweise nach anfänglicher Reduktion mit zunehmender Zeit eine Wiederherstellung bei Temperaturen unter 120 °C.


1 Introduction

1.1 Motivation of the thesis

Clays are natural materials widely used in industrial applications. The unique rheological properties of clay slurries make them especially important in civil and geotechnical engineering (Harvey & Lagaly, 2006). Environmentally most valuable property of clays is, however, their low hydraulic conductivity, the basic prerequisite for isolation of dangerous materials from biosphere. A clay particularly suitable for this purpose is bentonite. A substantial component of this clay rock is montmorillonite, a swelling clay mineral able to prevent further movement of the cationic species and heavy metals by cation exchange (Bergaya & Lagaly, 2006; Pusch, 2006).

Usage of bentonite as the main barrier element in landfills of hazardous waste is a standard practice (Czurda, 2006). From a future perspective, bentonite is planned as the mineral engineered barrier in deep geological repositories for radioactive waste. A repository is foreseen as the most suitable solution for the issue of nuclear waste disposal in many countries. A repository in Switzerland is designed as a multi-barrier complex of horizontal galleries several hundreds of meters below the Earth’s surface in clay sedimentary facies (Russell & Facella, 2006). Based on the scale of view, the multi-barrier can be seen in scope of the far-field and the near-field. The far-field represents a greater scope of the host rock fulfilling the task of the natural barrier, in which the repository is constructed. The near-field stands for the engineered barrier system together with the encapsulated waste (IAEA, 2003).

Besides its isolating function, the engineered barrier will transmit decay heat from the radioactive waste into the host rock. The bentonite barrier just after its emplacement will be therefore a subject to dehydration. Decay heat will drive initial bentonite humidity towards the host rock out of which, on the other hand, the pore water diffusion will counteract. Activity and temperature of the waste will decrease in time which will facilitate bentonite resaturation. A drying-wetting cycle will accompany the near-field during first decades to centuries until the water front reaches the surface of the canister with radioactive waste and its corrosion commences (Nagra, 2002).

The task of the multi-barrier system must be fulfilled especially during canister corrosion and thereafter over a time span exceeding several hundreds of thousands of years. Barriers will be exposed to various physical factors. The most significant will be ionizing radiation, high temperature and, in case of an eventual tectonic event in the far future, high compressive stress. Physicochemical properties of contained clay minerals will react on them and could be altered undesirably. This concerns in the first line their sorption capacity and surface area, prerequisites for the retention
of radioactive compounds (Nagra, 2002). However, the extent of the bentonite sensitivity to changing conditions within the engineered barrier remained still not entirely understood. The alteration is supposed to be time-dependent. Different water contents should also play a significant role. Simultaneously, the physical character of the engineered barrier will change in dependence on the mentioned aspects. Two main issues were therefore to answer concerning temperature:

- time-dependent changes of bentonite physicochemical properties in the near-field of a repository in dependence on the temperature field and water content
- detailed view on the heat transfer in the bentonite barrier and its evolution with physical factors changing in time

Research of the clay alteration induced by high compressive stress was up to now oriented on the impact of compressive stress coupled with high temperature to study conditions in depths of the Earth’s crust and mantle where oceanic sediments with clays succeeded after their consumption in subduction zones. Investigation of the sole influence of pressure was, however, neglected. Clays as part of the natural and engineered barriers in future deep geological repositories for radioactive waste can eventually be exposed to high compressive stresses. If clays are stable under exaggerated compressive conditions, their stability can also be extrapolated to realistic, much lower stress levels applicable to waste disposal.

The question how do different properties of powdered clays react on high compressive stress was unanswered what offered an opportunity for an investigation included in the dissertation. Specific aspects of investigation included:

- interconnection of awaited compressive-stress-induced structural alterations with alterations of the physicochemical properties and their amplitude at different pressures
- pressure alteration differences among different clay types

1.2 Objectives of the thesis

The first goal of presented work was to determine and to better understand the influence of the temperature on essential properties of bentonite with special consideration of conditions in the repository for radioactive waste. To reach the goal, a laboratory experiment simulating conditions in the near-field was started. Results of the experiment led to determination of the critical conditions leading to an undesirable alteration of the bentonite properties. Finite element modelling of the heat transfer in the barrier helped to determine structural properties of the granular bentonite which can enhance heat transfer from the waste in direction to the host rock.
The second goal of the thesis was to investigate how a high pressure influences the structural, physico- and crystallochemical properties of different clays. For this purpose, three clays were compressed under high pressure during two compression periods. The laboratory analysis outcomes of compressed clays helped to underline the most sensitive properties and to elaborate an outline of the clay compression stability.

1.3 Structure of the thesis

The thesis is composed of three scientific papers, out of which one is already published (chapter 3) and two are submitted for a publication (chapters 4-5).

Chapter 3 is focused on the reaction of physicochemical parameters of bentonite on near-field relevant temperatures and saturations. Different portions of the granular bentonite MX-80 were variably saturated with artificial pore water and stored in closed containers at different temperatures between 50-150 °C to simulate mineral barrier during resaturation at different distances from heat-generating radioactive waste. Different portions of bentonite enclosed in separate containers were analysed after 3, 6, 12 and 18 months. Temperatures higher than 105 °C appeared to be critical inducing a decrease of the bentonite cation exchange capacity, specific surface area, water uptake and water adsorption capacity.

Finite element model of the heat transfer through the granular bentonite is presented in the chapter 4. It represents the first step towards a solution of the resaturation time scale problem. Different structural parameters of the granular body and saturation levels were considered. Results of the model and its comparison with the laboratory measurements of the granular bentonite thermal conductivity confirmed awaited strong influence of water on heat transfer. Heat transfer in dry or partially saturated systems is on the other hand primarily governed by structural features of the granular material. The model is able to calculate temperature equilibrium periods what represents an important step towards the problem solution.

Chapter 5 is focused on the influence of high compressive stress on three clays present in the natural and engineered barriers of a future repository for radioactive wastes in Switzerland. The study is connected with production of pre-compressed green bodies in ceramic industry by means of isostatic pressing. This approach allowed obtaining uniformly compressed pressings with an assumption that the alteration of compressed clays is also uniform in the entire volume of the pressings. Their analysis was thus easier since preferred orientation of clay particles could have been excluded. Kaolin, illite and bentonite were exposed to an isostatic compressive stress of 1.5 and 3 GPa during one and four days. Two compression periods were chosen to investigate the time aspect of the awaited alterations.
Analysis of physicochemical properties was carried out before and after compression with focus on the microporosity, surface area, cation exchange capacity, and crystallochemical features of clays. The pressure-induced alteration was most pronounced in kaolin, illite was intermediately sensitive to the applied pressure, whereas bentonite was the most stable among the tested clays.

Paper chapters 3-5 are positioned before the outline of the topic and state of the art in chapter 2. Thesis is finished with conclusions and outlook in chapter 6.

References


Chapter 2 Outline and state of the art

2 Outline and state of the art

2.1 Temperature

Bentonite universally counts as the backbone of the engineered barrier concept. Despite being stable against weathering, it can react on intense physical factors like high temperature accompanying the radioactive decay in the nuclear waste (Sato et al., 1998; Laine & Karttunen, 2010). Investigations of the bentonite alteration were conducted within many laboratory experiments studying geochemical reactions within water-saturated bentonite at elevated temperatures (Montes-H & Geraud, 2004; Herbert et al., 2008; Kaufhold & Dohrmann, 2009, 2010, 2011; Gómez-Espina & Villar, 2010; Perdrial & Warr 2011; Kasbohm et al., 2012). The most significant changes confirmed in all studies were related to the cation exchange processes.

A couple of countries started experiments in situ – in the host rock planned for hosting the repository to most closely achieve the far-to-near-field conditions. In the underground rock laboratory Mont Terri in Switzerland is situated the HEATER experiment (Göbel, et al., 2006). The experiment was started in highly consolidated Jurassic clay stone (Opalinus clay). It consists of a vertical borehole filled with pre-compactated bentonite (Almeria, Spain) enclosing the heater element with a constant surface temperature of 100 °C simulating the waste canister. Heating period took eighteen months after which the bentonite was taken out and analysed in the laboratory. The analysis showed only very weak modifications of the bentonite. The alteration was mostly related to dehydration and dehydroxylation characteristics, mean layer charge, interlayer cation composition and cementing phenomena (Plötze, et al., 2007).

The Alternative Buffer Materials (ABM) project started in 2006 in Äspö Hard Rock Laboratory, Sweden. Eleven different clays are still tested in the experiment built according to the Swedish KBS-3 repository design. The experiment consists of three vertical boreholes with axially situated heaters (130 °C) and different compacted clay blocks stacked one onto another. The first of three clay packages was heated during about a year (Svensson, et al., 2011). One of the tested materials was MX-80 ESDRED “E”, sodium bentonite occurring in every part of presented thesis. The most obvious change of the bentonite was a decrease of its specific surface area by 25-50%. Interestingly, the cation exchange capacity (CEC) of the bentonite increased in direction to the heater. Other changes were connected with the mean layer charge and porosity (Nagra, 2011).

The same rock laboratory in Äspö hosts The Long Term Test of Buffer Material (LOT). Blocks of compacted MX-80 surrounding copper heaters were emplaced in the boreholes in the crystalline host rock at a depth of ca. 500 m. A temperature of 130 °C was reached at the contact heater-bentonite.
The first package was analysed after almost six years of heating. A certain bentonite alteration occurred which was confirmed by laboratory analyses. Contained anhydrite and gypsum were axially redistributed within bentonite proportionally to the temperature field. Anhydrite precipitated in the heater vicinity, whereas gypsum was found in the hydrated parts of the bentonite near the host rock. Carbonate dissolution was recognized as well. Its rate increased with increasing temperature. Consequently, the exchangeable sodium in the montmorillonite interlayer was replaced by calcium and even by magnesium in the warmest zones. Like in the ABM project, an increase of the CEC of bentonite in the heated zone was observed. The increase of the CEC was connected with an increase of the mean layer charge of montmorillonite (Olsson & Karnland, 2011).

A formation of highly charged expandable layers in smectite under hydrothermal treatment is a known phenomenon (Howard & Roy, 1985) and is mentioned practically in all works dealing with hydrothermal treatment of smectites. The increase of the layer charge is one of the initial requirements to convert a smectite to illite – a process known as illitization (Sawhney, 1970).

During illitization, smectite loses a proportion of its expandable layers and its ordering (Reichweite) in favour of creation of non-expandable, collapsed layers (Inoue, 1995). The process is determined by a simultaneous exchange of original smectite interlayer cations (e.g. Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)) for almost exclusive K\(^+\). The fixation of K\(^+\) in the interlayer is the results of the process (Meunier & Velde, 2013).

Hydrothermal requirements for smectite-to-illite conversion other than an elevated temperature are considered to be time, pressure, chemical composition of the system, high liquid/solid ratio, dioctahedral nature of smectite, as compared to a trioctahedral nature, and – a crucial requirement – an access to potassium (Velde, 1992; Huang et al., 1993; Pusch & Karnland, 1996; Ferrage et al., 2011). Namely, hydrothermal treatment alone does not lead to the collapse of the smectite layers but can increase layer charge (Howard & Roy, 1983). The increasing layer charge, however, leads to the selectivity of smectite for K\(^+\) (Sawhney, 1970). When sufficient layer charge is provided, K\(^+\) must be introduced for illitization to proceed. If other mobile cations are present in the system, e.g. Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), these can inhibit the illitization rate (Howard & Roy, 1985). It appears that these cations possess the inhibitory ability due to their sufficient hydration energy and ionic potential which both are higher than those of K (Eberl, 1980; Roberson & Lahann, 1981; Güven, 1990).

Illitization seems to be kinetically controlled (Pytte & Reynolds, 1989). The kinetic law describing the process is a chain of various reactions with different kinetic constants. A general kinetic expression of illitization exists:
\[ \frac{-dS}{dt} = S^o \left( \frac{K}{Na} \right)^b A \left[ \frac{U}{RT} \right] \]

where \( S \) is the mole fraction of smectite in illite/smectite, \( t \) is the time, \( K/Na \) is the ratio of potassium and sodium concentrations, \( a \) and \( b \) are integers whose sum is the reaction order, \( A \) is the frequency factor, \( R \) is the gas constant, \( T \) is the absolute temperature and \( U \) is the Arrhenius’ activation energy of the reaction. Temperature has a dominant control over the reaction progress (Pytte & Reynolds, 1989). Moreover, the activation energy itself appears to be determined by the thermodynamic temperature (Lasaga, 1984).

Temperature is not only important for the mineral alteration of clays but also in the heat regime of a repository for radioactive waste. In terms of the heat transport, thermo-hydro-mechanical processes awaited in the repository are modelled. The focus has been put on both the far-field and near-field. Different approaches were applied. For instance, Sato et al. (1998) considered in their numerical model that heat is transported through the engineered barrier only by conduction with thermal conductivities and heat capacities of all materials assumed as temperature independent. In the finite element model of the Boom clay (Belgium), François, Laloui and Laurent (2009) consider the medium as a deformable two-phase material in which heat and mass flow occur. The experience from the FEBEX experiment was utilized in the constitutive far- to near-field model of Gens et al. (1998) capable of the 1-D and 2-D thermo-hydro-mechanical analyses.

### 2.2 Compressive stress

The effect of high compressive stress on clay minerals has been intensively studied in field of geotechnics, civil engineering and fundamental geology. Clays are usually investigated under uniaxial or triaxial compression regimes to simulate natural conditions. Research of clays being exposed to a uniform compressive stress field (isostatic stress) is mainly attractive for industrial applications like production of ceramics. Results of the research are, however, universally applicable for studies of the influence of compressive stress on clays. Testing of the stability of compressed clay minerals has its value also for the radioactive waste disposal.

Cold isostatic pressing is a routine technique in the production of ceramics when a powder is compacted solely by mechanical means through a uniform compressive stress without being heated (Turner & Ashby, 1996; Ekşi & Saritaş, 2002). Applied compressive stress can induce alteration to clay mineral properties even at room temperature. Isostatic compressive stress causes a reversible structural phase transition in dickite at about 2.2 GPa (Johnston et al., 2002; Dera et al., 2003). In the case of kaolinite, isostatic stress decreases its crystalline order and crystallite size at a threshold of about 2 GPa (La Iglesia, 1993; La Iglesia & Aznar, 1996). Isostatic stress can lead to an alteration
of the unit-cell dimensions of layer silicates. Regardless of the type of clay minerals, the geometrical accommodations of the octahedral sheet in a compressed mineral provoke ditrigonalization of the tetrahedral layer (Hazen & Finger, 1978; Comodi & Zanazzi, 1995). The stress-induced alteration depends on the chemical composition and, more significantly, on the water content of compressed clay minerals (Comodi & Zanazzi, 1995; Galán et al., 2006).

Alteration effects of high compressive stress are accompanied with structural transitions of water in the clay mineral interlayer. Water can change its structure to ice VI at about 0.8 GPa and 20 °C resulting in a 30% volume reduction (Choukroun & Grasset, 2007). Phase transition of the interlayer ice VI into ice VII above 2 GPa can additionally take place during compaction (Somayazulu et al., 2008; Salzmann et al., 2011). The ice VI transition to its denser phase ice VII is a volume reduction phenomenon as well (Mishima & Endo, 1978). An alternative description of phenomena concerning the interlayer water in compressed smectite offered You et al. (2013). According to their study, water molecules are capable to (re)enter the smectite interlayer when a sufficient pressure is provided. It has been shown that the basal distance of hydrated synthetic smectite starts to increase at about 1.7 GPa.

Non-isostatic compressive stress induces structural alteration to clay minerals which is largely comparable with the isostatic stress effects. Kaolinite experiences alteration of its vibrational parameters (Fourier transform infrared analysis; Bell et al., 1991). A decrease of the crystalline order of uniaxially compressed kaolinite and illite was recognized at 0.32 GPa (Plötze & Kahr, 2002). A uniaxial compressive stress of about 2 GPa is likewise capable of decreasing illite's specific surface area and influencing its microporosity (Gregg & Langford, 1977).

As mentioned previously, the chemical composition of the compressed system determines the art and extent of clay minerals’ alteration. Adhesion energies between the interlayer surfaces depend on the type of interlayer cations. Different cations thus effectively influence the compressibility of clay minerals (Sakuma, 2013). Since kaolinite group minerals possess no interlayer cations, it is expected that the compressibility of their sheets is the managing structural factor under compressive stress.

References


Chapter 2 Outline and state of the art


3 Characteristics of variably saturated granular bentonite after long-term storage at near-field relevant temperature

Authors

M. Valter, M. Plötze

Publication

Published in Clay Minerals, Journal of Fine Particle Science (DOI: 10.1180/claymin.2013.048.2.14)

Abstract

Bentonite is a potential material in the engineered barrier of radioactive waste repositories because of its low hydraulic permeability, self-sealing capability and retention capacity. It is expected that bentonite reacts to the elevated temperatures accompanying the radioactive decay in the nuclear waste. The presented study was started in order to improve the understanding of the coupled influence of temperature and (pore) water on the physicochemical and mineralogical properties of bentonite during thermal treatment under near-field relevant conditions. Granular Na-bentonite MX-80 was differently saturated ($S_r=1-0.05$) and stored at different temperatures (50-150 °C) in a closed system. Upon dismantling after several periods of time (3 to 18 months) mineralogical characteristics, cation exchange capacity and content of leachable cations as well as physicochemical properties like surface area and water adsorption were investigated. The results showed a high mineralogical stability. A slight conversion from the sodium to an earth alkali form of the bentonite was observed. However, considerable changes in the physicochemical properties of the bentonite were observed particularly by treatment above the critical temperature of 120 °C. The cation exchange capacity decreased during heating at 150 °C by appr. 10%. The specific surface area dropped by more than 50%. The water uptake capacity under free swelling conditions showed a slight tendency to lower values especially for samples heated for more than 12 months. The water vapour adsorption ability in contrast drops by 25% already within three months at $T=120$ °C. These changes are mostly related to the variations in the interlayer cation composition and to smectite aggregation processes. The observed alterations are rather subtle. However, temperatures $\geq120$ °C had a remarkable negative influence on different properties of MX-80.

Keywords

radioactive waste repository, thermal treatment, Na-bentonite, bentonite alteration
3.1 Introduction

In several countries, a deep geological repository is foreseen as the most suitable solutions for the issue of radioactive waste disposal (Russell & Facella, 2006). Such an underground facility should isolate radioactive waste from the biosphere and ensure the dissipation of the heat of decay (Kahr & Müller Vonmoos, 1982). Currently designed repositories for radioactive waste are multibarrier systems composed of the natural barrier (host rock) and a combination of several engineered barriers (Nagra, 2002). An important part of the engineered barrier system is the bentonite backfill. The use of bentonite as the engineered barrier is of crucial importance because of its low hydraulic permeability, self-sealing capability and retention capacity (Pusch, 2001). Bentonite is a natural material predominantly consisting of smectite and represents a product of the early diagenetic alteration of vitric fallout ash in subaqueous, mainly marine environments (Chamley, 1989). Bentonite shows a great stability against weathering (Laine & Karttunen, 2010). Nevertheless, its properties can alter under harsh conditions like elevated temperature and pressure or wetting-drying cycles (Galán, 2006; Pusch, 2006). The exposure of bentonite to hot steam leads to a decrease in swelling capability and to an increase in hydraulic conductivity, all of which are mirrored also in the bentonite microstructure (Couture, 1985; Pusch, 2000). It is expected that bentonite reacts to the elevated temperatures accompanying the radioactive decay in the nuclear waste (Sato et al., 1998). Temperatures below 50 °C in the repository bentonite buffer and its full saturation are expected within 100-200 years (Senger & Ewing, 2008). The swelling behaviour and geochemical reactions of bentonite have been studied by saturation with pore water solutions with different chemical composition and ionic strength under confined conditions at elevated temperatures in short-term lab experiments (Montes-H & Geraud, 2004; Herbert et al., 2008; Kaufhold & Dohrmann, 2009, 2010, 2011; Gómez-Espina & Villar, 2010; Perdrial & Warr 2011; Kasbohm et al., 2012). Only minor alteration of the bentonite was reported. The described initial transformation of smectite to interstratified illite-smectite, and the decrease in layer charge are rather insignificant. Significant chemical changes are related to cation exchange processes only. The sorption ability of MX-80 remained unchanged up to 250 °C of heating for 24 h.

Several in-situ experiments have been started, in order to investigate the behaviour of bentonite under elevated temperature in the potential host rock to closely study the far-to-near-field conditions. Some of these projects are the FEBEX in Grimsel (enersa, 2000) and the Heater Experiment in Mont Terri (Göbel et al., 2006) both in Switzerland as well as the Alternative Buffer Materials project (ABM; Svensson et al., 2011), and the Long Term Test of Buffer Material project (LOT; Olsson & Karland, 2011), both situated in the Äspö Hard Rock Laboratory, Sweden. Generally, these experiments demonstrated a high chemical and mineralogical stability of the bentonite during thermal treatment. However, not all experiments showed the same reactions. The investigation of the thermo-hydro-mechanical (THM) properties of the bentonite after five years treatment at repository conditions
in the FEBEX experiment revealed unchanged retention and swelling capacity (Villar & Lloret, 2007). The analysis of the treated bentonite from the HEATER experiment discovered slight alterations related to cementing processes (by precipitation of amorphous Si/Al compounds). The specific surface area (SSA) decreased by about 20%. Besides the interlayer cation exchange an insignificant decrease of the mean layer charge (MLC) was detected (Plötze et al., 2007). In the ABM project, besides slight tendencies of cation exchange, an increase of the cation exchange capacity (CEC) of the bentonite was measured in the direction of the heating source (Nagra, 2011; Svensson et al., 2011). However, the differences appear to border the line of analytical error. As in the HEATER experiment, a significant decrease of the SSA of the MX-80 bentonite was measured as well. Additionally, in the LOT project, carbonate dissolution and gypsum dehydration in MX-80 according to the temperature gradient were observed. Close to the heater in the A2 parcel test, calcite was dissolved and gypsum dehydrated within the almost six-years of heating whereas gypsum precipitated in the colder and more humid part near the host rock (Olsson & Karnland, 2011).

The presented study was started in order to improve the understanding of the coupled influence of temperature and (pore) water on the physicochemical and mineralogical as well as the hydraulic and mechanical properties of bentonite during thermal treatment. The temperature and the hydration state of the bentonite were adapted to the expected conditions in the near-field of a planned repository for radioactive waste (Fig. 3-1).

![Fig. 3-1 Evolution of the saturation degree (blue curve) and temperature (orange curve) in the engineered barrier between the container and host rock (adapted from Senger & Ewing, 2008)](image)
In the experiment the Na-bentonite MX-80 was used, which is one of the possible buffer materials. The bentonite was saturated with artificial pore water of the same chemical composition as the pore water of the Opalinus clay – a potential host rock for the radioactive waste repository in Switzerland. The thermal treatment was carried out under laboratory conditions in a small-scaled closed system, providing full control of physical and chemical factors (mass and bulk density of the bentonite, content and chemical composition of the pore water, and temperature). The time scale of the experiment with more than three years of treatment will be in the same range as most of the in-situ long-term experiments.

The chosen setup allows to observe in short time steps the initial changes of the important bentonite properties under near-field relevant conditions comparable with large-scale in-situ experiments but in a closed system under controlled environmental conditions.

3.2 Materials and description of the experiment

3.2.1 Bentonite

The Na-bentonite MX-80 (Wyoming, AMCOL International Corp.) was used in this experiment. The mineralogical composition of the bentonite is characterised by a high content of smectite and about 10 wt.% of mica-like minerals and tectosilicates each. In traces, cristobalite, calcite and gypsum were found but also pyrite (Tab. 3-1). The bentonite is a granular material from the ESDRED experiment (Engineering Studies and Demonstration of REpository Design), where different granulometric distributions were tested in emplacement studies (Plötze & Weber, 2007). The chosen granular mixture ESDRED “E” (uniformity index $C_u=13.22$, curvature index $C_c=1.65$, $d_{50} = 1.61$ mm, dry bulk density of bentonite granules $\rho_d=1.962$ g/cm$^3$) achieved the highest dry emplacement density ($\rho_d=1.513$ g/cm$^3$). Various portions of bentonite (26 – 46 g) were filled with a dry bulk density of $\rho_d=1.5$ g/cm$^3$ in tight containers (Fig. 3-2). The containers consisted of an ematal coated aluminium shell with an inner PTFE casing. The PTFE casing prevents the contact of the bentonite material with the aluminium shell to avoid the formation of corrosion products to exclude an uncontrolled chemical influence. The containers had an inner diameter of 40 mm and an inner height of 25 mm.
Tab. 3-1 Mineral composition of the bentonite MX-80 before and after the thermal treatment

<table>
<thead>
<tr>
<th></th>
<th>50 °C</th>
<th>65 °C</th>
<th>105 °C</th>
<th>120 °C</th>
<th>150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bassanite</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Calcite</td>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>2.2</td>
<td>0.2</td>
<td>2.0</td>
<td>0.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.8</td>
<td>0.3</td>
<td>1.8</td>
<td>0.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Mica/S.c.l.</td>
<td>12.4</td>
<td>1.5</td>
<td>11.8</td>
<td>1.2</td>
<td>12.5</td>
</tr>
<tr>
<td>Feldspar</td>
<td>4.5</td>
<td>0.7</td>
<td>6.5</td>
<td>0.9</td>
<td>4.4</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.5</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Quartz</td>
<td>6.0</td>
<td>0.2</td>
<td>5.8</td>
<td>0.3</td>
<td>5.8</td>
</tr>
<tr>
<td>Smectite</td>
<td>72.7</td>
<td>1.2</td>
<td>70.8</td>
<td>1.3</td>
<td>72.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>12 months</th>
<th>18 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bassanite</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Gypsum</td>
<td>1.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Mica/S.c.l.</td>
<td>15.1</td>
<td>14.1</td>
</tr>
<tr>
<td>Feldspar</td>
<td>5.4</td>
<td>5.7</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Quartz</td>
<td>4.7</td>
<td>5.5</td>
</tr>
<tr>
<td>Smectite</td>
<td>70.7</td>
<td>70.3</td>
</tr>
</tbody>
</table>

nd – not detected; *30 absolute error
3.2.2 Artificial pore water

The bentonite was saturated with artificial pore water (APW) at five saturation degrees ($S_r$): 0.05, 0.25, 0.5, 0.75, and 1 (compare Fig. 3-1) corresponding to solution to dry clay weight ratios of 0.02, 0.08, 0.19, 0.33, and 0.53, respectively. The chemical composition of the APW (pH 7.9, alkalinity 0.55, ionic strength 0.23, Na-Ca-Mg-K type, main cation Na) corresponded to the pore water of the Opalinus Clay formation in the Brown Dogger facies (Mäder, 2009). The precise chemical composition of the APW (Tab. 3-2) was calculated using Phreeqc (version 2.15.07) software and NAGRA-PSI database Version 01/01.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>25</th>
<th>7.861</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.861</td>
<td>7.861</td>
</tr>
<tr>
<td>[mmol/kg]</td>
<td>[g/L]</td>
<td>[g/L]</td>
</tr>
<tr>
<td>Na (total)</td>
<td>163.8</td>
<td>3.766</td>
</tr>
<tr>
<td>K (total)</td>
<td>2.551</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca (total)</td>
<td>11.91</td>
<td>0.477</td>
</tr>
<tr>
<td>Mg (total)</td>
<td>9.166</td>
<td>0.223</td>
</tr>
<tr>
<td>Cl (total)</td>
<td>160</td>
<td>5.672</td>
</tr>
<tr>
<td>$S^{VI}$ (total)</td>
<td>24</td>
<td>0.77</td>
</tr>
<tr>
<td>$C^{IV}$ (total)</td>
<td>0.5431</td>
<td>0.007</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>0.5494</td>
<td>0.5494</td>
</tr>
<tr>
<td>P (CO$_2$)</td>
<td>1E-3.5</td>
<td>1E-3.5</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>0.2264</td>
<td>0.2264</td>
</tr>
<tr>
<td>SI (calcite)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SI (dolomite, ord.)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SI (gypsum)</td>
<td>-0.31</td>
<td>-0.31</td>
</tr>
</tbody>
</table>

Tab. 3-2: Artificial pore water (APW) characteristics corresponding to the chemical composition of the pore water in Opalinus clay.
3.2.3 Thermal treatment

The variably saturated bentonite were stored in the tight containers at temperatures (50, 65, 105, 120, and 150 °C) according to the expected temperature conditions at the different distances between the canister with the radioactive waste and the host rock (Fig. 3-1; Senger & Ewing, 2008). Accordingly, bentonite with $S_r=1$ was stored at 50 °C (vicinity of the host rock) and the $S_r=0.05$ sample at 150 °C (vicinity of the canister). One container was prepared for each temperature level and heating time. The heating time intervals are 3, 6, 12, 18, and ≥36 months. The material was taken out of the container, dried overnight at 50 °C, crushed in an agate mortar and homogenized for further analysis.

3.3 Analytical methods

3.3.1 Mineralogical characterization

X-ray diffraction analysis

The samples were characterized by X-ray powder diffraction using a Bruker AXS D8 Advance diffractometer (source Co Kα radiation $\lambda = 1.790 \, \text{Å}$) equipped with primary and secondary soller and automatic theta compensating divergence and antiscatter slits. Data were collected from 2-80°2θ (2-40°2θ for textured specimens) with a step size of 0.02°2θ and a counting time of 4 s/step. The mineral composition of the samples was determined on randomly oriented powder and textured smear specimens. The samples were micronized in ethanol to <20 μm using a McCrone micronizing mill equipped with agate grinding elements. After drying, the samples were front-loaded into the sample holders by taping a razor blade onto the sample within the sample holder in order to, both, maximize the random orientation of the minerals and to achieve a flat surface of the sample (Zhang et al., 2003). The textured specimens were prepared to easier identify the clay minerals. The basal reflections of the oriented clay minerals are enhanced through this technique (Brindley & Brown, 1980). An amount of each sample was mixed with deionised water. The paste was smeared onto the flat glass, dried in the laboratory atmosphere and analysed. The textured specimens were then saturated with ethylene glycol (EG) to examine smectite swelling (Brindley & Brown, 1980). The (00l) diffraction peaks can be observed as a rational series of d-values for a discrete clay mineral. The coefficient of variation (CV) for the (00l) diffractions of samples saturated with propane-1,3-diol (instead of EG) were determined in order to detect the possible formation of interstratified irregular illite/smectite with a CV≥0.75 (Moore & Reynolds, 1997). The XRD was also used for the determination of the mean layer charge (MLC). The samples were intercalated with dodecyl ammonium (chain length nC=12) and washed with ethanol (Lagaly, 1994). A few mg of talc was added.
to the intercalated samples as line positioning standard for the XRD pattern. The prepared suspension was then dropped onto a glass slide, dried in vacuum at 40 °C and immediately measured. The MLC was calculated as $\text{MLC} = \frac{d(001) - 5.52}{32.98}$ (Olis et al., 1990). The determination of the basal spacing, as well as the qualitative phase analyses were carried out by processing the diffraction pattern in the DIFFRACplus EVA software (Bruker AXS). The quantitative composition was calculated by Rietveld analysis using the BGMN®/AutoQuan software (Bergmann & Kleeberg, 1998).

**FT-IR spectroscopy**

The Fourier Transform Infrared Spectroscopy (FT-IR) was used as an additional method for the mineral composition analysis. Particularly, the presence of amorphous silica and the ion allocation in the octahedral position in smectite were investigated (Madejová et al., 2011). The IR spectra were measured in the middle-infrared region (4000-380 cm$^{-1}$) with a Perkin Elmer FT-IR 2000 device. The measurements were carried out in transmission mode using KBr pellets with two different weights (0.5 mg and 3 mg in 200 mg of KBr) for each sample.

**Thermal analysis**

Thermogravimetric and mass spectrometric analysis (TG-MS) was used as additional diagnostic tool particularly for the investigation of the dehydration and dehydroxylation characteristics of the smectite, the latter particularly for the analysis of the cis-/trans-vacancy character of its octahedral sheet (Emmerich, 2011). The measurements were carried out with a thermobalance Mettler-Toledo TGA/SDTA851°. With the coupled mass spectrometer Balzers ThermoStar GSD 300 T the evolved water, CO$_2$ and SO$_2$ were investigated as a part of the mineral composition analysis. 110 mg of each sample was thermally analysed in a platinum crucible between 25-1000 °C (heating rate 10 °C/min) in a dry and CO$_2$-free airflow atmosphere (50 mL/min).

**Cation exchange capacity, leachable cations and pore water chemistry**

The CEC of the samples was determined using the complexes of copper (II) with triethylenetetramine (Meier & Kahr, 1999). The CEC should be comparable with the amount of exchangeable cations that entered the exchanging solution. However, this amount of exchangeable cations is not only represented by the interlayer cations, but also includes the dissolved cations in the pore water (including the added APW) and additionally, the cations from the soluble minerals dissolved during the exchange procedure. Therefore, the term “amount of exchangeable cations” was replaced here with the “amount of leachable cations” (ALC). The ALC was determined by the analysis of cation concentrations ($\text{Na}^+$, $\text{K}^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$) in the exchanging solutions after CEC measurement using atomic absorption spectrometry (AAS; device Perkin Elmer AAnalyst400). The chemistry of the pore water
itself was determined by three times washing 2 g of each sample (in replicates) in 15 mL methanol. The suspension was centrifuged and the supernatant decanted and analysed by AAS.

3.3.2 Physical and physicochemical properties

Specific surface area determination by gas adsorption

The SSA represents ideally the external surfaces of crystals excluding the interlayers of sheet silicates but is for bentonites also influenced by the microporosity (Kaufhold et al., 2010b). The SSA of the samples (300-700 mg) was determined by N\textsubscript{2} adsorption using a 11-point BET method (Brunauer et al., 1938). The adsorption isotherm measurements were carried out with a Quantachrome Autosorb-1MP surface area analyser (N\textsubscript{2} relative pressure p/p\textsubscript{0} 0.05-0.3).

Water vapour adsorption and water uptake under free swelling conditions

The ability of MX-80 to adsorb water vapour was determined in an atmosphere with a relative humidity (RH) of 75% (Keeling et al., 1980), which was achieved in a closed desiccator above an oversaturated NaCl solution (Madsen & Kahr, 1992). The sample weight was checked until constant weight (after ca. 6-9 weeks). The water content of such a treated sample (dried at 105 °C until weight constancy) (DIN ISO 11465, 1996) represents the level of the water vapour adsorption ability (WVAA).

The uptake capacity for liquid water under free swelling conditions was determined with the Enslin-Neff technique (DIN 18132, 1995; Kaufhold et al., 2010a). About 85 mg of each sample (particles <400 \textmu m) was used for the analysis. The water-uptake capacity (WUC) was related to the initial dry weight of the bentonite, taking into account the separately determined initial water content. The influence of evaporation during the measurements was eliminated by subtracting the evaporation determined in a separate Enslin-Neff apparatus filled with milled quartz.

To investigate the possible influence of heating on the gas adsorption behaviour of the bentonite (smectite aggregation/cementation, Couture effect), the SSA and WVAA were measured on selected samples again after remoulding. It is expected that the shearing in excess of water will break up the aggregates. The remoulding was carried out by mixing a certain amount of the differently treated bentonite (appr. 2 g) with deionized water and mechanically shearing with a pestle to form a homogeneous paste without lumps. After air-drying at ambient conditions, the samples were crushed in an agate mortar and homogenized.
3.4 Results

3.4.1 Mineralogical characterization

The mineral composition of the pristine and the thermally treated MX-80 is shown in Tab. 3-1. The bentonite experienced some slight changes in mineral composition during the thermal treatment. The gypsum content in the pristine material was $1.0 \pm 0.3$ wt.\% and did not change in the samples stored at temperatures below $105 \, ^\circ C$. No gypsum was found in the samples stored at $T>65 \, ^\circ C$ due to its dehydration and simultaneous bassanite formation. The calcite content in the pristine and treated MX-80 varies between $0.5-1.0 \pm 0.3$ wt.\%. However, the ambiguous tendency of its decrease with temperature borders the line of the analytical error. No amorphous silica was detected by FT-IR analysis (Fig. 3-3a, b).

![IR transmission spectra of MX-80 stored for 12 months at 50-150 °C. No band of amorphous silica at appr. 1090 cm$^{-1}$ was observed](image)
The smectite content seems to be slightly reduced over time regardless of treatment temperature. The sum of mica and mica-type layers/collapsed smectite layers showed a weak opposite tendency (Fig. 3-4a, b).

![Diagram of smectite content and Mica/S.c.l. content](image)

Fig. 3-4 Development of (a) the smectite content and (b) the sum of mica and mica-type layers/collapsed smectite layers (Mica/S.c.l.) in thermally treated MX-80 over time (NT…pristine MX-80)

However, this increase is in the range of measurement error as well as additionally influenced by the heterogeneity of the pristine MX-80 and therefore rather ambiguous. The coefficient of variation (CV) in the basal spacing was determined for two specific samples to proof this increase of the content of mica-type layers as a tendency of illitization, which would be probably connected with the formation of interstratified illite/smectite (I/S). The CV of the pristine material was 0.2. For the sample with the highest content of mica and mica-type layers/collapsed smectite, which was the sample heated at 120 °C for 12 months, a CV of 0.38 was calculated. This insignificant increase does not indicate illitization. The slight increase of the MLC from 0.27-0.28 for samples heated up to 3 months to values of 0.29 – 0.30 for longer heated samples seemed to show the transformation of the smectite into a higher-charged form (Tab. 3-3). However, considering the measurement error of 6-13% (Lagaly & Weiss, 1969) all measured changes of MLC lay within the measurement error. The thermal analyses revealed for bentonites with higher saturation degree S_r=1 and 0.75 stored at 50 and 65 °C, resp., a shoulder at appr. 140 °C in their dehydration curves (Fig. 3-5a). The dehydroxylation curves showed an unchanged cis-/trans-vacant character of the smectite in all samples (Fig. 3-5b).
Tab. 3-3 The changes of the smectite mean layer charge (MLC). All changes of the MLC after heating MX-80 over time are ambiguous when considering the measurement error (6-13%; Lagaly & Weiss, 1969)

<table>
<thead>
<tr>
<th>MLC (±0.02)</th>
<th>Months</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>25 °C</td>
<td>0.28</td>
</tr>
<tr>
<td>50 °C</td>
<td>-</td>
</tr>
<tr>
<td>65 °C</td>
<td>-</td>
</tr>
<tr>
<td>105 °C</td>
<td>-</td>
</tr>
<tr>
<td>120 °C</td>
<td>-</td>
</tr>
<tr>
<td>150 °C</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 3-5 Mass spectrometry curves of the thermally released H2O from the pristine (curve 0) and MX-80 treated for 12 months at 50 °C (1), 65 °C (2), 105 °C (3), 120 °C (4), and 150 °C (5). A second dehydration shoulder evolved in the dehydration curves of the samples with higher saturation degree (1, 2) at a temperature of appr. 140 °C (a). The dehydroxylation curves (b) showed the predominant cis-vacant character of the octahedral layer in the dioctahedral smectite. The ratio of trans-vacant octahedral domains was low and stayed independent from the thermal treatment.

No change in the basal distances (17.0 Å) of the smectite saturated with EG was observed (Fig. 3-6). The small shift of the basal (00l) spacing of smectite from pristine 12.3 Å towards 12.5 Å would indicate a partial replacement of interlayer Na⁺ by bivalent cations. However, these measurements were not carried out under controlled relative humidity and are therefore not entirely unambiguous.
Fig. 3-6 Diffraction patterns showing the basal spacing of smectite in the pristine MX-80 (black) and heated at 150 °C for 18 months (red). The small increase was caused by partly exchange with bivalent cations. The basal spacing was similar after saturation with EG (green and blue curve resp.)

Cation exchange capacity, leachable cations and pore water chemistry

No significant changes in the CEC were observed for samples stored at temperatures up to 120 °C. A slight reduction seemed to occur after 6 months of heating. By longer heating, the CEC increased and even exceeded the value of the pristine material. But, these variations lay within the measurement error and were also influenced by the heterogeneity of the MX-80. However, the CEC of the MX-80 samples stored at T=150 °C showed a distinct decrease in CEC of appr. 10% (Tab. 3-4, Fig. 3-7a).
Tab. 3-4 Cation exchange capacity (CEC), amount of leachable cations (ALC) and concentration of Na⁺ in the pore water (PW) of the pristine and thermally treated MX-80. The concentration of leachable Ca²⁺ was overdetermined due to the dissolved water-soluble Ca-phases. The concentrations of Mg²⁺, K⁺ and Ca²⁺ in the PW are below the detection limit.

<table>
<thead>
<tr>
<th>CEC</th>
<th>ALC</th>
<th>PW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na⁺</td>
<td>K⁺</td>
</tr>
<tr>
<td></td>
<td>cmol(+)/kg</td>
<td></td>
</tr>
<tr>
<td>MX-80 ESDRED &quot;E&quot;</td>
<td>84</td>
<td>57 ± 1</td>
</tr>
<tr>
<td>3 months</td>
<td>50 °C</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>65 °C</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>105 °C</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>120 °C</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>150 °C</td>
<td>82</td>
</tr>
<tr>
<td>6 months</td>
<td>50 °C</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>65 °C</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>105 °C</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>120 °C</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>150 °C</td>
<td>77</td>
</tr>
<tr>
<td>12 months</td>
<td>50 °C</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>65 °C</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>105 °C</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>120 °C</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>150 °C</td>
<td>77</td>
</tr>
<tr>
<td>18 months</td>
<td>50 °C</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>65 °C</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>105 °C</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>120 °C</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>150 °C</td>
<td>79</td>
</tr>
</tbody>
</table>

No clear trends in the leachable Na⁺, K⁺, Mg²⁺, and Ca²⁺ concentrations with treatment time and temperature could be observed. The amount of leachable Na⁺ of the bentonite MX-80 is, as expected, the highest in comparison with the other cations (57 ± 4 cmol(+)/kg in pristine MX-80; Tab. 3-4, Fig. 3-7b). However, considering the measurement error, a slight decrease could be observed for samples stored at 150 °C and at 120 °C for 18 months, which is similar to the trend in CEC.

Variation in the concentrations of leachable cations was influenced by the amount of added APW. In the samples with higher saturation degrees, the higher amount of added Mg²⁺ was mirrored in the higher amount of leachable Mg²⁺ (Tab. 3-4, Fig. 3-7c). The amount of leachable Ca²⁺, instead, seemed...
to be more dependent on the dissolved Ca\textsuperscript{2+} from the soluble Ca-phases. The dissolution of calcite and gypsum/bassanite is a known effect that occurs during CEC determination when using complexes of Cu- triethylenetetramine (Dohrmann & Kaufhold, 2010). The concentration of leachable Ca\textsuperscript{2+} of appr. 30 cmol(+)/kg is similar for all samples and originates from the dissolution of calcite and gypsum in the pristine material during the CEC analysis.

![Graphs](image)

**Fig. 3-7** Development of the CEC (a), the amount of leachable Na\textsuperscript{+} (b) and Mg\textsuperscript{2+} (c) of the thermally treated MX-80 over time (NT…pristine MX-80). The decrease of the CEC and the amount of leachable Na\textsuperscript{+} of samples heated up to 120 °C were within the error of the measurements (±2 and ±3 cmol(+)/kg respectively). The amount of the leachable Mg\textsuperscript{2+} depended on the added amount of the artificial pore water.

The major cation in the pore water of the MX-80 Na-bentonite was as expected Na\textsuperscript{+}. The content in the initial pore water of the pristine MX-80 was 1.8 ± 0.3 cmol(+)/kg. The concentration of Na\textsuperscript{+} in the pore water decreases from appr. 9 to 1 cmol(+)/kg. The values of K\textsuperscript{+}, Mg\textsuperscript{2+} and Ca\textsuperscript{2+} in the pore water of both, heated and pristine bentonite, were below the limit of detection by AAS (Tab. 3-4; compare with Tab. 3-1).
3.4.2 Physical and physicochemical properties

Specific surface area

The specific surface area (SSA) of MX-80 decreased with increasing temperature over time (Tab. 3-5, Fig. 3-8a). The SSA of the pristine material (33 m²/g) dropped by more than 50% to 15 m²/g of the material stored at 150 °C for 18 months. The samples stored at other temperatures followed a similar trend. Even after remoulding, none of the samples reached the SSA values of the pristine material (Tab. 3-5, Fig. 3-8b). Only the SSA of samples stored at 120 °C for 12 and 18 months showed a clear trend of recovery reaching the values of samples heated for 3 and 6 months. Rather a tendency of a decreasing SSA was observed for samples stored at 50 °C.

Tab. 3-5 The specific surface area (SSA) of thermally treated MX-80 before and after remoulding determined by N₂-BET

<table>
<thead>
<tr>
<th>SSA [m²/g] ± 2%</th>
<th>SSA [m²/g] ± 2%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MX-80 ESDRED &quot;E&quot;</strong></td>
<td>33.1</td>
</tr>
<tr>
<td><strong>3 months</strong></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>28.9</td>
</tr>
<tr>
<td>65 °C</td>
<td>26.7</td>
</tr>
<tr>
<td>105 °C</td>
<td>24.0</td>
</tr>
<tr>
<td>120 °C</td>
<td>22.8</td>
</tr>
<tr>
<td>150 °C</td>
<td>16.8</td>
</tr>
<tr>
<td><strong>6 months</strong></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>30.6</td>
</tr>
<tr>
<td>65 °C</td>
<td>29.0</td>
</tr>
<tr>
<td>105 °C</td>
<td>22.1</td>
</tr>
<tr>
<td>120 °C</td>
<td>23.9</td>
</tr>
<tr>
<td>150 °C</td>
<td>17.7</td>
</tr>
<tr>
<td><strong>Remoulded material</strong></td>
<td></td>
</tr>
<tr>
<td><strong>3 months</strong></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>24.8</td>
</tr>
<tr>
<td>120 °C</td>
<td>23.9</td>
</tr>
<tr>
<td><strong>6 months</strong></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>16.3</td>
</tr>
<tr>
<td>120 °C</td>
<td>21.3</td>
</tr>
<tr>
<td><strong>12 months</strong></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>23.6</td>
</tr>
<tr>
<td>65 °C</td>
<td>23.3</td>
</tr>
<tr>
<td>105 °C</td>
<td>20.8</td>
</tr>
<tr>
<td>120 °C</td>
<td>14.9</td>
</tr>
<tr>
<td>150 °C</td>
<td>14.5</td>
</tr>
<tr>
<td><strong>18 months</strong></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>25.9</td>
</tr>
<tr>
<td>65 °C</td>
<td>24.8</td>
</tr>
<tr>
<td>105 °C</td>
<td>20.4</td>
</tr>
<tr>
<td>120 °C</td>
<td>15.0</td>
</tr>
<tr>
<td>150 °C</td>
<td>14.8</td>
</tr>
<tr>
<td><strong>12 months</strong></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>19.8</td>
</tr>
<tr>
<td>120 °C</td>
<td>23.2</td>
</tr>
<tr>
<td><strong>18 months</strong></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>29.3</td>
</tr>
<tr>
<td>120 °C</td>
<td>25.2</td>
</tr>
</tbody>
</table>
Water vapour adsorption

The water vapour adsorption ability (WVAA) of the pristine MX-80 stored at 75% RH atmosphere was $17 \pm 0.3$ wt.%. This value did not change up to 105 °C (Tab. 3-6, Fig. 3-9a). The WVAA decreased over time for MX-80 thermally treated at T>105 °C to values of $13-12 \pm 0.3$ wt.%. The measurements of the remoulded samples showed a clear recovery of the WVAA reaching the value of the pristine material (Fig. 3-9b).
Tab. 3-6 The water vapour adsorption ability at 75% relative humidity (WVAA) of thermally treated MX-80 before and after remoulding

<table>
<thead>
<tr>
<th></th>
<th>WVAA [wt. %]</th>
<th></th>
<th>WVAA [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MX-80 ESDRED &quot;E&quot;</strong></td>
<td></td>
<td><strong>3 months</strong></td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>16.7</td>
<td>50 °C</td>
<td>16.5</td>
</tr>
<tr>
<td>65 °C</td>
<td>16.5</td>
<td>65 °C</td>
<td>16.5</td>
</tr>
<tr>
<td>105 °C</td>
<td>16.1</td>
<td>105 °C</td>
<td>15.9</td>
</tr>
<tr>
<td>120 °C</td>
<td>13.4</td>
<td>120 °C</td>
<td>12.4</td>
</tr>
<tr>
<td>150 °C</td>
<td>12.6</td>
<td>150 °C</td>
<td>12.0</td>
</tr>
<tr>
<td><strong>6 months</strong></td>
<td></td>
<td>12 months</td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>16.6</td>
<td>50 °C</td>
<td>16.8</td>
</tr>
<tr>
<td>65 °C</td>
<td>16.5</td>
<td>65 °C</td>
<td>16.8</td>
</tr>
<tr>
<td>105 °C</td>
<td>16.2</td>
<td>105 °C</td>
<td>16.3</td>
</tr>
<tr>
<td>120 °C</td>
<td>13.2</td>
<td>120 °C</td>
<td>12.8</td>
</tr>
<tr>
<td>150 °C</td>
<td>12.3</td>
<td>150 °C</td>
<td>12.2</td>
</tr>
<tr>
<td><strong>Remoulded material</strong></td>
<td></td>
<td>18 months</td>
<td></td>
</tr>
<tr>
<td>3 months</td>
<td>16.8</td>
<td>50 °C</td>
<td>16.8</td>
</tr>
<tr>
<td>12 months</td>
<td>15.8</td>
<td>50 °C</td>
<td>15.5</td>
</tr>
<tr>
<td><strong>6 months</strong></td>
<td>16.8</td>
<td>120 °C</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Fig. 3-9 Development of the water vapour adsorption ability at 75% relative humidity (WVAA) of thermally treated MX-80 over time (a) and (b) after remoulding of selected samples (r…remoulded samples, NT…pristine MX-80)

**Water uptake under free swelling conditions**

The WUC of the heated samples did not change up to 105 °C. Even taking into account that the variations of the WUC values lay within the measurement error of about 25%, a tendency of decrease
with time could be observed for samples heated at $T \geq 105 °C$ for more than 12 months (Tab. 3-7, Fig. 3-10).

Tab. 3-7 The water uptake of thermally treated MX-80 under free swelling conditions

<table>
<thead>
<tr>
<th></th>
<th>Water uptake after 24 h [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MX-80 ESDRED &quot;E&quot;</strong></td>
<td></td>
</tr>
<tr>
<td>3 months</td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>781%</td>
</tr>
<tr>
<td>65 °C</td>
<td>725%</td>
</tr>
<tr>
<td>105 °C</td>
<td>781%</td>
</tr>
<tr>
<td>120 °C</td>
<td>650%</td>
</tr>
<tr>
<td>150 °C</td>
<td>613%</td>
</tr>
<tr>
<td>6 months</td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>688%</td>
</tr>
<tr>
<td>65 °C</td>
<td>775%</td>
</tr>
<tr>
<td>105 °C</td>
<td>638%</td>
</tr>
<tr>
<td>120 °C</td>
<td>706%</td>
</tr>
<tr>
<td>150 °C</td>
<td>631%</td>
</tr>
<tr>
<td>12 months</td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>688%</td>
</tr>
<tr>
<td>65 °C</td>
<td>662%</td>
</tr>
<tr>
<td>105 °C</td>
<td>709%</td>
</tr>
<tr>
<td>120 °C</td>
<td>627%</td>
</tr>
<tr>
<td>150 °C</td>
<td>566%</td>
</tr>
<tr>
<td>18 months</td>
<td></td>
</tr>
<tr>
<td>50 °C</td>
<td>606%</td>
</tr>
<tr>
<td>65 °C</td>
<td>606%</td>
</tr>
<tr>
<td>105 °C</td>
<td>488%</td>
</tr>
<tr>
<td>120 °C</td>
<td>463%</td>
</tr>
<tr>
<td>150 °C</td>
<td>463%</td>
</tr>
</tbody>
</table>

Fig. 3-10 Development of the water-uptake capacity (WUC) of thermally treated MX-80 over time (NT...pristine MX-80)
3.5 Discussion

The analysis of the Na-bentonite MX-80 ESDRED “E” treated under near-field thermal and saturation conditions in a closed system showed an overall good stability of its mineral composition and physicochemical properties over the 18-months test period. Elevated temperature (≥105 °C) causes some minor changes.

The smectite content seems to be slightly reduced over time regardless of treatment temperature. However, this decrease is in the range of measurement error as well as additionally influenced by the heterogeneity of the pristine MX-80 and therefore rather ambiguous. Interestingly, the sum of mica and mica-type layers/collapsed smectite layers showed a weak opposite tendency (Fig. 3-4a, b). These changes could possibly indicate an initial illitization, which would be probably connected with the formation of interstratified illite/smectite (I/S). However, the insignificant increase of the coefficient of variation (CV) in the basal spacing from 0.2 of the pristine material to 0.38 of the sample with the highest content of mica and mica-type layers/collapsed smectite does not reflect a formation of interstratified I/S. The slight increase of the MLC from 0.28 to 0.30 for longer heated samples reflects more likely the formation of more highly charged smectite, rather than the formation of illite. In contrast, a very weak decrease of the MLC of smectite from initial 0.35 to 0.33 ± 0.01 was found in the HEATER experiment (Plötze et al., 2007). However, all these insignificant changes lie within the measurement error. Nevertheless, significant mineral changes in MX-80 were predicted by modelling its reaction with a representative geological fluid from Callovo-Oxfordian (COX) formation (Gaucher et al., 2006) under repository thermal conditions (T=100 °C) (Montes-H et al., 2005; Marty et al., 2010). A formation of saponite, vermiculite, illite, and chlorite by simultaneously decreasing content of smectite within 10’000 years was described.

The CEC is one of the most valuable properties for assessing the radionuclide retention of bentonite. Therefore, bentonite alteration connected with changes in CEC is an important process to monitor. A weak increase of the CEC towards the heating source was observed in the in-situ ABM and LOT experiments (Nagra, 2011; Svensson et al., 2011, Olsson & Karmland, 2011). The investigation of long-term heated samples in an open system showed after an initial decrease of the CEC within one year a slight increase by further heating at temperatures >120 °C (Valter & Plötze, 2010). The tendency of CEC increase over time after an initial decrease was also observed in the presented work. However, the measured CEC variations are close to the analytical error of the method in all these experiments. In contrast, in the presented work the CEC of the samples stored above the critical temperature of 120 °C decreases non-ambiguously. The same observation was reported by Gómez-Espina & Villar (2010). This decrease in CEC cannot be explained with the measured changes in
Chapter 3 Bentonite after storage at near field temperature

Olsson & Karnland (2011) reported in the LOT project a redistribution of Ca-sulphate phases. Their results indicate the dissolution of gypsum in the colder part of the bentonite barrier at the contact to the host rock with ground water and the precipitation of anhydrite in the bentonite close to the heater within almost six years. These observations could be reproduced also by modelling (Itälä & Olin, 2011). In the closed systems of our experiment, such redistribution was excluded. Gypsum was dissolved in the samples with higher saturation degrees $S_r > 0.5$ at temperatures $T < 105$ °C. The Ca$^{2+}$ and Mg$^{2+}$ from the dissolved gypsum and from the added APW exchanged the Na$^+$ in the smectite interlayer. This is clearly visible in the dehydration curves of the bentonites in thermal analysis. The dehydration curves show a shoulder at appr. 140 °C, which corresponds to the release of the second water layer attached to the bivalent cations (Emmerich, 2011). In the samples stored at temperatures $>65$ °C gypsum dehydrated to bassanite but not to anhydrite. For this thermal decomposition probably higher temperatures or longer time are necessary.

The type of adsorbed and exchangeable cations influences such mechanical and physicochemical properties like plasticity and shear strength, water adsorption and swelling, specific surface area, microstructure and hydraulic conductivity. The amount of leachable Na$^+$ of the bentonite MX-80 is, as expected, the highest in comparison with the other cations (Tab. 3-4, Fig. 3-7b). The amount of leachable cations was influenced by the added amount of APW. The Na$^+$ in the bentonite was exchanged by the K$^+$, Mg$^{2+}$ and Ca$^{2+}$ particularly in the samples with higher saturation degree ($S_r=1-0.75$). Additionally, the Na$^+$ was partly exchanged by Ca$^{2+}$ from dissolved gypsum and calcite. Consequently, the concentration of Na$^+$ in the pore water in these samples is higher as the initial concentration (7-9 vs. 2 cmol(+)/kg, Tab. 3-4). The same cation exchange was observed in the LOT experiment (Olsson & Karnland, 2011; Itälä & Olin, 2011).

Generally, the specific surface area of Ca/Mg-bentonites is higher than that of Na-bentonites (Kaufhold et al., 2010b). This is in agreement with our findings. The samples with the higher Ca$^{2+}$/Mg$^{2+}$ content showed higher values of SSA. The SSA decreased by about 50% after thermal treatment with increasing temperature over time. A similar decrease of SSA was also observed in the ABM-project and the HEATER experiment (Nagra, 2011; Plötze, et al., 2007). The variations in SSA between the Ca/Mg- and Na-bentonite were explained with differences in their microporosity from the quasi-crystalline overlap region of smectite and the accessible area of the interlayer (Kaufhold et al. 2010b), i.e. the “roughness” of the smectite platelet edges. However, with increasing treatment temperature the SSA decreases as well for samples with higher amount of leachable Na$^+$. Therefore, additional effects on the microporosity have to be considered, e.g. dissolution and precipitation processes leading to aggregation effects. The influence of such effects was investigated.
by measurement of the SSA of some samples after remoulding. However, the changes in SSA after remoulding bordered the line of analytical error and did not show non-ambiguous trends (Tab. 3-5, Fig. 3-8b). None of the samples reached the SSA value of the pristine material. Only for samples stored at 120 °C for 12 and 18 months, a tendency of SSA recovery was observed reaching the values of samples heated over shorter time.

Swelling is a typical feature of bentonite when in contact with water in gaseous or liquid form. The amount of adsorbed water depends on the type of smectite, the layer charge density, and on the type of exchangeable cations in the interlayer (Laird, 1999; Kaufhold et al., 2010a). In addition, the water adsorption under free swelling conditions (WUC) is strongly affected by the microporosity of bentonite (Kaufhold et al., 2010a). The lower the amount of leachable Na⁺, the lower is the WUC (Kaufhold et al., 2010a). The WUC of the thermally treated MX-80 in the presented experiment decreased with increasing temperature over time and had a similar development as the SSA. This decrease could be observed especially for samples heated at $T \geq 105$ °C for more than 12 months (Tab. 3-7, Fig. 3-10). However, these samples have a higher content of leachable Na⁺ and consequently should have a higher WUC. The sole influence of the type of the interlayer cation could be thus excluded. The WUC of the thermally treated bentonite is, as the SSA, rather dependent on the bentonite aggregation and microstructure.

A link between the SSA and the WVAA has been observed previously by Kaufhold et al. (2010b). Both methods are based on gas adsorption. However, the adsorption mechanisms are rather different. In contrast to N₂, which will be adsorbed on external surfaces and micropores, the polar water molecules mainly hydrate the adsorbed cations. The WVAA is therefore strongly influenced by the type of these cations. However, at the applied relative humidity of 75% the difference in the water adsorption between Ca²⁺ and Na⁺ is not significant (Bérend et al., 1995; Cases et al., 1997; Plötze & Kahr, 2003). The presented results show in WVAA two plateaus independent from time with a significant drop at $T > 105$ °C (Fig. 3-9). A similar decrease of the WVAA of MX-80 (by appr. 20%) after its long-term heating in an open system at temperatures up to 200 °C was also described by Valter & Plötze (2010). The clear recovery of the WVAA reaching the value of the pristine material was observed for remoulded samples (Fig. 3-9b). This behaviour can be explained by cementing processes during thermal treatment, which “glue” the smectite platelets. The remoulding procedure breaks up the cemented platelets. The water molecules can enter the interlayer and hydrate the interlayer cations. The WVAA of the thermally treated bentonite is rather dependent on the bentonite aggregation and microstructure than caused by the so-called Couture effect, which describes an irreversibly reduced water uptake of bentonite after steam treatment at 250 °C (Couture, 1985).
3.6 Conclusions

The analysis of the Na-bentonite MX-80 treated under near-field thermal and saturation conditions in a closed system showed a high mineralogical stability over the 18-months test period. Only minor changes occurred at elevated temperature (≥105 °C): (i) The smectite content seems to be slightly reduced over time regardless of treatment temperature. However, this decrease is in the range of measurement error as well as additionally influenced by the heterogeneity of the pristine MX-80. Furthermore, the insignificant increase of the coefficient of variation in the basal spacing and of the MLC indicated more likely the formation of higher charged smectite, rather than of illite. Amorphous silica could also not be detected. (ii) The gypsum content did not change in samples stored at temperatures below 105 °C. At T≥105 °C gypsum dehydrated to bassanite. (iii) The calcite content showed a subtle tendency of decrease with temperature.

Whereas the mineralogical alterations are close to insignificance, considerable changes in physicochemical properties were observed: (i) The cation exchange capacity is one of the most valuable properties for assessing the radionuclide retention of bentonite. A very weak increase towards the heating source was observed in several in-situ experiments. In contrast, in our experiment the CEC decreased non-ambiguously for the samples stored above the critical temperature of 120 °C. (ii) A slight conversion from the sodium to an earth alkali form of the bentonite was observed. The Ca²⁺ and Mg²⁺ from the dissolved Ca-phases (gypsum, calcite) and from the added artificial pore water exchanged the Na⁺ in the smectite interlayer. The type of exchangeable cations as well as aggregation processes connected with dissolution/precipitation influenced physicochemical properties like water adsorption and swelling, specific surface area and microstructure. (iii) The SSA decreased by about 50% after thermal treatment with increasing temperature over time. (iv) The water uptake capacity under free swelling conditions decreased with increasing temperature over time especially for samples heated at T≥105 °C for more than 12 months. (v) The water vapour adsorption ability showed a significant drop at T=120 °C. The ability to recover by mechanical remoulding can be explained with cementing processes during the thermal treatment.

The observed alterations are mostly subtle. However, temperatures ≥120 °C had a remarkable negative influence on different properties of MX-80.

Acknowledgements

The presented work is part of the project “Mineralogical, geochemical and geotechnical characteristics of granular bentonite after storage at near-field relevant conditions (T, w)” within the ESDRED project and co-financed by the Swiss National Cooperative for the Disposal of Radioactive Waste (NAGRA)
and the European Community under the SP6 Program (contract number FI6W-CT-2004-508851). Hanspeter Weber from NAGRA is acknowledged for the coordination of the project. We acknowledge Urs Mäder (University Bern) for the calculation of the chemical composition and delivery of the recipe of the artificial pore water. Adrian Zweidler is thanked for designing the thermal treatment containers. The manuscript was kindly improved by Laurence Noel Warr and an anonymous reviewer.

References


4 Discrete geometry model of heat in granular bentonite barriers

Authors

M. Valter, A. Puzrin, M. Plötze

Publication

Status: Resubmitted for a re-review to Environmental Geotechnics on November 4, 2015

Abstract

The mineral engineered barrier in the planned repository for radioactive waste in Switzerland is being designed as a granular bentonite mixture. The infiltrating pore water from the (clayey) host rock will start to resaturate the granular barrier after its emplacement. Discrete structure of the mineral barrier requires more detailed analysis, because the porosity alone applied in the continuum approach cannot describe the heat transfer adequately. Towards this analysis, three granular size fractions have been arranged into square or hexagonal packings, and considered in the heat transfer model presented in this paper. The six different granular arrangements are set either in a planar or a cylindrical spatial system. A major feature of the approach is providing the modelled systems with an interstitial fluid of smoothly adjustable thermo-physical parameters, approximating variable water contents. Effective thermal conductivity of various systems is an important output of the model. Calculation of the temperature equilibrium period directly depends on this parameter and represents a step towards a solution for the reliable determination of the resaturation time scale. The validity of the modelled effective thermal conductivities was confirmed by laboratory experiments on real granular bentonite.

Keywords

Contaminated material; Fabric/structure of soils; Finite-element modelling

List of notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_c$</td>
<td>area of circles in a unit cell</td>
</tr>
<tr>
<td>$A_p$</td>
<td>area of a unit cell including interstices</td>
</tr>
<tr>
<td>$c_p$</td>
<td>heat capacity</td>
</tr>
<tr>
<td>$E_{SDRED}$</td>
<td>Engineering Studies and Demonstrations of Repository Designs</td>
</tr>
<tr>
<td>$E_{TC}$</td>
<td>effective thermal conductivity</td>
</tr>
<tr>
<td>$F_w$</td>
<td>weighing factor</td>
</tr>
<tr>
<td>$h_x$</td>
<td>hexagonal circle packing</td>
</tr>
<tr>
<td>$k$</td>
<td>thermal conductivity</td>
</tr>
<tr>
<td>$k_{LB}$</td>
<td>thermal conductivity lower bound</td>
</tr>
<tr>
<td>$k_{UB}$</td>
<td>thermal conductivity upper bound</td>
</tr>
<tr>
<td>$L$</td>
<td>total length of the heat transfer path</td>
</tr>
<tr>
<td>$q_x$</td>
<td>heat flux</td>
</tr>
<tr>
<td>$r$</td>
<td>radial distance or circle radius</td>
</tr>
<tr>
<td>$\rho$</td>
<td>bulk density</td>
</tr>
<tr>
<td>$\rho_d$</td>
<td>dry emplacement density</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>fluid density</td>
</tr>
<tr>
<td>$S_r$</td>
<td>saturation</td>
</tr>
<tr>
<td>$sq$</td>
<td>square circle packing</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$t_{eq}$</td>
<td>equilibrium period</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$x$</td>
<td>unit length</td>
</tr>
</tbody>
</table>
4.1 Introduction

A deep geological repository is a safe long-term option for the disposal of radioactive waste. The repository is projected as a complex of underground galleries, with a multi-barrier system consisting of engineered and natural barriers (host rock). The engineered barrier has two main functions: isolating the waste from the biosphere; and transferring the decay heat from the waste into the host rock (Nagra, 2002). In a repository for spent fuel and high-level waste, a substantial part of the engineered barrier is the bentonite backfill. Pre-compressed bentonite blocks filling the annulus between the waste canister and the surrounding host rock are planned in the repository designs of many countries, such as Sweden, Finland, France or Spain (Berkeley Lab, 2006). In the Swiss concept, a granular bentonite backfill is being considered instead of bentonite blocks.

Granular bentonite is designed as a mixture of dry pre-compressed quasi-spherical pellets (about 80% by volume) and bentonite powder (about 20% by volume) with a water content below 10 wt. % (Nagra, 2002). Dry bulk density of pellets (>2000 kg/m³) is comparable to the bulk density of the bentonite blocks (Plötz and Weber, 2007), while the dry emplacement density of the mixture is required to be >1500 kg/m³ (De Bock et al., 2009). The loose granular mixture has a non-linear character, which is common for all granular materials. Physical laws applying to solids, liquids or gases cannot satisfactorily describe the entire macroscopic behaviour of a granular body (Hinrichsen and Wolf, 2004). This non-linearity is, of course, translated into the mechanisms of the heat transfer. Unlike in coherent solid materials, heat may be transferred in granular materials by means of radiation, convection and conduction; the last contributing most significantly to the heat transfer (Argento and Bouvard, 1996). The temperature field consequently differs in granular and continuous materials, assuming the same boundary conditions.

Fourier’s law of heat conduction is a good approximation of the heat transfer in most materials. It states that the heat flux is determined by the temperature gradient and thermal conductivity of the medium. Fourier’s law when adapted to the heat transfer in granular materials contains a modified thermal conductivity parameter applicable to the whole granular body, including solid entities with fluids or vacuum in the interstices. This parameter is the effective thermal conductivity (ETC; Massoudi, 2006), and depends on several variables, such as the thermal conductivity of concerned phases, porosity, size and shape of grains, the number of contacts per unit volume or packing geometry (Aichlmayr and Kulacki, 2006; Buyevich, 1974; Löf and Hawley, 1948). Heat is transferred both by the solids and the interstitial fluid if the solid-fluid conductivity ratio is equal to about one. When the ratio starts to increase, the heat conduction is gradually adopted by solids, and vice versa (Bahrami et al., 2006; Gonzo, 2002). With an increasing number of particle sizes, there is an increase in the number of particle contacts, with a simultaneous enlargement of the total contact area per unit volume.
In this way, heat has more opportunities to spread. Therefore, the ETC of an n-sized granular system is expected to be higher than that of a mono-sized system (Dias et al., 2007; Yun and Santamarina, 2008). The geometry of the particle arrangement in granular systems also determines the effectiveness of heat conduction. Dense packing and random packing will produce different coordination numbers and hence different heat-flux vectors. The variability of the particle sizes and geometry of packing are closely associated with porosity, which directly determines the proportion of the fluid (or vacuum) in the system. The role of the fluid thermal conductivity can be intensified or attenuated depending on the system porosity and its spatial distribution (Augier et al., 2010; Massoudi, 2006).

The main mechanism governing thermal evolution in the dry granular bentonite barrier is heat conduction, with a certain contribution of the radiative heat in the air gaps (Sato et al., 1998; Senger and Ewing, 2008). Heat conduction becomes the sole heat transfer mode upon water entering the system. Namely, heat convection contributing substantially to the heat transfer in highly porous environments with a high hydraulic conductivity like gravels and sands, will be completely absent (Wagner, 2013). The heat conduction exclusiveness inheres in the enlargement of the bentonite volume proportion by its absorption of humidity – bentonite swelling. The swelling actually takes place due to montmorillonite – a swelling clay mineral abundantly contained in bentonite (Bergaya and Lagaly, 2006). Owing to the swelling of bentonite, the granular backfill will turn into a single solid block through its resaturation by the pore water from the surrounding host rock. The swelling of bentonite will at the same time lead to a rapid decrease of the gas and hydraulic permeability of the backfill because the overall (macro)porosity will be reduced to minimum (Johnson et al., 2002; Wagner, 2013). This mechanism will also ensure the necessary sealing performance of the originally granular bentonite (Nagra, 2002).

Simultaneously, the temperature in the barrier will decrease with the decreasing activity of the nuclear waste, holding the water front at a distance through generated heat. The air-water borderline will shift towards the direction of the canister until the water front reaches its surface and the canister corrosion commences. The resaturation phase under conditions expected in the planned repository in Switzerland is estimated to take about a hundred to several hundreds of years (Nagra, 2002). It is expected that part of the bentonite barrier in the vicinity of canisters will still remain granular and loose for the greatest part of this period. The entire heat transfer will thus be determined by the non-linear character of the granular bentonite.

The resaturation period, calculated by means of continuum mechanics, is a rather rough estimation and needs to be specified more reliably, in order to assess the start of the canister corrosion with greater certainty. Continuum mechanics is unfortunately insufficient for an approximation of the heat transfer in such a non-linear system. The packed structure of the granular bentonite requires a more detailed
The goal of this study is to improve understanding of the heat transfer in the granular bentonite by means of discrete geometry modelling and to help specify the resaturation period more reliably. Towards this goal, a finite element model was developed, which enables the quantification of different heat transport and thermodynamic parameters of variably saturated granular bentonite. Additionally, the parameters of granular mixtures with different void fractions are compared, which can help to adjust the pellet size distribution in the granular bentonite to reach the best heat transfer characteristics.

In this paper, heat transfer in granular bentonite is presented on example of three metastable states. Bentonite is modelled as a completely dry, a partially saturated and a fully saturated system. All three states can be found within the bentonite backfill at any time point between the backfilling the gallery and the water front reaching the canister (an interval of dozens of years of resaturation). Simultaneously, all three states are also expected to occur in any spatial point within the bentonite barrier annulus (an interval of 0.725 m; Senger and Ewing, 2008).

The bentonite swelling is not included in the presented simulation. Therefore, porosity of the system remains constant regardless of being dry or fully saturated. Interstices among solids are filled with fluid of variable thermo-physical parameters approximating variable water contents. The fluid properties can be smoothly adjusted to those of dry air, humid air or liquid water.

The model is intended for further development. It represents a base for a more advanced solution which will also consider the bentonite swelling (described in 6.7 Outlook section). The output of the presented model should underline the differences between the various granular mixtures and the influence of water on the heat transfer. The model is also designed to be able to calculate the equilibrium periods necessary to reach a uniform temperature field in the entire system which represents an important step towards the solution of the granular barrier resaturation time-scale problem.

4.2 Physics

4.2.1 Constitutive relations

Heat is a physical phenomenon when thermal energy is being transmitted, owing to the temperature difference between two boundaries. It is governed by the first law of thermodynamics: the principle of
energy conservation. Three modes of heat transfer are known: conduction; convection; and thermal radiation (e.g. Incropera et al., 2007; Kittel and Kroemer, 1980; Zemansky and Dittman, 1997).

Fourier’s law of thermal conduction is the basic equation quantifying conductive heat transfer in homogeneous systems. Under steady-state conditions, the heat flux \( q_x \) [W/m²] is proportional to the thermal conductivity \( k \) [W/(m*K)] and to the temperature gradient (a temperature change \( dT \) per unit length \( dx \) [K/m])

\[
q_x = -k \frac{dT}{dx}
\]  
(1)

The thermal conductivity is characteristic of every material and determines how fast heat can be transferred. While equation (1) describes the heat flow in homogeneous materials, it can also be applied to studying non-homogeneous systems containing a number of materials whose thermal conductivities differ significantly (e.g. in soil). In such a case it is necessary to define the effective thermal conductivity (ETC). The ETC is a function of the thermal conductivity and the surface radiative properties of the solids, and of the properties and volumetric fraction of the fluid in the interstices (Incropera et al., 2007). The ETC of a multiphase discrete system is limited by the weighted sum of its lower and upper bounds. The bounds are given by the actual thermal conductivities of concerned phases

\[
ETC = (1 - F_w)k_{LB} + F_wk_{UB}
\]  
(2)

with thermal conductivity of the lower bound \( k_{LB} \), upper bound \( k_{UB} \) and with a weighing factor \( F_w \) (Francl and Kingery, 1954; Grujicic et al., 2005).

Fourier’s law enables the calculation of the amount of energy transferred per unit time. To do this, the heat equation must be solved first. In the Cartesian coordinates, it states:

\[
\frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) = \rho c_p \frac{\partial T}{\partial t}
\]  
(3)

The heat equation is a relationship between a transport component and a thermodynamic component of the heat. The transport component describes how the temperature \( T \) [K] changes with the distance from a reference boundary \( x \) [m] in a material with a thermal conductivity \( k \) [W/(m*K)]. The thermodynamic component defines the time-dependent temperature change \( \frac{\partial T}{\partial t} \) in the material with a bulk density \( \rho \) [kg/m³] and a heat capacity \( c_p \) [J/(kg*K)].

The transport component of the heat equation has a different form in cylindrical coordinates. The transport component considers a radial distance of the analysed point \( r \) [m] from a reference boundary.
\[
\frac{1}{r} \frac{\partial}{\partial r} \left( kr \frac{\partial T}{\partial r} \right) = \rho c_p \frac{\partial T}{\partial t}
\]  \hspace{1cm} (4)

The solution of the heat equation is the temperature distribution in the system in space and time. In the Cartesian coordinates, the steady-state temperature distribution in a medium with a \( k = \text{constant} \) can be calculated using the following equation:

\[
T(x) = \left( T_{B,2} - T_{B,1} \right) \frac{x}{L} + T_{B,1}
\]  \hspace{1cm} (5)

where \( x \text{ [m]} \) is the distance of the studied point from a boundary with a constant temperature \( T_{B,1} \text{ [K]} \), \( L \text{ [m]} \) is the total length of the heat transfer path, and \( T_{B,2} \text{ [K]} \) the constant temperature at the second boundary, whereas \( T_{B,1} > T_{B,2} \). The steady-state temperature distribution equation for a cylindrical space has a logarithmic form:

\[
T(r) = \frac{T_{B,1} - T_{B,2}}{ln \left( \frac{r_1}{r_2} \right)} ln \left( \frac{r}{r_2} \right) + T_{B,2}
\]  \hspace{1cm} (6)

where \( r, r_1 \text{ and } r_2 \text{ [m]} \) are cylindrical coordinates of the studied point, and the inner and outer boundaries, respectively. Once the time-dependent temperature distribution is specified, the heat flux at any coordinate in the system can be calculated from Fourier’s law (Eq. 1; Incropera et al., 2007).

### 4.2.2 The simulation software

The model was generated in Comsol Multiphysics 5.0 software, which is an interactive finite element modelling platform for solving scientific and engineering problems. Comsol consists of a package of numerical analysis tools, based on partial differential equations. Its modular scheme is composed of a basic package and several optional modules (Comsol AB, 2014). The optional Heat Transfer module was used in this study, and the physics of the conductive heat transfer in solids and fluids was considered.

### 4.3 The model

#### 4.3.1 Geometry of the model

The basic structural components of the two-dimensional model were solid circles of different sizes, representing bentonite pellets in the real granular bentonite barrier. The surface of the real bentonite pellets is fairly irregular. Their general outline is, however, variably oval, roughly rounded and quasi-
spherical (Plötze and Weber, 2007). The shape of a circle in the model was chosen as a simplification of the faceted surface of a real bentonite pellet. In order to accurately simulate the pellet shapes and randomness of the pellet arrangements would be necessary to implement special algorithms (e.g. Bagi, 2005; Mollon and Zhao, 2014), making the model inevitably more complex. Circles and their arrangement into two packings were used in order to keep the model as simple as possible, simultaneously reliably imitating the bentonite pellet system. The porosity of the real pellets was not considered in the model – circles were designed as portions of dense continuum. The spatial arrangement of circles conformed either to square or hexagonal packing (Fig. 4-1; Stephenson, 2005). The two packings were also a simplification of the real pellet arrangement in the granular bentonite.

![Fig. 4-1 (a) square and (b) hexagonal circle packing (Stephenson, 2005)](image)

The biggest circle has a radius of \( C1 = 0.25 \) cm (the first-order circle). The circle diameter is one tenth of the smallest dimension of a vessel used in a real laboratory experiment described later in this section. The selected size of the circle also corresponds to proportions of one pellet fraction in the real granular bentonite. The shapes and sizes (grain size up to 4 cm) of contained pellets vary in order to achieve as dense emplacement density as possible (De Bock *et al.*, 2009). To approximate the pellet size variation, interstices between the first-order circles were filled with circles of the second order \( (C2) \). The third-order circles \( (C3) \) fill the interstices amid circles of the first two orders. All circles are mutually tangential and do not overlap with each other.

The square packing could be constructed using basic trigonometric functions. The construction of the circles in the hexagonal packing required other mathematical tools. Descartes’ theorem was applied to determine the radii of \( C2 \) and \( C3 \) (Lagarias *et al.*, 2002). Once the dimensions of circles were known, the Cartesian coordinates of \( C2 \) and \( C3 \) could be specified by means of inverse trigonometric functions (Gianella, 2014, personal communication).
The circles were arranged into six unit cells: cornerstones of the discrete geometry (Fig. 4-2). The code name of each unit cell was based on the type of packing, and on the variety of the circle sizes. A 2sq contained circles of the first and second order in the square packing. A 3hx contained circles of all three orders in the hexagonal packing, etc.

Fig. 4-2 Unit cells with their codes used for construction of the model. Circles were positioned in square (sq) or hexagonal packing (hx)

The area occupied by circles in a unit cell evidently increases with increasing complexity of a unit cell. Simultaneously, differences between the area occupied by circles in the square and hexagonal packings diminish. The areal coverages of the unit cells thus start to resemble each other with increasing system complexity (Fig. 4-3).
Fig. 4-3 Normalized unit cell areas of the square and hexagonal packings increases with increasing complexity of a unit cell. The areal differences between the two packings simultaneously diminish. The normalized area is a ratio between the area of circles in a unit cell ($A_c$) and the whole area of a unit cell including interstices ($A_u$).

The unit cells were repeated in the x and y directions, to fill either a planar or a cylindrical space (Fig. 4-4). The model dimensions were based on a rectangle, with a width of 8 cm and a height of 5 cm (the inner dimensions of a vessel used in a real laboratory experiment with the same granular bentonite, as in the model; see 4 Laboratory measurements section; Valter and Plötze, 2013). The planar system had a height of 5 cm and a width of the C1 diameter to reduce computational costs (Fig. 4-4a). The cylindrical system was a 90° segment of an annulus (Fig. 4-4b). Its proportions (inner and outer radii: 3.621 cm and 8.621 cm, respectively) were analogous to the proportions of the bentonite annulus in an underground gallery of the planned repository (radius of the radioactive waste canister, 0.525 m; gallery radius, 1.25 m; Senger and Ewing, 2008). The small scale of the simulated systems dramatically reduces computation time while still allowing for conceptual modelling of the underground gallery.
Fig. 4-4 Two examples of (a) a planar and (b) a cylindrical system. All systems were composed of pellets (light grey circles) and fluid in the interstices (dark grey). Black squares at the top indicate the reference points for the calculation of the temperature equilibrium periods.

4.3.2 Parameters of subdomains

Solids

The model utilized properties of a pellet made from sodium bentonite MX-80 (Wyoming, AMCOL International Corp.). The bentonite powder was compressed and shaped into pellets of different sizes, out of which different granular mixtures were produced. The mixtures were tested as part of the ESDRED (Engineering Studies and Demonstrations of Repository Designs) project (De Bock et al., 2009; Plötze and Weber, 2007).

Several parameters of a dry bentonite pellet were used in the model. These are a bulk density of 2070 kg/m$^3$ (Plötze and Weber, 2007), a heat capacity of 964 J/(kg*K) (Senger and Ewing, 2008) and a thermal conductivity of 0.671 W/(m*K) (Kahr and Müller-von Moos, 1982). In the model, pellets were defined as rigid discrete portions of dense continuum with no porosity. The void fraction of the whole system was given by the type of unit cell. Values of the void fraction are just inverted values of the circle packing density (Tab. 4-1). The void fraction in the model represents an equivalent to the macroporosity (pores bigger than 50 nm; Rouquerol et al., 1994) between the pellets of the real granular bentonite. Real bentonite pellets, however, have their own meso- (pore size 50-2 nm) and
microporosity (pores smaller than 2 nm). The entire porosity of the real bentonite is therefore higher than the proportion of voids between rigid continuum portions in the model.

Tab. 4-1 Packing density (normalized volume of solids) and void fraction (normalized volume of void space, or porosity in the real bentonite) of the geometries and of the real granular bentonite MX-80

<table>
<thead>
<tr>
<th>geometry</th>
<th>1sq</th>
<th>2sq</th>
<th>3sq</th>
<th>1hx</th>
<th>2hx</th>
<th>3hx</th>
</tr>
</thead>
<tbody>
<tr>
<td>packing density</td>
<td>0.7854</td>
<td>0.9202</td>
<td>0.9569</td>
<td>0.9069</td>
<td>0.9503</td>
<td>0.9718</td>
</tr>
<tr>
<td>void fraction</td>
<td>0.2146</td>
<td>0.0798</td>
<td>0.0431</td>
<td>0.0931</td>
<td>0.0497</td>
<td>0.0282</td>
</tr>
</tbody>
</table>

Low-consolidated granular bentonite

<table>
<thead>
<tr>
<th>( \rho_b ) [kg/m(^3)]</th>
<th>1500</th>
<th>1478</th>
<th>1617</th>
<th>1701</th>
<th>1778</th>
</tr>
</thead>
<tbody>
<tr>
<td>packing density</td>
<td>0.5587</td>
<td>0.5504</td>
<td>0.6023</td>
<td>0.6334</td>
<td>0.6623</td>
</tr>
<tr>
<td>void fraction (porosity)</td>
<td>0.4413</td>
<td>0.4496</td>
<td>0.3977</td>
<td>0.3666</td>
<td>0.3377</td>
</tr>
</tbody>
</table>

High-consolidated bentonite

The fluid

Interstices were filled with a fluid of variable thermo-physical parameters to approximate different bentonite water contents. It was assumed that bentonite at the contact with canister accommodating hot radioactive waste is completely dry and it contains dry air in its interstices. Just opposite the canister, fully saturated bentonite in the vicinity of the host rock contains water in its pores (no bentonite swelling was considered in the model; see Introduction). Between these two limit states, a hypothetical steam-like fluid resides in the interstices of the modelled system, being not entirely dry air and not entirely liquid water.

The parameters of the interstitial fluid were characterized by linear functions with the saturation as a variable \( (S_r = 0 \rightarrow 1; \) Figures 4-5a–d). The functions were found for four parameters of the fluid required by Comsol: thermal conductivity; density; heat capacity; and ratio of specific heats (the ratio of the heat capacity at constant pressure to the heat capacity at constant volume \( (\)Kundu et al., 2012\( )\).

In these functions, one limit was given for the dry air, another for the liquid water. The functions represent a smooth interpolation between these two limiting states. Any point along the linear function displays properties of a steam-like fluid (non-dry air/non-liquid water).

The procedure is reminiscent of thermodynamic mixture theory. A logarithmic function describes the air-water mixing, as is evident from the equation for the total Gibbs energy of binary mixtures (Atkins and de Paula, 2014). For simplification, no thermodynamics of mixing was considered in the model. The logarithmic functions were substituted with linear functions.
Fig. 4-5 Parameters of the fluid were defined by linear functions of their dependence on the water content. Every parameter has two limits corresponding to liquid water \((S_r = 1)\) and dry air \((S_r = 0)\). The limits come from the Comsol’s database of material properties at \(T = 20 \, ^{\circ}\)C. Parametrization was calculated for: (a) fluid thermal conductivity; (b) density; (c) heat capacity; and (d) specific heat ratio.

A similar procedure was used to define a function for the saturation \((S_r = 0 \rightarrow 1)\) and temperature \((T = 50 \rightarrow 200 \, ^{\circ}\)C; Fig. 4-6). The model assumes that, like in the real bentonite, the water is still present at temperatures below 200 °C at atmospheric pressure (Colten-Bradley, 1987; Heller-Kallai, 2013).

Montmorillonite abundantly contained in bentonite MX-80 readily adsorbs liquid water into its interlayer. The thickness of the interlayer, or basal distance, increases with increasing amount of adsorbed water – montmorillonite swells (Bergaya and Lagaly, 2006). Water is held in the interlayer by the hydration energy of the interlayer cation. It is adsorbed as one or more individual hydration layer(s) (Sposito and Prost, 1982; Kaufhold et al., 2010). The number of hydration water layers is a function of the water vapour pressure, temperature, type of montmorillonite, its layer charge and its interlayer cation (Brigatti et al., 2006). Hydration and dehydration of the montmorillonite interlayer is thus managed by molecular forces. Therefore, no phase transition of liquid water to steam (boiling) or vice versa (condensation) is applicable in the bentonite system at any temperature.

The water movement during the isothermal bentonite resaturation can be satisfactorily described by means of the Fick’s second law of diffusion (Kröhn, 2006). This partial differential equation characterizes the relation between the change rate of (water) concentration at a point and the spatial variation of the (water) concentration at that point (Atkins and de Paula, 2014). For the non-isothermal conditions, a suitable solution is currently being elaborated (Kröhn, 2006). Therefore, a simple linear
dependence of the system saturation on temperature was used in the model (Fig. 4-6). Since the bentonite swelling is not considered, the hypothetical steam-like fluid fills the interstices among two limits of the dry air (at \( T = 200 \, ^{\circ}C \) or 473.15 K) and the liquid water (at \( T = 50 \, ^{\circ}C \) or 323.15 K).

![Saturation/temperature dependence](image)

Fig. 4-6 Function of the saturation dependence on temperature. The values at \( S_r = 1 \) and 0 are for the liquid water and dry air, respectively

### 4.3.3 Boundary conditions

A gallery in the planned Swiss repository for radioactive waste is projected as a line structure – a tunnel. A canister with radioactive waste is planned to be positioned in the centre of a gallery, along its horizontal axis (Nagra, 2002). Heat from the waste will be spread radially around the canister vertical cross-section. The layout of the disposal concept therefore enabled to solve the problem as a two-dimensional one. The 2D solving was also completely valid comparing to a 3D solution due to circles used as a simplification of the quasi-spherical shape of bentonite pellets (see 3.1 Geometry of the model section).

Physics of the heat transfer in solids and liquids was applied in the model. The heat transfer in liquids was only solved by means of the heat conduction, with no convection contribution (see 1 Introduction section).

The initial temperature of the system was 20 °C, which was increased to 50, 120 and 200 °C. The temperatures are related to the spent fuel and high-level waste. The temperature of 50 °C is relevant for the positions within the barrier at a distance from the canister. A temperature of 120 °C counts as critical for the mineral barrier: the favourable properties of bentonite start to deteriorate at this temperature (Sato et al., 1998; Senger and Ewing, 2008). A temperature of 200 °C was examined as a completely dry case (Heller-Kallai, 2013). The saturation of the fluid was a function of temperature, as described in the previous 3.2.2 The fluid section. A correlation overview of temperatures and saturations used in the model is in Tab. 4-2.
Tab. 4-2 Matrix of modelled temperatures at Temperature boundaries with corresponding saturations

<table>
<thead>
<tr>
<th>$T$ [°C]</th>
<th>$S_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>120</td>
<td>0.5</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
</tr>
</tbody>
</table>

The lower horizontal boundary in the planar system and the circular boundary of the smaller radius in the cylindrical system were set as Temperature boundaries (heaters; Tab. 4-2). The remaining three boundaries in the planar system and the circular boundary of the larger radius in the cylindrical system were Thermally insulated. A Thermally insulated boundary ensures that the modelled system is not additionally heated or cooled down by a source other than the heaters, like it would be, for instance, in case of a Constant temperature boundary or an Open boundary. A definite temperature would have to be specified at the Constant temperature boundary, whereas the temperature of the exterior would be required for an Open boundary (Comsol AB, 2014). The two straight boundaries in the cylindrical system were Symmetries.

4.3.4 Meshing and study settings

Physics-Controlled Triangular mesh with Normal element size was used. The problem was solved as a Time-Dependent study, with a Time Step of 172.8 s, which was one thousandth of the whole Time Range (172800 s = 48 hours). The study was computed with a Relative Tolerance of 0.0001. Other solver configurations remained in their default settings.

4.3.5 Post-processing

The heat flux, temperature gradient and heat capacity were derived from the model solutions using Surface Average utility. The values are spatially averaged over the entire system, including all domains for each solution in a dataset, taken at discrete time intervals over 48 hours. The averaging was necessary in order to numerically homogenize different heat transfer conditions in different parts of the discrete model, for the calculation of the average ETC, based on the proportionality between the heat fluxes and temperature gradients prescribed by Equation 1. The procedure used Automatic Integration Settings with Average as the dataset operation. The stability of the ETC values in time was validated.

The effective thermal conductivity was calculated from Fourier’s law, using values of the derived heat flux and the temperature gradient. Values of the effective thermal conductivity were compared with experimentally measured thermal conductivities of the granular bentonite (Plötze and Valter, 2011; Valter and Plötze, 2013).
The temperature-equilibrium period is an important parameter by means of which the temperature distribution in a system can be illustrated. The spatial dimension of the heat is expressed by means of a time dimension. It was derived from the 1D Point Graph of the temperature evolution in time. A point on the insulated boundary (opposite the heater boundary; Fig. 4-4) was used as the reference in all systems. The equilibrium period was a time after which the temperature in this point became equal to the temperature of the heater.

4.4 Laboratory measurements

The thermal conductivity of the granular bentonite mixture ‘E’ from the ESDRED project was analysed in two laboratories; one series was carried out in the ClayLab of the Institute for Geotechnical Engineering, ETH Zurich, in Switzerland and the other at the Institute for Applied Geophysics and Geothermal Energy, RWTH Aachen, in Germany. The granular mixture was composed of pellets whose properties are described in the 3.3.1 Solids section. Thermal conductivity was measured at room temperature with a half-space probe in the ClayLab (ISOMET 2114, Applied Precision Slovakia), and with a full-space probe at the RWTH (TK04, TeKa Germany). Both probes utilized the transient hot-wire technique (Assael et al., 2002). Analysed samples had various dry densities and water contents (Tab. 4-3). Samples analysed in the ClayLab were low-consolidated whereas those analysed in the RWTH were high-consolidated.

Tab. 4-3 Water content ($S_r$), dry emplacement density ($\rho_D$) and thermal conductivity ($k$) of the low-consolidated (measurements in the ClayLab Zurich) and high-consolidated granular sodium bentonite MX-80 ESDRED ‘E’ (measurements in the RWTH Aachen)

<table>
<thead>
<tr>
<th></th>
<th>$S_r$</th>
<th>$\rho_D$ [kg/m$^3$]</th>
<th>$k$ [W/(m*K)]</th>
<th>Measurement error [W/(m*K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClayLab</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(low-consolidated)</td>
<td>1.0</td>
<td>0.75</td>
<td>0.75</td>
<td>± 10%</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>1500</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td></td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td></td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>RWTH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(high-consolidated)</td>
<td>0.64</td>
<td>1478</td>
<td>0.74</td>
<td>± 0.05</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
<td>1617</td>
<td>0.70</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>1701</td>
<td>0.63</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>1778</td>
<td>0.55</td>
<td>0.02</td>
</tr>
</tbody>
</table>
4.5 Results

4.5.1 The model

Effective thermal conductivity

Different spatial systems have no influence on the ETC, which is equal for both planar and cylindrical systems (Fig. 4-7). On the other hand, the ETC of different packings varies, the hexagonal systems having generally a higher ETC than the square systems.

The system complexity plays a crucial role for the resulting ETC, giving a maximum difference of 40% between the dry 1sq and 3sq. The relative contrasts are gradually fading out upon increasing saturation/decreasing temperature, resulting in an almost identical ETC in all systems at $S_r = 1$ (50 °C). Nevertheless, the ETC never exceeds the value of the pellet thermal conductivity ($k = 0.671 \text{ W/(m*K)}$).

![Effective thermal conductivity](image)

**Fig. 4-7** Average ETCs of all systems during the 48-hour time range. The variable saturation corresponds to different temperatures (Tab. 4-2; Fig. 4-6)

Equilibrium period

The time taken to reach a uniform temperature field is longer in the cylindrical systems, being extended by 40% relative to the planar systems (Fig. 4-8). Differences between packings reach 20% in favour of the hexagonal systems, and diminish logarithmically with increasing geometrical complexity. Saturation accelerates the temperature equilibrium, causing an average 30% shortening between the same systems at $S_r = 0$ and 1.
Fig. 4-8 Equilibrium periods vary among spatial systems, packings, complexities and saturations/temperatures (Tab. 4-2, Fig. 4-6). Periods were calculated at the points situated just opposite the Heater boundaries (Fig. 4-4). Equations 3–6 are concerned with their calculation.

The ETC of different systems is plotted against normalized time to confirm the proportionality of the heat flux and temperature gradient during every Time Step; i.e. the independence of the modelled ETC on time (Fig. 4-9). Two dry and saturated systems (1sq and 1hx at $S_r = 0$ and 1) are shown. However the validity of the diagram in Fig. 4-9 holds for every system in a planar or cylindrical geometry.

Fig. 4-9 ETC time evolution of dry and saturated 1sq and 1hx systems. ETC of other systems likewise remain stable in time. The time scale on the x-axis is normalized in order to compare systems with different equilibrium periods.
**Specific heat capacity**

Specific heat capacity was only determined for the planar space. The heat capacities are unique for each system, as long as a system contains a certain level of saturation (Fig. 4-10); namely, the heat capacities of all dry systems are equal to the heat capacity of bentonite (964 J/(kg*K)). Under saturated conditions, the heat capacity increases with the proportion of humidity as a function of temperature (Fig. 4-6).

Different packings have variable heat capacities, which are higher in the square systems than in the equivalent hexagonal systems. At the same time, increasing geometrical complexity leads to a decrease in the porosity (Tab. 4-1) and thus in the heat capacity.

![Specific heat capacity graph](image)

Fig. 4-10 Heat capacity of all systems with various saturations/temperatures

**4.5.2 Comparison with laboratory measurements**

From the comparison of the modelled ETC with the experimentally measured thermal conductivity, it can be seen that the values correlate very well (Fig. 4-11). The influence of the geometrical complexity is most obvious under dry conditions. The simplest system, 1sq, has an ETC corresponding to the conductivity of the low-consolidated bentonite ($S_r = 0; T = 200 \, ^\circ C$). At the same saturation level, the ETC of the systems with the highest geometrical complexity is near the conductivity of the high-consolidated bentonite. The ETC of all systems at $S_r = 1$ (50 °C) is very similar, however, only in the range of the low-consolidated bentonite.
Chapter 4 Discrete geometry model of heat in granular bentonite barriers

Fig. 4-11 Measured (grey) and modelled (black) effective thermal conductivity (ETC). Dependency on geometries/saturation in the model reflects the consolidation/saturation of bentonite in the laboratory measurements.

From the trend diagram (Fig. 4-12) it is apparent that the modelled ETC converges into a value near the input bentonite thermal conductivity ($k = 0.671 \text{ W/(m*K)}$; Fig. 4-12). The experimental values increase above the level of the modelled ETC and their convergence point lies beyond the scope of this study.

Trends of the 1sq system and of the low-consolidated bentonite (two dashed lines) are similar along the whole $S_r$ span, whereas the trends of the 3hx system and of the high-consolidated bentonite (two solid lines) are only comparable up to about $S_r = 0.5$. 
Fig. 4-12 Trend lines of the modelled ETC and experimentally measured thermal conductivity. Thin and thick dashed lines represent the low-consolidated bentonite mixture and the simplest system (1sq), respectively. Thin and thick solid lines represent the high-consolidated bentonite mixture and the most complex system (3hx), respectively.

4.6 Discussion

Results are discussed according to different aspects of the heat transfer mechanisms. The spatial geometry, circle packings and geometric complexity are analysed with regard to dry systems \((S_r = 0; T = 200 \, ^\circ C)\), whereas the influence of humidity follows afterwards in a separate section.

4.6.1 Spatial geometry

The spatial shape of studied systems (Fig. 4-4) determines the heat transfer mechanisms, which are described by two different forms of heat equation (Eq. 4 and 5; Incropera et al., 2007). The equilibrium periods thus evolve differently (Fig. 4-8), unlike the ETC, which is equivalent in both spatial systems and remained time-independent (Fig. 4-7 and Fig. 4-9), confirming the validity of the ETC for representing the thermal conductivity of a discrete system.

Heat-transfer mechanisms in the planar system are relevant for the immediate vicinity of the canister with the heat-generating radioactive waste, whereas the cylindrical system is applicable to the larger scale of the entire repository gallery cross-section.

For the experimental measurement of the thermal conductivity, the cylindrical system is only adequate. The transient hot-wire technique utilized in the experimental analyses has a character of a line source from which the heat spreads into a semi-circular space of the analysed medium (Assael et al., 2002).
4.6.2 Circle packing

The type of packing (Fig. 4-1) is important in affecting the way heat is transferred. As suggested by their designations, the square and hexagonal packings have different coordination numbers and hence different void fractions (Tab. 4-1). An increase in the coordination number and a reduction of the void fraction causes an increased tortuosity, inflicting an improved thermal dispersion (Dias et al., 2007; Tavman, 1996; Zhang et al., 2011). The ETC of the hexagonal arrangements is thus larger than that of the square arrangements (Fig. 4-7; van Brakel and Heertjes, 1974; Epstein, 1989). A consequence of the higher heat-transfer effectiveness in hexagonal systems is their shortened equilibrium periods with regard to square systems (Fig. 4-8).

4.6.3 Geometric complexity

Effects of different packings are intensified with increasing geometric complexity (Figures 4-7 – 4-9). More particle sizes in a unit cell produce a decrease in the void fraction, a coordination number enlargement, more variability of contact angles and finally a further increase in the tortuosity (van Antwerpen et al., 2010). Heat can be transferred more effectively in this manner, which is mirrored by a higher ETC and shortened equilibrium periods in more complex systems.

Differences in the values of the ETC for dry square and hexagonal systems ($S_r = 0$) diminish considerably as the number of particle sizes in a unit cell increases (Fig. 4-7 and Fig. 4-11). The same observation is valid for the case of the equilibrium period (Fig. 4-8). This can be explained by the fact that a large amount of particle sizes in a unit cell provide a larger area for the heat to spread. Because the normalized area of the most complex 3sq and 3hx systems is almost identical as seen in Fig. 4-3, the heat fluxes in these two systems are very similar. Therefore, the relative differences between their ETC and equilibrium period at $S_r = 0$ are small. The close values of ETC in the dry 3sq and 3hx systems are related to their equivalent heat capacity which is discussed later.

4.6.4 Water content

The influence of the fluid and its properties on the heat transfer is huge. All systems saturated with liquid water ($S_r = 1$; $T = 50 ^\circ$C; Fig. 4-6, Tab. 4-2) show a high, uniform and very similar ETC, despite being variously packed or complex (Figures 4-7 and 4-9).

The geometric differences between systems start to be emphasized in decreasing water content, while the solid-fluid conductivity ratio increases and the ETC declines (Bahrami et al., 2006; Gonzo, 2002).

Equilibrium periods in the saturated systems are significantly shorter than in the dry systems (Fig. 4-8). Dry air is a good thermal insulator (Incropera et al., 2007). Therefore heat in dry systems can be transferred almost exclusively through the contact points between the particles. On the other hand,
water facilitates heat transfer and virtually increases the effective heat-transfer area, enabling heat conduction not only through the circle contacts but also through the fluid and circle surfaces.

4.6.5 Heat capacity

Heat capacity offers an overview of all aspects influencing the heat transfer. Heat capacity varies with different packings, complexity and water contents, the last being the ultimate controlling factor (Sato et al., 1998): that is, the dry systems have the same heat capacity, regardless of packing or complexity, which is equal to the heat capacity of the bentonite \( c_p = 964 \, \text{J/(kg*K)} \); Fig. 4-10), and the differences in geometry are not pronounced until the fluid starts to conduct heat.

Humid systems with a high void fraction (Tab. 4-1) have a higher heat capacity than systems with a low one. An increase in the heat capacity is caused by an increase in the fluid proportion accompanying the decreasing system complexity.

4.6.6 Modelled and experimental ETC

The modelled ETC shows a close agreement with the experimentally measured thermal conductivity. The conductivity of two bentonite mixtures varied, as a result of the different consolidation of the same granular bentonite (Tab. 4-3; Figures 4-11 and 4-12). The low-consolidated mixture was poured into a vessel without any special mechanical treatment \( (\rho_D = 1500 \, \text{kg/m}^3) \), whereas the high-consolidated mixture was tamped on purpose \( (\rho_D = 1778 \, \text{kg/m}^3) \). The contact between pellets improved accordingly during the consolidation, and the porosity of the mixture decreased. The differences between the thermal conductivity of the high- and low-consolidated bentonite gradually declined with increasing water content, which is also well proven in the model.

Nevertheless, the trend lines in Fig. 4-12 suggest that important differences can be expected between model and experimental values of ETC for high-consolidation and high degree of saturation. The cause of the differences is swelling of the real bentonite. Bentonite shows extensive swelling in contact with water (Wagner, 2013). Under confined conditions, the distances between particles decrease and the (macro)porosity diminishes during this process. The effectivity of the heat transfer simultaneously increases firstly because of the presence of water and secondly due to increasing proportion of bentonite at the expense of the air volume. Swelling of bentonite lies beyond the scope of presented study. The ETC of the real saturated bentonite is therefore higher than modelled systems at a comparable saturation level.

The ETC of modelled systems would also potentially grow above the bentonite thermal conductivity if the bentonite swelling would be considered. Based on the experimental results, thermal conductivity of swelling bentonite (a mixture of bentonite and water) appears to be a sum of the partial thermal
conductivities of dry bentonite and liquid water, and to be simultaneously dependent on the proportion of water (Figures 4-11 and 4-12). The Eq. 2 is not applicable any more in this case.

Since presented model simulates a system of two mutually segregated, discrete phases, the ultimate thermal conductivity is given by the system’s upper bound (Eq. 2; Franel and Kingery, 1954; Grujicic et al., 2005) which is in our case the thermal conductivity of bentonite (see 3.2 Parameters of subdomains section). The ETC of modelled systems therefore converges into the value of the input dry bentonite thermal conductivity (\(k = 0.671 \text{ W/(m*K)}\); Fig. 4-12) which is higher than the maximum thermal conductivity of the interstitial fluid – water (\(k = 0.594 \text{ W/(m*K)}\)).

4.6.7 Outlook

The presented model will be directed towards the ultimate solution of the heat transfer problem in granular bentonite and it also offers a base for possible complementary studies. The next steps in the modelling would be considering the porosity of the single pellet. The double porosity of the real bentonite granulate could be taken into account by specifying the pellet porosity within the framework of the Heat Transfer in Porous Media interface (Comsol AB, 2014).

Heat transfer in the metastable state of swollen pellets just before turning into a continuous medium could be approximated well by a system of Voronoï polygons (Galindo-Torres et al., 2010; Voronoï, 1908). The heat transfer along very thin or even one-dimensional boundaries between the pellets would shed light on the question of whether the heat transfer is accelerated in this short state of swelling pellets. The Voronoï polygon study would be positioned between the discrete geometry and continuum mechanics studies. Modelling of the heat transfer in completely swollen bentonite would be modelled entirely by means of continuum mechanics like it is common in existing studies (e.g. Johnson et al., 2002; Sato et al., 1998; Senger and Ewing, 2008). The ETC of the real bentonite barrier will, however, change in time due to the swelling of bentonite. The variable ETC of bentonite with different water contents will be thus modelled as a function of time and temperature.

Finally, the model could be applied at the scale of the underground repository. However, a continuum mechanics solution has to be elaborated, owing to the computational costs of the discrete geometry approach. To reach such a solution, an implementation of the discrete geometry approach into the continuum mechanics framework would be necessary. The challenge is to create a continuum mechanics model that provides estimates in the same way as the discrete geometry model. The resaturation period of the real-scaled bentonite barrier might be specified simultaneously during a short computing time with the temperature-distribution evolution. Nonetheless, to construct an ultimate model corresponding to the reality in the repository, similar studies on the time dependent bentonite swelling due to water diffusion should be undertaken (Kröhn, 2006). Together with the diffusion implementation, the theory of air-water mixing must be considered (Gibbs equation...
for binary mixtures; Atkins and de Paula, 2014). The final part of the study would be both the time and space variability of the barrier ETC, enabling the modelling of the heat transfer and water diffusion in any arbitrary time scale.

A complementary study would consider the gravity effects on the dry granular system. To account for these, the Gravity parameter, together with the Multibody Dynamics interface of the Comsol’s Structural Mechanics module, could be applied (Comsol AB, 2014). At the same time, the kinetics of pouring the granular bentonite onto the canister would be simulated. A randomly oriented granular arrangement with contact forces spread into the force chains produces stress-induced anisotropy, which would be particularly attractive for studying the compression-caused enhancement of the heat conduction (Majmudar and Behringer, 2005).

### 4.7 Conclusions

The mineral engineered barrier in the planned repository for radioactive waste in Switzerland is being designed as a granular bentonite mixture. The infiltrating pore water from the (clayey) host rock will start to resaturate the granular barrier after its emplacement. Resaturation should take one hundred to several hundreds of years based on continuum mechanics calculations. This estimation does not appear to be entirely satisfactory and could lead to an inaccurate assessment of the time when the corrosion of the waste canister commences. Discrete structure of the mineral barrier requires a more detailed parametrization than the porosity alone applied in the continuum approach. To help solve this problem, a discrete geometry model was constructed.

The finite-element model allows for a calculation of the temperature evolution time scales, together with a quantification of the transport and thermodynamic parameters of the granular system at variable water contents. The model solution is well supported by the experimental measurements. The laboratory measurements validate the modelled observation that the water content is the major parameter, which decisively facilitates the heat transport and strongly suppresses the differences between various structural features of the granular media. As expected, the temperature field equilibrates in water-saturated systems faster than in dry systems, having the nature of thermal insulators. On the other hand, the heat transfer in dry systems is determined by structural features, which may affect the heat transfer efficiency can vary significantly. Dry granular bentonite should have as low porosity as possible to ensure a high tortuosity of the system, enabling an effective transversal thermal dispersion. The model confirms this premise by calculating shorter temperature equilibrium periods in the systems with a relatively high proportion of solids.
The presented model is intended for further development and can serve as a core of a more advanced model. In its actual version, it represents a useful instrument for estimating the ETC of a granular body calculated from the bulk density and thermal conductivity of a grain, and from the void fraction and water content of the whole system. The method is especially advantageous for calculations of the ETC in fast-drying granular materials when measurements under laboratory conditions could alter the water (or fluid) content and thus the ETC of the entire analysed system.

Acknowledgements

Part of the model computations was performed in Brutus, the central high-performance cluster of ETH Zurich. Authors are grateful to Ľuboš Horný (LPC, ETH Zurich) for his assistance in using the cluster. Thermal conductivity measurements on granular bentonite carried out by Andreas Koch (Institute for Applied Geophysics and Geothermal Energy, RWTH Aachen) are highly appreciated. Valerio Gianella (Mathematics Department, ETH Zurich) is acknowledged for his help with solving geometry issues. The Comsol team in Zurich is thanked for its support.

References


Chapter 4 Discrete geometry model of heat in granular bentonite barriers


5 Response of kaolin, bentonite and illite to cold isostatic pressing

Authors
M. Valter, P. Ulmer, M. Plötze

Publication

Abstract
Cold isostatic pressing at room temperature is a compaction technique applied in ceramics production. During this process, the properties of clay minerals contained in the ceramic mixtures are subject to alteration. Research on the influence of high compressive stress on clays under room temperature conditions is scarce despite their abundance in many kinds of ceramic materials. The purpose of the presented study is to quantify the alteration of compressed kaolin, bentonite and illite powders. Isostatic stress of 1.5 and 3 GPa was applied on air-dry clays for one and four days at room temperature. Compressive stress induces a decrease of the specific surface area and, in general, a reduction of the micropore volume of clays. The effect is more pronounced at 1.5 GPa where cold welding most probably takes place. At 3 GPa delamination of clay minerals dominates. Compressive stress also induces alteration of the clay minerals' crystalline order and of the bentonite cation exchange capacity. The three clays are amenable to the compressive stress. Nonetheless, they largely retain their valuable properties. This is relevant not only to the ceramics production but likewise to various engineering applications and geological processes where clays are exposed to the compressive stress.

Keywords
Cold isostatic pressing, microporosity, surface area, crystalline order, cation exchange capacity, clay minerals
5.1 Introduction

Isostatic pressing is a routine technique in the production of ceramics (Turner & Ashby, 1996). The procedure features the application of a uniform compressive stress simultaneously to all the external surfaces of a powder body (Ekşi & Saritaş, 2002). Pressures applied during pressing reach several hundreds of MPa to a few GPa (Prokhorov & Akimov, 1997; Kim et al., 2000; Ekşi & Saritaş, 2002). When a powder is compacted solely by mechanical means through an external pressure without being heated, the process is called cold isostatic pressing (Ekşi & Saritaş, 2002). Cold isostatic pressing has the advantage of manufacturing high quality green ceramic products with close to uniform density (Henderson et al., 2000).

The cold-welding response of materials to a high-energy mechanical impulse is an important characteristic determining the compaction behaviour of a powder body during isostatic pressing of ceramic powders (Henderson et al., 2000; Carlone & Palazzo, 2006). Cold welding is a process of interaction between the surface energies of two materials brought into sufficiently close proximity (Marshall et al., 1989). It proceeds at contacting surfaces where atomically clean interfaces overlap (Schaffer & McCormick, 1989). The interaction results in an irreversible adhesion of the particles (Baláž, 2008).

Research of cold welding is connected almost solely with the compaction of metal and ceramic powders. Clay minerals are usually not included in the problematics. An example is the work of Gregg (1968) dealing with kaolinite and mica. Cold welding of mica should occur during uniaxial compression of up to 96 ton/in² (about 1.3 GPa). Research of cold welding in compressed clays is otherwise limited.

Studies of the influence of the isostatic (or hydrostatic), triaxial and normal stress on clays have been elaborated for decades. In the presented study, hydrostatic stress means the stress acting in fluids filling the pore space of clay, whereas the term isostatic stress designates a shear-free state of stress in clay (Kaselow, 2004).

Compressive stress can induce considerable alteration to clay mineral properties even at room temperature. Isostatic compressive stress causes a reversible structural phase transition in dickite at about 2.2 GPa (Johnston et al., 2002; Dera et al., 2003). In the case of kaolinite, isostatic stress decreases its crystalline order and crystallite size at a threshold of about 2 GPa (La Iglesia, 1993; La Iglesia & Aznar, 1996). Stress-induced alteration of clay minerals depends on their water content, as documented in the experiments of Galán et al. (2006). In their works, several different kaolinites, dry ones or kaolinite–water suspensions were compressed under isostatic stress of 0.4 GPa. Interestingly,
the wet runs induced an increase of the kaolinite crystalline order whereas the dry runs decreased it. Isostatic stress causes a change of the unit-cell dimensions of layer silicates (Hazen & Finger, 1978). The alteration depends also on the chemical composition of minerals. Muscovite with different Na/Na+K interlayer substitution demonstrates variable compressibility. The K-muscovite has a greater compressibility than the Na- muscovite. Simultaneously, ditrigonalization of the tetrahedral layer increases with pressure due to the geometrical accommodations of the octahedral sheet, regardless of the type of muscovite (Comodi & Zanazzi, 1995).

Structural transitions of the water in the clay mineral interlayer accompany the alteration effects of high compressive stress. A reduced interlayer distance of montmorillonite has been described. However, studies suggest that water does not leave the interlayer during compression. It rather experiences a phase transition to several ice polymorphs in dependence on the actual pressure and temperature (Alabarse et al., 2011). Water changes its structure to ice VI at about 0.8 GPa and 20 °C. The phase change is accompanied with a 30% volume reduction (Choukroun & Grasset, 2007). Phase transition of the interlayer ice VI into ice VII above 2 GPa (Somayazulu et al., 2008; Salzmann et al., 2011) can additionally take place during compaction. The ice VI transition to its denser phase ice VII is a volume reduction phenomenon (Mishima & Endo, 1978). The interlayer compressibility actually depends on the total average potential energy of the interlayer. The interlayer potential energy is given by the pressure, interlayer cation(s) type and amount of adsorbed water (Boek et al., 1995; Chávez-Páez et al., 2001; de Pablo et al., 2004; Miranda-Pascual & Chávez-Garcia, 2015). An alternative description of phenomena in compressed smectite is offered in the study by You et al. (2013). According to this study, water molecules are most probably capable of (re)entering the smectite interlayer when a sufficient pressure is provided. It has been shown that the basal distance of hydrated synthetic Na-hectorite (d001 = 15.3 Å) starts to increase at about 1.7 GPa (You et al. 2013). Pressures up to 1.7 GPa induce an initial decrease of the hectorite basal distance to about 14.2 Å, after which an abrupt increase of the basal distance is observed. The maximum basal distance (d001 = 16.5 Å) is measured at about 2.2 GPa. A second stage of the basal distance decrease (a re-expulsion of the interlayer water) follows at pressures above 2.2 GPa. You et al. state that water (the compression medium) around the hectorite tactoids remained liquid up to 2.2 GPa when the water turned to ice VII, contrary to the known water equilibrium isotherms. They assumed that increase of the basal distance occurs due to the pressure-induced water insertion into the interlayer. The water insertion into the hectorite interlayer was found to be fully reversible during decompression.

Non-isostatic compressive stress induces structural alteration to clay minerals which are largely comparable with the isostatic stress effects. Kaolinite experiences alteration of its vibrational parameters (Fourier transform infrared analysis; Bell et al., 1991). A decrease of the crystalline order of uniaxially compressed kaolinite and illite was recognized at 0.32 GPa (Plötze & Kahr, 2002).
uniaxial compressive stress of about 2 GPa is likewise capable of decreasing illite’s specific surface area and influencing its microporosity (Gregg & Langford, 1977).

Alteration of clay mineral properties was anticipated in the presented study as well. The focus was on three clays: kaolin, bentonite and illite. Compressive stress of 1.5 GPa and 3 GPa was applied on air-dry clays during cold isostatic pressing procedures taking 24 and 96 hours at room temperature. Pressure levels were carefully chosen below and above 2 GPa which seems to be the threshold pressure for many properties of clay minerals (Holtz et al., 1993; La Iglesia, 1993; Dera et al., 2003). At the same time, the chosen pressure levels are relevant in the industrial cold isostatic pressing procedures.

The clays in the presented study have different interlayer cations (predominantly Na/Ca-montmorillonite in bentonite MX-80, and K-illite Füzérradvány). Different interlayer cations determine different adhesion energies between the interlayer surfaces (Sakuma, 2013). The actual adhesion energy can be determined by the layer charge and the variable location on a clay particle where the cations are predominantly adsorbed. Planar sites have the lowest affinity for cations of low hydration energy like K, Rb or Cs. The edges of the clay particles are, in turn, less accessible to cations with high hydration energy, like Na, Ca or Mg (Sawhney, 1964; Van Loon et al., 2009). Different cations effectively influence the compressibility of clay minerals. For instance, the K-muscovite has a higher compressibility than the Na-muscovite (Comodi & Zanazzi, 1995). Hence, the effective stress evolved in illite has the potential to cause a relatively greater volume change than in montmorillonite. Since kaolinite possesses no interlayer cations the compressibility of its tetrahedral-octahedral sheet is the managing structural factor under compressive stress. In general, the highest compressibility of sheet silicates is measured in a perpendicular direction to the layers (Hazen & Finger, 1978). This axial anisotropy is a result of bonding differences within, as opposed to between, the tetrahedral and octahedral layers. Moreover, the tetrahedral layer is less compressible than the octahedral layer (Comodi & Zanazzi, 1995 & 1997). The volume change of a single crystal of kaolinite H1 thus depends predominantly on the geometrical accommodations of the octahedra.

The single crystal compressibility is translated into the compressibility of the clay mineral accumulations. Powdered kaolinite shows a larger compressibility than powdered illite, which in turn has a larger compressibility than powdered montmorillonite (Meade, 1963; Mondol et al., 2007). Based on this assumption, the greatest stress-induced volume reduction and thus the lowest effective stress evolved in kaolin, followed by illite and bentonite. Simultaneously, the montmorillonite particles in bentonite are smaller than those of illite and kaolinite. Pressure can thus be relaxed on a larger number of grain–grain contacts in montmorillonite than in illite or kaolinite (Mondol et al., 2007).
The purpose of the presented study was to investigate if clay minerals are amenable to cold welding under isostatic compressive stress. If cold welding occurs, it is anticipated that the specific surface area and microporosity of the compressed clays will experience alteration. The specific surface area will be reduced, the micropore volume will decrease and the finer end of the micropore size distribution will be prevalent (Gregg & Langford, 1977).

Analysis of the specific surface area of clay compacts and mapping of their microporosity is the primary part of the study. Besides these two parameters, the crystal structure of compressed clays, their cation exchange capacity and the amount of leachable cations were investigated.

The presented study is in the line of works focused on physical (clay) mineral alteration and the investigation of the influences on their physicochemical properties (Plötze & Kahr, 2002; Plötze et al., 2003; Valter & Plötze, 2013), e.g. in various applications in environmental mineralogy and geotechnical engineering. Clays as part of the natural and engineered barriers in future deep geological repositories for radioactive waste can eventually be exposed to high pressures. Compressive stress levels in the presented study are rather extremely exaggerated in the scope of waste disposal. Nevertheless, if clays are stable under such extreme stresses, their stability can then be extrapolated to realistic, much lower stress levels applicable to waste disposal. Another research field where the results of the presented study may be applicable is the burial and consumption of sediments in subduction zones. An applied stress of 1.5 and 3 GPa is assumed at depths of about 55 km and 110 km below the Earth’s surface. Temperatures at these depths are estimated as about 300 °C and 600 °C respectively. Clay minerals do not exist under these conditions and are already recrystallized into more stable mineral species (Bucher & Grapes, 2011). Since the presented study was carried out at room temperature (25 °C), the sole influence of high stresses on the properties of clay minerals can be considered. The stress-induced alteration of clay minerals can be separated from the coupled thermo-barometric alteration of clays in natural environments. For instance, the level of the illite crystalline order is usually used as an indicator for the environment temperature in crustal depths defining the metamorphic grade of facies (Weaver, 1959; Kübler, 1967; Warr, 1996). Similarly, the K-micas are important as indicators for the geobarometry (Sassi & Scolari, 1974). Within the presented study, given the coupled role of temperature and pressure in diagenetic and low-grade metamorphic processes, an attempt can be made to distinguish these from each other.
5.2 Materials and experimental setup

5.2.1 Clay materials

Three commercial clays were studied in the experiments: kaolin H1 (Dorfner, DE), illite sarospatakite (Füzérradvány, HU) and bentonite MX-80 (AMCOL International Corp., US-WY). Their mineralogical composition is given in Tab. 5-1. Particle size distribution analysis was carried out to test the homogeneity of the analyzed clays. The grain size distribution stability of different portions of the same clay represents one sign of clay homogeneity. The homogeneity of the clays can also be proven e.g. by the mineral composition stability. All three clay materials exhibited a high level of homogeneity confirmed by their almost identical particle size distribution in non-sonicated and sonicated runs (Fig. 5-1). Only bentonite showed a certain level of inhomogeneity in the grain size region above 8 µm after sonication. Nevertheless, differences between runs are so low that their influence on the results is considered as too small to cross the measurement error of analyses in the paper.

Tab. 5-1 Mineral composition of clays (bentonite composition adopted from Valter & Plötze, 2013)

<table>
<thead>
<tr>
<th>Kaolin H1</th>
<th>wt. %</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite</td>
<td>4.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>86.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Microcline</td>
<td>4.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Muscovite</td>
<td>2.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Quartz</td>
<td>3.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bentonite MX-80</th>
<th>wt. %</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>2.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Feldspar</td>
<td>4.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Mica-type layers/collapsed smectite layers</td>
<td>12.4</td>
<td>1.5</td>
</tr>
<tr>
<td>Quartz</td>
<td>6.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Smectite</td>
<td>72.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Illite Füzérradvány</th>
<th>wt. %</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite/smectite R3 I/S90</td>
<td>84.2</td>
<td>4.0</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>&lt;0.5</td>
<td></td>
</tr>
<tr>
<td>K-feldspar</td>
<td>13.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.4</td>
<td>0.1</td>
</tr>
</tbody>
</table>
5.2.2 High pressure apparatus

Clay samples were compressed at 1.5 GPa in a single stage, non-end-loaded, Johannes-type piston cylinder apparatus (piston bore 22 mm; Johannes, 1973) and at 3.0 GPa in an end-loaded piston cylinder module mounted in a 600-ton O-frame press (piston bore 14 mm; Schmidt & Ulmer, 2004) at room temperature (25 °C). Compression was carried out by uniaxially displacing a cylindrical tungsten-carbide (WC) piston into the central bore of the WC pressure vessel containing the...
compression assembly. The compression assembly evolved isostatic compressive stress on a copper capsule containing clay.

The compression assembly consisted of a large NaCl sleeve (inner diameter 14.1 mm, outer diameter 21.9 mm, length 42.0 mm; component 4 in Fig. 5-2), an NaCl shell around the copper capsule (inner diameter 10.1 mm, outer diameter 14.0 mm, length 16.0 mm; component 2 in Fig. 5-2) and two solid NaCl cylinders (diameter 14.0 mm, length 13.0 mm; components 3 in Fig. 5-2) positioned above and below the NaCl capsule shell.

Air-dry clays (Tab. 5-2) were tightly packed into prefabricated copper capsules. The copper capsule (inner diameter 7 mm, outer diameter 10 mm, inner height 9.5 mm, inner volume ca. 0.4 mL; component 1 in Fig. 5-2) was filled stepwise with about 0.5–0.7 g of clay. Clays were stamped with a glass rod to reach the highest initial bulk density possible. The filled copper capsule was closed with a tight-fitting lid (total length of the copper capsule including the lid 16.0 mm). The filled capsules were encased and centrally positioned in the compression assembly (Fig. 5-2).

Fig. 5-2 Schematic drawing of the pressure assembly used for the compression of clays. The assembly composed of a sample-containing copper capsule with a lid (component 1) that was enclosed within an NaCl sleeve (component 2), between two NaCl cylinders (components 3) and encased in a large NaCl sleeve (component 4). A complete assembly is depicted on the right.

5.3 Analytical methods

The particle size distribution was tested with a laser grain/particle size analyzer Horiba Partica LA-950 (Horiba, JP). Samples were dispersed in 0.1% Na-polyphosphate solution. Measurements of non-sonicated samples were followed by sonicated measurements until there was no further change in the particle size distribution curve. Three runs for each of the three clays were measured.
The specific surface area of the clays was determined by the 11-point N₂ adsorption method (Brunauer et al., 1938). An Autosorb-1MP surface area and pore size analyzer (Quantachrome, USA; N₂ relative pressure p/p₀ = 0.05–0.3) was used for the measurements.

The microporosity distribution was analyzed by the same Quantachrome Autosorb-1MP analyzer. The CO₂ adsorption was applied at a temperature of 273.15 K (CO₂ relative pressure p/p₀ = 3.10⁻⁵ to 3.10⁻²). The range of the analyzed pore diameters was 3.0–15.0 Å. Samples were outgassed for 24 hours prior to the analysis.

Electron microscopy with a Quanta 600 Scanning Electron Microscope (FEI, USA) was applied for the surface topography observations. The microscope was operated in the low-vacuum mode (0.5 torr), at a voltage of 20.0 kV and employing an SE large-field detector. The magnification ranged between 50-6000x. Before scanning, samples were dried at 105 °C until no further weight change occurred. Loose clay as well as the surfaces of freshly broken compressed clay were examined.

The cation exchange capacity of montmorillonite and illite was determined using the copper (II) triethylenetetramine complexes (Meier & Kahr, 1999). Approximately 150 and 275 mg of each of the bentonite and illite samples, respectively, were treated ultrasonically for three minutes prior to the cation exchange. Concentrations of leachable Na⁺, K⁺, Mg²⁺ and Ca²⁺ were determined using atomic absorption spectrometry (device AAnalyst400, Perkin Elmer, USA).

X-ray diffraction was used to determine the mineral composition of the clays and to analyze the crystalline order and swelling ability of the contained clay minerals. An AXS D8 Advance diffractometer (Bruker, DE; source Co Kα radiation λ = 1.790 Å) equipped with the primary and secondary soller and automatic theta compensating divergence and antiscatter slits was used for the X-ray diffraction analysis. Data were collected within an interval of 2–80°2θ with a step of 0.02°2θ and a counting time of 10 s/step (samples powdered on an off-axis cut silicon plate providing a zero-background used for the crystalline order analysis) and 2–15°2θ with a step of 0.02°2θ and a counting time of 4 s/step (textured specimens). Randomly oriented powder and textured smear specimens were used to determine the mineral composition of the clays. A McCrone micronizing mill equipped with agate grinding elements was used to micronize ethanol-dispersed clays to <20 μm. Micronized clays were left to dry at room temperature. Dry clays were front-loaded into the sample holders. The textured specimens were prepared to more easily identify the clay minerals and to determine the basal distances d(001) of smectite and illite. After their X-ray diffraction analysis, textured specimens of bentonite were treated in ethylene glycol vapour at 60 °C to examine eventual alterations of the montmorillonite intracrystalline swelling ability (MacEwan & Wilson, 1980). The full-widths at half-maximum (FWHM) of the 001 peak (or Kübler index of illite) in the X-ray diffractograms of all samples (Kübler, 1967; Kübler & Jaboyedoff, 2000), and the Hinckley index for kaolinite were
calculated to determine eventual stress-induced alterations of the clay mineral crystalline order. The FWHM of the 001 reflections were determined in the software DIFFRACplus TOPAS P (BrukerAXS). The intensities of the 020, 1-10 and 11-1 reflections of kaolinite were used to calculate the Hinckley index (Hinckley, 1963). The mean layer charge of montmorillonite was determined by X-ray diffraction after its intercalation with a dodecyl ammonium salt (Olis et al., 1990; Lagaly, 1994). An addition of a small amount of talc to the suspensions served as the line positioning standard in the X-ray diffraction pattern. Prepared suspensions were dripped on a glass slide and dried in vacuum at 40 °C before measurement. Values of the montmorillonite basal distance were used for the mean layer charge calculation: charge = (d001-5.52)/32.98. Diffraction patterns were processed in the software DIFFRACplus EVA (Bruker AXS) to implement the qualitative phase analysis and to determine the basal spacing of montmorillonite and interstratified illite/smectite. The quantitative phase analysis was carried out by the Rietveld algorithm implemented in the BGMN®/AutoQuan software (Bergmann & Kleeberg, 1998).

Thermogravimetric and mass spectrometric analysis was applied as a diagnostic tool for the examination of the dehydration and dehydroxylation characteristics of the clays (Emmerich, 2011). Thermal analysis was carried out in a thermobalance TGA/SDTA851e (Mettler-Toledo, CH). The quantities of the released water and CO₂ were registered by a coupled mass spectrometer ThermoStar GSD 300 T (Balzers, LI) as part of the mineral composition analysis. Each sample was thermally analyzed in a platinum crucible between 25 and 1000 °C (heating rate 10 °C/min) in a dry and carbon-dioxide-free airflow atmosphere (50 mL/min).

5.4 Results

5.4.1 Specific surface area

Compressive stress demonstrably induced alteration to the surface area in kaolin only when compressed at 1.5 GPa for 96 hours. Its surface area decreased by about 14% (Tab. 5-2). The surface area alteration of kaolin compressed under other compression regimes lies within the range of the measurement error. Kaolin compressed at 1.5 GPa for 24 hours was drilled out of the copper cylinder and pulverized during which its originally compressed structure was modified. This sample was thus not included in the interpretation of the pressure induced alteration of the specific surface area.

A compressive stress of 1.5 GPa decreased the bentonite’s specific surface area by about one third and 15% after 24 and 96 hours, respectively, (Tab. 5-2). In contrast, an increase of its surface area by about the same one third and 15% was observed after 21 and 96 hours, respectively, at a pressure of 3 GPa.
Chapter 5 Response of kaolin, bentonite and illite to cold isostatic pressing

The specific surface area of illite exhibited a rather ambiguous reaction to compressive stress. A pressure of 1.5 GPa applied for 24 hours induced an increase of the illite’s specific surface area by 11%. On the other hand, compression for 97 hours at 1.5 GPa and for 24 hours at 3 GPa caused a surface area decrease by about 10% (Tab. 5-2). Compressive stress of 3 GPa for 97 hours seemingly had no influence on the illite’s specific surface area.

5.4.2 Microporosity

Stress-induced reduction of the micropore volume and change of the micropore size distribution were clearly observed in kaolin and illite, whereas the alteration of the bentonite’s microporosity was moderate. Again, the properties of kaolin compressed at 1.5 GPa for 24 hours were not included in the interpretation of the pressure-induced alteration of the kaolin’s microporosity.

Of the three clays, the microporosity of kaolin H1 responded most sensitively to the applied stress. The microporosity of the pristine kaolin was distributed fairly uniformly (Fig. 5-3aa); however, compression led to an overall micropore volume reduction by about 50% (Fig. 5-3ba). Only pores with a diameter of about 4.4–6.6 Å were accessible for the CO₂ adsorption (Fig. 5-3aa). The micropore size distribution was similar for all three compressed kaolin samples (Fig. 5-3aa, ba and ca). Micropores with a diameter of about 4.4–5.0 Å and 5.0–6.6 Å covered 40% and 60% of the kaolin microporosity, respectively, regardless of the compression conditions. The micropore volume alteration of kaolin appears to be sensitive to compressive stress in general.

The microporosity of bentonite only experienced a moderate alteration during compression. The micropore size distribution of all the compressed samples largely resembled that of the pristine bentonite (Fig. 5-3ab). However, certain alterations occurred in the relative pore volume. The volume of 4.4–8.6 Å pores increased during compression. Outside this size region, the micropore volume decreased. The overall micropore volume decreased at 1.5 GPa regardless of the time. At 3 GPa, the micropore volume almost reached the level of the pristine bentonite (Fig. 5-3bb). The alteration of bentonite’s microporosity seems to be sensitive to the level of the applied compressive stress.

Compressive stress influenced the illite’s micropore distribution irregularly (Fig. 5-3ac). The most significant stress-induced change occurred after 97 hours at 3 GPa. Only pores with a diameter of approximately 5–6.5 Å remained open. After applying stress of 1.5 GPa for 97 hours, micropores with a diameter larger than about 6.5 Å remained closed. Pores of about 5–6.5 Å constituted about 80% of the preserved micropore volume (Fig. 5-3ac and bc). Illite compressed at both stress levels for 24 hours preserved its entire microporosity. The differences lie within the measurement error (Fig. 5-3bc and cc). Illite was time-sensitive. Its microporosity reacted predominantly to the duration of the stress.
Fig. 5-3 Micropore size distribution charts for the clays. The upper (a)-row depicts histograms with relative pore volume, the middle (b)-row shows the cumulative pore volume curves, and the lower (c)-row are isotherms from the analysis. Results for kaolin, bentonite, and illite are in the left, middle, and right columns, respectively. Depicted are distributions in pristine and compressed clays. Results for kaolin compressed at 1.5 GPa for 24 hours, and bentonite compressed at 2 GPa for 72 hours were not considered because insufficient data was collected. The sample of illite compressed at 3 GPa for 97 hours was not included in the results — the insufficient amount of this sample produced unrealistic results.
5.4.3 Clay fabrics

The system of mineral platelets of kaolin H1 before and after compression at 3 GPa for 24 was visualized by electron microscopy. Micrographs of the pristine, loose kaolin are illustrated in Fig. 5-4. Freely lying kaolinite platelets, as well as a detailed view of a kaolinite stack consisting of several superimposed lamellae, are depicted in Fig. 5-4a (250x magnification) and 5-4b (6000x magnification), respectively. Kaolinite was compressed into a compact, macroscopically glossy mass with coarse, anastomosing (micro-)fabrics on broken surfaces (Fig. 5-4c and d; 50 x and 800x magnification, respectively). Separate lamellae are no longer identifiable after the compression. Kaolin samples compressed under different compression conditions look very similar.

Fig. 5-4 ESEM image of the pristine kaolin H1. (a) Individual mineral platelets lie freely on the adhesive liner; magnification 250x. (b) A detailed image of a kaolinite platelet with lamellae; magnification 6000x. (c) and (d) Images of the kaolin compressed at 3 GPa for 24 hours; magnification 50 x and 800x respectively. Lamellae within platelets are no longer identifiable.
5.4.4 Mean layer charge, cation exchange capacity and the amount of leachable cations

Compressive stress induced an ambiguous response in the bentonite cation exchange capacity. The exchange capacity of the pristine bentonite is $89 \pm 2 \text{ cmole}(+)/\text{kg}$. A pressure of 1.5 GPa diminished the cation exchange capacity to $80–83 \pm 2 \text{ cmole}(+)/\text{kg}$ (Tab. 5-2). The exchange capacity of bentonite compressed at 3 GPa (87–88 ± 2 cmole(+)/kg) appears to remain identical to the exchange capacity of the pristine bentonite.

The cation exchange capacity analysis was followed by analysis of the amount of leachable cations. This amount represents the sum of exchangeable cations, cations in the pore water and the cations from the minerals dissolved during the exchange procedure. Compressive stress had a limited effect on the amount of leachable cations. A trace of alteration was only observed in concentrations of leachable Na⁺ (Tab. 5-2). In addition, only a compressive stress of 1.5 GPa for 96 hours seems to have an effect on it. The original amount of $57 \pm 6 \text{ cmole(Na⁺)/kg}$ decreased to $42 \pm 6 \text{ cmole(Na⁺)/kg}$.

The montmorillonite mean layer charge remained unchanged after the experiments. The compression also appears to have no influence on the intracrystalline swelling ability of montmorillonite in bentonite.

5.4.5 Crystalline order of clay minerals

Kaolinite experienced the most severe alteration of its crystalline order among all three clays. Compressive stress caused a decrease of the Hinckley index from about 1.0 to $0.3–0.5 \pm 0.2$ (Tab. 5-2). Differences in the crystalline order of kaolinite before and after compression are illustrated by the diffractograms in Fig. 5-5 (region for calculation of the Hinckley index).

Compressive stress induced minute alteration to illite. In contrast to the decreased crystalline order in kaolinite, an applied stress of 3 GPa for 97 hours even caused an improvement of the illite crystalline order. The Kübler index of the 10 Å peak slightly decreased from 1.3 to $1.0 \pm 0.1 [°2\theta]$ (Tab. 5-2).

The montmorillonite crystalline order and basal distance of all the clay minerals remained unaltered after compression. All deviations remained within the statistical margin of error.
5.4.6 Thermal behaviour

Stress-induced structural and crystalline order alteration was translated into the thermal behavior of kaolin. Compressive stress clearly influenced the kaolinite’s dehydroxylation temperature. The dehydroxylation temperature of the pristine kaolinite (538 °C ± 1 °C) decreased to about 520 °C (Tab. 5-2). The mass loss on dehydroxylation decreased from about 12.5 wt.% of pristine kaolin to about 11.5 wt.% after 96 hours at both pressure levels (Tab. 5-2). Compressive stress led to an increase of the mass loss on dehydration from pristine 0.3 wt.% to almost 3 wt.% after 96 hours at both pressures.

All changes in the bentonite’s thermal behaviour remained within the statistical margin of error. Nevertheless, the dehydroxylation temperature of montmorillonite decreased very slightly from 706 to 702 ± 2 °C, bordering the measurement error. The mass loss on dehydroxylation only decreased in bentonite compressed at 3 GPa for 96 hours, from 4.2% (pristine bentonite) to about 3.8 %.

The major dehydroxylation of the pristine illite Füzérradvány occurred at 582 ± 1 °C (Tab. 5-2). Compressive stress induced a uniform decrease of the illite’s dehydroxylation temperature by about 15 ± 1 °C, regardless of the stress level or duration. As in the case of bentonite, a decrease of the illite mass loss in dehydroxylation was registered only after compression at 3 GPa for 97 hours, from 4.2% (pristine illite) to 3.6%. The dehydration and dehydroxylation curves of the illite samples are depicted in Fig. 5-6 in order to show the decomposition processes at temperatures above dehydroxylation up to 1000 °C. The shape of the TGA curves (thermal gravimetry analysis indicates the relative sample mass of a sample at a given temperature; Fig. 5-6a) and DTG curves (differential thermal gravimetry curves indicate the change of the sample mass per degree Kelvin; Fig. 5-6b; Emmerich, 2011) of the illite samples, except for the one compressed at 3 GPa for 97 hours, resemble each other. However,
the shape of the last sample, especially at temperatures above about 600 °C is unlike the others. Above all, the lower mass loss on dehydroxylation of illite compressed at 3 GPa for 97 hours with respect to the other illite samples is mirrored in this part of the TGA and DTG curves.

Fig. 5-6 Curves of the thermal gravimetry analysis (TGA) and differential thermal gravimetry (DTG) of pristine and compressed illite. The decomposition processes above 600 °C distinguish illite compressed at 3 GPa for 97 hours from the rest of the samples
Tab. 5-2 Experimental conditions, specific surface area, and results of the thermal, X-ray diffraction and the cation exchange capacity (CEC) analyses of the pristine and compressed clays

<table>
<thead>
<tr>
<th>Water content [wt. %]</th>
<th>Isostatic compressive stress</th>
<th>Period [h]</th>
<th>Temperature [°C]</th>
<th>Specific surface area [m²/g]</th>
<th>Dehydroxylation temperature [°C]</th>
<th>Mass loss on dehydroxylation [%]</th>
<th>Mass loss on dehydration [%]</th>
<th>Hinckley index</th>
<th>Kübler index [°2θ] ± 0.1</th>
<th>CEC [cmole(+) / kg]</th>
<th>Na⁺ ± 0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>± 4%</td>
<td>Δ [%]</td>
<td>± 0.2</td>
<td>± 0.0%</td>
<td>± 0.0%</td>
<td>± 6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolin H1 (five different specimens, one for each condition)</td>
<td>0.3%</td>
<td>-</td>
<td>-</td>
<td>25</td>
<td>4.9</td>
<td>-</td>
<td>538 ± 1 (40 mg)</td>
<td>12.4% (± 0.0%)</td>
<td>0.3% (± 0.0%)</td>
<td>1.0</td>
<td>89</td>
</tr>
<tr>
<td>Bentonite MX-80 (five different specimens, one for each condition)</td>
<td>9%</td>
<td>1.5</td>
<td>24</td>
<td>10.1</td>
<td>-34%</td>
<td>703</td>
<td>4.2%</td>
<td>83</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>24</td>
<td>12.9</td>
<td>-16%</td>
<td>702</td>
<td>4.2%</td>
<td>80</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>21</td>
<td>20.2</td>
<td>31%</td>
<td>702</td>
<td>4.2%</td>
<td>87</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>96</td>
<td>17.8</td>
<td>16%</td>
<td>702</td>
<td>3.8%</td>
<td>88</td>
<td>57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Illite Füzéravány (five different specimens, one for each condition)</td>
<td>3%</td>
<td>1.5</td>
<td>24</td>
<td>31.0</td>
<td>11%</td>
<td>568</td>
<td>4.2%</td>
<td>1.3</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>97</td>
<td>24.8</td>
<td>-11%</td>
<td>567</td>
<td>4.1%</td>
<td>1.2</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>24</td>
<td>25.5</td>
<td>-9%</td>
<td>567</td>
<td>4.2%</td>
<td>1.3</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>97</td>
<td>27.6</td>
<td>-1%</td>
<td>568</td>
<td>3.6%</td>
<td>1.0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Hinckley index and Kübler index are used as crystalline order indicators for kaolinite and illite, respectively. Measurement/statistical errors are indicated as percentage or absolute values at the head of each parameter. Sample weights for the thermal analysis are included in parentheses after the value of the dehydroxylation temperature of pristine samples. The specific surface area of kaolin compressed at 1.5 GPa for 24 hours was not considered for the results.
5.5 Discussion

The presented experiments must be considered with regard to the effective isostatic stress. The effective stress represents the real stress acting on the clay and originates as a complex interaction of many different factors.

Since the clays in the presented study contain fluids in their pores and in the interlayer (water content; Tab. 5-2), hydrostatic stress evolves in the fluid-filled volume and acts against the applied outer stress. Water acts as an inhibitor of the direct contact between the clay mineral surfaces. The friction coefficient of wet clays is consequently lower than that of dry clays (Behnsen & Faulkner, 2012). The effective stress (applied isostatic stress minus hydrostatic pore stress) depends on the actual water content; i.e., the fluid pressure only acts over part of the partially saturated soil (Mitchell, 1960). From the water content point of view, the highest effective stress evolves in almost dry kaolin, unlike in the more humid bentonite and illite.

The stiffness of clay mineral platelets is another decisive factor. The highest stiffness expressed as bulk modulus (the inverse of the compressibility; the ratio of the infinitesimal pressure increase to the resulting relative decrease of the volume; Walker et al., 2014) and shear modulus (the ratio of shear stress to the shear strain; IUPAC, 2014) is found in illite, followed by kaolinite and montmorillonite, respectively (Fig. 5-7). The lower stiffness of montmorillonite (bentonite MX-80) relative to kaolinite H1 and illite Füzérradvány is consistent with its smallest particle size among the three clays. The brittleness of montmorillonite most probably causes that this clay mineral is composed of particles that are much smaller than the relatively stiffer kaolinite or illite (Fig. 5-1; Stotzky, 1966).

Fig. 5-7 Bulk and shear moduli of kaolinite, illite and smectite. Depicted values are averages of moduli published in several works and summarized in Bayuk et al. (2007)
Kaolin H1

Cold welding is a phenomenon which was expected to take place in the presented study. Cold welding would be mirrored particularly in the alteration of the specific surface area and of the microporosity. However, its traces in kaolin’s specific surface area are minute. A demonstrable decrease of the kaolin’s specific surface area only occurs at 1.5 GPa for 96 hours (Tab. 5-2). The area decrease can be considered as a sign of the cold welding. Nevertheless, seemingly no alteration of the surface area can be seen during compression at 3 GPa for 24 and 96 hours. Most likely, the compression in fact causes a decrease of the surface area at 3 GPa and cold welding in the first stages of compression. Later on, kaolinite crystals potentially start to cleave along the basal planes and they expose new surfaces while being delaminated (Gregg & Langford, 1977). Newly exposed surfaces could also originate from the fragmentation (breakage) of kaolinite crystals (La Iglesia, 1993; La Iglesia & Aznar, 1996). The area of the new surfaces after 3 GPa compression would then contribute to the original surface area, which is reduced after 96 hours at 1.5 GPa.

In contrast to the specific surface area, compressive stress causes a uniform micropore volume decrease – another sign of the cold welding (Fig. 5-3ba and 5-5a). Most of the remaining microporosity thus most probably originates in delaminated (and/or broken) kaolinite surfaces. Microporosity can predominantly be found on the edges of the clay mineral crystals (Kaufhold et al., 2013). The mechanism of the microporosity reduction can thus be described by compression of these edges.

The contrast between the stable specific surface area and the reduced microporosity of kaolin can be explained by the presence of pores bigger than micropores. Part of the whole mesoporosity in compressed kaolin H1 most probably originates from eliminated macropore volume. Some of the water adsorbed in the macropores and mesopores of the pristine kaolin H1 can potentially be squeezed out. The evidence for the stress-induced squeezing-out of adsorbed water is the liquid water found on the surface of the dismantled kaolin pressing (the same holds for bentonite MX-80 and illite Füzérradvány).

Gregg & Langford (1977) likewise reported a virtually unaltered specific surface area and a significant proportion of mesoporosity in kaolin compressed at about 1.48 GPa. The N₂ can be adsorbed on the surfaces of all the accessible porosity. Hence, the apparently unaltered specific surface area of the kaolin compact is measured. The proportion of microporosity relative to the whole kaolin porosity is most probably low. This is also obvious from the lower kaolin micropore volume relative to bentonite and illite (Fig. 5-8a). The measured 50% decrease of the kaolin micropore volume (Fig. 5-3ba) could have influenced the whole surface area only marginally. To determine the extent to which compressive
stress influences mesoporosity (and macroporosity), an additional analysis, for instance mercury intrusion porosimetry, would be necessary.

Fig. 5-8 Trend comparison of the specific surface area with the cumulative micropore volume of kaolin (a), bentonite (b) and illite (c). Kaolin compressed at 1.5 GPa for 24 hours was not considered. The sample of illite compressed at 3 GPa for 97 hours was not included in the results. The insufficient amount of this sample produced unrealistic results. The error intervals are depicted as error bars or are already included in the size of symbols.
The evidence of cold welding in compressed kaolin is weak. However, the compressive stress influences other kaolin parameters more distinctively. Alteration of the kaolinite crystalline order appears to be largely sensitive to the compression period. The compression during the 96 hour period only induces a reduction of the Hinckley index (Plötze & Kahr, 2002; Galán et al., 2006). The Hinckley index decreases by more than 50% (Tab. 5-2). A comparable reduction was reported by La Iglesia (1993).

The stress-induced deterioration of the kaolinite crystalline order can be confirmed by the thermal analysis. The hydroxyl groups of octahedra most probably become destabilized along the crystalline order alterations. The stress-induced destabilization of hydroxyl groups is evident as a reduction of the dehydroxylation temperature (Tab. 5-2; Hlavay et al., 1977; La Iglesia, 1993; La Iglesia & Aznar, 1996; Suraj et al., 1997; Vizcayno et al., 2010) and a decrease of the mass loss on dehydroxylation with a simultaneous increase of the mass loss on dehydration (Tab. 5-2; Franco et al., 2004). The intracrystalline deformations of kaolinite revealed by the X-ray diffraction and thermal gravimetry analyses apparently occurred after the compression could no longer be accommodated by closure of pores or by easy-slip across crystal surfaces.

**Bentonite MX-80**

The specific surface area and micropore volume of bentonite react similarly to the isostatic compressive stress (Fig. 5-8b). The specific surface area decreases as the micropore volume decreases, and vice versa. These two parameters most probably change as a reaction to the clay compaction and accompanying void ratio reduction (Ekşi & Saritas, 2002). The inter-particle distance could decrease enough to reach the attractive van der Waals forces and cold welding takes place.

In contrast to 1.5 GPa, a compressive stress of 3 GPa leads to an increase of both specific surface area and micropore volume (Tab. 5-2; Fig. 5-3bb and cb). The increase can be explained by delamination of montmorillonite, assuming some of the (meso)porosity remains preserved (Gregg & Langford, 1977) and offers open space for the slipping montmorillonite lamellae along the basal planes. The surface of all the dismantled bentonite pressings was macroscopically wet, as in the case of kaolin H1. Some of the adsorbed water in the macro- and mesopores of the pristine bentonite was most probably squeezed out during compression.

An additional effect of the water phase transition can occur during the process of compression. Water in the interlayer (water content; Tab. 5-2) responds to the compressive stress by changing its structure into ice VI at about 0.8 GPa (Alabarse et al., 2011) and to the denser ice VII above 2 GPa (Somayazulu et al., 2008; Salzmann et al., 2011), causing >30% volume reduction (Mishima & Endo, 1978, Choukroun & Grasset, 2007). The interlayer volume could thus be reduced and the delamination
of montmorillonite can gain additional free space to move to. The volume reduction due to the ice phase transitions can potentially lead to a partial increase of the interparticle porosity, which facilitates delamination of montmorillonite. Delaminated montmorillonite provides more sites for the N₂ and CO₂ adsorption (Aylmore & Quirk, 1967; Rutherford, et al., 1997; Kaufhold et al., 2013) and the surface area and micropore volume thus increase (Tab. 5-2; Figures 5-3 and 5-6).

However, an alternative description of the phenomena in compressed smectites is offered in the study by You et al. (2013). According to this study, water molecules are most probably capable of (re)entering the smectite interlayer when a sufficient pressure is provided. Pressures up to 1.7 GPa induced an initial decrease of the hectorite basal distance, after which an abrupt increase of the basal distance until 2.2 GPa was observed. At pressures above 2.2 GPa the basal distance decreased due to a re-expulsion of the interlayer water. The authors state that water around the hectorite tactoids remained liquid up to 2.2 GPa and the pressure induced water insertion into the interlayer. A comparable phenomenon could have occurred in the montmorillonite of the compressed bentonite MX-80. If water insertion into the montmorillonite interlayer takes place, the mesopore volume would indeed be reduced. However, the increased basal distance and the implied reduction of the forces holding the interlayer together would possibly also facilitate the montmorillonite delamination. Furthermore, delaminating montmorillonite would eventually contribute to the partial reduction of the mesopore volume. Yet both hypotheses appear to be equally possible, based on the actual knowledge and results. An in-situ measurement of the basal distance of montmorillonite under compressive stress would be necessary to verify the two hypotheses. If the montmorillonite’s basal distance gradually decreased during compression up to 3 GPa, the water–ice transition would be confirmed. If the basal distance increases at some point during compression, the more plausible explanation would be the water insertion into the montmorillonite interlayer.

The subtle alteration of the bentonite cation exchange capacity correlates well with the alteration of the specific surface area (Fig. 5-9a) and microporosity (Fig. 5-9b). Isostatic compressive stress causes a decrease of the accessible surface area of bentonite compressed at 1.5 GPa, regardless of the time. Diminished accessibility, in turn, leads to the decreased cation exchange capacity and amount of leachable Na⁺ (Tab. 5-2).
The mechanism of diminishing interlayer accessibility can be explained by stress-induced migration of the interlayer cations. Cations could travel into the hexagonal cavities on the tetrahedra-octahedra-tetrahedra layers of the dioctahedral montmorillonite. Here, they could remain partially fixed and inaccessible for the cation exchange. The cation migration and fixation could be induced or accompanied by changes in the layer charge distribution, as in the case of thermally treated smectite described by Kaufhold & Dohrmann (2010).

However, the cation exchange capacity (both time periods) and the amount of leachable Na⁺ (96 hours) seem to remain unaltered under a pressure of 3 GPa. The already described pressure-induced facilitation of the montmorillonite delamination at 3 GPa most probably leads to an improved interlayer accessibility.

Furthermore hydroxyl groups of this sample after compression at 3 GPa for 96 hours are destabilized (Tab. 5-2). The bentonite mass loss on dehydroxylation is detectably lower compared to the pristine and all other compressed samples. The structural destabilization is most probably accompanied by the process of smectite delamination. The friction between the smectite sheets which evolves during delamination is a possible agent causing the OH-groups destabilization.

**Illite Füzérradvány**

Compressive stress causes an ambiguous alteration of illite properties, which is largely difficult to interpret. The isostatic compressive stress induces a distinct alteration of the illite’s specific surface area (Tab. 5-2). The specific surface area increases at 1.5 GPa after 24 hours most probably due to stress-induced delamination. The increase of the micropore volume would also confirm this.
assumption (Fig. 5-8c). Delamination of illite could be suppressed by cold welding during 97 hours at 1.5 GPa. The specific surface area of this sample decreases together with the micropore volume.

About the same specific surface area is measured in illite compressed at 3 GPa for 24 hours. Its micropore volume is, however, clearly higher. An explanation for this discrepancy could be a second stage of delamination of illite particles along the non-welded (interlayer) planes. CO₂ can be adsorbed on the new lateral sites of the illite platelet edges and an increased micropore volume is then measured. The new sites could, however, remain inaccessible for the N₂ adsorption. The specific surface area thus remains lower than expected.

The difference in specific surface area between the pristine illite and illite compressed at 3 GPa for 97 hours borders the measurement error. The delamination rate was most probably the highest among the compressed illite samples, assuming preserved mesoporosity (Gregg & Langford, 1977) and/or considering the reduction in thickness of the smectitic layers in illite (5%, Tab. 5-1) due to the recrystallization of the interlayer water into ice VI/VII in the smectite layers of the interstratified illite, as discussed previously with bentonite (Mishima & Endo, 1978; Somayazulu et al., 2008).

Compressive stress is probably capable of squeezing out water from illite’s macro- and mesopores, as described for kaolin and bentonite. The illite pressings were covered with water when dismantled.

The isostatic compressive stress had practically no influence on the illite crystalline order, with the exception of the sample compressed at 3 GPa for 97 hours. The Kübler index of this sample is higher than that of pristine illite (Tab. 5-2). The crystalline order of illite appears to be improved during compression at 3 GPa for 97 hours. The stress-induced increase of the crystalline order of illite can also be followed in the results of the thermal analysis. Its mass loss on dehydroxylation (3.6%) is lower than that of the pristine illite and illite compressed under different compression regimes (4.2%; Tab. 5-2). The mass loss curve of illite compressed at 3 GPa for 97 hours above 600 °C up to 1000 °C is flatter than that of the other illite samples (Fig. 5-6a & b). Additionally, the mass loss on dehydration (25–200 °C) is similar in all the samples – the hydroxyl groups thus do not leave the structure in the form of sample humidity. This means that a portion of the hydroxyl groups remains fixed within the sample.

The decrease of the mass loss on dehydroxylation of illite compressed at 3 GPa for 97 hours (3.6%) is similar to that of bentonite compressed in comparable conditions (3.8%). The TGA and DTG curves of bentonite, however, confirmed the stability of the montmorillonite crystalline order.

The improvement of the illite’s crystalline order just by high compressive stress and without the contribution of elevated temperature may have interesting consequences for studies of burial diagenesis and metamorphosis of sediments.
5.6 Conclusions

Three clays tested in the presented study are amenable to the compressive stress. Cold isostatic pressing of kaolin, bentonite and illite at 1.5 and 3 GPa during one and four days at room temperature induces alteration to the clay properties. Several more or less distinct signs of cold welding could be identified in the clays as well.

Nevertheless, the extent of the alteration is, in general, moderate and the clays largely retain their valuable properties. This is relevant not only to the ceramics production but likewise to various engineering applications and geological processes where clays and compressive stress interact.

Compressive stress causes a decrease of the micropore volume and the prevalence of the finer end of the micropore size distribution. In general, the specific surface area of clays decreases at 1.5 GPa due to the stress-induced compaction and cold welding. Surprisingly, the surface area appears to increase at 3 GPa. This can be explained as a reaction to the clay mineral delamination.

The space for movement of delaminating clay mineral platelets should provide still preserved mesoporosity. The interlayer water potentially experiences transition into ice VI and VII polymorphs. This structural transition of water is accompanied by a volume reduction and should also provide an additional space for delamination. The water may possibly re-enter the interlayer at about 2.2 GPa as well. However, an in-situ basal distance measurement of the compressed minerals would be necessary to prove the two hypotheses.

A subtle alteration of the cation exchange capacity of bentonite correlates well with the alteration of its specific surface area and microporosity. Compression leads to a diminished accessibility of montmorillonite due to compaction and interlayer cation fixation in the hexagonal cavities of the tetrahedra-octahedra-tetrahedra layers. Compressive stress of 3 GPa, on the other hand, induces more intensive delamination of montmorillonite facilitating cation exchange. The alteration of bentonite under high compressive stress is in general subtle. In the scope of the presented study, bentonite retains its properties, which is important, for instance, in the geological disposal of radioactive wastes.

Compressive stress is translated into the structural integrity of clay minerals. Alteration of the kaolinite crystalline order appears to be primarily sensitive to the compression period. Montmorillonite and illite experience a rather subtle crystalline order alteration. The crystalline order of illite compressed at 3 GPa for 97 hours even shows signs of improvement – its Kübler index is lower than that of the pristine illite. The improved crystalline order of this illite sample is mirrored in its lower mass loss on dehydroxylation compared with the pristine illite.
Acknowledgment

The authors would like to acknowledge Stefanie Luginbühl (IGP, ETH Zürich) for her kind assistance with the compression experiments. Gabriele Peschke (IFB, ETH Zürich) is thanked for carrying out the ESEM imaging and for helping with the textural studies. Annette Röthlisberger (IGT, ETH Zürich) is acknowledged for conducting the AAS analyses.

References


106


6 Conclusions and outlook

6.1 Main findings

The first part of the thesis handled about the influence of temperature on physicochemical properties of sodium bentonite. Portions of bentonite were saturated with artificial pore water and their water content represented presumed water content within the engineered barrier in different radial distances from the heater. Portions of bentonite with different water content were accordingly stored at corresponding temperatures. In scope of the radioactive waste disposal, bentonite showed its overall stability against acting temperature. However minor changes occurred. The most important finding is its sensitivity to temperatures above 105 °C. The specific surface area decreased by 50% during thermal treatment. A significant decrease of the water uptake capacity under free swelling and of the water vapor adsorption most probably correlates with this phenomenon. Treated bentonite was remoulded and analysed. The procedure revealed cementing processes which were induced by high temperature. The cation exchange capacity (CEC), on the other hand, improved at temperatures above 105 °C. At first, it decreased after six months of heating at all temperatures. The CEC of bentonite heated for twelve and eighteen months showed, however, signs of recovery. This can be related to an in time slightly increasing mean layer charge of the montmorillonite. The interlayer cation of montmorillonite (predominantly Na⁺) was simultaneously exchanged with Ca²⁺ and Mg²⁺ originating in the soluble calcium and gypsum but also in the added pore water itself. The sensitivity of bentonite to temperatures above 105 °C can be related to reaching and overcoming certain activation energy necessary for alterations to take place. The mechanism of these kinetic effects, however, seems to require a more elegant description rather than just by means of the activation energy. The problem is that the activation energy is generally not known with any certainty (Pusch, 2008). Moreover, it is not clear what the calculated activation energy represents because several parameters that could modify the rate of alteration are probably not yet completely known (Ferrage et al., 2011). A promising way for a description of the alteration processes in such complex system like bentonite (and clay minerals in general) can possibly offer quantum mechanics. Each of reactions leading to alteration of clay minerals has its own propagation manner expressed as a cluster of various kinetic constants (Pytte & Reynolds, 1989). The vagueness of dozens of possible factors can potentially be clarified by means of quantum mechanics. Quantum chemistry could, for instance, explain the mechanisms of the time-dependent alteration and recovery of the bentonite cation exchange capacity described in Chapter 3 of the thesis. Research of clays in this direction already runs for decades (e.g. Gibbs, 1982; Bleam, 1993; Skipper et al., 1995; Sposito et al., 1999; Liu et al., 2012). Nevertheless, it largely remains out of the main focus of researchers, most probably due to its extreme computational demand (Skipper, 1998).
The finite element model of the heat transfer in granular bentonite presented in chapter 4 was designed to help solving the resaturation time scale problem. The model was based on the discrete circle geometries which represent mixtures of granular bentonite with different emplacement densities. Water content of the granular bentonite was simulated by adjustable thermodynamic properties of the fluid in the circle system interstices. The main factor regulating the heat transfer appeared to be the water content, whereas the structural features were decisive in partially saturated or dry systems. A dry granular material of low porosity is therefore expected to have a high effective thermal conductivity due to a high tortuosity facilitating thermal dispersion. The outcomes of the model were also very good proven experimentally which represents a step towards a solution for the reliable determination of the resaturation time scale.

The last part of the thesis reported about the compressive-stress-induced alterations of clays. Kaolinite, illite and sodium bentonite were compressed under isostatic compressive stress of 1.5 and 3 GPa during one and four days. In general, bentonite was the most stable clay material in the experiment, followed by illite, whereas the reaction of various properties indicated kaolinite the most pronounced sensitivity among all tested clays. Their different particle/crystal size distribution, elastic properties and compressibilities were most probably responsible for their different stability. Compressive stress caused a decrease of the overall micropore volume. A compressive stress of 1.5 GPa generally caused a decrease of the specific surface area of clays due to the stress-induced pore volume reduction and cold welding. However, the surface area tends to increase at 3 GPa most probably as a consequence of the clay mineral delamination. The crystalline order of kaolinite was incomparably more sensitive to the compressive stress that that of montmorillonite (in bentonite) or illite which even showed signs of a stress-induced improvement.

All clays retained most of their valuable properties in a satisfactory extent despite being exposed to for clays considerable levels of high temperature and compressive stress. In scope of the radioactive waste disposal, they (again) proved their qualities for their consideration as barrier components in a deep geological repository for radioactive waste. A temperature level, however, has to be controlled or ensured not to cross certain border value in order to provide perfect performance of the barriers for an extensive long time. High compressive stress influences each clay mineral in a different way. Nevertheless, the stress-induced alteration can even be advantageous.

References


Chapter 6 Conclusions and outlook


6.2 Research outlook

The main outcome of the first study about bentonite stored under near-field relevant conditions (chapter 3) revealed a critical temperature interval of \( T = 105-120 \) °C inducing an alteration to properties of clay. This interval of temperatures is relatively broad and a more precise specification of the threshold temperature would be beneficial. The same experiment could be carried out under the same conditions like in presented study with a few improvements.

Four sets of bentonite encapsulated in tight containers would be prepared. First set would encapsulate freeze-dried bentonite. Second set would contain bentonite stored at 75% of relative humidity (RH) until a weight equilibrium (procedure described in chapter 3) to achieve a known content of water in the interlayer. Bentonite in the second and third set would be saturated with deionized water and artificial pore water, respectively, to \( S_r = 1 \) to control the liquid water content and to study the influence of its chemical composition. Each set would contain two identically prepared specimens to reduce random errors.

The sets would be prepared for five batches to store them at five different temperatures: four batches within the critical temperature interval graded in 5 °C intervals \((4 \times 2 \times 4 \text{ specimens}) \) and one batch to store at the room temperature \((2 \times 4 \text{ specimens})\). The one batch stored at room temperature would be a reference case to study the influence of the amount of water and of its chemical composition with
exclusion of temperature. The experiment would take 18 months to compare the outcome of the analysis with results in chapter 3.

The model of the heat transfer in granular bentonite offers a lot of opportunities for additional research. Some ideas were already proposed in the end of the chapter 4.

Studies of the two physical factors could be broadened with a third one, the radiation. Knowledge base concerning different types of ionizing radiation and their influence on clays already includes the most common ones, the alpha, beta and gamma. Studies of the neutron radiation effects on clays are, however, scarce. Investigation of the neutron radiation effects could help for instance by prospecting of uranium-bearing deposits which contain californium, the neutron emitter. Neutrons originating in spontaneous fission of californium could have a potential alteration effect on clays in its vicinity.

Better controlled boundary conditions would also improve the compression experiments (chapter 5). Illite will only be discussed for an easier outline. Similar to the heating experiment, two sets of illite would be compressed. One portion of illite would be freeze-dried. The second portion would be weight-equilibrated at 75% RH to control the water content. Again, each set would be doubled for random error reduction (2 × 2 specimens).

The analyses of microporosity and specific surface area with gas adsorption were possibly the most sensitive elements in the study. To consolidate the results, several portions of illite (and other clays) should be compressed under identical conditions to obtain a bigger amount of material for the gas adsorption analysis. Analyses of the microporosity and surface area were pioneering for the compressed clays. Proper attention to this topic will for sure bring interesting and valuable results in the future. Especially, when a systematic study will be elaborated, comprising a finer pressure level gradation than in presented study, e.g. a step of 0.3 GPa.
Acknowledgments

My first and greatest express of gratitude belongs to my supervisor, Dr. Michael Plötze for his steady guidance, scientific coaching, everyday support and never-ending willingness to engage in valuable discussions about the research throughout my entire doctoral studies. He not only dedicated me to practices of scientific work, he also substantially broadened my professional and personal horizons. I’m utmost thankful to him for it.

I would like to pay a special expression of gratitude to my second supervisor Prof. Dr. Alexander Puzrin for his bottomless knowledge, motivational input and positive attitude helping me to enrich the scope and increase the value of the thesis. I’m sincerely thankful for his constant support during my studies creating relaxed atmosphere especially in their finale.

My particular gratitude is reserved for Prof. Dr. Laurence Warr for his willingness to be my co-examiner and whose expert’s opinion and experienced review of my work essentially improved the standard of the thesis.

A part of the thesis could be elaborated upon the patronage of NAGRA which is gratefully appreciated. Dr. Hanspeter Weber is thanked for his readiness in our fruitful conversations.

My work could be sustained with qualified backing of many members of the D-BAUG and D-ERDW. I would like to thank Ralf Herzog for smoothly enabling long-term laboratory measurements. I’m thankful to Dr. Pierre Andre Mayor for providing his scientific outcomes and works related to my topic. Prof. Dr. Robert Flatt and Prof. Dr. Peter Niemz are thanked for permitting access to devices. The dedication of Gabriele Peschke by ESEM analyses is likewise highly appreciated. A part of my thesis could be realized with a contribution of Prof. Dr. Peter Ulmer and Stefanie Luginbühel whose help are kindly acknowledged.

An exceptional thank-you goes to the colleagues in the ClayLab who created a perfect working atmosphere invaluable for my performance and were unceasingly prepared to help. Dr. Günter Kahr was a great scholar with an immense grasp of knowledge. The skillfulness and devotion of Annette Röthlisberger and Marion Rothaupt was flavored with a feeling of human touch during the everyday routine. My competence and abilities in the laboratory practice were periodically perfected by the patient mentoring of Beat Hornung who so markedly shaped the spirit of the ClayLab. I want to thank Dr. Nuttakan Wongfung as well who, besides being a cheerful colleague, was a great pal also outside the lab.
The experimental part of the thesis resides on the technical framework formed by the IGT workshop and administrative staff. I would like to thank Alfred Ehrbar, Ernst Bleiker, Andreas Kieper and Adrian Zweidler for their workaday support and inventions.

My great appreciation goes to the members of the Geomechanics group, especially Esther Schilling, Ingrid Mettler, Ivo Sterba and René Rohr. I’m thankful Pascal Minder and Dr. Dominik Hauswirth for their enlightening advices and discussions.

I would like to express a particular thanks to Dr. Rolf Zumsteg, Dr. Sophie Messerklinger and Dr. Erich Saurer who made the start of my PhD studies and whole stay in Zurich easier and I highly appreciate their warm welcome and involvement thereafter.

I would heartily reminisce of and acknowledge my former supervisor on the Comenius University in Bratislava, Dr. Renáta Adamcová who helped me to come to the ClayLab where I made the most part of my master thesis and where I finally returned for my PhD studies. Without her encouragement, nothing of this would ever happen.

Finally, I would like to thank my family who made my education possible and for their keen interest about my studies. I am likewise grateful to all my friends for their moral support.