

Mechanisms of Mineralogical Alteration of Diocahedral Smectites in Contact with Water – A Review

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Abstract

Bentonites are a suitable buffer- and backfill-material in the multibarrier-concept for high level radioactive waste - repositories. The geotechnical performance of engineered barriers using bentonite is to predict for the next 1 million of years. This review of experiments and phase-analytical investigations on more than 25 different bentonites and clays lets recognize few mechanisms in mineralogical alteration processes of smectite, gives first indications as possible impact on geotechnical properties of these bentonites and offers further screening tools for bentonites concerning their rate of alteration (slow or fast reacting phases).

Each bentonite and clay are characterized by a specific rate of alteration (sleeper or sprinter). This specific rate is determined by the geological background during the bentonite formation (parent rocks, marine or freshwater environment, heat impact during smectite formation). The geological background is controlling the active mechanisms of alteration by dissolution/precipitation and solid state-transformation. The composition of octahedral sheet (Al-rich bentonites have the lowest sheet stress by ion radius) and two interlayer mechanisms protect smectite aggregates (a: Na⁺-cations and/or b: Ca²⁺- and Mg²⁺-cations are responsible for stabilization). The reported mechanisms help to understand the variable response of bentonites in mineralogical and geotechnical performance in different zones in a repository like at interfaces “Canister / Bentonite”, “Host rock / Bentonite” as well as partially also

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for “Concrete /Bentonite”.

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1. Introduction

The behaviour of bentonite at changing water contents is a very complex phenomenon, influenced by coupled thermal, hydraulic, mechanical and chemical as well as sometimes also biological processes (THMC/B) (Pusch, 2006; Pusch and Yong, 2006; Sena et al., 2010; Wilson et al., 2011; Davies et al., 2017)

Most aspects of bentonite performance as barrier material are likely to be specifically related to the site (e.g. flow rate and composition of groundwater) and also to the properties of particular bentonite that will be used (Pusch, 2001a; Wilson et al., 2011; Herbert et al., 2004; Herbert et al., 2008, Nguyen-Thanh et al., 2014; Nguyen-Thanh et al., 2017).

A series of papers delivered certain indications for mineralogical alteration processes in bentonite as barrier material in contact with water. Altaner and Ylagan (1997) introduced a system of solid state-alteration of mixed layer phases and smectites explaining possible alteration processes without dissolution of full stacks. Pusch (1998; 2001a, b) described Si-precipitations and cementations of smectite stacks in compacted bentonite after heat impacts. Herbert et al. (2004) recorded a different behaviour of smectite in chemically closed or in chemically open systems. They identified in closed systems a charge reduction of smectite phases and in open systems a rising of charge. Lantenoise et al. (2005) developed a conceptual model leading to destabilization of dioctahedral smectite. X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) were applied as analytical tool to identify destabilized smectites after contact with water. They found that trioctahedral smectites were stable under the same experimental conditions. Furthermore, they described the catalytic function of Fe^{3+} in dioctahedral smectites supporting alteration processes. K, Na and Ca affect dissolution processes, but that was driven by particle's thickness. Herbert et al. (2004, 2008, 2011, 2016) combined XRD-measurements with transmissions electron microscopy (TEM) linked with energy-dispersive X-ray fluorescence spectroscopy (EDX). Using this analytical combination, they found and confirmed the different behaviour of illite-smectite mixed layer phases (IS-ml). Normal charged IS-ml in sense of Środon et al. (1992) formed thicker particles and have shown a higher degree of stability in contact with water. In comparison to those IS-ml phases, K- and charge deficient IS-ml phases (so-called dioctahedral vermiculite-smectite mixed layer phases – diVS-ml) were formed as thinner particles and underwent a faster alteration in contact with water. Pusch (2006) summarized repeated the hypothesis that smectite alteration can take place either by successive transformation to mixed smectite/illite and further to pure illite or by dissolution of smectite and neoformation of illite and used for that the natural analoga Ordovician Kinnekulle bentonite and Silurian Hamra bentonite.

Herbert et al. (2008) rearranged their former experiments and confirmed the different charge development of smectite in close and open systems. They have shown also the different impact of ionic strength on ‘double-layer’-swelling and swelling pressure. A larger series of swelling pressure and permeability experiments indicated that in cases of cementation by Fe and after heat impact also by Si will break the typical behaviour “swelling pressure \sim 1/permeability” (Herbert et al., 2011). Christidis and Huff (2009) described alteration processes of smectite from sections in bentonite deposits and the impact of parent rocks on chemical composition of smectite. Experiments with more than 25 bentonites under same conditions have shown that each bentonite has on own specific dissolution behaviour (Herbert et al., 2011; Nguyen-Thanh et al., 2014). Some bentonites underwent only a slow alteration related to montmorillonite layer probability (so-called “Sleepers”), other bentonites were characterized as fast reacting material (so-called “Sprinters”).

This report should summarize the in the different papers described mechanisms of smectite alteration and should visualize the possible meaning of these mechanisms for the different behaviour of bentonite in the different main interaction spaces “canister / bentonite”, “host rock / bentonite” and “concrete / bentonite”.

In this report, the bentonite barrier performance is reduced only to coupled processes determined by factors ‘solution’, ‘corrosion’ and ‘smectite’. The intensity of these factors (chemical activity) is determining the degree of action of mechanisms ‘solid-state-alteration’, ‘dissolution’ & ‘precipitation/cementation’. These mechanisms influence the process ‘double-layer’-swelling as important key property for the barrier performance. The effect “co-volume swelling” (Laird, 2006) is one of important parameters to control the rate of alteration (sleeper, sprinter).

2. Materials and experiments

The following materials were considered in this review: 12 bentonites from the BGR (Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany) collection (04F, 09F, 11F, 12F, 13F, 16F, 22F, 23F, 28F, 31F, 37F, 38F); nine bentonites of the API (American Petroleum Institute Clay Mineral Standards) series Polkville, Mississippi (API #20), Amory, Mississippi (API #22a), Chambers, Arizona (API #23), Otay, California (API #24), Belle Fourche, South Dakota (API #27), Bayard, New Mexico (API #30), Pioche, Nevada (API #32), Cameron, Arizona (API #31), and Garfield (nontronite), Washington (API #33a)], MX80 (a commercial product, obtained from Süd-Chemie AG, Moosburg, Germany in 1998 and in 2005), and illite-smectite interstratified structures (ISml) bearing clays such as Friedland clay (taken from core TB97/1 of the ore body from ‘Burgfeld Scholle’ quarry, Germany), GeoHellas clay (from western Macedonia, Greece, sample DA1206-02), and Vietnam clay from Nui Nua, Thanh Hoa province, north central Vietnam (Nguyen-Thanh et al., 2014, 2017).

The experiments were commonly designed approaching two different solid/solution ratios (1:3 and 1:10) of full saturated and compacted bentonite (raw dry density of

1.60 g/cm³). The experiments were carried out mainly under low temperatures like 25°, 60° and 90°C and with different solutions (aqua dest.; solutions with low ionic strength like Äspö granitic ground water and Opalinus clay pore water; solutions with high ionic strength like saturated NaCl-solution, IP21 solution as a MgCl₂-rich brine and young Portland cement pore water representing pore water of concretes; details see Herbert et al., 2004 and Herbert et al., 2008). Experiments to investigate the possible catalytic effect of Fe were arranged under percolation with different FeCl₂-enriched solutions and powdered native Fe as additive to the sample (Herbert et al., 2016).

Batch experiments should simulate a more closed chemical reaction system (Herbert et al., 2004), experiments with percolation (Herbert et al., 2008, 2016) or with overhead rotation of powdered, non-compacted samples (Nguyen-Thanh et al., 2014) should represent a more dynamic and so open chemical reaction system. The overhead rotation was applied for 20 days at different rates (20 rpm, 60 rpm) at room temperature to classify the bentonites and clays as slow or fast reacting material (Nguyen-Thanh et al., 2014; Pusch et al., 2015).

3. Mineralogical methodology

Transmission electron microscopy linked with energy-dispersive X-ray spectroscopy (TEM-EDX) was applied to characterize mineralogical signals of possible alteration processes of smectites at the fraction < 2 µm (details in Hoang-Minh et al., 2019). About 200 individual clay particles per sample were characterized by TEM-EDX with respect to crystal size, crystal habit, particle morphology, element distribution and stack order of particles.

The XRD analyses were performed on oriented samples of <2 mm material (separated by sedimentation) in air-dried and ethylene glycol-solvated specimens for identification of expandable clay minerals. Obtained XRD patterns were modelled with the Sybilla software developed by Chevron Inc. (Aplin et al., 2006), which is a software routine to compare the measured X-ray diffractogram with a modelled pattern of the basal reflections to better determine discrete clay minerals and interstratifications. The quantities of interlayer ion species and octahedral Fe as well as the mean value of coherent scattering domain sizes (T_{mean}) were considered as variables in the fitting process. This modelling of oriented XRD patterns was applied to validate the TEM-EDX measurements concerning possible precipitations of Fe, Al or amorphous silica on particles (details in Pusch et al., 2015; Hoang-Minh et al., 2019).

Additionally, bulk samples were analysed by XRD to determine their general mineral composition. The bulk samples were ground in an agate mortar by hand to <32 µm for XRD investigation. The processing of XRD powder patterns included also Rietveld refinement for semi-quantitative determination of essential mineral components by using the PROFEX software package (Doebelin & Kleeberg, 2015) as a graphical interface, which has embedded the BGMN software package (Bergmann et al., 1998; Ufer et al., 2004, 2008).

Fourier-transform infrared spectroscopy (FTIR) was applied commonly as further essential analytical method to verify the TEM-EDX-results. The bulk samples of approximately 1–2 mg were milled, wet sieved to <40 µm and dispersed in 120 mg of KBr, and then the mixtures were pressed to form pellets of 13 mm in diameter. The analyses were recorded in the mid-infrared range (400–4000 cm⁻¹). X-ray fluorescence spectroscopy (XRF) of bulk samples supported the validation of semi-quantification of mineral matter by BGMN-refinement of XRD-pattern of powdered bulk samples.

3.1 Mixed layers: Illite-smectite vs. dioctahedral vermiculite-smectite

Random interstratifications between illite and montmorillonite (IS-ml) are common components of clays and bentonites. Środoń et al. (1992) determined the principal charge distribution in IS-ml (in stricto sensu) with 0.89 for illite layers and 0.4 for smectitic layers per (OH)₂ O₁₀. In comparison to this statement, K- and/or charge-deficient IS-ml phases are denoted in this report as dioctahedral vermiculite–smectite (diVS-ml) interstratifications.

3.2 Alteration processes of smectites-*Rearrangement of stacks*

Untreated bentonites like MX80 (Figure 1a) show under transmission electron microscope a mixture of dark and flaky aggregates (thick particles) and non-discrete, fine particles forming a film-like matrix (Figure 1c). Especially, the morphology of particles forming this film-like matrix is transformed into discrete, xenomorphic or hypidiomorphic particles without any morphological swelling marks after a certain contact time with water (Figure 1d). Electron diffraction visualizes a rearrangement of initially turbostratic ordered layers per stack of the untreated montmorillonite (inlet of Figure 1c) into a 1 M polytype in the reaction products (inlet of Figure 1d). Such transformation of layers in stacks is sometimes also to recognize in larger aggregates in first steps, where the original turbostratic order of such stacks (inlet of Figure 1a) is showing after a certain contact time with water intermediate states between turbostratic and 1M polytype order of stacks (inlet of Figure 1b).

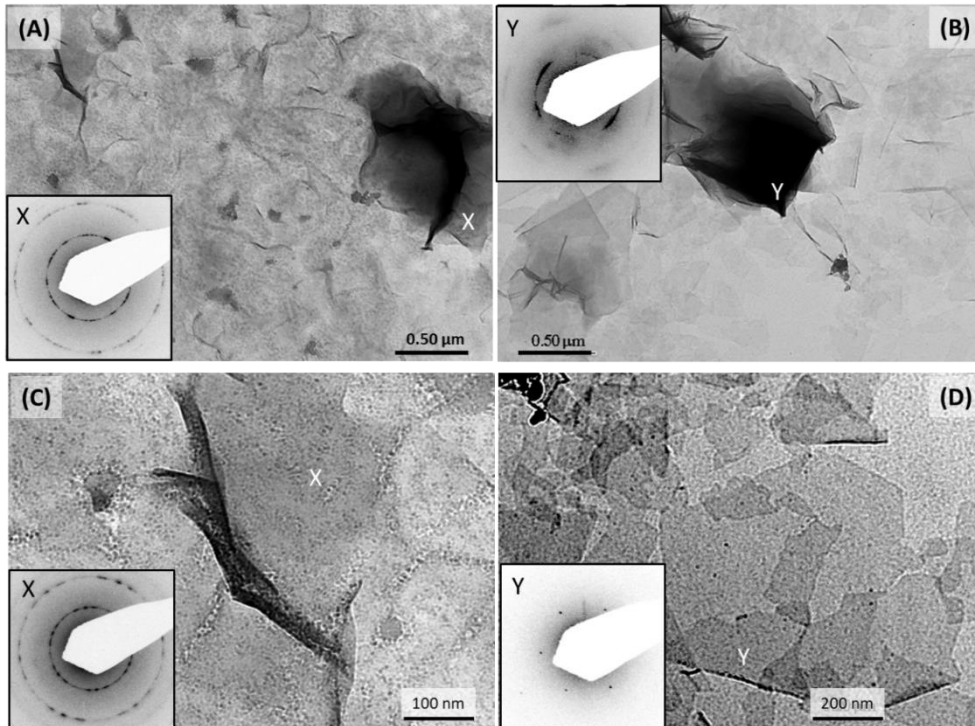


Figure 1: TEM-micrographs and electron diffractions (inlets) of bentonite MX80 (year 2000)

MX80 - contact time in deionized water: < 4 hours

(a) Particles distributed as dark aggregates and as fine non-discrete particles forming a film-like matrix (stack order of dark aggregates: turbostratic)

(b) Zoom of image (A) – no discrete particles are to recognize in the film-like matrix (stack order of matrix: turbostratic). MX80 - contact time in deionized water: 13 days

(c) Particles distributed as dark aggregates and as fine discrete particles (stack order of dark aggregates: intermediate state between turbostratic and 1M-polytype)

(d) Zoom of image (C) – only discrete fine particles with idiomorphic and xenomorphic morphology are to recognize (stack order of fine particles: 1M-polytype)

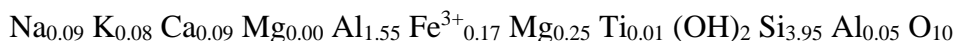
The “coherent scattering domains” (CSD) by XRD techniques of the starting montmorillonite show CSD values between 8.5 and 10.5 nm for ethylene-glycol saturated montmorillonite indicating that in general stacks are formed mostly by 5 - 6 layers. These CSD values are decreased to 3-4 nm (2-3 layers) related to contact time, temperature and type of solutions (Herbert et al., 2004).

Altaner & Ylagan (1997) described similar processes in illite-smectite mixed layer phases as ‘solid state transformation’. In case of MX80 (trade ware from year 2000), a contact time of 13 days was already enough for these complete rearrangements of stacks (Figure 1).

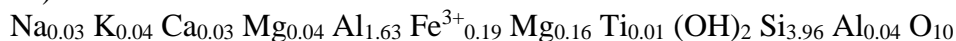
3.3 Chemical alterations of smectite accompanying the rearrangement of stacks

TEM–EDX analyses of montmorillonite particles show for the untreated MX80 an interlayer charge of 0.36 per (OH)₂O₁₀ and for montmorillonite after contact time with water for 13 days (Figure 1b) a reduced interlayer charge of 0.21. This low interlayer charge for this altered smectite was also verified by n-alkylammonium methodology as 0.20 (written communication by R. Dohrmann, 2002).

Montmorillonite (untreated MX80, Figure 1a):



Montmorillonite (treated MX80, 13 days in contact with deionized water, Figure 1b):



The averaged mineral formulae of montmorillonite in untreated and treated MX80 (Figure 1) were calculated using TEM-EDX-data. Mg-substitution by Al has caused the above-mentioned lowering in the interlayer charge.

This trend to decreasing interlayer charges of smectite for reaction products was confirmed also in other experiments in chemically closed reaction systems (Herbert et al., 2004; Herbert et al., 2008). Experiments in a more dynamic, chemically open reaction system (e.g. percolation, overhead rotation) can cause a rising interlayer charge of montmorillonite by higher charge deficit in octahedral layer (Pusch et al., 2007; Herbert et al., 2008).

3.4 Mineralogical alterations of smectite accompanying the rearrangement of stacks

The described chemical alteration of smectite is accompanied by changes in the distribution of IS-ml series. Środoń et al. (1992) postulated for IS-ml in *senso stricto* certain interlayer charge of illite (0.89) and montmorillonite (0.4). Bentonites contain in this concept full charged IS-ml (with montmorillonite as an end member of this series) and K- and charge deficit IS-ml phases. These K- and/or charge deficit phases are called here as dioctahedral vermiculite-montmorillonite mixed layer phases (diVS-ml). The charge deficit of diVS-ml phases is causing thinner particles

than for IS-ml phases. In result of that IS-ml phases resist longer dissolution processes than diVS-ml phases. The visualized example of MX80 bentonite saturated with Äspö-pore solution in a more chemically closed reaction system (Herbert et al., 2008) is demonstrating this different resistance (Figure 2).

The IS-/diVS-ml – ratio alters with contact time between smectite particles and solution (inlets in Figure 2). As first step diVS-ml phases are dissolved and the ratio IS/diVS is rising (see the first 7 days in Figure 2). In a further step a disaggregation of IS-ml phases is accompanied by charge reduction. So, IS-ml phases are converted stepwise into diVS-ml mainly as solid-state transformation (see diagrams for 1 year and 2 years in Figure 2). Normal charged and deficit-charged montmorillonite is commonly the most frequent member of these IS- and diVS-ml series during this alteration process (Figure 2), because a remarkable mitigation of dissolved elements is excluded in chemically closed reaction systems. Typically for this chemically closed reaction system the interlayer charge of montmorillonite in this example with Äspö-pore solution (Figure 2) is decreased from 0.40 per $(\text{OH})_2 \text{O}_{10}$ of original MX80 to 0.35 after 7 days to 0.28 after 1 year and 0.16 after 2 years. Based on TEM-EDX-data, octahedral Al increased from 1.54 – 1.54 – 1.57 – 1.64 and octahedral Mg decreased 0.26 – 0.25 – 0.22 – 0.15 (Herbert et al., 2008).

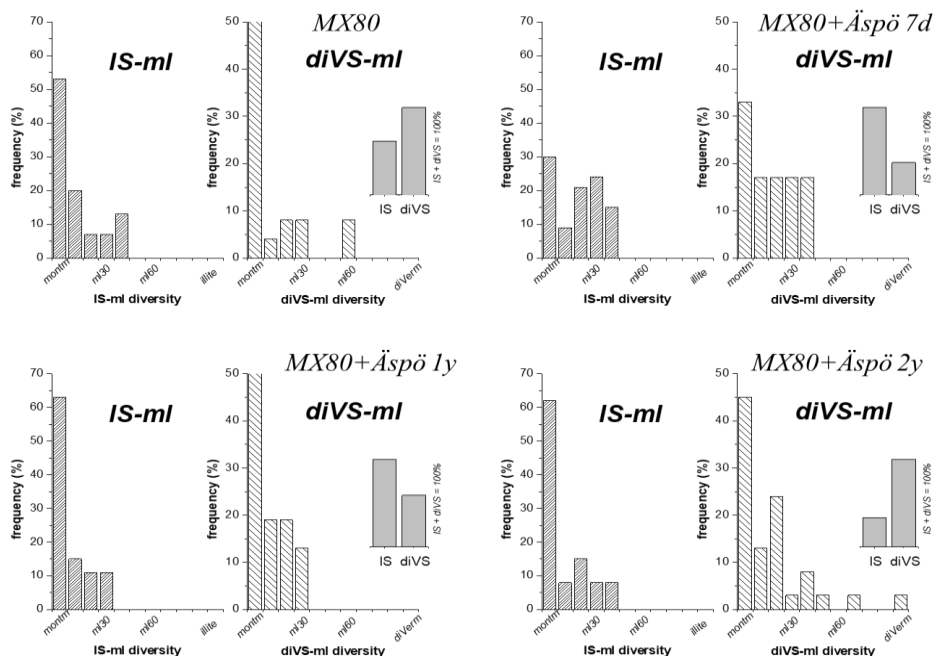


Figure 2: Changing distribution of members in the illite-montmorillonite- (IS) and dioctahedral vermiculite-montmorillonite (diVS) mixed layer series during long term experiments with MX80 bentonite and Äspö-pore solution (using mineral formulae calculated by TEM-EDX-data) – experimental setup in Herbert et al., 2008.

Semi-quantitative XRD-measurements using Rietveld-routines (Kasbohm et al., 2018) has shown also a slight reduction of the smectite amount in the treated samples (from 1% - 7%) in case of Gaomiaozi bentonite deposit (GMZ) (Xinghe County, Inner Mongolia Autonomous Region, China).

3.5 Have chemical and mineralogical alterations an impact on geotechnical parameters?

Closed chemical reaction system: Herbert et al. (2008) reported about the behaviour of MX80 bentonite in different pore solutions representing different ionic strengths using two years batch experiments. MX80 saturated by pure water has shown a decreasing swelling pressure with decreasing interlayer charge. MX80 in pore solutions of low (e.g. Äspö, Bure, Opalinus) and high ionic strength (e.g. NaCl, IP21) have drawn an opposite trend: slightly rising swelling pressure with decreasing interlayer charge of run products. Swelling pressure of MX80 in pore solution with low ionic strength was higher than for high ionic strength.

Jasmund & Lagaly (1993) described already the different development of swelling pressure in relation to different salt concentrations in solution. These different states of repulsive and attractive forces explain the observed behaviour in Herbert et al. (2008).

Herbert et al. (2008) described also decreased ENSLIN-water absorption and cation exchange capacity (CEC) with decreasing interlayer charge.

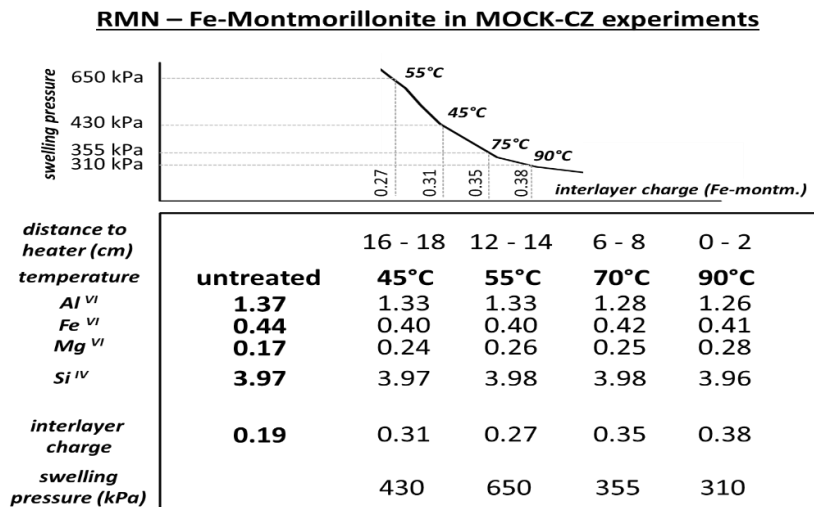


Figure 3: Chemical composition and interlayer charge development of Fe-montmorillonite (calculated by TEM-EDX-data) in relation to swelling pressure influenced by heat and pore solution impact in a 2-year Czech Mock-up experiment using RMN-bentonite (experimental design and database in Pusch et al., 2007)

3.6 Open chemical reaction system

A Czech Mock-up test simulating the so called KBS-3V concept with a “canister” temperature of 95°C showed that the Ca montmorillonite clay with 17% Fe lost more than half of its swelling pressure and became about 10 times more permeable than untreated clay. During this two years Mock-up experiment the used compacted RMN-bentonite underwent a rising interlayer charge with strongest impact close to the heater. The amount of octahedral Al decreased and octahedral Mg increased (Figure 3). The increasing interlayer charge is accompanied by decreased swelling pressure. This Mock-up experiment is so to consider as a chemically open reaction system until in a depth from 18 cm far from heater during these two years of this experiment (Pusch et al., 2007).

A further parameter, additionally to the heat impact, is influencing the mineralogical alteration. The lowest heat impact 45°C at the end of the sampled section is not the lowest affected material. The lowest affected bentonite was recognized at 55°C, located closer to the heater than the 45°C heated material (Figure 3). This special role of 45°C sample is also mirrored in the development of layer probability of montmorillonite (%S) as average of all members of IS- and diVS-ml series in the samples: RMN original %S=89%, 45°C %S=48%, 55°C 87%, 75°C=89% and 90°C %S=67%. An illitisation-like process is indicated close to the heater (90°C) an even far from the heater (45°C). The layer probability of montmorillonite between these two positions is comparable to the averaged %S of the original RMN-bentonite. The heat-driven mitigation of dissolved Si away from the heater is responsible for the illitization-like effect at 90°C and is feeding the zones of 75°C and 55°C to stabilize the %S-level. A critical concentration of pore solution caused by heat-driven mitigated elements into the zone of 45°C could increase the reactivity of smectite promoting again an illitisation-like alteration.

3.7 Have precipitation and cementation an impact on geotechnical parameters?

Flow rate, reactivity of smectite, role of montmorillonite and IS-/diVS-ml phases for the behaviour of dissolved Si

Overhead rotation experiments with a large series of different bentonites (Herbert et al., 2011; Nguyen-Thanh et al., 2014; Herbert et al., 2016) indicated an impact of flow rate and dissolution rate on behaviour of dissolved Fe and Si in the system. Fe-precipitation and cementation of smectite stacks were observed in case flow rate (mitigating iron ions) was lower than the dissolution rate of Fe-bearing phases. Dissolved Si underwent two options under low flow rate conditions: (i) in IS- and diVS-ml phases: conversion of illite layers into montmorillonite layers and (ii) in montmorillonite: precipitation of Si and cementation of stacks. So, IS- and diVS-ml phases seem to offer a certain buffer for Si-uptake.

This concept supported a discussion of the swelling pressure and permeability behaviour of MX80 (that means a low buffer for dissolved Si) under percolation with different solutions (e.g. NaCl, IP21, Opalinus). Subsequent these basic

solutions were spiked with iron-(II)-chloride in concentrations of 10^{-1} to 10^{-4} mol/litre concentrations of FeCl_2 -solutions (Herbert et al., 2011). Finally, the development of swelling pressure was compared with development of permeability (SP vs. Perm). Three different patterns of “SP vs. Perm”-behaviour were classified in relation to rising concentration of FeCl_2 -solution: (i) swelling pressure $\sim 1/\text{permeability}$, (ii) swelling pressure $\sim \text{permeability}$ and (iii) swelling pressure \pm constant, but rising permeability.

The class “swelling pressure $\sim 1/\text{permeability}$ ” is to consider as standard rule – rising swelling pressure is densifying the barrier, mirrored in a lower permeability. The class “swelling pressure $\sim \text{permeability}$ ” was to recognize in cases of rising concentrations of FeCl_2 -solution, where the swelling pressure decreased and permeability decreased, too. Herbert et al. (2011) discussed this as effect of precipitation and cementation of stacks by Fe-oxyhydroxides. Cemented stacks were limited to develop a swelling pressure. Otherwise, cementation limited also the flow of pore solution densifying the barrier system. Higher pressure can break such cemented areas opening channels for a fast transport of solutions. This situation was discussed as possible background for the class “swelling pressure \pm constant, but rising permeability”.

Kasbohm et al. (2013) published investigations about Cu-penetration of compacted MX80 bentonite, Friedland clay and saponite clay in direct contact with a hot Cu-plate. The deepest degree of penetration by Cu was identified in MX80 bentonite (see Figure 7 in Kasbohm et al., 2013). The distribution of higher Cu-concentration in the contact zone of MX80 bentonite was shaped in the depth more channel-like than like a diffusion front. Furthermore, the contact between MX80 bentonite and the Cu-plate has shown the highest degree of corrosion for the Cu-plate. The depth of penetration and the degree of corrosion for Friedland clay was much lower. Otherwise, the swelling pressure of untreated Friedland clay (dominated by Fe-rich IS-ml phases) was lower than for untreated MX80 bentonite (> 1.000 kPa vs. 4.000 kPa).

They explained this situation with channel-like broken zones of before heat-affected cemented stacks in MX80 bentonite. Dissolved Si couldn't mitigate in deeper parts of MX80. So, dissolved Si precipitated and formed cemented larger areas close to the Cu-plate. Otherwise, the dominating IS-ml phases in Friedland clay offer a Si-buffer by conversion of illite layers in montmorillonite layers. This partial smectitisation of IS-ml phases is avoiding Si-precipitation and cementation and is avoiding so also the forming of channel-like structures as observed in MX80 bentonite.

4. Rate of smectite alteration

4.1 Specific alteration rate

25 bentonites and clays were treated under same experimental conditions by overhead rotation (Herbert et al., 2011; Nguyen-Thanh et al., 2014; Herbert et al., 2016). These authors found that bentonites have a specific dissolution potential. Some bentonites have shown in interaction with water a very fast alteration of chemical composition (these bentonites were called as “Sprinter”), other bentonites were nearby unchanged under the same experimental conditions (called as “Sleeper”). This potential was identified by degree of “illitisation” or smectitisation for each sample (proofed by TEM-EDX, FT-IR, XRD). The authors defined themselves bentonites with a loss of smectite layer probability less than 5% (e.g. from %S = 90% to %S = 86%) as sleeper and bentonites with a loss of smectite layer probability after the test experiments higher than 20% as sprinter.

Bentonites with illite-smectite mixed layer phase in the original material have shown commonly smectitisation. It seems that such mixed layer phases can buffer dissolved Si. Otherwise, fast reacting bentonites with a tetrahedral Si amount close to 4 per half unit cell (phuc) are preferred for cementation of aggregates by precipitated Si. This cementation can have drastically impact to the properties of engineered barrier.

4.2 Driving forces for specific alteration rate

The following parameters were identified as driving forces for the mentioned specific dissolution potential: (i) original distribution of Al, Fe and Mg in octahedral sheet and (ii) Na/(Ca+Mg)-ratio characterising the composition in the interlayer space.

4.2.1 Cations in the octahedral sheet

Increasing octahedral Fe- and Mg-amounts are promoting a faster dissolution of smectite. Larger quantities of Fe and/or Mg in the octahedral sheets enhanced the rates of alteration because of the associated stress by higher ion radius of Fe- and Mg-ions than for Al, which affects the particle lattice structure. This finding is in agreement with previous studies concerning the stability of smectites (Čičel and Novak, 1977).

4.2.2 Cations in the interlayer space – Two principles for sleeper/sprinter-behaviour

The mentioned overhead rotation-experiments indicated that the composition of the interlayer affects also strongly the degree of alteration of smectite. These experiments under different conditions (20 rpm, 60 rpm; deionized water, saturated NaCl-solution; all for 20 days) on 25 bentonites have drawn two general types of interlayer impact on the specific rate of alteration of smectite: type A – Na-cations in interlayer space act as protector against alteration as well as type B – Ca+Mg-

cations in the interlayer space protect the stacks (Nguyen-Thanh et al., 2014). High Na/(Na+Ca+Mg)-ratio in interlayer space of type A-smectites (e.g. Polkville API #20, Otay API #24, Pioche API #32, Cameron API #31, Kunipia F) stabilize the smectite aggregates against any dissolution attacks in contact with pore solution. The result is a slow alteration (sleeper). Otherwise, a lowered Na/(Na+Ca+Mg)-ratio in interlayer space of type A-smectites (e.g. MX80, trade ware from 2005) undergo a fast alteration in contact with pore solution (sprinter).

A similar situation is drawn for type B-smectites, where Ca+Mg cations in the interlayer are responsible to resist possible attacks by pore solution. Low Na/(Na+Ca+Mg)-ratio in interlayer space of type B-smectites (Ca+Mg cations are dominating) are characterised by a slow alteration (sleeper) like Belle Fourche (API #27). Smectites with a high Na/(Na+Ca+Mg)-ratio in interlayer space (e.g. Garfield API #33a, Friedland clay) are easier to attack and to alter (sprinter).

Especially, Fe-rich bentonites (e.g. Garfield, API #33a) and Fe-rich clays composed by IS-/diVS-ml phases mainly (e.g. Friedland clay, Holmehus clay) are commonly sprinters. The dissolution of Si from the tetrahedral sheets (“illitisation”) is faster as it can mitigate driven by ruling flow rate. IS-/diVS-ml phases offer a certain Si-buffer by conversion of illite layers into montmorillonite layers (smectitisation), but precipitation of the dissolved Si occurs in montmorillonite-rich smectites because of its limited Si-buffer.

4.2.3 Cations in the interlayer space – Type A, B - Classification by mineralogical analyses

Empirically, the experimental results indicated a way to predict the different behaviour of bentonites in low level energy experiments by chemical parameters of smectite (Herbert et al., 2011). Following that, smectites with dominating octahedral Al [$Al_{oct} > 1.4$ per $(OH)_2 O_{10}$] and a remarkable amount of octahedral Fe [$Fe^{3+}_{oct} > 0.19$ per $(OH)_2 O_{10}$] were classified as members of group A. These smectites were protected by high Na in the interlayer space. Otherwise, smectites also with dominating octahedral Al [$Al_{oct} > 1.4$ per $(OH)_2 O_{10}$] and low amount of octahedral Fe [$Fe^{3+} < 0.19$ per $(OH)_2 O_{10}$] or smectites generally with reduced octahedral Al [$Al_{oct} < 1.4$ per $(OH)_2 O_{10}$] belonged to group B. Such smectites were protected by Ca and Mg in the interlayer space (see also Figure 9 in Nguyen-Thanh et al., 2014). The composition of octahedral sheet was determined by TEM-EDX.

A comparison of TEM-EDX-based octahedral Al vs. FTIR-based position of the δ_{AlAlOH} -band and octahedral Fe vs. δ_{AlFeOH} -band shows two different trends (see Figure 5 in Nguyen-Thanh et al., 2014). These trends divide the samples again into the two groups referred to as types A and B. This comparison between TEM-EDX-based mineral formulae and FTIR measurements have shown strong linear trends within each group. The positions of the δ_{AlAlOH} -bands show a rising linear trend with rising octahedral Al-amount (type A) and a decreasing linear trend of the positions of δ_{AlAlOH} -bands with rising octahedral Al-amount (type B).

Muller et al. (2000) and Wolters (2005) used thermal analysis to classify smectites

into three types. Based on their octahedral Al^{3+} and Fe^{3+} contents, those authors identified smectites with $\text{Al}^{3+}_{\text{VI}} < 1.4$ per $[\text{O}_{10}(\text{OH})_2]$ and $\text{Fe}^{3+}_{\text{VI}} > 0.3$ per $[\text{O}_{10}(\text{OH})_2]$ which were trans-vacant; the smectites with $\text{Al}^{3+}_{\text{VI}} > 1.4$ per $[\text{O}_{10}(\text{OH})_2]$ and $\text{Fe}^{3+}_{\text{VI}} < 0.3$ per $[\text{O}_{10}(\text{OH})_2]$ were cis-vacant, and the smectites with $\text{Al}^{3+}_{\text{VI}} > 1.4$ per $[\text{O}_{10}(\text{OH})_2]$ and $\text{Fe}^{3+}_{\text{VI}} > 0.3$ per $[\text{O}_{10}(\text{OH})_2]$ tended to be trans-vacant mostly and were predominantly ferrian.

4.2.4 Cations in the interlayer space – Assumed mechanisms to protect smectite

Type A – Na^+ as protector: Laird (2006) claimed that an increase in the amount of Na^+ in the interlayer can enhance the viscosity of water in the interlayer or can enlarge the co-volume swelling between the particles. Both mechanisms result in the limitation of particle movement, and thus Na-smectites have greater resistance. A large Na concentration therefore has the effect of retarding the dissolution impact on smectite particles and favours delamination of relatively stable quasicrystals. For Na-dominant populations of the interlayer, a co-volume process increases the swelling pressure between the delaminated layers as the particle number increases (Laird, 2006). As a result, the co-volume processes cause a limitation of the particle mobility during rotating activities. Such Na-montmorillonites have only a low specific dissolution potential and are stable phases.

Type B – Ca^{2+} & Mg^{2+} as protectors: In the other cases, type B bentonite with charge sites oriented opposite to one another on adjacent layers will be protected. Divalent cations (Ca, Mg) in the interlayer can fix the sheet stacks and balance the opposing charges in adjacent layers (Kaufhold and Dohrmann, 2008). The smectite aggregates will be protected from alteration by an increase in the overall stack stability. Due to the relative number of platelets per tactoid and hydrolysis properties, Ca-montmorillonite is more stable than Na-montmorillonite in water (Banin and Lahav, 1968; Eyal and Singer, 1987; Kaufhold and Dohrmann, 2008). An increase in the number of Ca+Mg cations in the interlayer promotes the unmixing of monovalent and divalent cations to particles of different sheet structures. Quasicrystals can therefore be broken along Na-bearing interlayer and help to maintain the quasicrystal (Laird, 2006). Such bentonite with Ca- and Mg-montmorillonites can be also taken as slow-reacting bentonite due to their low specific dissolution potential.

4.2.5 Cations in the interlayer space – Role of barrier environment on smectite reactivity

Nguyen-Thanh et al. (2014) classified different reaction environments by their short-term alteration experiments. The specific dissolution potential of the same bentonite was partially different under changed experimental conditions for solution and rotation speed.

Type A - Highly transport-controlled alteration experiments in contact with 1 M NaCl solution (60 rpm + NaCl): The saturated concentration of NaCl is increasing

the alteration of smectite. Furthermore, the high rotation speed of 60 rpm offers a higher flow rate for a fast transfer of dissolved elements into the bulk solution of the experiment. The authors found under these highly transport-controlled alteration experiments for each bentonite and clay only type A (Na⁺ in interlayer space as protector) as only active interlayer mechanism. Type B (Ca²⁺ & Mg²⁺ as protectors) was never identified as active interlayer mechanism in all experiment under these conditions.

Type A - Moderate transport-controlled alteration experiments: Smectites of type A for the interlayer impact show under all other experimental conditions the same behaviour of specific dissolution potential (20 rpm + deionized water; 60 rpm + deionized water; 20 rpm + 1M NaCl).

Type B - Moderate transport-controlled alteration experiments (20 rpm + 1 M NaCl): The NaCl-solution is initiating an additional impact to the specific dissolution potential for smectites of type B. So, the specific dissolution potential in 1 M NaCl-solution is slightly different the behaviour in deionized water.

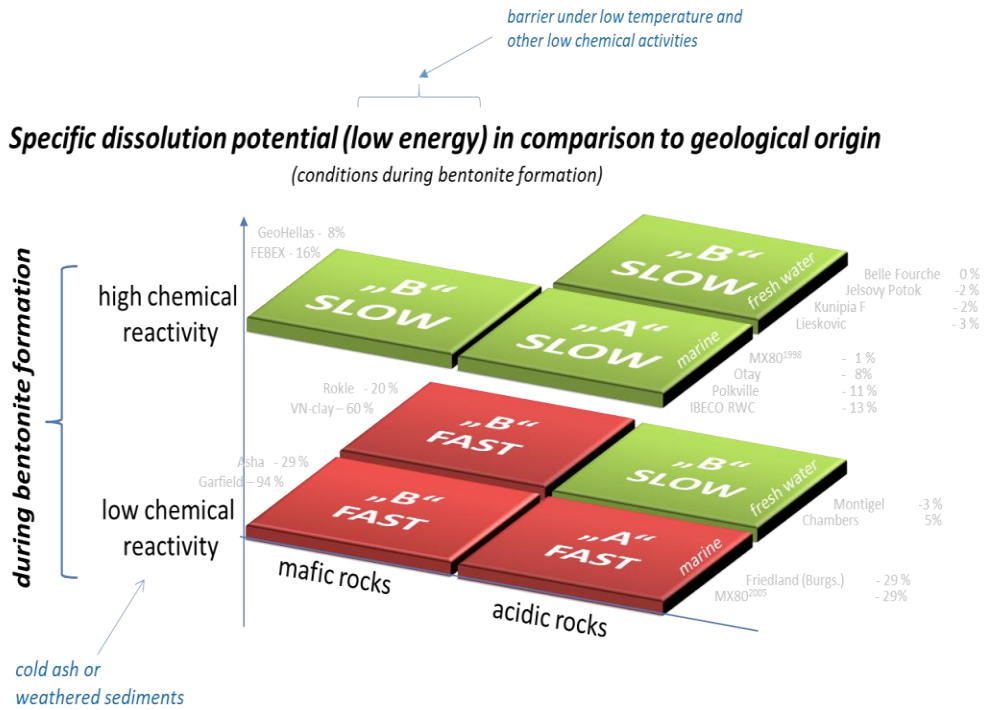


Figure 4: Specific dissolution potential in relation to the geological origin of bentonites – case: barrier under low temperature and other low chemical activities. X-axis: main chemical composition of the parent rocks; y-axis: environment of bentonite formation; z-axis: degree of temperature during bentonite formation; “A”, “B” - interlayer impact type of original bentonite on specific dissolution potential; FAST, SLOW - fast alteration of bentonite ("sprinter") or slow alteration of bentonite ("sleeper").

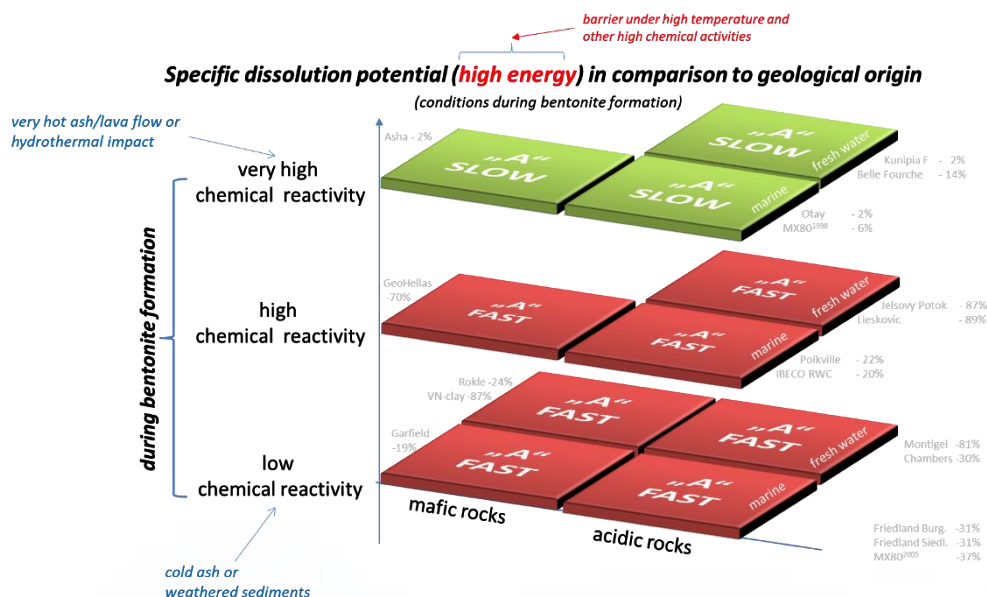


Figure 5: Specific dissolution potential in relation to the geological origin of bentonites – case: barrier under high temperature (e.g. hot phase of canister) and other high chemical activities (e.g. brines).

Legend: Chambers -30% - The probability of montmorillonite layers (%S) in Chambers bentonite is reduced by 30% (“illitisation”) after 20 days of overhead rotation (here: 60 rpm, 1 M NaCl-solution) from %S_{orig} = 93% (S_{tetrahedra} = 3.94) to %S_{treated} = 63% (S_{tetrahedra} = 3.76).

Type B - Low transport-controlled alteration experiments (20 rpm + deionized water): The additional impact of NaCl-solution is not available in this experimental design. So, only the rotation speed affects the dissolution behaviour.

Summarizing, the type A-smectites are more resistant against any higher impacts by rotation speed and solution than type B-smectites.

Room temperature and a chemically closed reaction system (e.g. interface barrier – host rock) seems to correspond to low and moderate transport-controlled alteration experiments and the hot phase of the interface barrier – canister including contact with solutions of medium or higher ionic strength could be represented by highly transport-controlled alteration experiments. All later own measurements with other bentonites and clays under different conditions let also apply all these above-mentioned classes for the specific dissolution potential (e.g. Pusch et al., 2015; Herbert et al., 2016).

4.2.6 From the mineral formula of smectite to a sleeper/sprinter-evaluation

Nguyen-Thanh et al. (2014) developed also an Excel-based tool to calculate the expected specific dissolution potential under the described different experimental designs.

Type A - Highly transport-controlled alteration experiments in contact with 1 M NaCl solution (60 rpm + NaCl): The empirically determined effect of interlayer cations (Na, Mg, Ca) on loss of montmorillonite layer probability (expressed as ΔP_{XII}) followed the trend:

$$\Delta P_{XII} = 15.46 \ln [\text{Na}/(\text{Na}+\text{Ca}+\text{Mg})] - 68.83 \quad (1)$$

(see Fig. 8a in Nguyen-Thanh et al., 2014)

The impact of the octahedral sheet (ΔP_{VI}) on the specific dissolution potential modelled by regression equation

$$\Delta P_{VI} = -5.26 \ln [(\text{Fe}+\text{Mg})/(\text{Fe}+\text{Mg}+\text{Al})] - 9.09 \quad (2)$$

(see Fig. 8b in Nguyen-Thanh et al., 2014)

Type A - Moderate transport-controlled alteration experiments:

$$\Delta P_{XII} = 7.14 \ln [\text{Na}/(\text{Na}+\text{Ca}+\text{Mg})] - 32.76 \quad (3)$$

(see Fig. 8c in Nguyen-Thanh et al., 2014)

$$\Delta P_{VI} = -3.78 \ln [(\text{Fe}+\text{Mg})/(\text{Fe}+\text{Mg}+\text{Al})] + 6.52 \quad (4)$$

(see Fig. 8d in Nguyen-Thanh et al., 2014)

Type B - Moderate transport-controlled alteration experiments (20 rpm + 1 M NaCl):

$$\Delta P_{XII} = -9.70 \ln [\text{Na}/(\text{Na}+\text{Ca}+\text{Mg})] + 17.2 \quad (5)$$

(see Fig. 8e in Nguyen-Thanh et al., 2014)

$$\Delta P_{VI} = -79.8 \ln [(\text{Fe}+\text{Mg})/(\text{Fe}+\text{Mg}+\text{Al})] + 269.9 \quad (6)$$

(see Fig. 8f in Nguyen-Thanh et al., 2014)

Type B - Low transport-controlled alteration experiments (20 rpm + deionized water):

$$\Delta P_{XII} = -7.91 \ln [\text{Na}/(\text{Na}+\text{Ca}+\text{Mg})] + 14.53 \quad (7)$$

(see Fig. 8g in Nguyen-Thanh et al., 2014)

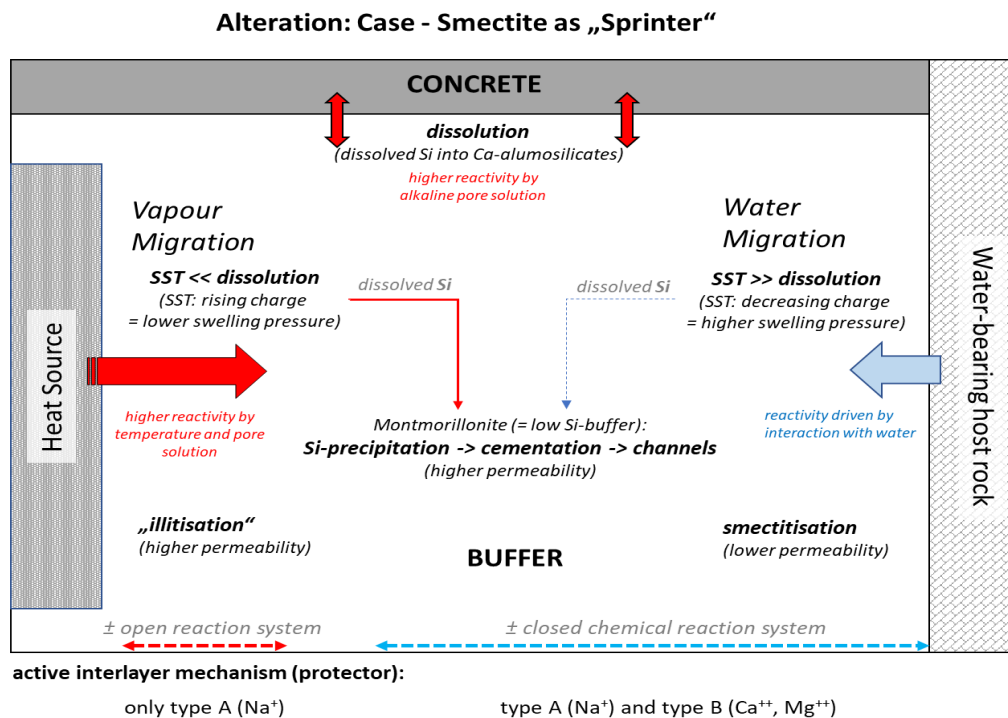


Figure 6: Possible interactions of barrier bentonite in a final repository (case: bentonite as sprinter) [Legend: SST – solid-state-transformation]

$$\Delta P_{VI} = -68.52 \ln \left[\frac{(\text{Fe}+\text{Mg})}{(\text{Fe}+\text{Mg}+\text{Al})} \right] + 230.5 \quad (8)$$

(see Fig. 8h in Nguyen-Thanh et al., 2014)

4.2.7 Assumed geological background for sleeper/sprinter-development

The geological background during the formation of bentonite was discussed for all bentonites and clays involved in above-mentioned overhead rotation experiments (Mingliang et al., 2012). In this context the bentonites and clays were classified by parent rocks (mafic rocks, acidic rocks), environment of deposition (marine, fresh water) and expected chemical reactivity (low, high, very high) during the main phase of bentonite formation (Figs. 4, 5).

This classification of geological background of bentonites leads to following indications:

Case “Low temperature & low pore solution impact” in an engineered barrier (Figure 4): Bentonites and clays of type A occur only under sedimentation of ashes from acidic parent rocks in a marine environment. Examples are MX80, Otay, Polkville and IBECO bentonites. Slow reacting bentonites of types A and B are possible commonly, if bentonite formation run under elevated temperatures (e.g. after hot ash fall, impact of hydrothermal solutions etc.). Probably, only stable smectite crystals and stacks (manifested by chemical composition and grain size distribution) could survive this environment with a high chemical activity during

the bentonite formation.

Case “Higher temperatures & high pore solution impact” in an engineered barrier (Figure 5): Under such strong environment in the barrier (e.g. at the hot contact with container), only type A is the active interlayer mechanism to protect the smectite phases in all bentonites and clays. Again, slow reacting bentonites are a result for those bentonites, which run during the bentonite formation processes under very high temperature and/or very high impact by pore solution (e.g. MX80 – trade ware 1998, Otay, Belle Fourche and Kunipia F).

4.2.8 How to apply the sleeper/sprinter-concept in final disposal of high radioactive waste?

Three different interfaces seem to consider in the engineered barrier system for final depository of radioactive waste: (i) Interface “Canister / Bentonite”, (ii) Interface “Host rock / Bentonite” and (iii) Interface “Concrete / Bentonite” (Figure 6).

Interface “Canister / Bentonite” (Figure 6)

Heat from the hot canister, critical concentration of pore solution by the heat-driven transport of steam in deeper part of bentonite barrier as well as corrosion of canister cause higher chemical activities to alter bentonite. Dissolution processes and then again precipitation are dominating the alteration of smectite in comparison to the occurrence of solid state-alteration. The more dynamic chemical reaction system is supporting a transfer of dissolved elements (e.g. Si) into deeper parts of barrier. The smectite phases close to the canister undergo so an “illitisation”-process. The rising charge of altered smectite phases is accompanied by a decreased swelling pressure. The heat-driven Si-dissolution deals to precipitation and then cementation of smectite aggregates. This cementation of smectite stacks can disrupt the principal geotechnical relation “swelling pressure ~ 1 / permeability”. Finally, higher heat-driven pressure can break cemented zones and could create channel-like structures with areas of high permeabilities (Pusch 1998; Mingliang et al, 2012; Kasbohm et al., 2013; Nguyen-Thanh et al., 2014).

The mentioned possibility of channel-formation caused by precipitated Si is to reduce using clays with IS-ml phases mainly instead of montmorillonite-rich bentonites.

The interlayer mechanism type A with Na for stabilisation (type B, the Ca-Mg-mechanism, is excluded here) and the composition of octahedral sheet are the active mechanisms influencing the rate of alteration. Na-bentonites with an octahedral composition for Al > 1.40 and for Fe³⁺ > 0.19 per (OH)₂ O₁₀ let expect a slow alteration under conditions of this interface. Bentonites formed by hot ash fall in sea water and with acidic parent rocks like MX80 (trade ware 1998), Otay (API #24) and Belle Fourche (API #27) or formed by hydrothermal activities like Kunipia F should follow this request (Figure 5).

4.2.9 Interface “Host Rock / Bentonite” (Figure 6)

The interaction with water (mainly with low ionic strength) is here the typical driving force for low grade alteration of smectite phases. Solid state-alteration is dominating the interaction with water in comparison to the other mechanism “dissolution/precipitation”. This zone is to consider as closed chemical reaction system caused by compacted bentonite and the only low chemical activity. The tetrahedral charge deficit is unchanged or reduced. The resulting lower total charge of smectite is accompanied by an increased swelling pressure. Cementation by precipitated Si is not to expect especially not for slow reacting bentonites (sleepers). The rising swelling pressure is causing commonly also a lower permeability. Exceptions are to expect from this behaviour in case of pore solutions with ionic strength like saturated NaCl-solutions (Herbert et al., 2004, 2008; Nguyen-Thanh et al., 2014).

The two interlayer mechanisms, type A and type B, and the composition of octahedral sheet are the active mechanisms influencing the rate of alteration. Bentonites and clays with high sum of octahedral Fe^{3+} and Mg are fast reacting.

Type A (Na acting for stabilisation): Na-bentonites with an octahedral composition for $\text{Al} > 1.40$ and for $\text{Fe}^{3+} > 0.19$ per $(\text{OH})_2 \text{O}_{10}$ let expect a slow alteration under conditions of this interface. Bentonites formed by hot ash fall in sea water and with acidic parent rocks like MX80 (trade ware 1998) and Otay (API #24) as well as partially also Polkville (API #20) and IBECO RWC could fulfil this request (Figure 4).

Type B (Ca^{2+} and Mg^{2+} acting for stabilisation): Ca- and Mg-bentonites (e.g. saponite-rich bentonite GeoHellas) with mafic parent rocks are only slow reacting (sleeper), if their smectite phases were formed under higher temperature conditions (e.g. hot ash fall etc.). Ca- and Mg-bentonites in freshwater milieu and from acidic parent rocks offer slow reacting smectite phases for low and high temperature conditions during the bentonite formation phase, e.g. Chambers, Belle Fourche (API #27), Jelsovy Potok, Kuniplia F and Lieskovic (Figure 4). The Chambers bentonite is an example that different interlayer mechanisms are active to protect the aggregates under different barrier conditions. Type B (Ca-Mg) is active under low chemical activity conditions like interface “Host rock / Bentonite”. Here, this Ca-bentonite is a sleeper. Type A (Na) is the active mechanism under higher chemical activities like interface “Canister / Bentonite”. Under those conditions Chambers bentonite is acting as a sprinter (Figures 4 and 5).

The impact of interlayer mechanisms is stronger than the effect of octahedral composition.

Interface “Concrete / Bentonite” (Figure 6)

The higher pH-level and the high affinity of dissolved Si to form Ca-alumosilicates are the driving forces for any alteration of smectite. Dissolution is the main alteration process. The former experiments have included to less different bentonites. So, no explanations to the different behaviour of smectite under those conditions are to present. Some special experiments have shown that certain

trioctahedral sheet silicates can offer a very low dissolution potential: saponite (Kasbohm et al., 2013) and talc (Pusch et al., 2013).

5. Conclusions

The relevance of mineralogical alteration processes of bentonite in an engineered barrier for its long-term performance is still under discussion in the scientific community. Mostly, groups could identify after their experiments only changes in CEC and only few groups found proofed mineralogical alterations and changes in the geotechnical performance of the barrier.

The in this report described mineralogical principles and mechanisms in possible alteration processes of smectite in contact with water are only to identify by differential phase analytical diagnostics (TEM-EDX proofed by FTIR and XRD). Standard X-ray diffraction methodology alone is mostly not sensitive enough to recognize the alteration of smectite phases (Pusch et al., 2015; Hoang-Minh et al., 2019). Furthermore, each bentonite has a specific behaviour and rate of alteration (slow, fast) as well as is reacting different under different conditions in the barrier (Nguyen-Thanh et al., 2014, 2017). A comparison of a series of different bentonites under same experimental conditions supports additionally the identification of degree and principles of alterations.

The described mineralogical principles and mechanisms allow a further screening of suitable bentonites as barrier candidates directly by overhead rotation experiments and indirectly by estimation of specific dissolution potential using the chemical composition of smectite (Nguyen-Thanh et al., 2014).

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