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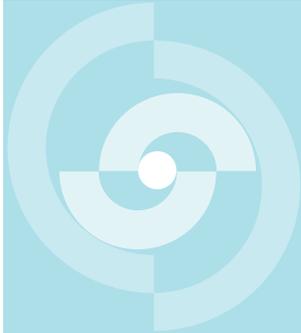
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TECHNICAL REPORT 88-24E

THE CHEMICAL BEHAVIOUR OF MONTMORILLONITE IN A REPOSITORY BACKFILL: SELECTED ASPECTS

ROLF GRAUER

MARCH 1990

PSI, Würenlingen and Villigen

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ABSTRACT

With a view to supplementing an earlier report (NTB 86-12E, EIR Report 576), publications appearing in the interim period have been evaluated. Particular emphasis was placed on the thermodynamic status of the clay minerals, the long-term stability of montmorillonite and interactions with other repository components.

Smectites and illites are presumably thermodynamically unstable and even the formation of metastable solubility equilibria is questionable. Basic problems are thus encountered when formulating equilibrium models for the clay/water interaction.

It can be concluded from investigations of argillaceous sediments that, given a repository temperature of 50 to 60°C, a maximum of 50 % of the montmorillonite will alter to illite over a period of around 10^8 years. The formation of such illite/smectite interstratifications does not impair the function of the backfill material. Since the alteration of calcium montmorillonite is very restricted in comparison with that of the sodium variant, a calcium bentonite should be foreseen as the backfill material.

Magnetite is probably unstable in the presence of montmorillonite. The thermodynamic data and experimental results necessary to allow a reliable assessment of potential interactions between the bentonite and the steel canister corrosion products are lacking. Given the current state of knowledge, the formation of iron-rich microcrystalline layer-silicates is to be expected.

Montmorillonite in contact with alkaline cement pore-waters reacts to form zeolites. This alteration is linked with a volume increase and a loss of plasticity.

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1. INTRODUCTION

An earlier report entitled "Bentonite as a Backfill Material in a High-level Waste Repository" (GRAUER, NTB 86-12E and EIR Report 576, 1986), dealt with the chemical parameters which are relevant to the behaviour of bentonite in a disposal system, the most important being swelling capacity, sorption and diffusion properties and long-term stability.

In the period since publication of the abovementioned report, further works on the illitisation of smectites have appeared in the clay mineralogy literature and the question of the thermodynamic stability of clay minerals has been raised once again. Reference should also be made to recent reports which deal specifically with the use of bentonite as a backfill and sealing material (BÖRGESSON & PUSCH, 1987; BRENNER, 1988; BUCHER et al., 1986; JOHNSTON & MILLER, 1985; PUSCH & BÖRGESSON, 1987a; PUSCH & BÖRGESSON, 1987b). The work done by HIGGO (1987) on "Clay as a Barrier to Radionuclide Migration" is particularly worthy of mention; it concentrates on disposal in clay formations rather than on bentonite backfills as such, but many aspects are the same for both subjects, e.g. nuclide migration and pore-water chemistry. The report also contains 130 literature references. Higgo's work is recommended as complementary reading to the present report.

The aim of this report is to provide an overview of recent literature on the subject of bentonite behaviour in a repository environment. Some aspects of the earlier report are also gone into in more depth. Emphasis will be on

- the thermodynamic status of clay minerals
- the long-term stability of montmorillonite and
- the interactions between bentonite and other engineered repository components.

Table 2 in reference GRAUER, NTB 86-12E and EIR Report 576 (1986), provides a summary of the nomenclature and systematics of the three-layer silicates. The "Lexikon der Mineralogie" (STRUEBEL & ZIMMER, 1982) may also be of assistance.

2. THE THERMODYNAMICS OF CLAY MINERALS

2.1 The phase problem

Because of their diversity and heterogeneity, smectites cannot be considered as single phases in the thermodynamic sense (MAY et al., 1986). The heterogeneity of this class of materials is apparent from the macro-range down to the dimensions of the unit cell. Variations in composition in the macro-range are the rule and heterogeneities are also found between, or even within, the individual T-O-T layer stacks (MAY et al., 1986). The microcrystallinity results in a solubility which is dependent on particle size and imperfection.

The formula for natural smectites generally contains trace elements in such small proportions that an atom is encountered only in every 10th or 50th unit cell. A further element of variability is provided by the distribution of layer charge over the tetrahedral and octahedral layers and the inhomogeneous lateral charge distribution.

Some of the problems arising from this heterogeneity can be avoided if the clay minerals are considered as idealised solid solutions. If the variability of the inter-layer ions is disregarded, illites, montmorillonites, beidellites and their mixed layers can be described with the ternary system mica/pyrophyllite/celadonite (LIPPMANN, 1979) (Fig. 1). An exact description of real phyllosilicates would necessitate a marked increase in the number of end-members required (FRITZ, 1985) (see Sect. 2.3).

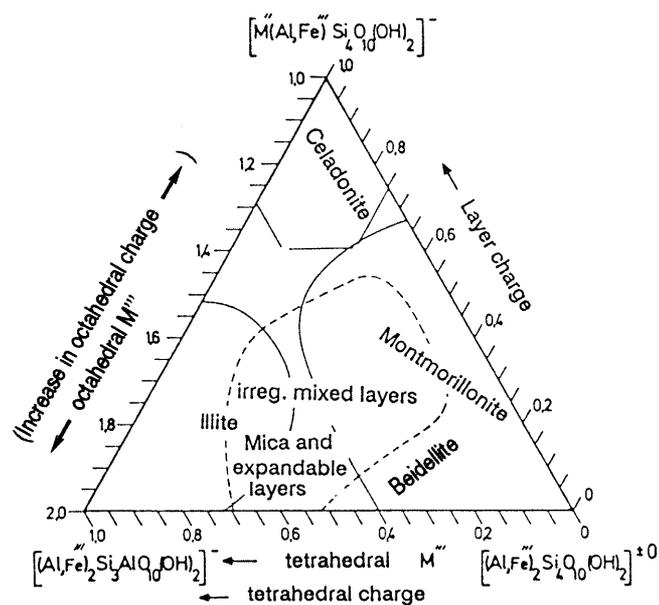


Figure 1: Chemical composition of the three-layer clay minerals in the system "muscovite" $[(Al,Fe)_2Si_3AlX]^-$, "pyrophyllite" $[(Al,Fe)_2Si_4X]^0$ and "celadonite" $[M'(Al,Fe)Si_4X]^-$ (WEAVER & POLLARD, 1973). X is $O_{10}(OH)_2$.

The question as to the ranges of composition within which natural clay minerals can be considered as homogeneous solid solutions still remains open. Basically, illite/smectite (I/S) interstratifications can be seen as solid solutions or two-phase mixtures. Garrels (GARRELS, 1984) attempts to clarify the situation by including the composition of formation waters in contact with clay minerals in the clay mineral stability diagrams (Fig. 75 in GRAUER, NTB 86-12E and EIR Report 576, 1986). This shows that the water compositions in the illite/montmorillonite field are concentrated around a phase boundary. This leads to the conclusion that the composition of co-existing solutions in contact with I/S interstratifications is compatible with the assumption of two discrete phases. According to GARRELS, 1984 and ROSENBERG et al., 1985, the existence of a single-phase solid solution is unlikely.

According to the findings of NADEAU et al. (1984a and b), irregular I/S interstratifications are to be considered as two-phase mixtures. The writers point out that sodium smectites can be dispersed into elementary layers with monocrystalline character. The fact that these clay minerals produce sharp base reflections during X-ray diffraction is explained by interparticular diffraction rather than by the existence of coherent crystals. Based on this premise, it was shown that the diffractograms for I/S interstratifications can be simulated with settled suspensions of smectite and potassium-rectorite.

NADEAU et al., 1984b found that **irregular** I/S interstratifications are made up of elementary smectite and rectorite layers with thicknesses of 10 and 20 Å respectively (Fig. 2) and are therefore two-phase interstratifications (cf. also AHN & PEACOR, 1986b).

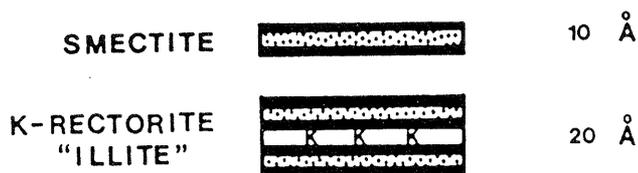


Figure 2: The elementary particles of the irregular I/S interstratifications (WILSON & NADEAU, 1985).

The diffractogram for the pure 20-Å-phase (rectorite) shows a **regular** interstratification. Regular interstratifications with a larger range (IIS and IIIS) should be considered as primary illite particles with a thickness of 30 to 40 Å (Fig. 3, McHARDY, 1986). If the illite crystals are thicker than around 50 Å, the diffraction is innerparticular and results in the normal 10 Å-spacing of illite. **Regular** interstratifications can therefore be considered as monophase "illite" with a thickness of 20 to 50 Å (NADEAU et al., 1984b).

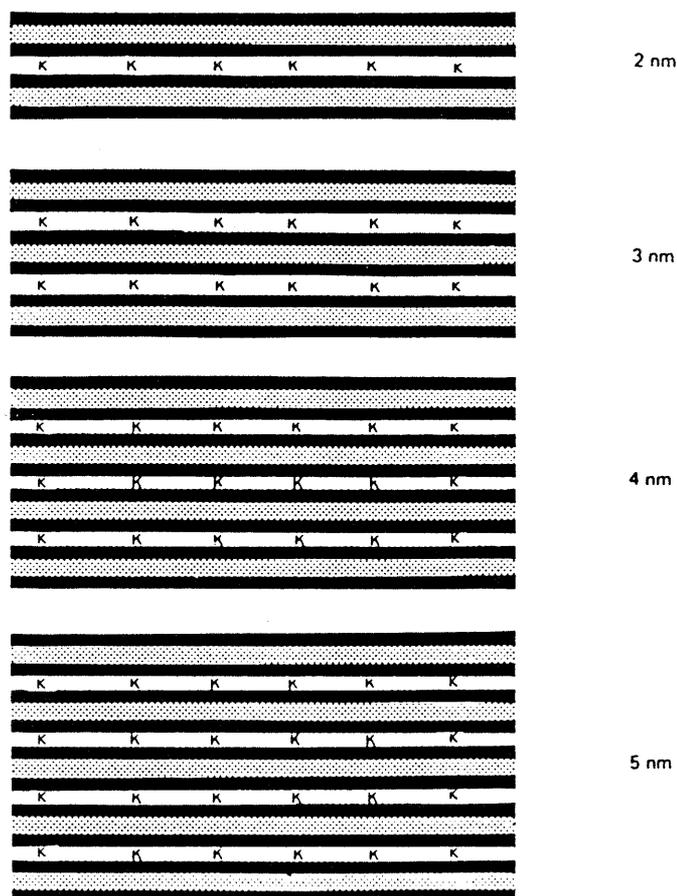


Figure 3: Schematic representation of the fundamental "illite" particles. Solid lines: tetrahedral layers. Dotted: octahedral layers (McHARDY, 1986).

WILSON & NADEAU (1985) and McHARDY (1986) indicate that this interstratification concept finds particular application in the case of diagenetically altered clays where the illite layers have been produced by dissolution and reprecipitation rather than by isomorphous substitution in existing T-O-T layer stacks.

The ideas of NADEAU and co-authors were accepted very rapidly into the body of literature on the diagenesis of smectites. Critiques of the work do exist (BELL, 1986; INOUE et al., 1987; MacKINNON, 1987), but there are also some which are constructive in nature (AHN & PEACOR, 1986) and do not call the basic model into question.

2.2 The thermodynamic stability of clay minerals

LIPPMANN (1981) maintains that application of the Gibbs phase rule to clay minerals results in "too many phases", i.e. the system is not in equilibrium. On the basis of crystal chemistry and thermodynamic considerations, he comes to the conclusion that illites and smectites are metastable or even completely unstable and never reach metastable equilibria (LIPPMANN, 1979; LIPPMANN 1981; Fig. 4). This throws the basic applicability of equilibrium calculations in clay/water systems into question.

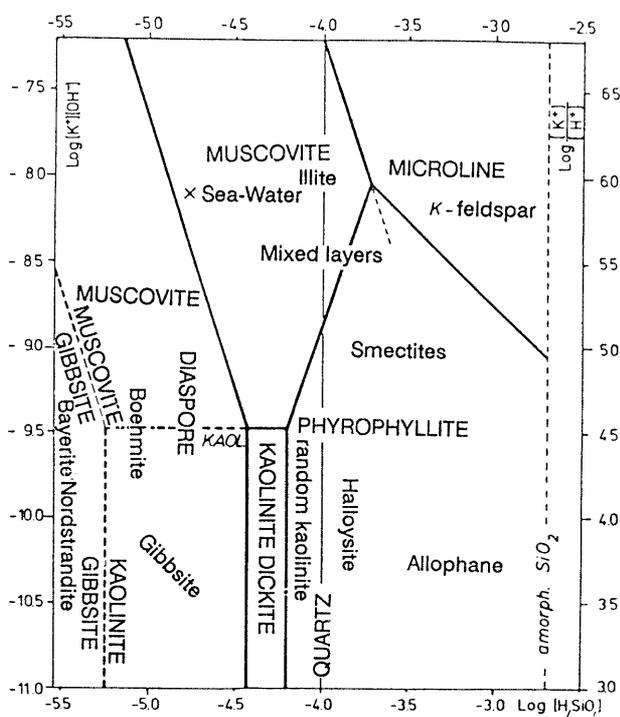


Figure 4: The system $K_2O-Al_2O_3-SiO_2-H_2O$ at $25^\circ C$. Stable minerals are shown in large print (e.g. DICKITE), minerals with metastable equilibrium formation in cursive capitals and unstable minerals in normal type (e.g. illite). Their positions in the diagram correspond more or less to their formation and stability conditions (LIPPMANN, 1979; LIPPMANN 1981).

On the basis of experiments on the dissolution behaviour of smectites, MAY et al. (1986) also concluded that these materials are not equilibrium phases. They mention that, at low temperatures, a reversible solution equilibrium for 2:1 phyllosilicates has not yet been proved to exist and they have confirmed this finding experimentally. The solution composition in contact with smectites is determined by aluminium hydroxides or possibly by an amorphous forerunner of kaolinite. This calls the results of other authors, who assume that an equilibrium is set up within the course of 2 to 3 years (e.g. REESMAN & KELLER, 1968; REESMAN, 1974), into question.

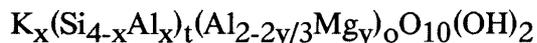
MAY et al. (1986) agree with LIPPMANN in concluding that, because of their inherent heterogeneity and variability and their dissolution behaviour, smectites are not real phases in the thermodynamic sense and that their stability in geochemical systems is due to kinetic reasons alone. This would mean that application of "equilibrium"-solubility products and estimation of enthalpies of formation for illites and smectites via dissolution experiments are not justified.

The debate on the thermodynamic stability of clay minerals is by no means closed. SASS et al. (1987) conclude on the basis of systematic investigations in the temperature range 25 to $250^\circ C$ that a metastable illite/smectite equilibrium does exist.

2.3 Free enthalpies of formation of clay minerals

Various approaches can be used for estimating the thermodynamic data of non-stoichiometric phyllosilicates (literature in MAY et al., 1986; SPOSITO, 1986; TARDY & FRITZ, 1981). Two representative examples will be given here.

Tardy and Fritz's model (FRITZ, 1985; TARDY & FRITZ, 1981; TARDY et al., 1987) treats clay minerals as ideal solid solutions of structurally related stoichiometric end-members. Thus, for example, the simply composed mineral



can be understood as a solid solution of four end-members:

muscovite ($\text{Si}_3\text{AlAl}_2\text{X}$), pyrophyllite ($\text{Si}_4\text{Al}_2\text{X}$), phlogopite ($\text{KSi}_3\text{AlMg}_3\text{X}$) and talc ($\text{Si}_4\text{Mg}_3\text{X}$) where X is $\text{O}_{10}(\text{OH})_2$. As the number of elements in the clay mineral increases (e.g. Fe(III) in octahedral positions, Na, Ca, Mg in the interlayer), the number of end-members required increases dramatically. The general model developed by TARDY & FRITZ (1981) has 36 end-members, 27 of which are required to describe Wyoming montmorillonite (FRITZ & KAM, 1985).

The law of mass action is formulated for each end-member i

$$K_i = Q_i/x_i$$

(Q_i : product of ionic activities; x_i : mol fraction of i in the solid phase). For the solubility product K^* of the solid solution, the following applies

$$\log K^* = \sum_i x_i \log Q_i.$$

Because

$$\log Q_i = \log K_i + \log x_i$$

then

$$\log K^* = \sum_i x_i \log K_i + \sum_i x_i \log x_i.$$

Table 2 of the report by TARDY & FRITZ (1981) shows that there can be differences of several orders of magnitude between solubility products derived from experiments and those calculated from the model. Potentially there are many reasons for this, which can be traced back to the inadequacy of the experimental data (MAY et al., 1986) but also to the inadequacy of the model which assumes **ideal** solid solutions. KITTRICK (1979) discusses different possibilities for formulating the solubility product of clay minerals.

Matigod and Sposito's model (MATIGOD & SPOSITO, 1978; SPOSITO, 1985; SPOSITO, 1986) approaches the difficulties involved in dealing with solid solutions by considering the clay mineral as a polymerizate of simple hydroxides for which the enthalpies of formation are known exactly. The enthalpy of polymerisation ΔG_r is initially unknown but can be determined for a specific class (e.g. for dioctahedral smectites) from known enthalpies of formation by way of linear regression. This gives the relationship

$$|\Delta G_r^\circ| = A + B(C \cdot R/Z).$$

A and B are adjustable parameters, C is the layer charge per $O_{10}(OH)_2$ -unit and R is the crystallographic ionic radius of the interlayer ion with charge Z. Figure 5 (SPOSITO, 1985) shows this relationship for homoionic montmorillonites and a similar correlation also exists for vermiculites (SPOSITO, 1985). Matigod and Sposito's model predicts the free enthalpies of formation with an uncertainty factor of less than ± 10 kJ/mol but is restricted to homoionic clays.

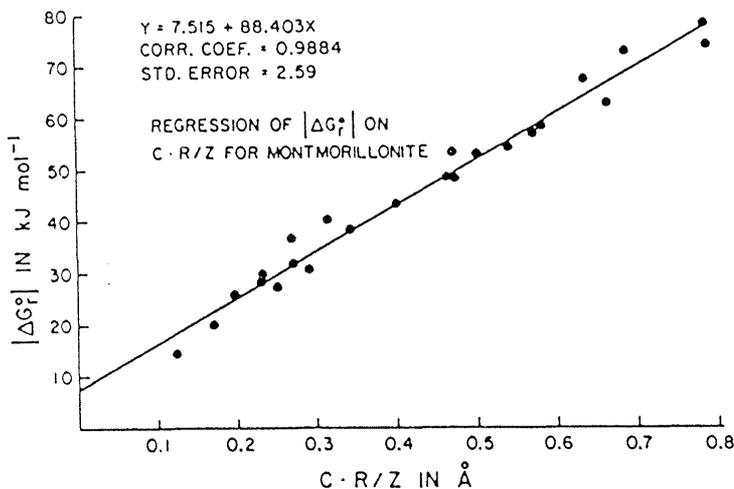


Figure 5: Regression line for the enthalpy of polymerisation for montmorillonite (SPOSITO, 1985).

3. THE SWELLING OF BENTONITES

3.1 Water uptake and swelling behaviour

Water uptake by the two reference bentonites MX-80 and Montigel was characterised by determining the heats of immersion and water vapour sorption isotherms (KAHR et al., NTB 86-14; KRAEHENBUEHL et al., 1987). The relevant sorption isotherms are shown in Figures 6 and 7. For both the sodium bentonite MX-80 and the calcium bentonite, increasing water-content leads to a step-wise increase in the c-spacing (Fig. 8). Figure 9 gives the hydration stages for the individual layer spacings. For an Na-smectite at around 25 % relative humidity, MOORE & HOWER (1986) found an ordered interstratification of hydrated and unhydrated layers with a c-spacing of 2.2 nm (= 0.96 + 1.24 nm).

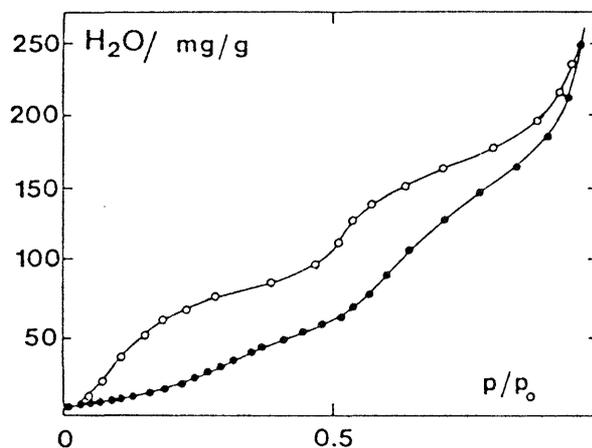


Figure 6: Adsorption- (•) and desorption- (o) isotherms for the water/Montigel system at 293 K (KRAEHENBUEHL et al., 1987).

It can be concluded from the adsorption data and the observed layer-expansion that free water can occur in pore-spaces only with water contents over 25 % (related to pure montmorillonite).

The swelling pressure of the montmorillonite can be calculated from the adsorption isotherms (GRAUER, NTB 86-12E and EIR Report 576, 1986, p. 48). As shown in Figure 10, the values calculated for MX-80 in the range of interest (water contents > 10 %) correlate well with measured swelling pressures. For Montigel, there is a systematic discrepancy between measured and calculated values. Investigations of this type have also been carried out for metabentonites and illites (KRAEHENBUEHL et al., 1987).

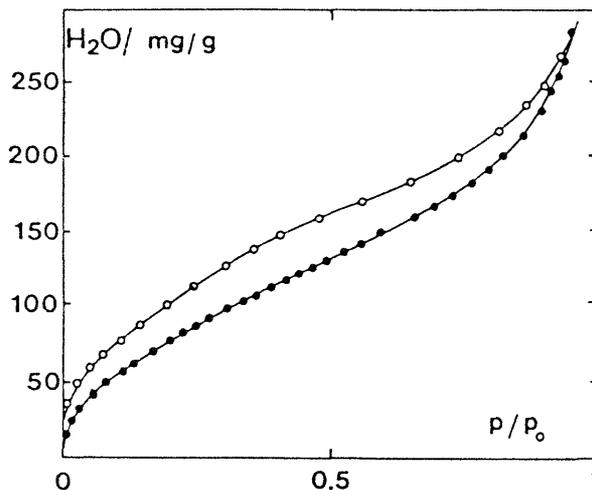


Figure 7: Adsorption- (●) and desorption- (○) isotherms for the water/MX-80 system at 293 K (KRAEHENBUEHL et al., 1987).

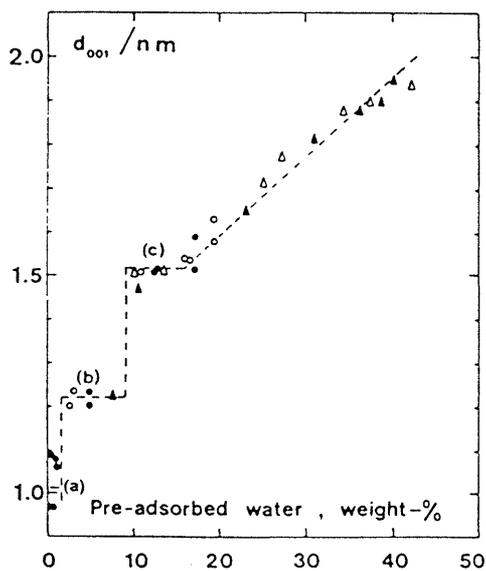


Figure 8: Alteration of the (001)-spacing of MX-80 (filled-in symbols) and Montigel (empty symbols) as a function of water adsorption (KRAEHENBUEHL et al., 1987).

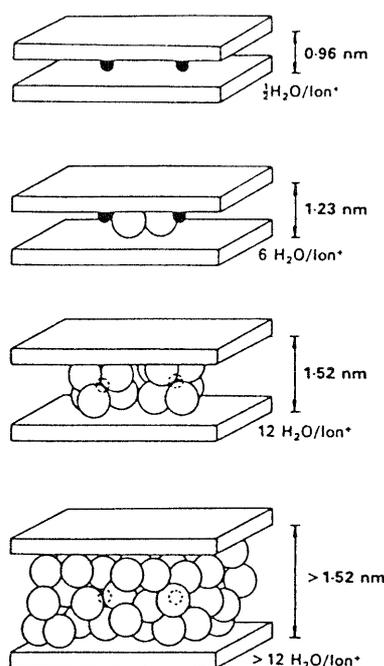


Figure 9: The expansion of the smectite structure as a function of water adsorption (maximum number of water molecules per sodium ion), KRAEHENBUEHL et al. (1987).

COLTEN (1986) used XRD to determine the c-spacing of a montmorillonite at high pressures and temperatures in 1 and 5 M sodium chloride solutions. Up to a temperature of 200°C and a pressure of 455 bars, the spacing is 1.52 to 1.57 nm, i.e. there is practically no difference from the value at ambient temperature and a pressure of 1 bar. Even under extreme conditions, which would not be expected in a repository in any event, the smectite thus contains at least two water layers in the interlayer space.

Mention was made in (GRAUER, NTB 86-12E and EIR Report 576, 1986, p. 41) that simple double layer models are unsuitable for a quantitative prediction of the swelling pressure of smectites. As a follow-up to previous work, LOW (1987) has further developed his critique of the application of such models. Compared with the summary in GRAUER, NTB 86-12E and EIR Report 576 (1986) no significant new points are raised in this recent work.

3.2 Loss of swelling capacity under special conditions

The loss of interlayer water from bentonites is reversible in the range 100 to 200°C (GRAUER, NTB 86-12E and EIR Report 576, 1986, p. 109). During the initial dry phase after sealing of the repository, loss of the swelling potential has therefore been ruled out.

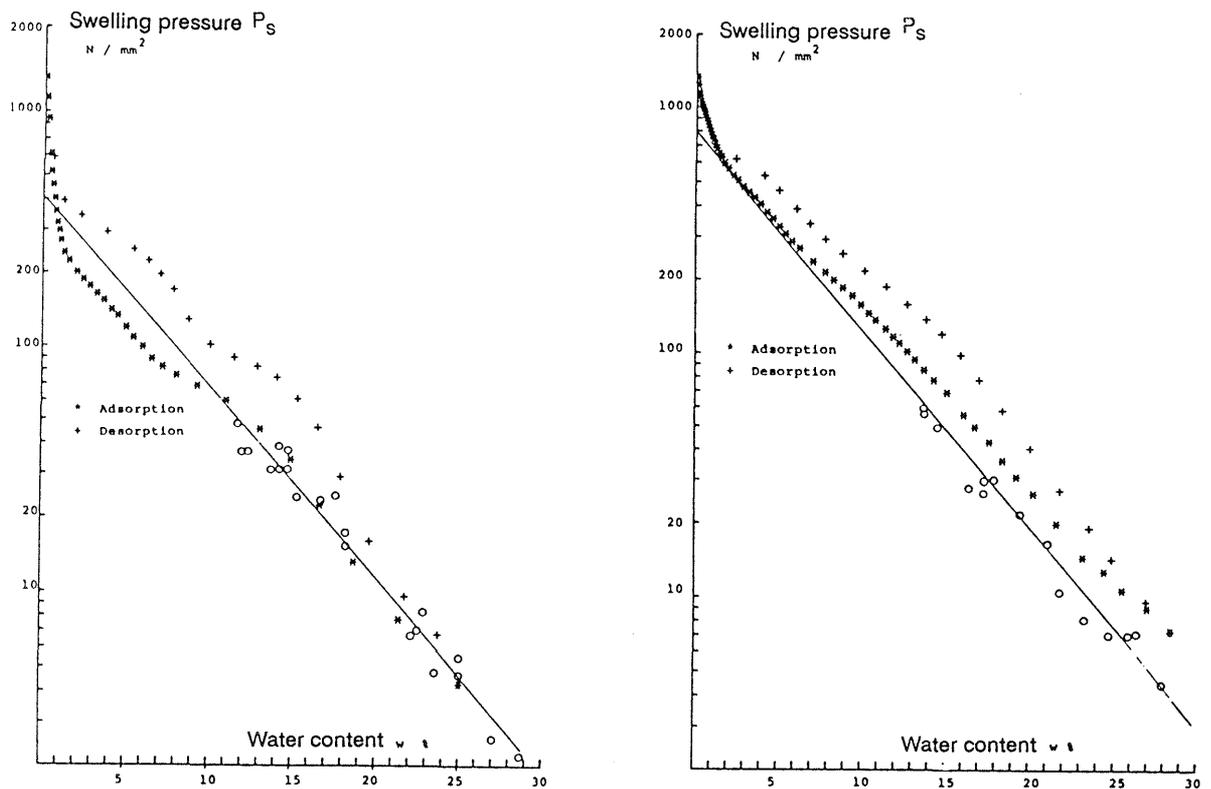


Figure 10: Swelling pressures calculated from the water vapour sorption isotherms for MX-80 (left) and Montigel (right) and comparison with measured swelling pressures (KAHR et al., 1986). (o): measured values.

However, according to the investigations carried out by Couture (COUTURE, 1985a), sodium-bentonite loses its swelling capacity to a large extent if it is exposed to water vapour in the temperature range 150 to 200°C. This process appears to be irreversible. If samples treated in this way are then stored in water at ambient temperature, their swelling properties show no improvement over a period of months.

Couture has also shown that the hydraulic permeability of quartz/bentonite mixtures with 25 % bentonite increases drastically if the samples were heated initially in steam (COUTURE, 1985b). As Figure 11 shows, this rise in permeability is irreversible.

Couture concludes from his results that the barrier effect of bentonite in a repository could be adversely affected if it comes into contact with water vapour over a long period during the initial high-temperature phase.

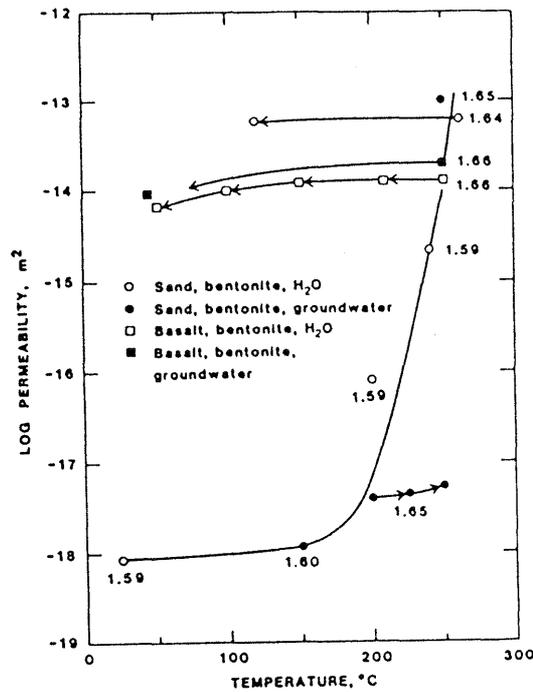


Figure 11: The hydraulic permeability of bentonite/basalt mixtures heated in water vapour. The permeability rises with the temperature of the vapour treatment but is only slightly dependent on the temperature during measurement (COUTURE, 1985b). The numbers are the dry densities in g/cm^3 .

These conclusions should not be applied indiscriminately to the Swiss repository concept since the latter foresees the use of highly compacted bentonite as a backfill material. Couture characterised the swelling capacity of clay in his experiments by **free** swelling in water. For the untreated sodium bentonite used, the figure obtained is naturally large, i.e. in the range 25 to $37 \text{ cm}^3/\text{g}$. Although the swelling capacity is reduced after treatment with water vapour, it is nevertheless still detectable; the treated samples swell to a volume of 4 to $13 \text{ cm}^3/\text{g}$ (COUTURE, 1985a). After water vapour treatment at 250°C and subsequent swelling in water, a c-spacing of 1.9 nm was detected (COUTURE, 1985b). This is equivalent to the innercrystalline swelling of calcium montmorillonite (GRAUER, NTB 86-12E and EIR Report 576, 1986, p. 23). For the dry density of bentonite foreseen for a Swiss repository, the innercrystalline swelling is sufficient to ensure a satisfactorily low permeability.

It must also be clarified whether the swelling behaviour of calcium montmorillonite is impaired by water vapour treatment. For the purpose of assessing barrier effect, swelling pressures of compacted, steam-treated bentonite would also be of interest.

In dioctahedral smectites with a low layer charge, there is a reversible exchange of potassium without layer collapse (literature in EBERL et al., 1986). There is however information to the effect that the swelling capacity of potassium montmorillonites is lost on drying (GRAUER, NTB 86-12E and EIR Report 576, 1986, pp. 109, 127). EBERL et al. (1986) have carried out a systematic investigation of this phenomenon and have demonstrated that potassium-saturated smectites irreversibly fix a proportion of the potassium when they undergo repeated drying and wetting cycles.

12 different smectites were saturated with potassium and dried and re-wetted up to 100 times at 60°C. After the wet/dry cycles, the potassium which had not been fixed was removed through ion-exchange with 0.1 N strontium chloride. The clays were also characterised by XRD.

The majority of the illite layers form during the first 20 cycles (Fig. 12). After 100 cycles, the percentage of illite layers in smectites with predominantly octahedral layer charge is proportional to the layer charge (Fig. 13).

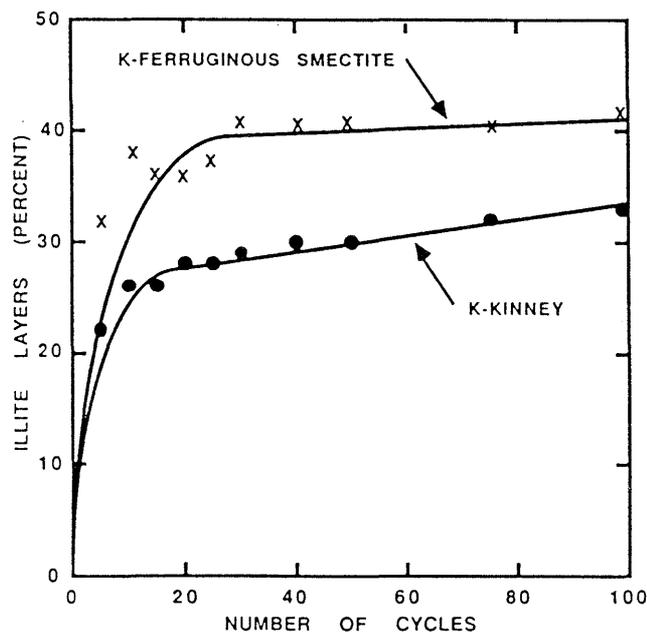


Figure 12: Kinetics of the illitisation of two potassium-saturated smectites with wet/dry cycles (EBERL et al., 1986).

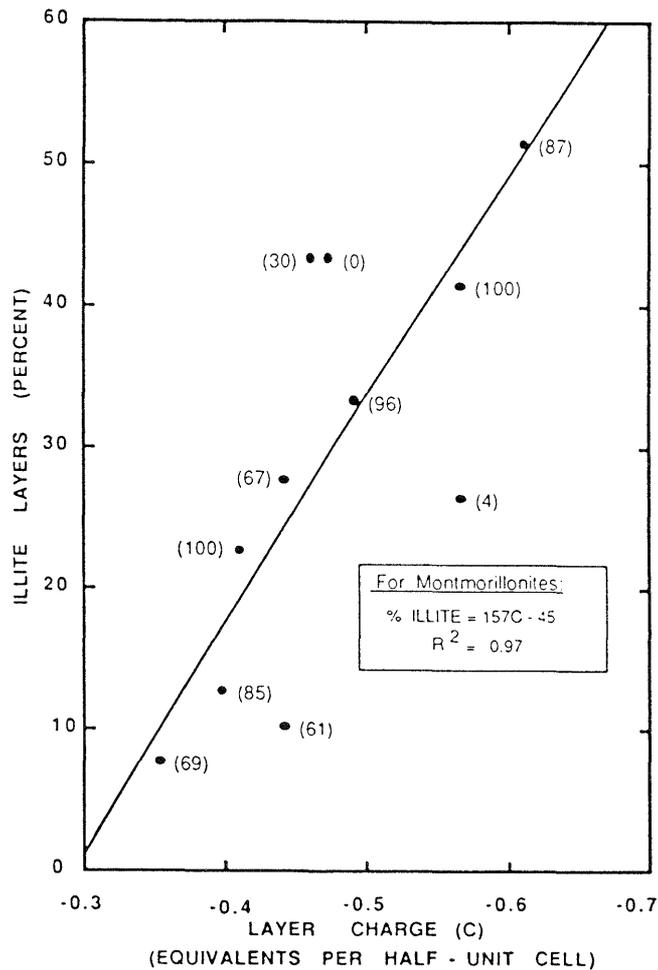


Figure 13: Percentage of illite layers in potassium smectites after 100 wet/dry cycles as a function of layer charge. The numbers in brackets are the percentage charge in the octahedral layer (EBERL et al., 1986).

The total cation content of the interlayers is not altered significantly by the wet/dry cycles. The smectite layers therefore stay intact and the irreversible fixing of the potassium is not the consequence of an increased layer charge. It must therefore be assumed that only dehydration and the associated re-orientation of the layers leads to more stable configurations. This ties in with the fact that, for a specific smectite, the number of cycles and not the drying temperature in the range 30 to 90°C determines the illite proportion.

It has also been shown (EBERL et al., 1986) that non-expandable layers are produced during wet/dry cycling of a mixture of sodium smectite and potassium feldspar. After 100 cycles, 40 % of the layers had lost their swelling capacity. However, if such mixtures were agitated under water for a period of one year, the swelling capacity of the smectite remains intact.

EBERL et al. (1986) assume that natural wet/dry cycles at low temperatures contribute significantly to the formation of illite/smectite interstratifications. A prerequisite is that the smectite should be loaded with potassium.

4. WATER COMPOSITION IN CONTACT WITH BENTONITE

The literature on water composition in contact with bentonite is still somewhat lacking. SNELLMAN et al. (1987) have examined the alteration of a model water caused by the bentonite MX-80 at ambient temperature over 540 days. At 27 g/litre, the bentonite/water ratio was too low to simulate the conditions in a repository. The rise in the pH of the solution from 8.2 to 9.2 was associated with a rise in the sodium and hydrogen carbonate concentration. These concentration changes can be explained with the reaction



(Z⁻: exchange equivalent of the montmorillonite).

Takahashi et al. (TAKAHASHI et al., 1987) measured pH values for different water/clay ratios for a purified sodium bentonite (Fig. 14). They found pH values over 10 in concentrated suspensions. The contact period can not be derived directly from the work (TAKAHASHI et al., 1987) but comparison with other experiments described would suggest that it was probably in the order of only one day.

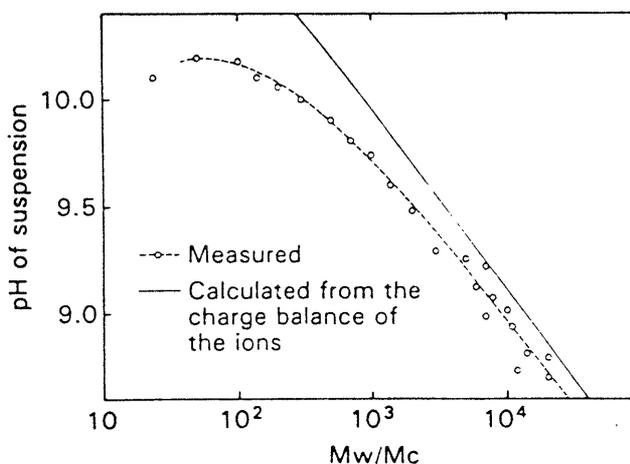


Figure 14: pH values of sodium bentonite suspensions as a function of the water-clay weight ratio (TAKAHASHI et al., 1987).

Smectites can affect the pH of the solution not only by dissolution but also by exchange of the interlayer ions against the hydrogen ion. Sodium is more easily exchanged than calcium and sodium smectites therefore give higher pH values (ca. 9.5) than the calcium varieties (ca. 8.5) (JOHNSTON & MILLER, 1985).

The values from Figure 14 contradict the data in Figure 10 in GRAUER, NTB 86-12E and EIR Report 576, 1986 where the highest pH values are found in **diluted** clay suspensions. It is impossible to identify the reasons for these discrepancies as the measurement methods are not described in sufficient detail. Reference has already been made to the problems involved in measuring pH in suspensions (GRAUER, NTB 86-12E and EIR Report 576, 1986, p. 20).

FRITZ & M. KAM (1985) used Tardy and Fritz's model (FRITZ, 1985; TARDY & FRITZ, 1981) to calculate the pH values of Wyoming bentonite in contact with two deep groundwaters from the Swedish drilling programme. Values of 8 to 8.6 result for high clay/water ratios, which is not very different to the pH values for the initial waters. Measurements carried out by TORSTENFELT (1986a) agree more or less with these calculated values. After one week, a Swedish model water in contact with the bentonite MX-80 had a pH of 8.8 to 9.0. The clay/water ratio is not given.

The earlier statement to the effect that the pH values of bentonite pore-waters lie in the range 8 to 10 (GRAUER, NTB 86-12E and EIR Report 576, 1986), can unfortunately not be narrowed down in the light of current knowledge.

FRITZ & KAM, 1985 carried out model calculations of the change in water chemistry caused by bentonite and the change in mineral content for the temperature range 25 to 100°C. It is worth noting that no illite is predicted.

WANNER (NTB 86-21 and EIR Report 589, 1986) has developed a model for the interaction between sodium bentonite and water which treats the montmorillonite as a chemically inert ion-exchanger. Dissolution and alteration reactions of the montmorillonite and Na⁺/H⁺ ion-exchange are ignored.

According to this model, the water composition is determined mainly by the reaction between sodium montmorillonite and the calcium carbonate present in the bentonite. Ion-exchange reactions with potassium and magnesium are also taken into consideration. The model can be used to calculate the alteration in the pore-water composition in the bentonite as a function of the number of water-exchange cycles (Fig. 15). The initial pH of 9.6 is determined by the reaction between calcite and sodium montmorillonite but, after around 60 exchange cycles, the montmorillonite is saturated with calcium and the pH of 6.8 corresponds to that of the groundwater. According to this model, a calcium montmorillonite would therefore have only a minimal effect on water composition.

Treating the montmorillonite as a chemically inert ion-exchanger is an oversimplification, particularly when this involves ignoring the participation of hydrogen ions in the ion-exchange. Many studies (e.g. BAR-ON & SHAINBERG, 1970) show that montmorillonite is partly dissolved after only a short time at ambient temperature. Modelling such reactions presents particular problems as solubility equilibria are not set up (MAY et al., 1986).

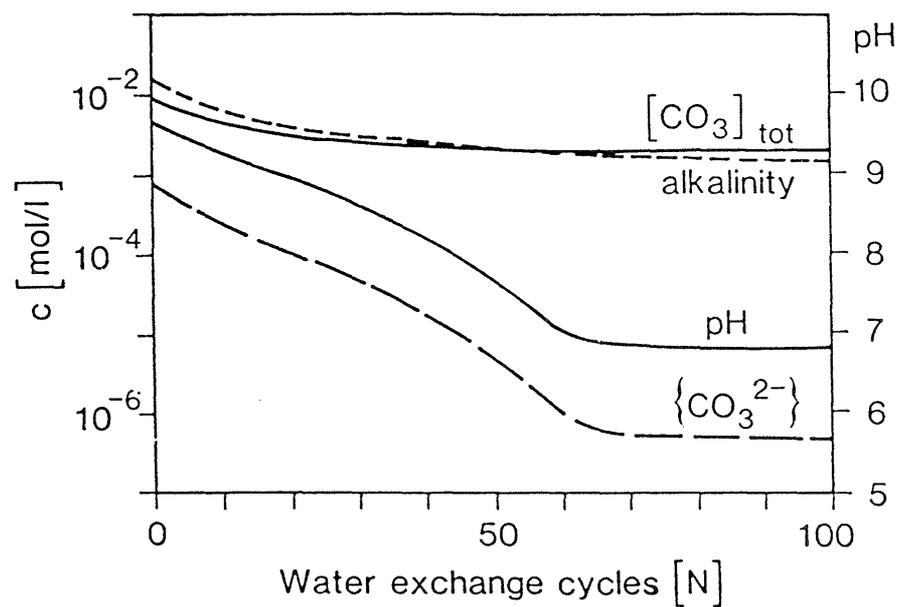


Figure 15: Modelled alteration of pore-water composition in sodium bentonite as a function of water exchange cycles with a Swiss model groundwater (WANNER, NTB 86-21 and EIR Report 589, 1986).

5. SORPTION AND DIFFUSION BEHAVIOUR

5.1 Cation exchange

Exchange of interlayer ions for potassium is of particular interest when considering the illitisation of montmorillonite.

INOUE & MINATO (1979) have investigated the calcium/potassium exchange of a montmorillonite at different temperatures (Fig. 16). The selectivity for calcium increases as the temperature rises and is also more marked in the case of lower overall concentrations.

If dried samples loaded with potassium are used for the sorption experiments, a hysteresis results, which is not the case for dried calcium montmorillonite (Fig. 17). This behaviour indicates a partly irreversible fixing of the potassium on drying (see Sect. 3.2).

If the calcium/potassium exchange is compared for different montmorillonites, it is seen that the selectivity for potassium increases with increasing layer charge (SHAINBERG et al., 1987). This is also true for the sodium/potassium exchange. The calcium/sodium exchange, on the other hand, is not dependent on layer charge.

In mixed-ion smectites, interstratifications with potassium- or calcium-containing interlayers can be formed (INOUE & MINATO, 1979). Segregations were also observed for mixed Na-Ca smectites (Fig. 18, IWASAKI & WATANABE, 1988).

BENSON (1982) has summarised and commented on the literature data on ion-exchange of smectites in tabular form.

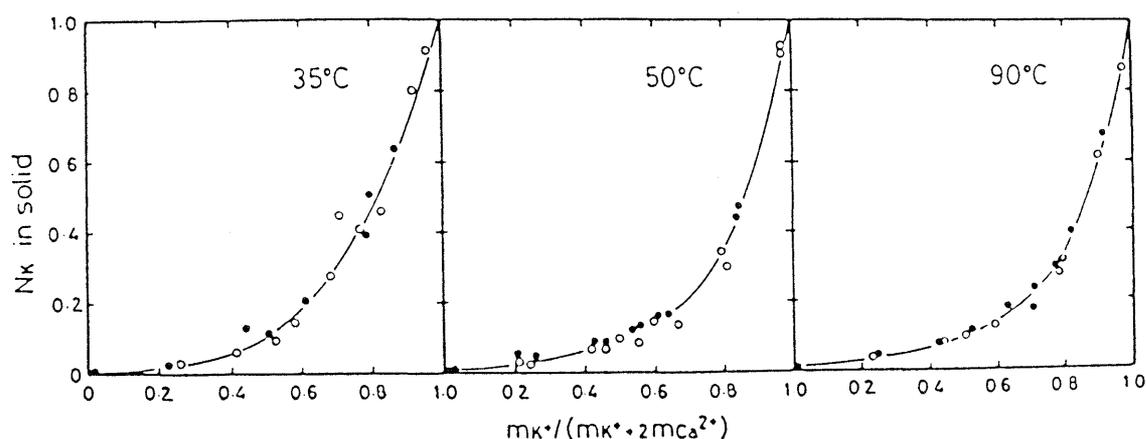


Figure 16: Potassium/calcium exchange isotherms at 35, 50 and 90°C in solutions with a total normality of 0.1. Filled and empty circles indicate a starting product of potassium and calcium montmorillonite respectively (INOUE & MINATO, 1979).

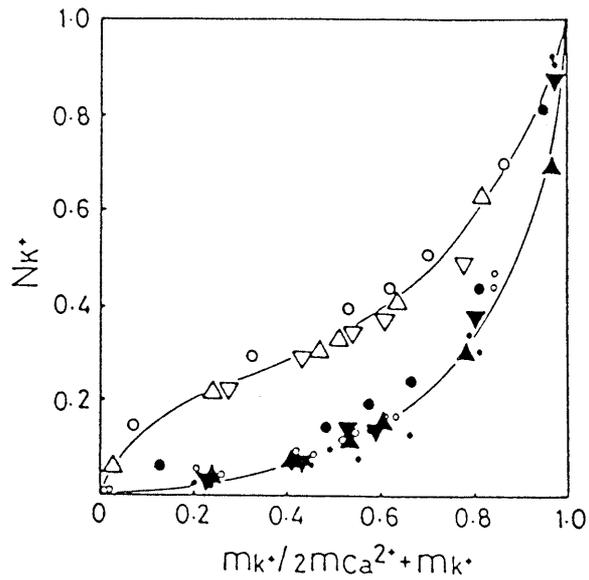


Figure 17: Potassium/calcium exchange isotherms for different sample pre-treatment. o: wet material; dried at 80°C (○), 200°C (△) and 300°C (▽). Filled symbols: Ca-montmorillonite; open symbols: K-montmorillonite as starting material (INOUE & MINATO, 1979).

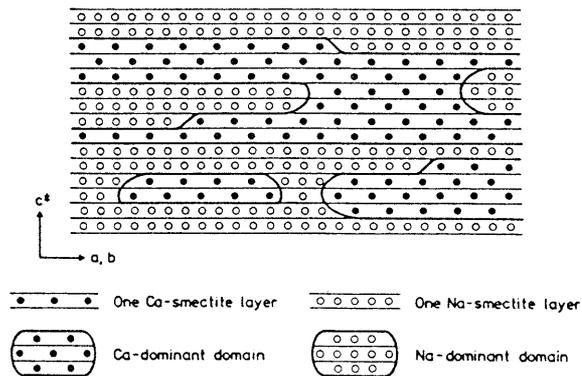


Figure 18: Schematic representation of the domain formation in Na-Ca-smeectites (IWASAKI & WATANABE, 1988).

5.2 Diffusion processes in compacted bentonite

Torstenfelt has recently published two reports (TORSTENFELT, 1986a and 1986b) on the migration behaviour of fission products and actinides in compacted Wyoming bentonite MX-80. These reports are in the nature of an overview of earlier KBS- and conference reports but the data have been re-evaluated. The apparent diffusion coefficients D_a were determined from non-stationary experiments. The bentonite was compacted to 2000 kg/m^3 and equilibrated with a model groundwater. In some experiments, iron or iron(II)-phosphate was added to the bentonite in order to create reducing conditions. It should be noted that, when evaluating the experiments, D_a was considered to be independent of concentration.

Table 1 summarises the results (cf. also Tab. 13 in GRAUER, NTB 86-12E and EIR Report 576, 1986). Where several D_a values are given for one nuclide, this means that diffusion occurs by way of several mechanisms (e.g. two for iodide, three for uranium).

The high value for strontium, also found by other authors (NERETNIEKS, 1985), is worth noting. For a suite of other elements, D_a is in the order of 10^{-11} to $10^{-12} \text{ m}^2/\text{s}$ (Cs, TcO_4^- and proportions of I, U, Np and Pu). This order of magnitude is typical of non-sorbing ions such as chloride ($D_a = 6 \times 10^{-12} \text{ m}^2/\text{s}$ (PUSCH & JACOBSSON, 1982).

In the case of uranium, neptunium and plutonium, only a small proportion behaves like a non-sorbing tracer. For the larger proportion of U and Np, D_a is $10^{-13} \text{ m}^2/\text{s}$. The value for protactinium also lies within this range so it appears to be valid for 5- and 6-valent actinides. Similarly, one would also expect that a proportion of the protactinium would diffuse rapidly; the absence of this could possibly be due to the tracer concentration which is orders of magnitude lower than those for U and Np. Other sources give a value of ca. $10^{-12} \text{ m}^2/\text{s}$ for protactinium (Tab. 13 in GRAUER, NTB 86-12E and EIR Report 576, 1986).

It could be speculated that some of the 5- and 6-valent actinides behave like strontium and caesium and are emplaced in the montmorillonite interlayers and diffuse rapidly, while the proportion which diffuses slowly is sorbed on surface OH-groups. The proportions of kaolinite and iron hydroxides in the bentonite would also be significant for the second mechanism.

The 4-valent actinides (thorium, neptunium under reducing conditions and the greater part of plutonium) and americium have diffusion coefficients which are still difficult to determine after periods of over a year. The figures given in Table 1 are to be understood as maximum values. Uranium(VI) is apparently not reduced to uranium(IV) by the iron(II) phosphate.

Of particular interest is the finding that the diffusion of americium and uranium(VI) is not increased by a higher hydrogen carbonate concentration in the model water (600 mg/l). This holds true for uranium(VI) even if 10 mg of humic acid per litre is added.

Table 1: Apparent diffusion coefficients for fission products and actinides in compacted bentonite (TORSTENFELT, 1986a and 1986b).

Element	Material Quantity (mol)	D_a (m ² /s)
Cs	E-12	2,4 E-12
Sr	E-12	2,0 E-11
TcO ₄ ⁻	E-06	1,2 E-12
Tc (reducing)	E-06	(0,8÷2,6) E-12
I	E-13	(1,2÷2,6) E-12 (1,1÷2,4) E-13
Th	E-14	< 7,7 E-15
Pa	E-13	6,2 E-13
U(VI)	3 E-07	3,4 E-12 6,4 E-13 2,7 E-13
U (reducing)	3 E-07	8,2 E-12 3,1 E-13 1,0 E-13
Np (V)	5 E-06	1,2 E-11 3,7 E-13 4,6 E-14
Np (reducing)	5 E-06	2,1 E-14
Pu	3 E-08	3,2 E-12 < 1,9 E-15
Am	4 E-09	< 1,3 E-14
Am + HCO ₃ ⁻	4 E-09	< 2,8 E-16

The diffusion behaviour of iodide is still difficult to understand. The two different diffusion coefficients do not alter significantly if the chemical milieu in the bentonite is altered by addition of iron, KMnO_4 , HgS , PbO or CuFeS_2 .

Torstenfelt compares the diffusivities determined directly with the pore diffusion model with reversible sorption (TORSTENFELT, 1986a, p. 92 in R. GRAUER, NTB 86-12E and EIR Report 576, 1986). K_d values from batch experiments are used. It is clear that this model is not applicable if sorption is by way of ion-exchange in the interlayers of the montmorillonite. Direct diffusion measurements are therefore a prerequisite to obtaining useful data.

There are also approaches for describing the diffusion of strontium and cesium with a combined pore- and surface diffusion model (CHARLES et al., 1986; JAHNKE & RADKE, 1985; MUURINEN et al., 1985 and 1987). However, the surface diffusion coefficients used by various authors differ by around three orders of magnitude (JAHNKE & RADKE, 1985; MUURINEN et al., 1985 and 1987).

RELYEA et al. (1986) have determined the effective diffusion coefficients of tritium-marked water and chloride-36 in basalt/bentonite mixtures in the temperature range 20 to 90°C. The regression equations are

$$\log D(\text{H}_2\text{O}) = -5.513 - 1120/T - 0.338 \times d \quad (D \text{ in } \text{m}^2/\text{s})$$

and

$$\log D(\text{Cl}^-) = -6.807 - 547/T - 1.195 \times d.$$

d is the bentonite bulk density in Mg/m^3 .

The activation energies are 10 kJ/mol for chloride and 21 kJ/mol for water. While the two diffusion coefficients are roughly the same at ambient temperature, at 60 and 90°C chloride diffuses more slowly than water.

6. THE ILLITISATION OF SMECTITES

6.1 Introduction

In phenomenological terms, the illitisation of smectites involves an increase in the (tetrahedral) layer charge to values over 0.6 per $O_{10}(OH)_2$ -unit and a loss of swelling capacity if the layer charge is compensated by potassium ions. Formally, the layer charge is increased through isomorphous substitution of silicon by aluminium. This can occur as a solid-state reaction or by dissolution and reprecipitation (literature in BETHKE & ALTANER, 1986).

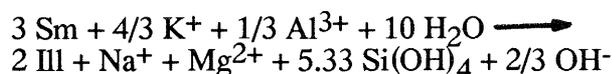
The solid-state reaction would have to be conceived in such a way that the original smectite layer remains intact during Si/Al-exchange. However, such a process is extremely unlikely at temperatures below around 200°C and this type of diagenetic reaction is ruled out by the literature (AHN & PEACOR, 1986a; INOUE et al., 1987; YAU et al., 1987a). Oxygen isotope ratios also point against a solid-state reaction; with increasing illite content they can be compared with the isotope ratios in the pore-water (YEH & SAVIN, 1977). The discovery that the illitic parts of a bentonite contain more octahedral aluminium and less magnesium than the original smectite (NADEAU & BAIN, 1986) is also incompatible with a solid-state reaction.

An external source of aluminium and potassium is often assumed for the formation of illite, e.g. according to the schematic reaction (HOWER et al., 1976).

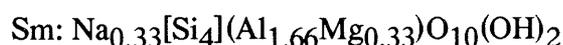


Chlorite can be formed from the magnesium and iron of the original smectite.

However, an increase in the layer charge is also possible without an external aluminium source, in that montmorillonite alters to illite by dissolution and reprecipitation. Around two illite layers are produced from three smectite layers (BOLES & FRANKS, 1979):



with the assumed ideal formulae



(The low Al-requirement on the left side is due to the fact that an exact 3:2 stoichiometry was forced.) Only the potassium must come from an external source; it can enter the clay either before or after the increase in the layer charge.

This layer cannibalism is now recognised as a possible illitisation mechanism, particularly in formations with low water-flow (e.g. (AHN & PEACOR, 1986a; BELL, 1986; INOUE et al., 1987; NADEAU & BAIN, 1986; POLLASTRO, 1985). The arguments for this type of reaction are supported by TEM investigations (Sect. 6.4).

6.2 Illite contents of natural smectites

Argillaceous sediments were deposited continually in the Gulf of Mexico over a period of around 200 megayears (Fig. 19) and have been investigated in detail because of the oil deposits found there. They are shallow-water sediments which became embedded due to the continual sinking of the Gulf basin (GARRELS & MACKENZIE, 1971). As there was no tectonic superposition, the geological conditions are clearly identifiable.

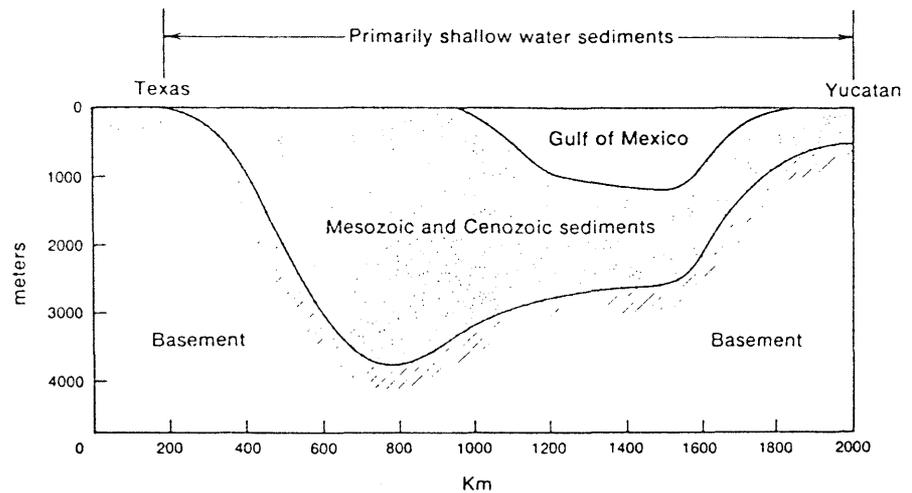


Figure 19: Schematic cross-Section through the sedimentary basin of the Gulf of Mexico (GARRELS & MACKENZIE, 1971).

The swelling layers of the clay minerals were investigated in a series of drill-core studies. Figure 20 (COUTO ANJOS, 1986) shows that there is considerable illitisation at temperatures over 80°C. Besides temperature, geological age is also a decisive factor (Pleistocene < 2 Ma; Pliocene 2 - 7 Ma; Oligocene 26 - 37 Ma). At temperatures below 140°C, and independent of geological age, the maximum illite content is around 80%. Similar information can be found in the work of SCHOONMAKER et al. (1986) and VELDE (1985).

The transition from irregular to ordered interstratifications occurs at temperatures over 90°C (CHANG et al., 1986; COUTO ANJOS, 1986), an arrangement similar to that of rectorite generally being achieved (BURTNER & WARNER, 1986).

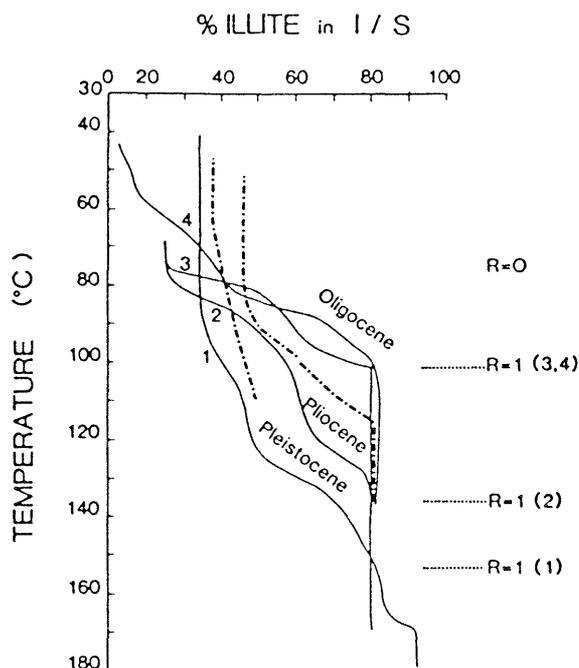


Figure 20: Proportions of illite in the clay fractions of shales. 1: Salton Sea. 2-4: Gulf Coast, different boreholes. Dashed: left Campos basin (Brasil) and right Gulf of Mexico. R = 0 irregular and R = 1 ordered interstratifications (COUTO ANJOS, 1986).

The investigations by Bell (BELL, 1986) on sediments from the Gulf of Texas from the Miocene up to recent deposits show that, down to a depth of 3000 m, the proportion of expandable layers decreases after saturation with potassium ions (Fig. 21). For these clays this means that, down to a depth of around 2500 m, an increase in the layer charge occurs but the swelling capacity remains intact due to the lack of potassium.

6.3 The stabilising effect of calcium

It has already been mentioned in GRAUER, NTB 86-12E and EIR Report 576 (1986), that calcium montmorillonite is more resistant to illitisation than the sodium variant. This statement has also been corroborated by other studies.

NADEAU & REYNOLDS (1981) investigated argillaceous sediments from the Cretaceous period and found that the presence of calcium inhibits the illitisation of a smectite. In an extreme case, pure smectites could be found in the same layer with calcite, as well as disordered I/S interstratifications in calcite-free areas.

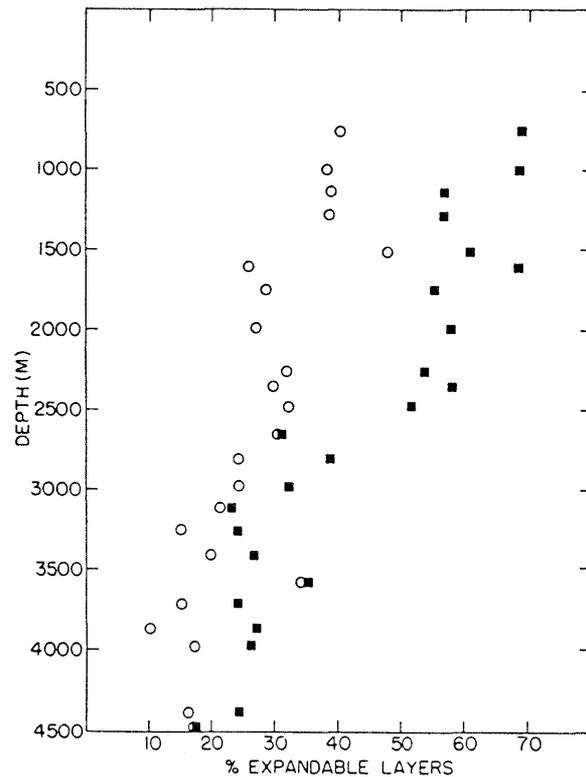


Figure 21: Proportion of expandable layers of I/S interstratifications as a function of depth (Gulf Coast). Squares: untreated samples; circles: samples saturated with potassium (BELL, 1986).

YAU et al. (1987a) show that calcium has such a stabilising effect on bentonite that it is not altered under hydrothermal conditions (200 and 300°C, 537 days). For these reasons it is recommended that the bentonite used as a repository backfill should be stabilised by addition of calcite.

INOUE (1983) has also shown that, under hydrothermal conditions (150 and 300°C), calcium montmorillonite fixes potassium irreversibly to a much lesser extent than the potassium variant. At 300°C in contact with 0.02 M KCl-solution, after 10 days the proportion of swelling layers was 80 % for the Ca-montmorillonite but only 40 % for the K-variant.

LAHANN & ROBERSON (1980) have also shown the stabilising effect of calcium and magnesium.

6.4 The mechanisms of illitisation

Investigations using high-resolution electron microscopy carried out by Bell (BELL, 1986) on sediments from the Gulf of Texas lead to the conclusion that the individual illite layers extend laterally and replace the montmorillonite (Fig. 22). The aluminium required for the increase in the layer charge originates from the dissolved smectite. The potassium in the illite layers comes from weathered potassium-feldspar (with etch pits) in the surrounding formations. Special reference is made in this work to the fact that the layer charge had already increased before entry of the potassium (cf. Fig. 21).

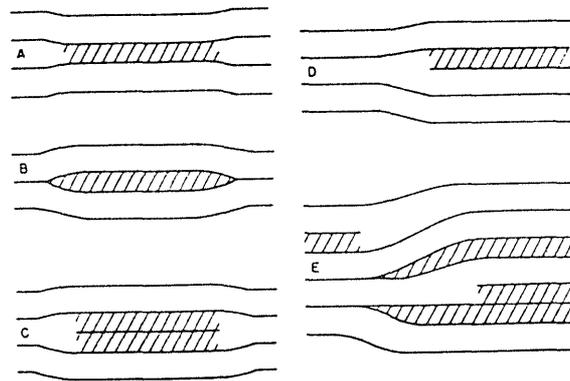


Figure 22: Schematic representation of the single layers in I/S interstratifications. Dashed: smectite. Open: illite. A: no alteration in number of layers. B-D: decrease in number of layers due to illitisation. E: combination of B-D (BELL, 1986).

Similar investigations by Lee, Ahn and Peacor (AHN & PEACOR, 1986a; LEE et al., 1985) - also on coastal sediments from the Gulf of Texas - confirm the local alteration of smectite to illite by dissolution and reprecipitation. With increasing depth, the illite occurred in almost ideal composition in the form of ordered layer stacks and not in the form of interstratifications (Fig. 23). Magnesium and iron released during the illitisation process are the source for the formation of chlorite and berthierin (kaolin-chamosite).

Only a minimum amount of water is required for these local isochemical alteration reactions. This situation is typical of compacted deep sediments, but also of a repository. In open hydrothermal systems, the dissolved smectite components are transported by water and the illite forms well-defined crystals isolated from montmorillonite (INOUE et al., 1987; YAU et al., 1987a and 1987b).

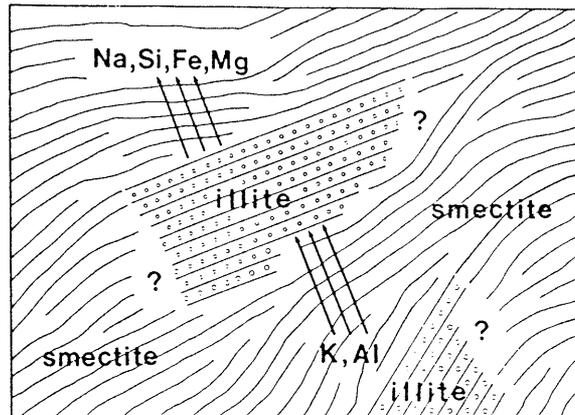


Figure 23: Alteration of smectite to illite in clay sediments AHN & PEACOR (1986a).

While it is widely agreed that the illitisation of smectites in compacted clays occurs by way of dissolution and reformation of layers, discrepancies still occur in the detailed model concepts. In agreement with Bell (BELL, 1986), Nadeau et al. (NADEAU et al., 1985) describe the formation of random interstratifications with a dissolution/precipitation reaction (Fig. 24). This model does not indicate at which stage the potassium ions are incorporated into the interlayers.

In contrast with this, Inoue et al. (INOUE et al., 1987) consider the random I/S interstratifications as largely unaltered smectite where the original interlayer ions have been replaced by potassium ions (Fig. 25). During this first stage, the layer charge is supposed to increase slightly by way of a mechanism which is not described and reach values of around 0.5. According to the authors, the smectite layers become unstable with a potassium content of around 0.4 per $O_{10}(OH)_2$ unit and change to regular interstratifications.

6.5 The kinetics of illitisation

Bethke and Altaner (BETHKE & ALTANER, 1986) have developed a Monte-Carlo model for layer-wise illitisation; the model is based on 1st order reaction kinetics. In contrast with previous studies (e.g. EBERL & HOWER, 1976), the reactivity or probability of alteration of a particular smectite layer depends in this case on the nature of its immediate neighbours (Tab. 2).

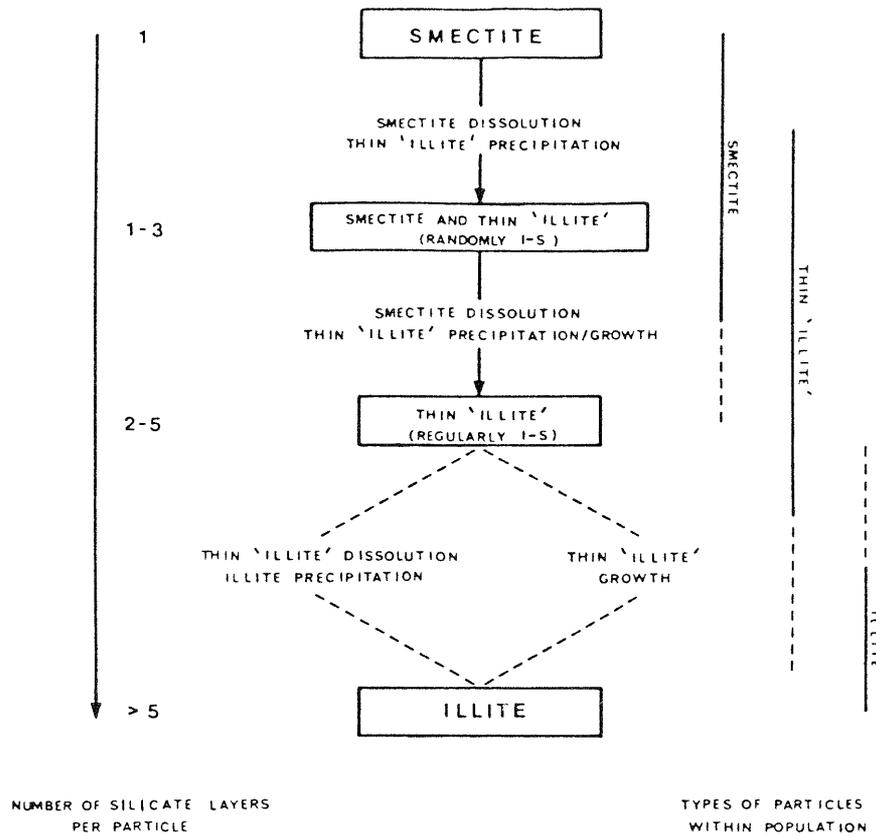


Figure 24: Mechanism for alteration of smectite to illite in bentonites (NADEAU et al., 1985).

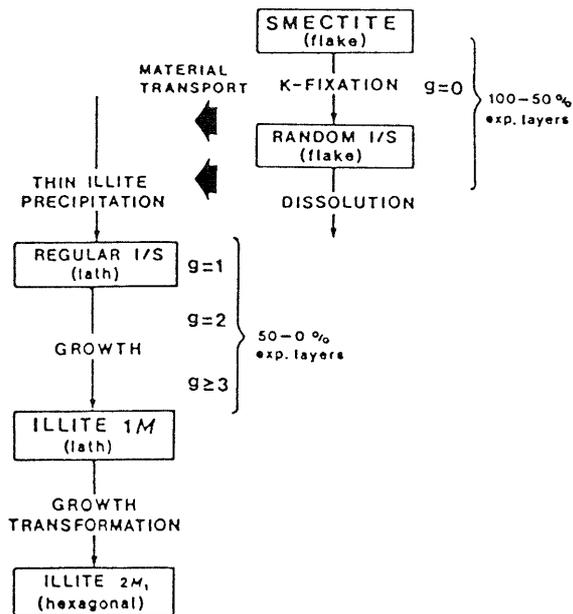


Figure 25: Possible mechanism for alteration of smectite to illite under hydrothermal conditions (INOUE et al., 1987).

It is assumed that each layer type reacts according to a 1st order law:

$$- dN_i/dt = k_i \times N_i$$

where k_i is a function of temperature according to the Arrhenius relationship:

$$k_i = A \times \exp(-E_i/RT).$$

A is the Arrhenius factor, E_i the activation energy.

Table 2: Relative reactivity of smectite layers in different environments (BETHKE & ALTANER, 1986).

Type	Neighbours	Reactivity
0	SSS	0,5
1	SSI ISS	1,0
2	ISI	0,1

If the proportion of illite layers is P and the smectite proportions $X_i = N_i/N$ (N: total number of layers), the following rate law can be formulated:

$$\frac{1}{(1-P)} \times \frac{dP}{dt} = k_0X_0 + k_1X_1 + k_2X_2$$

Figure 26 gives the solution of this equation for the illitisation of a smectite with an original illite content of 10 % in a geothermal gradient of 25°C/km with constant burial rate. Because of the temperature dependence, the rate of alteration increases with depth. With illite contents over 75 %, it decreases strongly because, in this range, type-2 layers with a high activation energy dominate. As shown in Figure 27, the model calculations agree well with the conditions observed in the deep boreholes.

The model of Bethke and Altaner is persuasive because it explains the incomplete illitisation in old clay sediments. The chemical basis for the different reactivity of the individual layer types is, however, largely speculative. Reference should be made to the original work (BETHKE & ALTANER, 1986), together with BETHKE et al. (1986) for a more complete understanding.

Bethke and Altaner formulated their model on the assumption that the illitisation occurs as a solid-state reaction, but this would not be contradictory to the existence of a dissolution/precipitation mechanism.

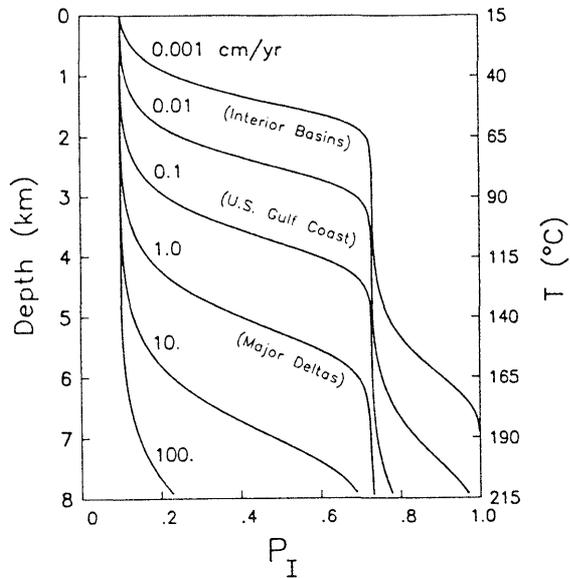


Figure 26: Model calculation for the alteration of smectite to I/S interstratifications with different burial rates for the sediments in a geothermal gradient of 25°C/km. For the reaction of layer types 0, 1 and 2, activation energies of 77.4, 75.3 and 100.4 kJ/mol respectively were used. A value of $10^{-3}/s$ was assumed for the Arrhenius factor A. P_I is the illite fraction of the interstratifications (BETHKE & ALTANER, 1986).

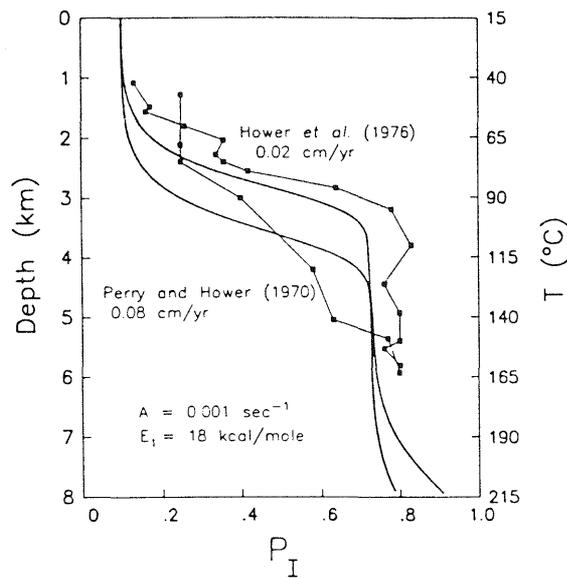


Figure 27: Comparison of model calculations with observed illite fractions in sediments (BETHKE & ALTANER, 1986).

7. INTERACTIONS BETWEEN BENTONITE AND MAGNETITE

7.1 Introduction

In a high-level waste repository, the steel canister must provide an initial barrier against radionuclide release for a period of at least 1000 years (NAGRA, NGB 85-04). Very little is known about the potential interactions between the backfill material and the steel canister or its corrosion products. At least it is certain that the bentonite has no adverse effect on the corrosion behaviour of the canister (SIMPSON, NTB 83-05 and NTB 84-01). It is still not clear whether interactions between montmorillonite and the canister corrosion products would occur to such an extent and in such a way that the function of the backfill could be impaired.

If one considers the material inventory expected in a Swiss repository (Tab. 3), it can be seen that iron and montmorillonite have comparable molar amounts. Chemical reactions between these partners could therefore affect a considerable percentage of the backfill and must be taken into account when considering the function of the bentonite. The potential reaction partners for iron in the glass are present in much smaller quantities. (The influence of steel and its corrosion products on the behaviour of the glass waste matrix will not be discussed here.)

After a short time, anaerobic conditions will be set up in a sealed repository and the corrosion products formed with the presence of oxygen will be negligible in terms of quantity (NAGRA, NGB 85-04). The product anticipated from the corrosion of the steel canister is a fine magnetite (GRAUER, 1981; GRAUER, NTB 84-19 and EIR Report 523, 1984) which was also found in corrosion experiments in compacted bentonite (SIMPSON, NTB 83-05 and NTB 84-01). A brown colouring of the bentonite in the vicinity of the steel samples (not investigated in depth) is an indication that the magnetite is still reacting.

Basically, there are several possible ways in which the steel corrosion products could affect the bentonite, for example

- destruction of the montmorillonite and formation of new solid phases
- intercalation of iron hydroxide layers in the interlayers of the montmorillonite (chloritisation)
- incorporation of iron ions into the montmorillonite structure (isomorphous substitution)
- blocking of part of the exchange capacity with iron ions
- precipitation of low-solubility, fine iron(III)-oxide/hydroxide phases, together with partial loss of swelling capacity.

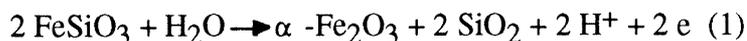
Table 3: Material inventory in a planned Swiss high-level waste repository, related to one waste canister (McKINLEY, NTB 84-48 and EIR Report 563, 1985; MUELLER-VONMOOS & KAHR, NTB 83-12).

	Volume (m ³)	Mass (kg)	Material quantity (kmol)
<u>Bentonite (dry)</u>	32,7	88'000	-
Montmorillonite	-	61'600	164
SiO ₂ in Montm.	-	39'400	657
CEC	-	-	61
<u>Pore-Water</u>	20,1	20'000	1110
<u>Iron, corroded to</u>	0,85	6'500	117
Fe ₃ O ₄	1,8	9'000	39
<u>Glass</u>	0,15	405	-
SiO ₂	-	183	3,1
B ₂ O ₃	-	56	0,8

A state-of-the-art discussion of these possibilities appears in the following Sects. Some aspects have already been discussed (GRAUER, NTB 86-12E and EIR Report 576, 1986). Experiments on the reaction between magnetite and montmorillonite have only begun recently (NAGRA, Personal Communication) and the discussion in this particular case will therefore be restricted to analogies and plausibility considerations.

7.2 Destruction of montmorillonite, formation of new phases

GARRELS & CHRIST (1965) have discussed the stability conditions in the system Fe/H₂O/SiO₂ and have determined that, in the presence of amorphous SiO₂, the magnetite is unstable with respect to ferrosilite (FeSiO₃). For the equilibrium



the redox potential according to these authors is

$$E = 258 - 59 \times \text{pH} \text{ (mV, } 25^\circ\text{C)}.$$

For the reaction



the silica equilibrium concentration was calculated with the data from BOWERS et al. (1984) for 25 and 75°C and compared with the saturation concentrations for amorphous silica and quartz:

	SiO ₂ equilibrium conc. (M)	
	25°C	75°C
Reaction (2)	1.20x10 ⁻³	4.57x10 ⁻³
SiO ₂ (amorph.)	1.95x10 ⁻³	4.57x10 ⁻³
Quartz	1.00x10 ⁻⁴	4.68x10 ⁻⁴

According to these data, magnetite is stable in a quartz-saturated solution at 25 and 75°C. In the presence of amorphous silica, it is unstable at 25°C while at 75°C it is stable beside ferrosilite.

In real terms, these calculations should be interpreted in a reserved manner. The magnetite corrosion product is fine-grained and has a different enthalpy of formation from the mineral Fe₃O₄. This is also true for the α-Fe₂O₃. Finally, formation of ferrosilite as an iron-rich end-member of the pyroxene series is unlikely. GARRELS & CHRIST (1965) selected FeSiO₃ as the silicate phase because - in contrast with other iron silicate phases - its enthalpy of formation is known.

Potential reaction products can be found among the numerous iron-containing clay minerals; some are presented in Table 4. Because the potassium supply in a repository will be low, the formation of micaceous compounds is unlikely, as is new formation of phases which are formed naturally under hydrothermal conditions. In accordance with the temperature and pressure conditions, one would expect to find those minerals which occur in sediments.

Iron-containing components of sediments are mainly chamosite, greenalite, cronstedtite and thuringite (HARDER, 1978) but minnesotaite and stilpnomelane are also found (JAMES, 1954). These iron-containing clays are often associated with magnetite in non-metamorphosed sediments (JAMES, 1954). It cannot be assumed a priori that such a clay/magnetite facies would correspond to an equilibrium state.

In the geohydrothermal system of the Red Sea, an iron (II/III)-nontronite with Fe(III)/Fe(II)-ratios from 2.7 to 8.9 was found (BISCHOFF, 1972). BADAUT et al. (1985) also isolated a trioctahedral iron(II)-smectite in the sediments of the Red Sea; on oxidation to the iron(III) form, this releases iron(III)-hydroxide which is deposited in the form of small grains on the clay platelets (cf. also DECARRAU & BONNIN, 1986).

Table 4: Iron-containing phyllosilicates (BAILEY, 1986; cf. also OTTOW, 1975).

Mineral	Ideal Formula	Structure Type
Berthierin	$(\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg})_{3-x-3y}(\text{Fe}^{3+}, \text{Al})_{x+2y}$ $\square_y(\text{Si}_{2-x}\text{Al}_x)\text{O}_5(\text{OH})_4$ (mit $x = 0.45$ 0.90 , $y = 0.0$ 0.3)	Serpentine
Cronstedite	$(\text{Fe}^{2+}, \text{Mg})_{3-x}\text{Fe}_x^{3+}(\text{Si}_{2-x}\text{Fe}_x^{3+})\text{O}_5(\text{OH})_4$	Serpentine
Greenalite	$\sim (\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4$	Kaolinite
Ferripyrophyllite	$\text{Fe}_2^{3+}\text{Si}_4\text{O}_{10}(\text{OH})_2$	Pyrophyllite
Nontronite	$\text{Fe}_2^{3+}(\text{Si}_{3.67}\text{Al}_{0.33})\text{O}_{10}(\text{OH})_2 \cdot \text{R}_{0.33}^{1+}$	Smectite
Annite	$\text{KFe}_3^{2+}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$	Mica
Ferriannite	$\text{KFe}_3^{2+}(\text{Si}_3\text{Fe}^{3+})\text{O}_{10}(\text{OH})_2$	Mica
Biotite	$\text{K}(\text{Mg}_{0.6-1.8}\text{Fe}_{2.4-1.2}\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$	Mica
Celadonite	$\text{K}(\text{Mg}, \text{Fe}^{2+})(\text{Fe}^{3+}, \text{Al})\text{Si}_4\text{O}_{10}(\text{OH})_2$	Mica
Glaucosite	$\sim \text{K}_{0.85}(\text{Fe}^{3+}, \text{Al})_{1.34}(\text{Mg}, \text{Fe}^{2+})_{0.66}(\text{Si}_{3.76}\text{Al}_{0.24})\text{O}_{10}(\text{OH})_2$	Mica
Zinnwaldite	$\text{K}[\text{Fe}_{1.5-0.5}^{2+}\text{Li}_{0.5-1.5}(\text{Al}, \text{Fe}^{3+})](\text{Si}_{3.5-2.5}\text{Al}_{0.5-1.5})\text{O}_{10}(\text{OH}, \text{F})_2$	Mica
Siderophyllite	$\text{K}(\text{Fe}_2^{2+}\text{Al})(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2$	Mica
Montdorite	$\text{K}(\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg})_{2.5}\text{Si}_4\text{O}_{10}(\text{OH})_2$	Mica
Anandite	$\text{BaFe}_3^{2+}(\text{Si}_3\text{Fe}^{3+})\text{O}_{10}(\text{OH})\text{S}$	Mica
Chamosite	$\text{Fe}_5^{2+}\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$	Kaolinite
Thuringite	$(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}, \text{Mg})_3(\text{Al}, \text{Si})_2\text{O}_5(\text{OH})_4$	Chlorite
Stilpnomelane	$\sim (\text{Ca}, \text{Na}, \text{K})_4(\text{Fe}_{35.5}\text{Mg}_{9.3}\text{Al}_{2.3}\text{Mn}_{0.8}\text{Ti}_{0.1})_{48}$ $(\text{Si}_{63}\text{Al}_9)(\text{O}, \text{OH})_{216} \cdot n\text{H}_2\text{O}$	2:1
Minnesotaite	$\sim (\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	2:1

In water, nontronite is formed by adsorption of silica on goethite particles followed by a reaction in deeper layers under reducing conditions (PEDRO et al., 1978). For 40 % conversion of goethite particles (diameter ca. 0.25 μm) under tropical conditions (Lake Chad), a time period of 1000 years is estimated. Similarly to the case of nontronite, chamosite (PEDRO et al., 1978), greenalite (BORCHERT, 1951) and glaucosite (PORRENGA, 1967) are formed.

EGGLETON (1987) describes a series of amorphous Fe-Si-Al hydroxides which are partly weathering products of crystalline silicates but are also forerunners of crystalline clay minerals. An iron(II) saponite is also known (KOHYAMA et al., 1973).

Colloidal iron silicates (which did not undergo close characterisation) form on corrosion of borosilicate glasses in the presence of iron (McVAY & BUCKWALTER, 1983). These experiments were carried out without addition of bentonite and oxygen was not excluded - their significance for repository conditions is therefore questionable.

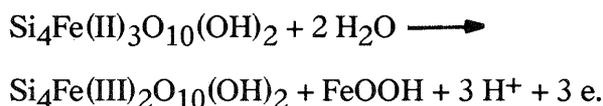
The systematic synthesis experiments carried out by HARDER, 1986 at ambient temperature give an insight into the genesis of iron-containing clay minerals. The experiments started with iron hydroxide/silica precipitates to which further ions such as aluminium, magnesium and potassium were added. Crystalline precipitates formed under reducing conditions over time periods ranging from hours to several days.

If oxygen is excluded and hyposulphite is present as a reducing agent, Fe(II)-berthierin, Fe(II)-smectite and Mg-Fe(II)-saponite (lembertite) are formed. The micaceous Fe(II)-glaucosite formed only with a high potassium supply.

Under slightly oxidising conditions, mixed-valence compounds of berthierin, nontronite and glaucosite formed. Crystalline phases of the chamosite- and greenalite-type also formed (HARDER, 1978). The optimum pH range for the formation of these substances is 8 to 9.

The synthesis of crystalline compounds is possible only with silica contents below 100 ppm because polymeric silica inhibits crystallisation. Berthierin is produced with silica contents of 6 to 10 ppm and low Si/(Fe + Al) ratios in the presence of magnesium. Nontronite formed with silica contents over 10 ppm and a high Si/(Fe + Al) ratio. At ambient temperature, formation of dioctahedral iron(III)-nontronite is possible only via reduced precursors (HARDER, 1976; HARDER, 1978).

DECARRAU & BONNIN (1986) have aged iron(II)/silica gels without further addition of cations (except Na⁺) at 75°C under reducing conditions. This produced nuclei of trioctahedral iron(II)-stevensite; crystal growth appears to have been inhibited by the relatively high silica content. Oxidation of this primary product led to the dioctahedral iron(III)-form, with a third of the iron being released as hydroxide:



The iron(III)-hydroxide was possibly emplaced in the interlayers.

To summarise, any prediction of potential reactions between magnetite and montmorillonite to form new phases will be uncertain, but such reactions are nevertheless very likely. The reaction products would be iron-rich clay minerals and possibly also amorphous reaction products which, although they show no intercrystalline swelling, have a large specific surface and are therefore good sorbents.

Because of the variable and complex stoichiometry of the potential reaction products, it is only possible to make a rough estimate of the extent of montmorillonite alteration. If the stoichiometry of reaction (2) is used as a basis, complete alteration of the magnetite would involve 6 % of the montmorillonite in the reaction.

The extremely unlikely corrosion reaction



would use up 18 % of the montmorillonite. Estimates with realistic end-products such as greenalite also lead to a montmorillonite alteration of between 5 and 20 %.

7.3 The chloritisation of montmorillonite

Chloritisation is understood to mean the emplacement of positively charged non-stoichiometric hydroxide layers in the interlayer spaces of three-layer silicates. These layers then become inaccessible for ion-exchange and the innercrystalline swelling capacity is lost. In chlorite, these interlayers consist of magnesium hydroxide. The emplacement of aluminium- and, more rarely, iron hydroxides in montmorillonite is a well-known pedological phenomenon (RICH, 1968).

The possible chloritisation of montmorillonite under repository conditions has already been discussed (GRAUER, NTB 86-12E and EIR Report 576, 1986) and the details need not be repeated here; reference should be made to the relevant literature.

As the following assessment shows, chloritisation of montmorillonite by canister corrosion products would have significant consequences. The overall montmorillonite surface is 750 m²/g (MUELLER-VONMOOS & KAHR, NTB 83-12). The data for a unit cell of lepidocrocite (γ -FeOOH) are used as an approximation for the dimensions of the Fe(O,OH)_x-interlayer: a = 0.387 nm, b = 1.252 nm, c = 0.307 nm, orthorhombic cell with z = 4. The iron present in the repository would therefore require 8.5 x 10⁹m² in the a x b-dimension and would block the montmorillonite surfaces (0.5 x 4.6 x 10¹⁰m²) to around 40 %. The same figure is also derived from BARNHISEL (1977) according to whom 4.5 moles of aluminium or iron per kg of montmorillonite are necessary for formation of a complete hydroxide interlayer.

From this brief consideration, it can be seen that the chloritisation of montmorillonite could be a serious problem, especially when one considers that deterioration of the montmorillonite properties can occur with a hydroxide content of only a few percent (APLEROVICH et. al., 1985). An in-depth discussion is therefore necessary.

As presented in GRAUER, NTB 86-12E and EIR Report 576 (1986), chloritisation of montmorillonite occurs by sorption of positively charged hydroxo-complexes and subsequent polycondensation. Positively charged hydroxo-complexes are generally sorbed in preference to the aquo-ion. For electro-neutrality reasons, negative hydroxo-complexes are not emplaced in the montmorillonite interlayers.

The potential for chloritisation of montmorillonite is therefore to be assessed in terms of the availability of mono- and polynuclear hydroxo-complexes. As shown in Figure 28, in the case of aluminium, polynuclear complexes occur in notable concentrations only at pHs below 5. The chloritisation of montmorillonite by aluminium will therefore occur only in acid soils (RICH, 1968). For iron(III), the stability ranges of polynuclear complexes are shifted to even lower pH values (Fig. 29). In the pH range relevant for repository conditions (7 to 10), only the complexes $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_4^-$ contribute to the solubility of goethite at a very low level. There are no known polynuclear complexes of iron(II). In the pH range of interest, besides the aquo-ion only the complex FeOH^+ is to be taken into account (Fig. 30).

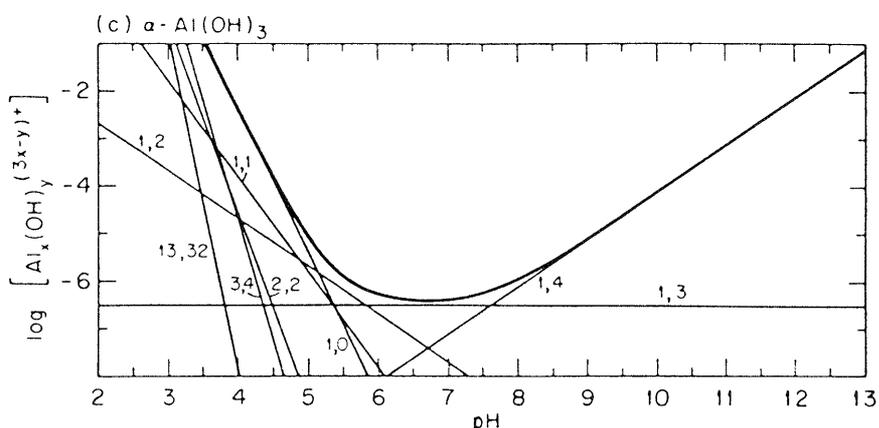


Figure 28: Distribution of aluminium hydroxo-complexes in equilibrium with gibbsite as a function of pH value at 25°C and ionic strength 1 M (BAES & MESMER, 1976).

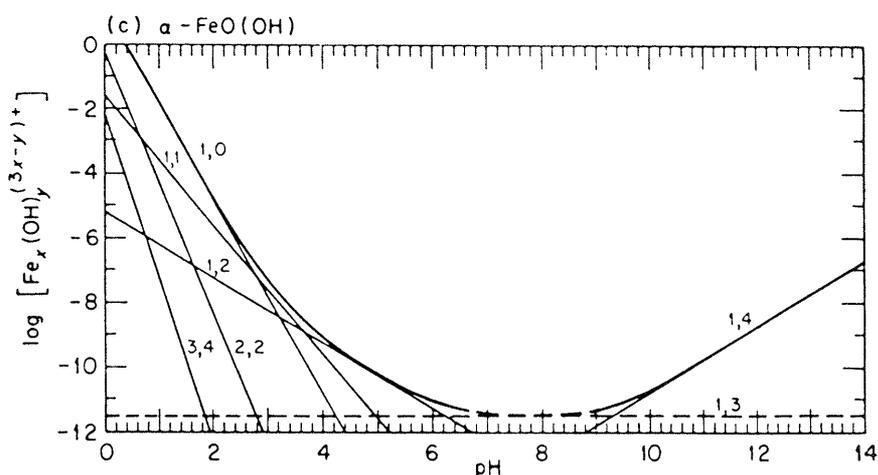


Figure 29: Distribution of iron(III)-hydroxo-complexes in equilibrium with goethite as a function of pH value at 25°C and ionic strength 1 M (BAES & MESMER, 1976).

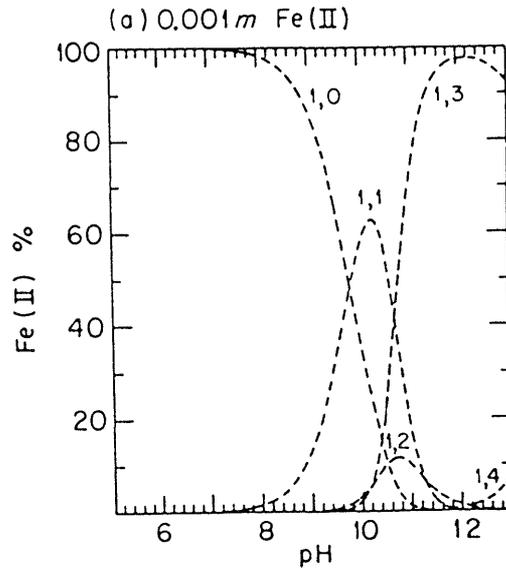
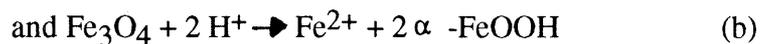
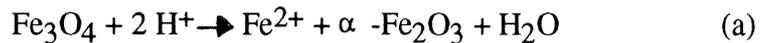


Figure 30: Percentage distribution of iron(II)-hydroxo-complexes as a function of pH value at 25°C and ionic strength 1 M. (BAES & MESMER, 1976).

Of interest in this connection is the iron(II)-concentration in equilibrium with magnetite. Magnetite dissolves incongruently according to



The equilibrium calculation is difficult as one cannot apply the enthalpies of formation of well-formed crystalline solid phases. It would not be unreasonable to assume that, for the reaction a, the non-ideality of the educt and product would compensate one another. Data from (STUMM & MORGAN, 1981) give $\log K = 8.1$. For reaction b, $\log K$ varies from 5.2 (for active FeOOH) to 7.8 (for inactive FeOOH). A conservative estimate of the iron(II) concentration at $\text{pH} > 8$ would be under $1 \mu \text{ mol/litre}$. HEUSLER (1985) also found concentrations of this order.

Because of the low availability of iron hydroxo-complexes in the pH range of bentonite pore-water, it seems unlikely that the montmorillonite will undergo chloritisation under repository conditions. It should also be mentioned that iron hydroxide interlayers have been found to be less stable than their aluminium counterparts (RICH, 1968). Whenever the interlayers are filled to a high degree with iron hydroxide, the chlorite structure becomes unstable and decomposes to smectite and iron hydroxides.

7.4 Isomorphous substitution of silicon and aluminium by iron in the montmorillonite structure

Nature provides many examples of three-layer silicates with high iron contents mainly in the octahedral positions (BADAUT et al., 1985 and Tab. 4). The montmorillonite of bentonites also contains iron (MUELLER-VONMOOS & KAHR, NTB 83-12). The iron(III)-content of the montmorillonite can have an adverse effect in that reduction to iron(II) increases the layer charge to such an extent that an irreversible layer collapse occurs if potassium is present (ESLINGER et al., 1979; GRAUER, NTB 86-12E, EIR Report 576, 1986). Reduction of iron in the smectite structure is reversible (LEAR & STUCKI, 1985; YARIV & CROSS, 1979). For this reason, only montmorillonites with low iron contents should be considered as a backfill material. In principle, the incorporation of iron from the canister corrosion products into the silicate lattice could also have an adverse effect on the backfill properties.

There appears to be little information on the extent and kinetics of such substitution reactions. They can, however, be considered as similar to illitisation by isomorphous substitution of silicon by aluminium. According to GRAUER, NTB 86-12E and EIR Report 576 (1986), under repository conditions illitisation of montmorillonite is not to be expected over a time period of over 10^6 years.

As with normal illitisation (Sect. 6.4), it is not to be expected that substitution of silicon or aluminium by iron will occur via a solid-state reaction. Based on ionic radius ratios and information on natural minerals, incorporation of iron into the tetrahedral layers appears unlikely (BADAUT et al., 1985; JOHNSTON & CARDILE, 1987). If the idea of a solid-state reaction is adhered to, aluminium would have to be replaced by iron in the shielded octahedral layers (non-tronitisation). This reaction is even more unlikely than isomorphous substitution of silicon by aluminium or iron by interdiffusion in the tetrahedral layers.

Direct incorporation of iron into the montmorillonite structure can therefore more or less be ruled out. Much more likely is incorporation of iron as a result of complete restructuring by a dissolution/precipitation reaction (Sect. 7.2).

7.5 Blocking of the cation-exchange capacity by iron

Around 80 % of the sorption capacity of montmorillonite is based on ion-exchange in the interlayers and around 20 % on reactions of surface OH-groups (broken bonds) see GRAUER, NTB 86-12E and EIR Report 576 (1986). Purely mathematically, the amount of iron present would suffice to block the total sorption capacity of the bentonite (Tab. 3). However, because of the low availability of dissolved iron, significant sorption is not to be expected. The possibility of sorption of hydroxo-complexes was discussed in Section 7.3. This also appears unlikely under repository conditions.

7.6 Loss of swelling capacity due to precipitated iron(III)-oxide/hydroxide phases

PUSCH (1983) describes a bentonite with strongly reduced plasticity and low swelling capacity (Magreteberg clay); these properties are in contrast with the high smectite content of the material. Electron-microscopy investigations have shown that this behaviour can be linked with the fact that the smectite-aggregates are covered by fine FeOOH. There are also accumulations of SiO₂ at the smectite edges. Grinding restores the swelling capacity of the clay. The conclusion is therefore that the observed precipitates somehow clamp the layer packages together.

It has been suggested that the swelling of the montmorillonite in a repository could be hindered in a similar way by the iron corrosion products.

Laboratory investigations (EL RAYAH & ROWELL, 1973) have shown that aluminium- and iron hydroxide-precipitates on montmorillonite inhibit its swelling properties. Reference is also made in the same work to the fact that the hydroxide "clamps" crack under sufficient swelling pressure.

It is not clear how the covering layers were formed on the smectite of the Margreteberg clay. The SiO₂ deposits possibly originated when the bentonite was formed as volcanic ash generally has an excess of SiO₂ (GRIM, 1968). PUSCH (1983) assumes that the iron hydroxides were formed by a hydrolytic and oxidative reaction of iron-containing silicates. According to the works by BADAUT et al. (1985) and by DECARRAU & BONNIN (1986), an oxidation of iron(II)-rich smectites with release of FeOOH would also be conceivable (cf. Sect. 7.3). In the case of such a reaction, the accumulation of iron(III)-compounds at the edges of the smectite crystals was electron microscopy (BADAUT et al., 1985). Formation of iron(III)-coatings could also conceivably originate from an external hydrothermal iron source or by oxidation of iron(II) minerals such as siderite and pyrite which occur frequently in bentonite. Iron transport due to biological activity is also possible (ZINDER & STUMM, 1985).

The effects on backfill function of a possible deposition of iron(III) compounds on the montmorillonite would not be serious. Since corrosion of the steel canister only begins after entry of water, the bentonite will already have swollen.

Finally, the percentage of montmorillonite affected by a precipitation should be estimated. From Figure 15, 1972 in PUSCH (1983), the particle size of the FeOOH can be estimated as around 30 nm. Assuming a low density of 3.0 g/cm³, for this particle size a surface requirement of 1.2 x 10⁸m² results for 117 kmol FeOOH. This value is to be compared with the outer surface (BET surface) of the montmorillonite, the latter being around 2.3 x 10⁹m² (based on information in GRIM, 1968 of 38 m²/g for Wyoming bentonite). The corrosion products would therefore be sufficient to coat around 5 % of the montmorillonite crystals.

7.7 Summary overview

The basic possibilities for reactions between montmorillonite and canister corrosion products in a repository environment are manifold. Because of the absence of relevant thermodynamic data and pertinent experiments, it is almost impossible to make any statements with certainty. There is still much room for speculation and arguments are based at best on analogies and plausibility considerations.

The potential interactions should be looked at from the point of view of how they will affect the barrier function of the backfill; this means that not only should the likelihood of their occurrence be investigated but the percentage of the bentonite affected by the reaction should also be determined. The properties of possible reaction products should also be assessed.

In nature, clay minerals are also found alongside magnetite but this association need not imply a stable situation. It does however indicate that alteration reactions occur extremely slowly.

In all probability, montmorillonite and magnetite will react to form new phases. The formation of chamosite, greenalite or nontronite would be conceivable, part of the iron reacting to form goethite. With the given quantity ratios, around 5 to 20 % of the montmorillonite would be altered.

Only a proportion of the potential reaction products will have swelling properties. Under repository conditions, they will occur in a microcrystalline or amorphous state and the sorption capacity of the backfill will not be affected.

The formation of products similar to chlorite with strongly reduced sorption capacity and swelling capacity due to emplacement of iron hydroxide in the interlayers of the montmorillonite is rather unlikely due to the low solubility of the iron compounds and the absence of polynuclear hydroxo-complexes in the pH range of the pore-water. If such a reaction were to occur, the quantity of iron present would be sufficient to affect all the montmorillonite.

Isomorphous substitution of silicon or aluminium in the montmorillonite structure by iron(II/III) via a solid-state mechanism is extremely unlikely. It is to be assumed that iron-containing clay minerals will be produced only by a dissolution/precipitation reaction.

It is known that iron(III)-oxyhydroxides precipitated onto the montmorillonite can affect its swelling potential. Under repository conditions, such a precipitation of corrosion products would be onto the already swollen bentonite. The amount would be sufficient to cover around 5 % of the montmorillonite surface.

The possible effects of microbial processes were not included in the discussion due to lack of knowledge on the author's part. They could however be important in nature in the formation of iron-containing silicates such as chamosite and glauconite (CAROLL, 1958).

Since statements on the interactions between bentonite and the canister corrosion products are only more or less plausible, experiments must be carried out. This is true particularly because the material ratios in the repository would imply that the effects of such reactions would not be insignificant.

8. INTERACTIONS BETWEEN BENTONITE AND PORTLAND CEMENT

In a repository for low- and intermediate-level waste, there is a possibility of contact between bentonite and concrete. Cement pore-waters are characterised by a high pH which is determined initially by alkali hydroxides and later by the incongruent dissolution of hydrated calcium silicates (BERNER et al., 1987). During this phase the pH is around 12.5 and the calcium concentration in the water is increased (Fig. 31).

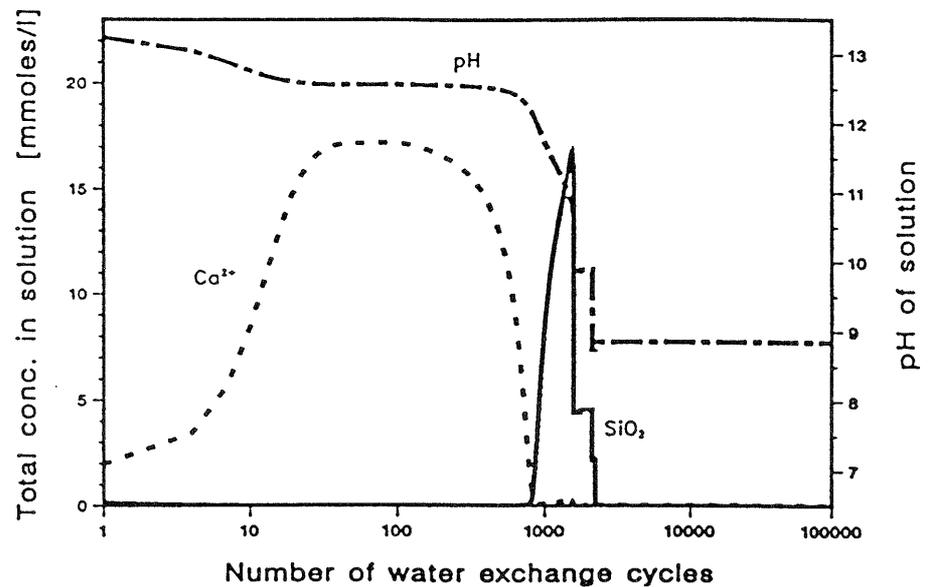


Figure 31: Curves for pH, calcium and silica concentrations obtained on leaching of Portland cement with a marl water (BERNER et al., 1987).

Under such conditions, the montmorillonite can be expected to alter to zeolite. Zeolites are water-containing tectosilicates with tetrahedral $(\text{Si,Al})_n\text{O}_{2n}$ building units. The negative lattice charge caused by incorporation of aluminium is compensated by the alkaline and alkaline earth ions in structural cavities (BARRER, 1982; GOTTARDI & GALLI, 1985). These ions are exchangeable. In contrast with smectites, the zeolites have no swelling capacity.

JOHNSTON & MILLER (1984 and JOHNSTON & MILLER, 1985) give an overview of the formation of zeolites; the following summary is based on this overview with no reference to any other literature data.

Zeolites are formed particularly at high pH values (over 9 to 10) and with relatively high calcium or sodium concentrations. In nature they are produced mainly by hydrothermal alteration of volcanic glasses but also from bentonite. In geothermal fields, zeolites are found in the temperature range 50 to 350°C. Zeolites also occur in sediments alongside smectites and illites but in this case it is not certain that the phyllosilicates are the zeolite forerunners.

PUSCH (1982) has investigated the interactions between compacted bentonite and cement. Zeolites could not be identified unambiguously. Based on different assumptions it was estimated that, at 10 to 20°C over a period of 500 to 1000 years, a clay layer of maximum thickness 1 cm would be altered to zeolite.

The loose structure of zeolites means that they have a low density. The alteration from smectite to zeolite therefore involves an increase in volume and permeability increases due to the cavities in the zeolite structure. Because the zeolite structure is rigid, the altered bentonite backfill loses its plasticity.

Although zeolites have a high cation-exchange capacity, their selectivity for heavy metal ions is low; this means that the sorption properties of an altered backfill would also deteriorate.

Under repository conditions, it is to be expected that the formation of zeolites will be dominated by transport processes.

9. SUMMARY DISCUSSION

9.1 The thermodynamics of clay minerals

There is as yet no satisfactory repository near-field model which includes the interaction between bentonite and water. Formulation of a thermodynamic equilibrium model comes up against basic difficulties because smectites and illites are presumably unstable, i.e. no metastable solution equilibria are set up (LIPPMANN, 1979; LIPPMANN, 1981; MAY et al., 1986).

Because of their inherent variability and heterogeneity, smectites and illites are not phases in the thermodynamic sense. If inhomogeneities on the single layer scale are ignored, irregular illite/smectite interstratifications are to be seen as two-phase while the ordered interstratifications are single-phase (NADEAU et al., 1984).

TARDY & FRITZ (1981) calculate the smectite and illite solubility products with a model which considers the clay minerals as ideal solid solutions with a maximum of 36 stoichiometric end-members. There are two basic objections to this model:

1. The assumption of continuous solid solutions between all 36 end-members is not justified (GIGGENBACH, 1985; VELDE, 1985)
2. The setting-up of solution equilibria with 2:1 phyllosilicates has not been demonstrated (MAY et al., 1986).

TARDY et al. (1987) meet these objections with the argument that, in every micro-system, there should be a metastable equilibrium from just one clay particle and the surrounding solution. The idea of a solid solution in the atomic range is given up in favour of the concept of the solid solution consisting of individual elementary layers, each of which should represent the chemical composition of one of the 36 end-members. Formally this deals with the objections but it remains to be discussed whether these assumptions are in fact realistic.

The semi-empirical model of Mattigod and Sposito (SPOSITO, 1986) allows the free enthalpies of formation of real homoionic smectites to be estimated. These are considered as polymerizates of simple hydroxides. Because enthalpies of formation (and not solubility products as with TARDY & FRITZ, 1981) are being calculated, the discussion of setting-up of solution equilibria is avoided.

In the case of stability diagrams which include clay minerals, it should be taken into account that not only is the equilibrium state questionable but that a graphic representation is possible with only a simple idealised formula (GIGGENBACH, 1985). The differences in the enthalpies of formation for ideal and real minerals can lead to false conclusions.

9.2 The swelling of bentonites

The water uptake of the reference bentonites MX-80 and Montigel was characterised by determining the heats of immersion and water vapour sorption isotherms (KAHR et al., NTB 86-14; KRAEHENBUEHL et al., NTB 87-01). Calculation of the swelling pressure from the sorption data gives a good agreement with the measured values. It is therefore possible, for example for the purpose of ongoing quality control, to assess the swelling behaviour of a bentonite by the less costly process of measuring water vapour sorption.

Observations that a sodium bentonite loses its swelling capacity after treatment with water vapour (COUTURE, 1985a and 1985b) have promoted the idea that such a situation could occur in a repository during the initial high-temperature phase. However, a resumé of the work carried out leads to the conclusion that the intercrystalline swelling of the smectite, which is all that is required in a repository, probably remains intact. Further critical experiments, including some with calcium bentonite, are necessary.

Montmorillonites loaded with potassium partly lose their swelling potential following repeated wet/dry cycles, without raising the layer charge of the montmorillonite (EBERL et al., 1986). The sodium and calcium variants do not show this phenomenon. Because the low potassium supply in a Swiss repository means that the necessary potassium saturation would only be achieved after 10^6 to 10^8 years (GRAUER NTB 86-12E and EIR Report 576, 1986, p. 127), it is highly unlikely that the bentonite will be adversely affected.

9.3 Water composition in contact with bentonite

There is still very little information on water composition in contact with bentonite. The Finnish work (SNELLMAN et al., 1987) should be mentioned but, in this case, the bentonite/water ratio was very low.

There is still confusion about the pH-determining reaction in bentonite/water mixtures. Besides the partial dissolution of the montmorillonite, exchange of the inter-layer ions for the hydrogen ion and also the reaction



can increase the pH (Z⁻: exchange equivalent of the montmorillonite).

According to the discussion in Section 9.1, there are problems involved in applying Tardy and Fritz's equilibrium model (TARDY & FRITZ, 1981) to bentonite/water systems (FRITZ & KAM, 1985; TARDY et al., 1987). Wanner's model (WAN-
NER, NTB 86-21 and EIR Report 589, 1986) of the interaction between sodium bentonite and water treats the montmorillonite as an inert ion-exchanger. This avoids most of the problems involved in quantitative treatment of the smectites but it tends towards oversimplification.

9.4 Sorption and diffusion behaviour

Exchange of interlayer ions of the montmorillonite for potassium is of interest when discussing illitisation. Two works have investigated the Ca/K-exchange, one dealing with temperature dependence (INOUE & MINATO, 1979) and the other with the effect of layer charge (SHAINBERG et al., 1987). The selectivity for calcium increases with increasing temperature but decreases with increasing layer charge.

The diffusion behaviour of fission products and actinides in compacted MX-80 bentonite is dealt with in two recent publications (TORSTENFELT, 1986a; TORSTENFELT, 1986b, see also Tab 1. p.5-4). Several individual ions have a complex diffusion behaviour which is only partially understood.

9.5 The illitisation of smectites

Investigations of Mesozoic up to recent clay sediments (mainly from the Gulf of Texas) show that, for typical repository temperatures of 50 to 60°C, complete illitisation of the montmorillonite would not be expected, even over a time period of 10^8 years (Fig. 20). The maximum illite contents of Cretaceous sediments are around 50 %. Investigations of sediments have also shown that potassium need not be present for an increase in the montmorillonite layer charge.

Calcium montmorillonite is significantly more resistant to alteration into illite than the sodium variant. This was shown by experiments on clay sediments (NADEAU & REYNOLDS, 1981) and in hydrothermal laboratory experiments (INOUE, 1983; LAHANN & ROBERSON, 1980; YAU et al., 1987).

In compact sediments with low water circulation (comparable with repository conditions), alteration of montmorillonite to illite is isochemically via the solution, producing around two illite layers from three montmorillonite layers. The potassium must come from an external source (e.g. K-feldspar; BELL, 1986; NADEAU et al., 1985).

The kinetic model of illitisation developed by BETHKE & ALTANER (1986) is of particular interest since it makes the reactivity of an elemental montmorillonite layer a function of the nature of its immediate neighbours and can thus give a good description of the depth distribution of the illite in the sediments. The model should take account of the role of the different interlayer ions and the variations in solution chemistry.

9.6 Interactions between bentonite and magnetite

The thermodynamic data and relevant experiments required to assess possible interactions between the montmorillonite of the backfill material and the canister corrosion products are lacking. It is therefore only possible to discuss basic possible reactions and to assess the likelihood of their occurring on the basis of analogies and plausibility considerations.

Given the present state of knowledge, the formation of new iron-containing phases such as chamosite, greenalite or nontronite would appear highly likely. With the given mass ratios, this could involve alteration of around 20 % of the montmorillonite. Some of these phases have no swelling capacity. As clay minerals, they will occur in microcrystalline form so that the sorption capacity of the backfill is not impaired.

Since the material ratios in a repository do not generally allow the effects of potential reactions to be classed as insignificant, experiments will have to be carried out.

9.7 Interactions between bentonite and Portland cement

If montmorillonite comes into contact with alkaline cement pore-waters, the clay can be expected to alter to form zeolites. This reaction is linked with an increase in volume and therefore leads to a pressure increase in a closed system. Zeolites are not plastic.

In a repository, the extent of the reaction will be determined by mass ratios and the diffusion of the cement pore-water into the bentonite.

Experiments in this area are also desirable.

10. CONCLUSIONS AND RECOMMENDATIONS

The conclusions drawn in the earlier report GRAUER, NTB 86-12E and EIR Report 576 (1986), remain valid. The time period of 10^6 years given in the report for the long-term stability of the montmorillonite appears now to be conservative. It is realistic to expect the formation of random illite/smectite interstratifications (50 % illite) within around 10^8 years.

Recent publications have also confirmed the increased resistance of calcium montmorillonite to an alteration into illite. It is therefore recommended that calcium bentonite should be used for backfilling the type C repository. It has recently been shown that the rheological properties of sodium and calcium bentonite differ only very slightly at high dry densities (BÖRGESSON & PUSCH, 1987).

Experiments still require to be carried out in the following areas:

- Swelling behaviour of montmorillonite after treatment with water vapour
- Interactions between magnetite and bentonite
- Interactions between cement and bentonite.

Attempts should also be made to develop a model for bentonite/water interaction and nuclide transport through the backfill.

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