

Chemical and mineralogical aspects of water-bentonite interaction in nuclear fuel disposal conditions

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ABSTRACT

In the field of nuclear fuel disposal, bentonite has been selected as the principal sealing and buffer material for placement around waste canisters, forming both a mechanical and chemical barrier between the radioactive waste and the surrounding groundwater.

Ion exchange and mineral alteration processes were investigated in a laboratory study of the long-term interaction between compacted Na-bentonite (Volclay MX-80) and groundwater solutions, conducted under simulated nuclear fuel disposal conditions. The possible alteration of montmorillonite into illite has been a major object of the mineralogical study. However, no analytical evidence was found, that would indicate the formation of this non-expandable clay type. Apparently, the change of montmorillonite from Na- to Ca-rich was found to be the major alteration process in bentonite. In the water, a concentration decrease in Ca, Mg, and K, and an increase in Na, HCO_3 and SO_4 were recorded. The amount of calcium ions available in the water was considered insufficient to account for the recorded formation of Ca-montmorillonite. It is therefore assumed that the accessory Ca-bearing minerals in bentonite provide the fundamental source of these cations, which exchange with sodium during the alteration process.

X-ray powder diffraction (XRD) analyses and optical microscope observations of the initial and reacted bentonite samples were conducted. Quartz, feldspars, pyrite, calcite and minor amounts of gypsum were revealed as the primary accessories. In reacted samples, goethite and siderite were identified as secondary mineral products in association with corroded pyrite grains, while calcite and gypsum were found to disappear. From these results it is assumed that oxygen present in the water and in the bentonite pore space promotes the oxidation reaction of pyrite (dissolved) and the precipitation of goethite. As a result, the pore water pH decreases and calcite is partly dissolved. This dissolution provides a significant amount of calcium ions, in addition to those that arise by diffusion from the water. Some of the reaction-released bicarbonate and ferric ions are found to re-precipitate in the bentonite as siderite, while the rest (also as sulphate ions) diffuse into the water.

Although the relative oxygen content in the experiment may be considered higher than that of the repository concept for nuclear fuel disposal (due to interaction in a semi-closed system with high water/bentonite ratio), the near field geochemistry predictions imply limited oxidising conditions, which are characterised by the above-described processes in sulphide-bearing bentonite and occur for some time after closure and sealing of the repository.

PREFACE

This report was prepared as part of the publicly-administrated research program (JYT) on nuclear waste disposal management, currently in progress at the Communities and Infrastructure Laboratory of the Technical Research Centre of Finland (VTT). The work is financed by the Ministry of Trade and Industry of Finland (KTM).

The interaction experiment and the chemical analyses of water were performed by the Chemical Laboratory of VTT. The X-ray powder diffraction analyses of bentonite were conducted by Mr. Kristian Lindqvist of the Geological Survey of Finland (GTK), the microprobe analyses by Mr. Bo Johansson (GTK), and the extraction treatments and chemical analyses of bentonite by Dr. Antti Vuorinen from the Department of Geology & Mineralogy of Helsinki University.

Espoo, December 1995

The Authors

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1 INTRODUCTION

In a repository for high level nuclear fuel, the buffer material should perform certain barrier functions in order to isolate and support the waste canisters. Sodium bentonites, uniquely characterised by their excellent swelling ability, adsorption properties, low hydraulic conductivity and good plasticity (Borchardt 1989), have been considered suitable candidates for this purpose (Pusch 1978, Anderson 1983, Güven 1990). The bentonite is expected to minimise the flow rate of percolating groundwater, retard the migration of radio nuclides, withstand mechanical stress in the host rocks, and seal open cracks and fissures. Since long-life radioactive fuel is to be disposed in the repository, the maintenance of the repository's material properties and the continuity of its buffering functions over a long period of time, i.e. the longevity of the bentonite, are of great significance.

Bentonites consist mainly of the expandable smectite clays of the montmorillonite-beidellite series. The mineralogical compositions of different bentonites vary, the main component being montmorillonite, generally in the range 50 - >90%. Bentonites also contain a number of associated minerals reflecting the volcanic origin or the alteration history of the rock. Accessory minerals commonly found in bentonites include aluminosilicates (feldspars, kaolinite and zeolites), oxides (quartz, cristobalite, hydrous ferric oxides), carbonates (calcite \pm dolomite), sulphides (pyrite), sulphates (gypsum, anhydrite) and residual unreacted volcanic glass (Grim & Güven 1978).

The mineralogical stability of the buffer material may change under the hydrothermal conditions expected in the repository. The transformation of smectite clay into illite (non-expandable clay type) may occur (Johnston 1983, Johnston & Miller 1985, Pusch & Karnland 1988a, Güven 1990), possibly followed by a gradual degradation in buffer performance, particularly in terms of its plasticity, water impermeability and sorption properties.

Alteration processes of bentonites in hydrothermal environments and in contact zones of magmatic intrusions have been the subject of continuous investigations of deposits at various locations (Velde & Brusewitz 1982, Pusch 1983, Brusewitz 1988, Pusch & Karnland 1988b, Müller-Vonmoos et al. 1990, Inoue et al. 1990, 1992). The most prominent factor usually deduced from the study of natural analogues is the alteration time of the clay material. However, the hydrothermal conditions and original mineralogical and chemical compositions of the reacting components, which determine the mechanism and rate of the alteration process, can only be evaluated.

In order to follow closely the characteristic hydrothermal-induced mineralogical changes of the buffer material and the changes in chemical composition of reacting water solutions, laboratory experiments on bentonite alteration were conducted under various hydrothermal conditions (Fritz & Kam 1985, Pusch & Güven 1990, Pusch & Karnland 1990, Bruno et al. 1992, Cuevas et al. 1992, Krupka & Conca 1992, Whitney 1992). Thus, the long-term interaction at intermediate temperatures between compacted sodium bentonite and two types of synthetic granitic groundwater solutions was investigated in a laboratory study (Melamed et al. 1992). The experimental conditions were set in accordance with those described, for example, in the safety analysis of disposal of spent nuclear fuel in Finland (Vieno 1994). The aim of the study was to determine and characterise the mineralogical behaviour and alteration process of bentonite in the repository. Examinations focused on the water chemistry, ion exchange processes and smectite alteration.

It is generally assumed that dissolution-precipitation and oxidation-reduction reactions in the bentonite are the principal aspects of buffering. They determine the pH and redox potential of the near-field groundwater, which are critical parameters of the material buffer performance. Thus, further investigations of reacted bentonite samples (Melamed & Pitkänen 1994) were conducted, which emphasised the role of accessory non-clay mineral reactions during the water-bentonite interaction and the alteration of the smectite clay.

Presented in the following chapters are the materials and interaction conditions used in the experiment, the analytic results for water and bentonite and their discussion, including an interpreted model of the accessory non-clay mineral reactions and their effects on bentonite alteration.

2 EXPERIMENTAL CONDITIONS AND METHODS

2.1 MATERIALS

2.1.1 Bentonite

The material used in the experiment was Volclay MX-80 bentonite, consisting mainly of sodium-montmorillonite (85 - 95 wt.%). Primary accessory minerals (Table 1) included quartz, feldspars, micas, calcite, pyrite and gypsum.

Table 1. Mineral content of MX-80 bentonite, based on XRD and optical microscope analyses.

Mineral	Volume %	Identification method
Montmorillonite	85 - 95	XRD
Illite	+	"
Kaolinite	+	"
Quartz	3 - 6	XRD + Opt. microscopy
Pyrite	1 - 3	"
Carbonates	1 - 3	"
Feldspars	1 - 3	"
Orthopyroxene	+	XRD
Amphibole	+	"
Micas	+	"
Gypsum	+	"
Iron oxides	+	Opt. microscopy

The typical chemical composition of the bentonite is shown in Table 2. According to the American Colloid Company (1970), the chemical formula of sodium-montmorillonite in the MX-80 bentonite is given as:

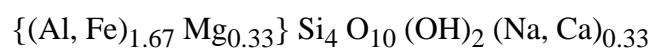


Table 2. Major elements in the MX-80 bentonite as determined by AAS, neutron activation and gravimetric analyses.

Element	Content (ppm)	Element	Content (ppm)
Si	290 500 - 291 400	La	46.4 - 50.1
Al	108 000 - 110 000	Sm	7.8 - 8.3
Fe	27 500 - 31 100	Lu	0.97 - 1.30
Na	17 500 - 19 800	Cr	34.2 - 35.3
Ca	10 000 - 11 000	Ni	33.1 - 34.5
K	3 800 - 4 400	Co	2.4 - 3.0
Mg	1 500 - 1 500	Sc	5.3 - 5.9
As	5.9 - 6.5	Ba	360 - 370
Sb	1.2 - 1.3	Cs	0.65 - 0.79
Zn	100 - 115	Rb	10.0 - 13.1
Sn	85 - 98	Ta	2.7 - 3.1
Ag	5.5 - 5.8	U	10 - 12
W	0.63 - 0.66	Th	34.3 - 35.9
Mo	2.2 - 3.4	Br	0.32 - 0.49
Au	0.0029 - 0.0031		

Based on Atomic Absorption Spectrometry (AAS) analyses of the original unreacted bentonite treated by NH_4Cl extractions, the Na/Ca ratio in the above formula is calculated as 1.54 (43/66 meq/100 g). X-ray powder diffraction (XRD) analyses show the sodium-montmorillonite to be characterised by a d value of 12.38 Å for the basal (001) spacing. The bentonite was compacted into a cylindrical shape having a dry density of 1.6 g/cm³.

2.1.2 Water

Two types of synthetic groundwater solutions (Table 3) were prepared and used in the experiment: 1) A, the Allard groundwater solution typical of granitic terrain (Allard et al. 1981), and 2) B, the Allard groundwater ionic concentrated (x 100) with potassium and chloride. The initial pH conditions and the concentrations of other ions and compounds in both water types were similar. It should be pointed out, however, that the Allard groundwater solution is now regarded as diluted compared with the latest chemical results of deep groundwater as reported, for

example, in granitic bedrock investigations for nuclear waste disposal in Finland (Pitkänen et al. 1992, Lampén & Snellman 1993). Some of these groundwater solutions, which were found with high concentrations of Cl (up to 20,000 mg/l), Na and Ca (4,000 mg/l), and a low concentration of K (10-100 mg/l) vary between brackish Na-Cl type waters to saline Ca-Na-Cl type.

2.2 PROCEDURES

The experimental set-up is illustrated in Figure 1. The compacted cylindrical bentonite samples were placed inside copper capsules to prevent the volumetric swelling of the clay and restrict the diffusion of water at the perforated outer-plain surfaces through a stone-disk filter. The wet density of the bentonite was 2.0 g/cm^3 and the swelling pressure estimated to be less than 10 Mpa. The air trapped in the pore space was expected to be replaced with water through the saturation of samples, encouraged by the typically strong water suction of the sodium-bentonite.

The sample-containing copper tubes were separately inserted into 500 ml polythene cans, of which half were filled with water of type A and the others with type B. The bentonite/water ratio was 30 g/450 cm^3 . All cans were well sealed and placed inside an open water evidently heated to a constant temperature of 75°C . The water-bentonite interaction in the cans proceeded through several time intervals up to 36 months. At the end of each time period, four cans (two of each water type) were extracted from the bath. The bentonite samples were left to dry inside the copper tubes at room temperature, then extracted. The water in the cans was sampled for chemical analysis.

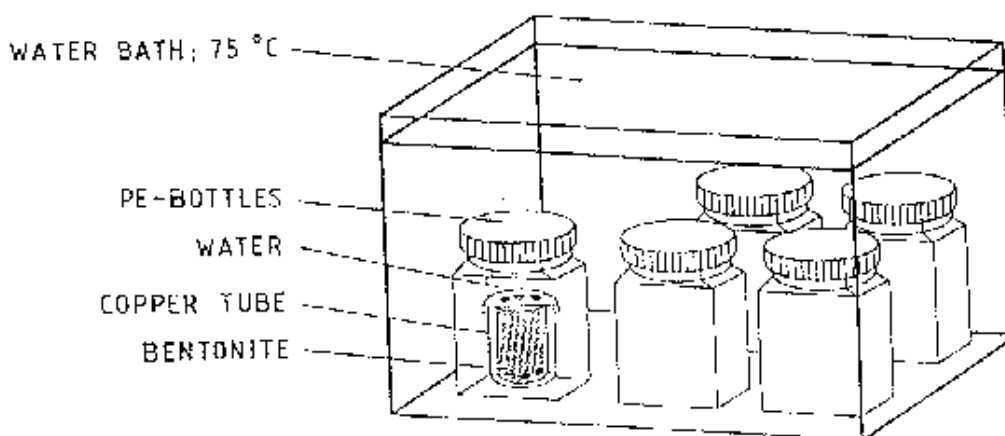


Figure 1. *Experimental set-up.*

An interruption in the experiment due to stumbling of the heating bath thermostat occurred after 24 months and lasted roughly 48 hours. At that time the water temperature in the bath increased to almost 100°C, causing some evaporation of water from the cans. All samples were extracted from the bath. The solution in the cans was sampled and analysed but the results showed low carbonate contents due to mixing and contamination, thus no additional water analyses were performed. The bentonite samples were left to dry and analysed later. The copper tubes originally intended to carry the long-term reacting bentonite samples were inserted into new cans filled with fresh water types and placed inside the bath while the temperature was re-set at 75°C.

2.3 PREPARATION FOR ANALYSES OF BENTONITE

The reacted, dry cylindrical bentonites were cut perpendicularly into 2 mm thick slices to obtain five isochronic layer samples at different distances from the interaction front with water (Fig. 2). Layers 1 and 5 represent the outer and inner parts, respectively. Each of the layer samples was divided into smaller parts, which were separated and prepared for chemical, microprobe and XRD analyses.

In order to increase the detection ability of accessory minerals in the original, unreacted bentonite by the XRD method, the non-clay fraction was enriched by 1) dry sieving of ground powder through a 74 µm mesh, and 2) separation of settled sediment from a water-bentonite suspension.

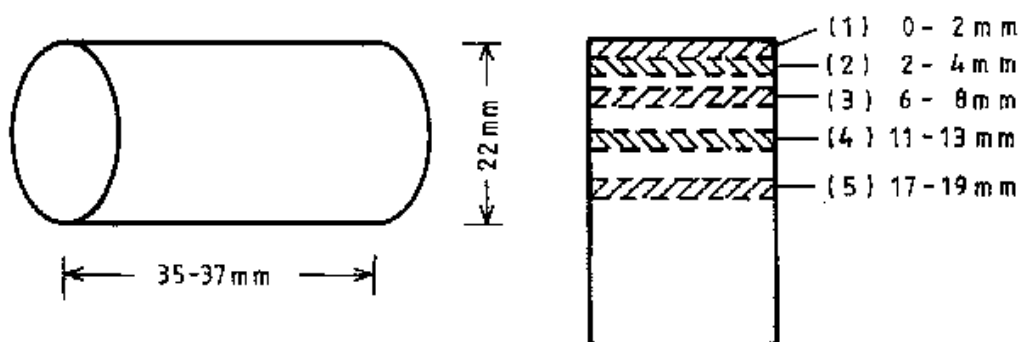


Figure 2. Sketch of sample preparation.

2.4 METHODS OF ANALYSIS

2.4.1 Water

The water chemistry analyses were conducted at the end of every reaction time period. The pH value was measured in the cabinet immediately after sampling. The elements Na, K, Al, Ca, Fe and Mn were determined by AAS, and compounds SiO₂, NO₃ and NH₄ by spectrophotometry. F was determined by a specific electrode and SO₄ by turbidimetric titration. Alkalinity and Cl were determined by titration. The precision of analytical concentrations is 5 - 10% for most elements but may be as low as 20% for elements close to the detection limit (Mn, Al, Fe in most of the samples, Ca and Mg in some samples).

2.4.2 Bentonite

AAS analyses of samples were carried out for determining the concentrations of exchangeable cations in the clay fraction. For this purpose, 50 - 60 mg of ground powder were weighed (exact values are recorded) in 20 ml plastic bottles. A further 10 ml of 1 M ammonium chloride (NH₄Cl) solution was added and the bottles were gently shaken for 24 hours and centrifuged (10 min, 3,500 r/min). Thereafter, the solution was diluted 2.5 and 10 times adding 0.5% La and 0.5% Cs as chlorides (0.3 M hydrochloric acid). La was used as an elaborating agent and Cs as an ionisation buffer when determining Ca, Mg, Na and K. The cation exchange capacity (CEC) was calculated as the sum of the exchangeable Ca, Mg, Na and K.

XRD analyses were conducted twice. First with a Philips PW 1050 vertical goniometre (max. 2 θ range from 3° to 30°) using Ni-filtered CuK α radiation for obtaining mainly the diffractograms of the smectite clay, and second with a Philips wide-angle goniometre (2 θ range from 2° to 70°) the complete detection of the minerals present. In some cases single grains of accessory non-clay minerals were selected under the stereomicroscope and analysed separately with the Debye-Scherrer method (camera diameter = 5.73 cm). The relative humidity during the run of XRD analyses varied between 53% and 70% but was usually stable at around 60%.

Energy dispersive spectrums were obtained using the JEOL JXA-733 super probe. The analyses were performed with a P6T system energy dispersive spectrometer (EDS) for determining the proportional amount and distribution of major cations in the bentonite. The method is limited, however, with regard to sodium which is hard to detect and does not appear in the spectrums.

Additional analyses of the bentonite material were performed with 1) an optical microscope for preliminary determination of the accessory non-clay minerals in thin sections of the original unreacted bentonite, and 2) a stereomicroscope for following the development in samples of mineral dissolution effects and precipitation products caused by the interaction of the material with the water solutions.

3 RESULTS

3.1 WATER

The results of the water chemistry analyses are summarised in Table 3. The calculated values of charge balance fall roughly in the 10% range, which indicates a reasonable accuracy. Concentration curves of major species are shown in Figure 3. Typical of both sample types was the concentration increase in sodium, sulphate, bicarbonate and somewhat also in silica, and the decrease in calcium, potassium and magnesium. Chloride was found to be inactive. The pH increased moderately from about 8 to slightly over 9. In water type B the potassium concentration decreased clearly and the increase in sodium concentration was marginally stronger than in water type A.

Table 3. Analytical data of water types at various reaction-time intervals. Concentrations are given in mg/l (after Melamed et al. 1992).

Type A					Type B				
Months	0	1	3	9	Months	0	1	3	9
pH	8.2	8.7	9.2	9.2	pH	8.1	9.4	9.5	9.4
HCO ₃	115.9	125	152	253	HCO ₃	115.9	124	141.5	264
CO ₃	0	17	27	24	CO ₃	0	18.1	22.5	21.1
Na	53	193	239	269	Na	53	243	330	457
K	3.9	4.8	4.9	5.5	K	390	305	188	127
Mg	4.3	1.3	0.8	0.8	Mg	4.3	1.8	0.4	0.2
Ca	18	3.7	2.1	2.9	Ca	17	3.8	2.6	2.5
Al	0.07	0.1	0.8	1.2	Al	0.07	0.08	0.16	0.47
Cu	0.01	0.06	0.07	0.03	Cu	0.01	0.05	0.03	0.03
SiO ₂	10	11.7	21.8	24	SiO ₂	9.8	10.1	18.5	20.5
Fe	0.1	0.1	0.1	0.13	Fe	0.1	0.06	0.05	0.06
F	7.8	7.1	9	9.9	F	6.2	7.1	8.9	11.5
Cl	59	51	53.5	55	Cl	420	420	430	415
PO ₄	0.3	<0.5	<0.5	<0.2	PO ₄	0.4	<0.5	<0.5	0.3
SO ₄	10	160	225	245	SO ₄	9.8	160	220	245

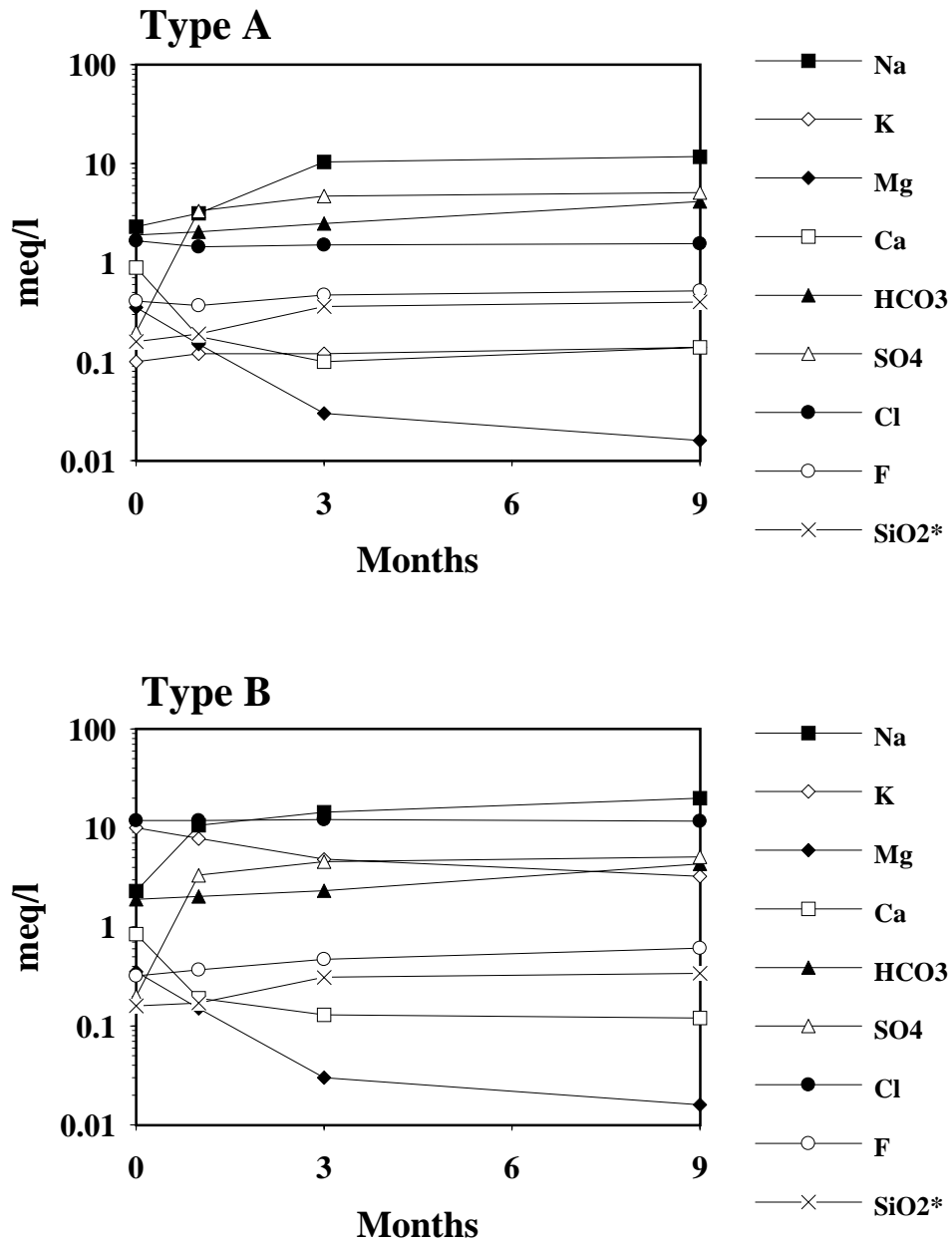


Figure 3. Time-dependent concentration curves of major species in water (after Melamed & Pitkänen 1994). *mmol/l.

3.2 BENTONITE

3.2.1 Cation exchange

The AAS analysis results of samples treated with NH_4Cl showed good conformity (reverse correlated) with the water chemistry analysis results. Time-dependent concentration changes of cations in reacted bentonite (Figs. 4 and 5) included: 1) a strong decrease in sodium which was clearly dominant in samples of case B, 2) a consistent and moderate increase in magnesium in both A and B cases, 3) a general concentration increase in calcium in both A and B cases. However, The calcium increase has a complex behaviour characterised by decrease/increase gaps and a clear consistent increase in the outer and inner layers, respectively, 4) no significant changes in potassium concentration in case A samples except for a proportional increase in the outer layers. In samples of case B, potassium was found to have a strong concentration increase (x 10) which was particularly dominant within the outer layers, and occurred for the most part already during the first 3 months of the interaction.

Concentration curves of cations with dependency on distance from the contact front with water are shown in Figure 6. Calcium is the principal cation found to have significant concentration changes seen as an increase towards the inner parts of the cylindrical bentonite samples and, particularly, at longer reaction-time intervals. The cations Na, Mg and K differ from calcium as they appear to have steady concentration profiles at various reaction-time intervals.

The reason for the increase trend of calcium in the bentonite is unclear. It may be that the NH_4Cl could, to a certain degree, dissolve calcite and/or gypsum during the extraction treatments of bentonite samples, which would result in what appear to be high detected amounts of exchangeable calcium ions in the smectite clay. This could mainly be the case in analyses of the initial, unreacted bentonite material and of the inner parts of reacted samples, in which the dissolution of calcium-bearing minerals during the interaction is assumed to have been limited. It should be noted that the relatively high cation exchange capacity (CEC) values (app. 120 meq/100 g) of the initial bentonite may also reflect partial dissolution of calcium-bearing minerals and the release of calcium ions during extraction treatments with NH_4Cl . The CEC values of the MX-80 bentonite are typically in the range 70 - 80 meq/100 g (Wanner et al. 1992).

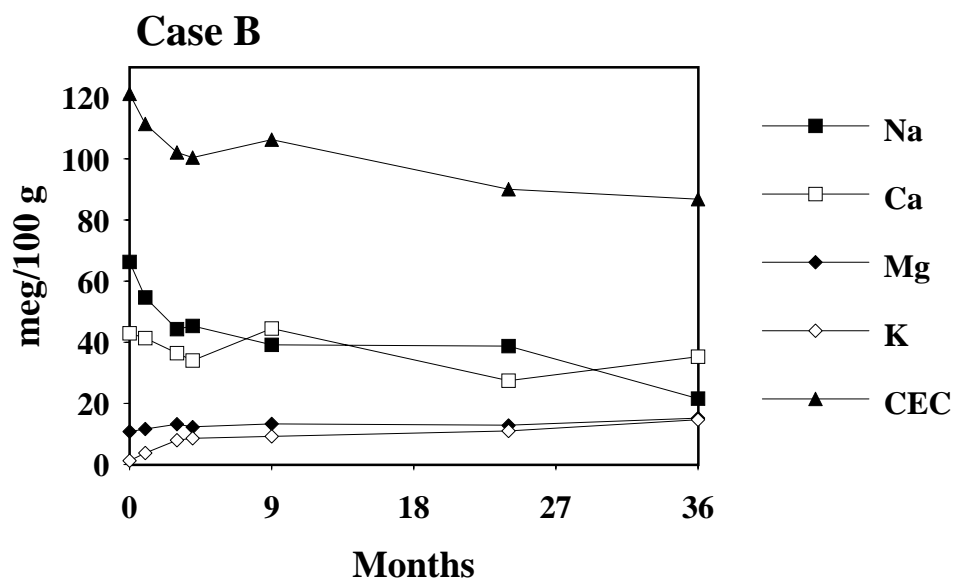
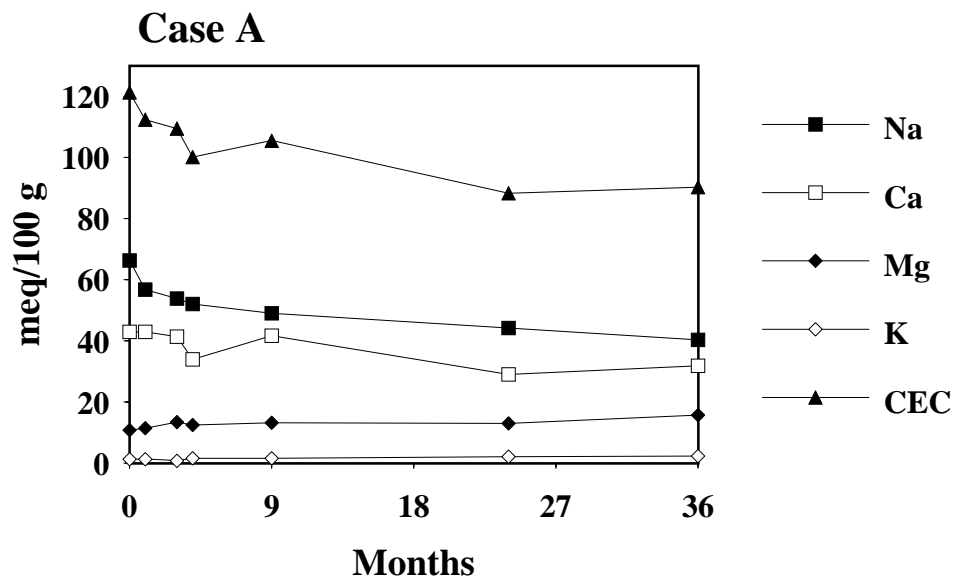


Figure 4. Time-dependent concentration curves of major cations in layer 1 (outer part) of reacted A and B bentonites (modified after Melamed et al. 1992.).

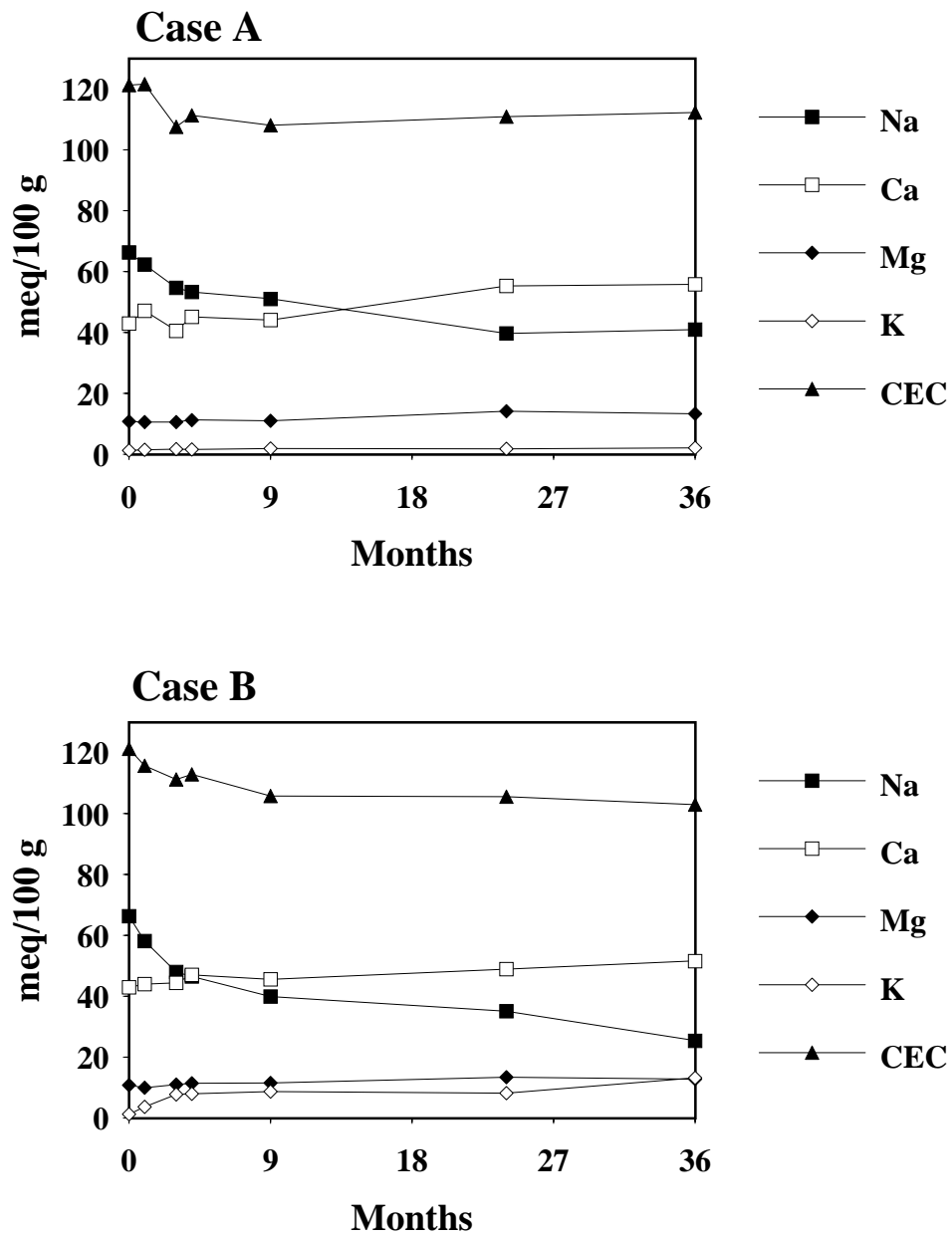


Figure 5. Time-dependent concentration curves of major cations in layer 5 (inner part) of reacted A and B bentonites (modified after Melamed et al. 1992).

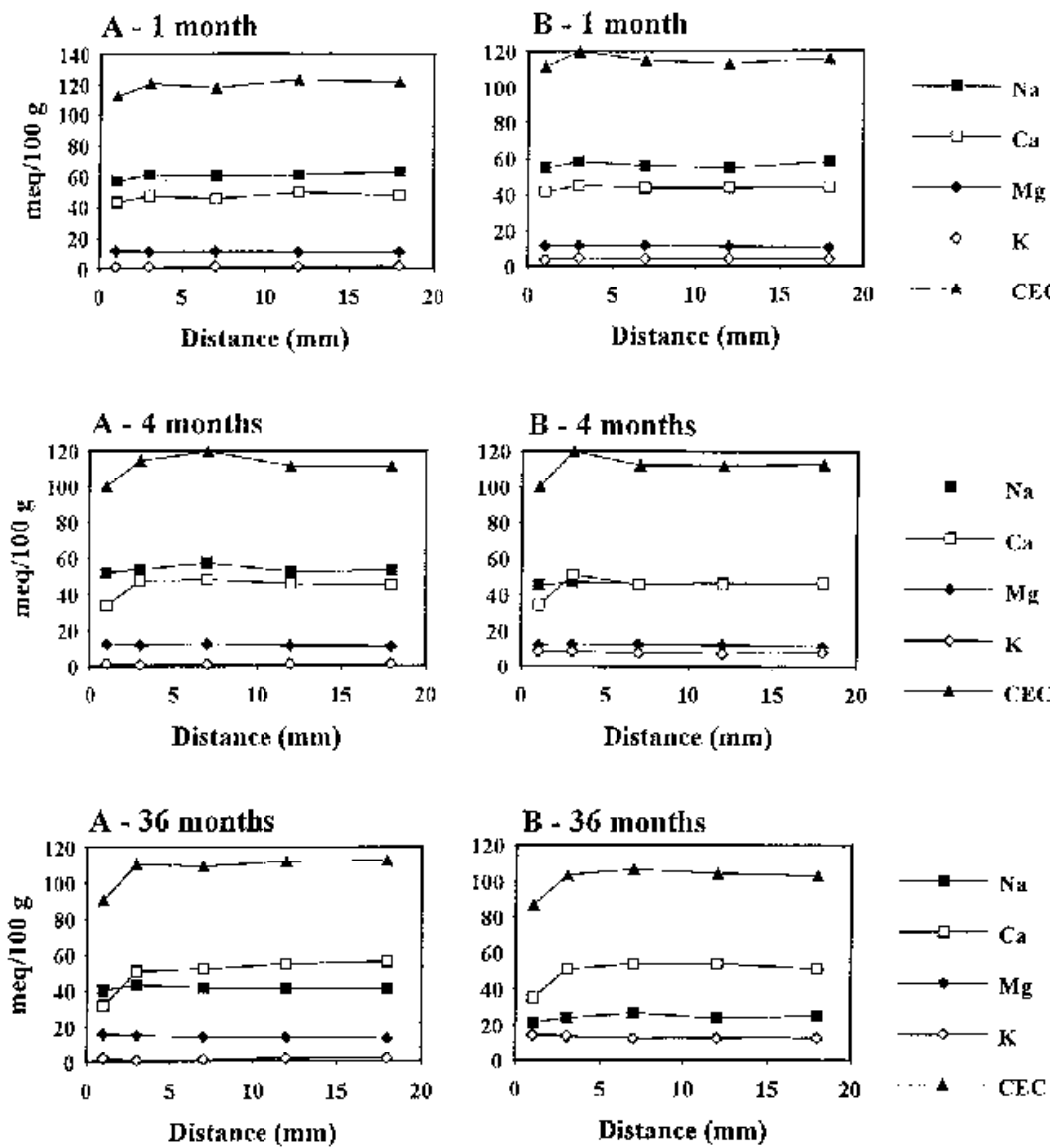


Figure 6. Concentration curves of exchangeable cations in bentonite with dependency on distance from the interaction front with water. The reference initial concentrations (meq/100 g) are: Na 66.3, Ca 42.9, Mg 10.8, and K 1.3 (modified after Melamed & Pitkänen 1994).

Energy dispersive spectrums obtained from analyses of the reacted bentonite indicate the development of a non-homogeneous distribution in smectite of calcium in case A, and of calcium and potassium in case B (Fig. 7). Also, in addition to the presence of the interlayer calcium, magnesium and potassium (case B) ions in montmorillonite, copper is identified as an exchangeable cation in the clay within an area restricted to the tippet zone of samples and close to the wall of the copper capsules. In this zone, a crystallised mineral containing copper, iron and sulphur was revealed and analysed (Fig. 8).

3.2.2 Smectite

In the X-ray diffractograms of the reacted, air-dried bentonite samples of both cases A and B (Figs. 9 and 10), the peak representing the basal reflection (001) of sodium montmorillonite appeared to change with the increase in reaction time from typically high and sharp to a lower and broader double peak. The change, which is also reflected in the position of the peak, appeared already after 3 months of interaction in case B, whereas in case A it was not observed before 9 months. The development of the broad double peak probably represents an increase in the 14 Å/12 Å components ratio, which indicates mainly the exchange of sodium in montmorillonite with calcium and magnesium. The appearance of a broad peak may also indicate a breakdown, to some degree, of the smectite clay lattice structure.

In the diffractograms of some of the air-dried samples (both A and B) a minor basal reflection of 10 Å typical of illite was obtained. However, the reflection, which appeared randomly in the diffractograms, shows no tendency to develop either as a function of the reaction time or of the distance from the contact front with water. The 10 Å reflection can be assumed to appear due to the presence of an accessory amount of illite in the clay fraction of the original, unreacted bentonite. It should be noted, however, that in the diffractograms of reacted samples treated with ethylene glycol (Fig. 11) the intensity of the 17 Å peak typical of montmorillonite appears to drop with the increase in reaction time. As described e.g. by Wilson (1987), the decrease in the intensity of the 17 Å peak may indicate the interstratifying increasing amounts of illite with smectite. In the current study, the decrease in peak intensity, which was more dominant in B samples, appeared stronger (in both A and B cases) in the outer layer samples.

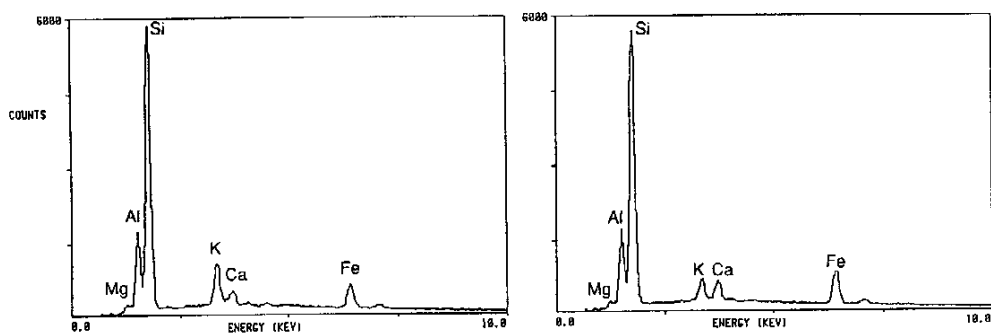


Figure 7. EDS spectrums obtained from two different locations on the inner surface of layer 1-B sample aged 36 months (after Melamed et al. 1992).

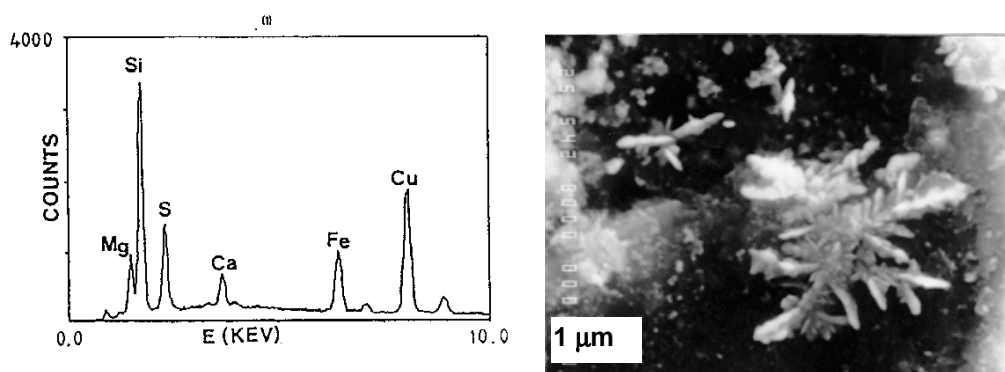


Figure 8. EDS spectrum (1) and micrograph (2) of a crystal containing Cu, Fe and S analysed from the tippet zone of layer 1-A bentonite sample aged 36 months (after Melamed et al. 1992).

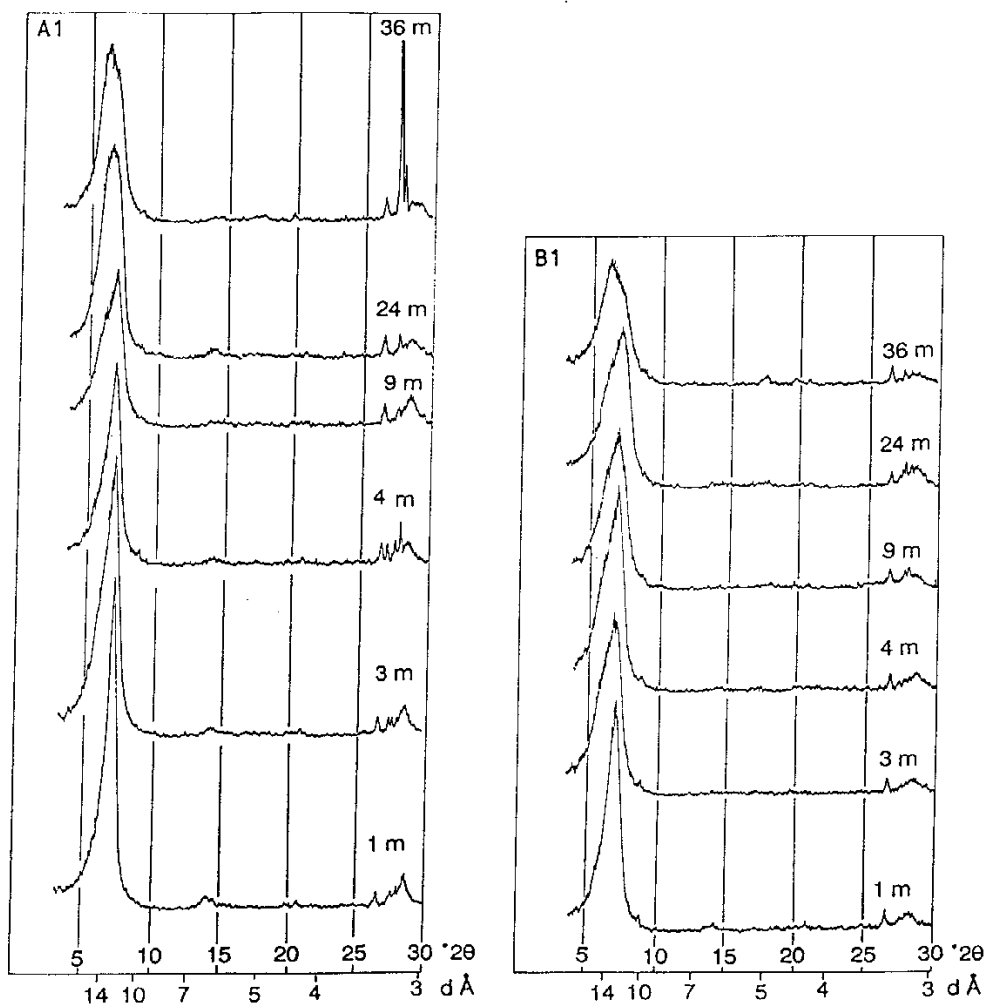


Figure 9. X-ray diffractograms of reacted, air-dried layer 1 (outer) of A and B bentonite samples at various reaction times (after Melamed et al. 1992).

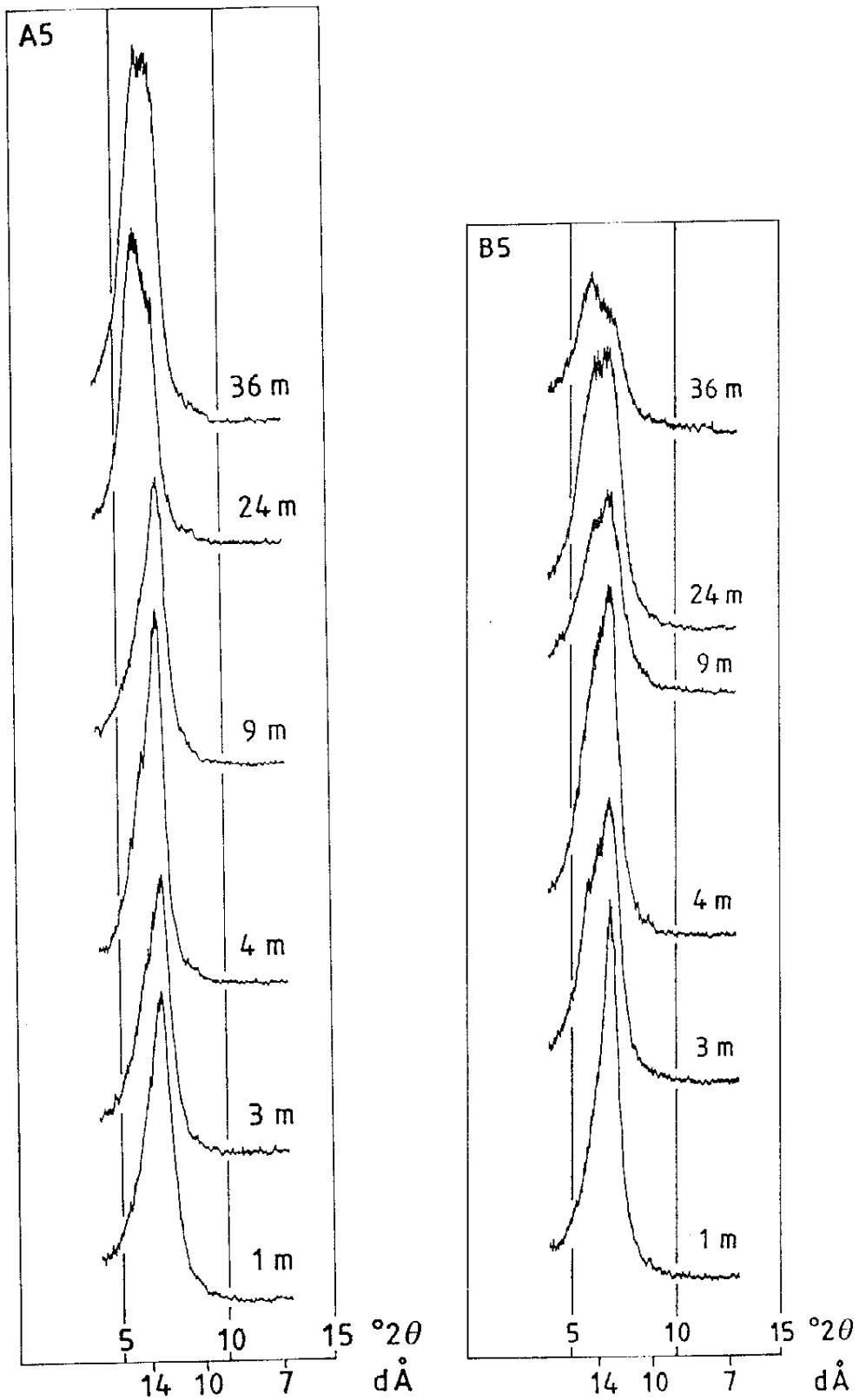


Figure 10. X-ray diffractograms of reacted, air-dried layer 5 (inner) of A and B bentonite samples at various reaction times (after Melamed et al. 1992).

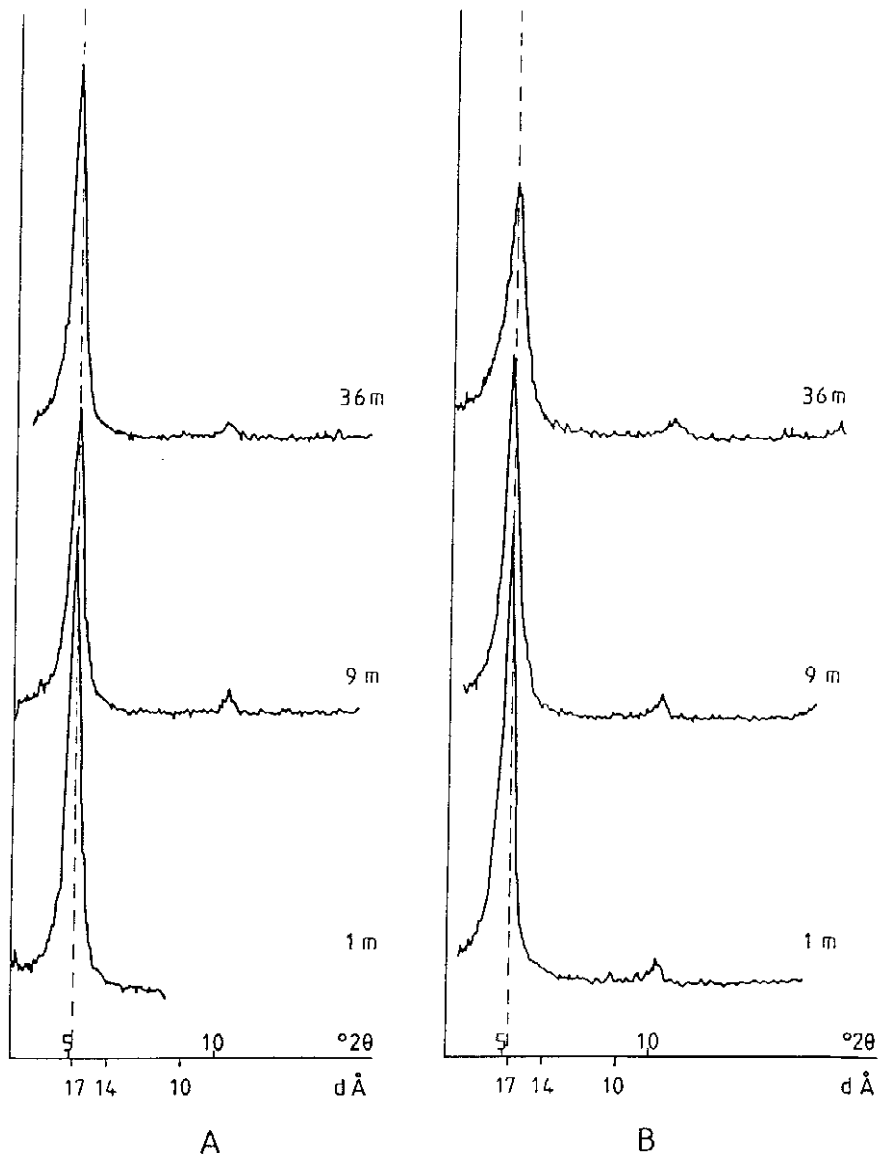


Figure 11. X-ray diffractograms of reacted, E.G.-treated layer 1 of A and B bentonite samples at various reaction-time intervals.

3.2.3 Accessory non-clay minerals

The observations made by optical microscope and the XRD analysis results of the original, unreacted bentonite clearly revealed the presence of quartz (dominant), feldspars, calcite, pyrite and gypsum (minor) as the major, primary accessory minerals of the MX-80 bentonite. In addition to these minerals, the material has been reported (Pirhonen 1986) to contain also traces of orthopyroxene, hornblende and micas.



Figure 12. Micrograph of reacted bentonite surface (case A, 36 months) showing the concentric precipitation of ferric compounds around pyrite. Magnification 40 x (after Melamed & Pitkänen 1994).



Figure 13. Micrograph of a crystallised grain of cuprite (copper oxide) located on a reacted bentonite surface (case A, 36 months). Magnification 40 x (after Melamed et al. 1992).

In the stereomicroscope observations, the principal mineralogical changes that appeared in samples through interaction with water included: 1) the development of reddish-brownish patches commonly associated with grains of pyrite (Fig. 12), and 2) the precipitation of bluish, copper-bearing minerals (Fig. 13), which were observed only in the tippet zone of the cylindrical bentonite samples.

In the X-ray diffractograms of reacted samples, gypsum is absent and calcite tends to disappear with the increase in reaction time, particularly within the outer layer samples, while goethite and siderite (reddish-brownish patches observed under the stereomicroscope) are regarded as the major secondary mineral products of the interaction. Owing to lack of crystallisation the bluish, copper-bearing minerals extracted from the tippet zone of samples could not have been identified even when analysed with the Debye Scherrer method. However, recently-conducted XRD analyses of the long-term reacted material clearly revealed the presence of cuprite (copper oxide).

4 DISCUSSION

4.1 CATION EXCHANGE AND SMECTITE ALTERATION

The cationexchange process in bentonite samples occurs mainly in terms of replacement of sodium ions in montmorillonite by calcium and magnesium in case A, and by calcium, magnesium and potassium in case B. From the ionic concentration profiles of reacted water solutions and bentonite it seems that the main part of the ion and compound diffusion is completed already after 3 - 4 months of interaction. Later, with continuation of the experiment over longer time periods the diffusion process slows down (reflected by moderate ionic concentration changes in water types) while the system tends to approach equilibrium.

The bulk mineral alteration in the MX-80 bentonite is of the clay fraction, in which montmorillonite changes from its sodium- to calcium-rich form. The alteration, clearly revealed on X-ray diffractograms by a change in the smectite basal-peak shape and position, occurs somewhat after the major part of the ion diffusion and the cation exchange process. Despite the rapid migration of potassium ions into bentonite during interaction with the potassium-rich water (case B), there is only limited analytic evidence, which may indicate fixation of these ions in the smectite interlayer position. If any amount of interstratified illite layers have been formed during the course of the experiment these are assumed to be in very low quantities (<5%), close to the detection limits of XRD.

The XRD and AAS analysis results of the reacted bentonite material show the cation exchange and smectite alteration processes to be mainly time-dependent. Thus, at any given reaction-time interval, the processes occur to a similar extent throughout the profile of the cylindrical bentonites. It should be noted, however, that the bentonite samples used in the experiment were perhaps too small to show the effect of distance from the contact front with water, particularly when taking into account the long interaction time-periods applied.

There is no clear evidence of dissolution and/or precipitation reactions involving silica. However, the recorded concentration increase of silica in the water from 10 mg/l initially to roughly 20 mg/l after 9 months may indicate minor dissolution of silicates in the bentonite by hydrolysis. Slight increases of silica concentration in the solution during the course of similar interaction experiments have been reported (Bateman et al. 1991, Yui et al. 1992). The moderate precipitation of silica in bentonite is likely to occur as described, for example, in

electron microscope examinations of hydrothermally treated bentonite (Pusch & Güven 1990). Although minor amounts of kaolinite can be expected to form as a result of silicate dissolution, no traces of this clay mineral were found in the X-ray diffractograms.

4.2 MINERAL-SOLUTION EQUILIBRIUM

The effective concentrations and activities of dissolved species in water were calculated by WATEQF program, the aqueous geochemical speciation/saturation model (Plummer and others 1976). Aqueous activity diagrams (Figs. 14 and 15) show the equilibrium relationship of water types and clay minerals at various reaction times.

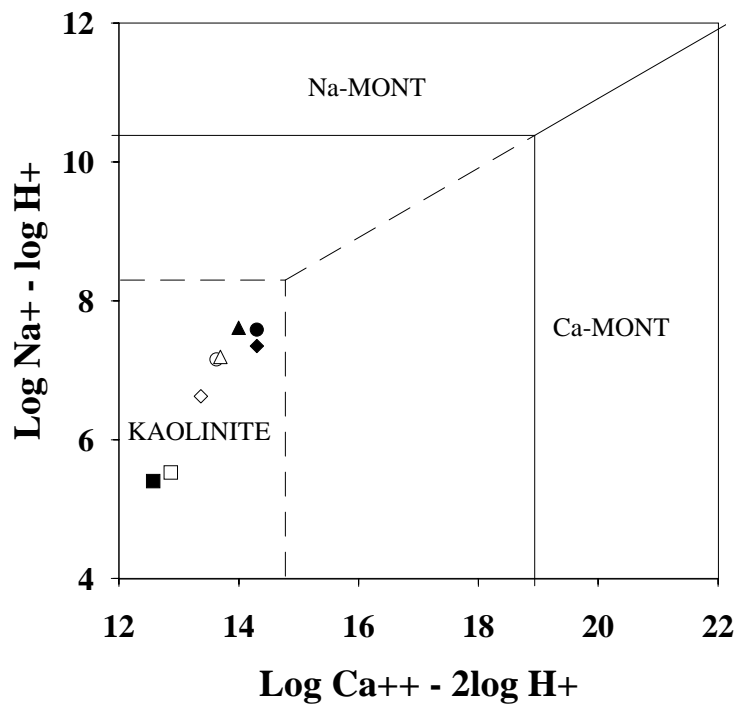


Figure 14. Aqueous activity diagram for the system $\text{CaO-NaO-Al}_2\text{O}_3\text{-SiO}_2\text{-HCl-H}_2\text{O}$ at 70°C , 1 bar. Mineral stability boundaries are indicated by dashed lines for $\log H_4\text{SiO}_4$ activity = -3.80 , and by continuous lines for $\log H_4\text{SiO}_4$ activity = -4.35 . The diagram is constructed from the data of Helgeson (1969).

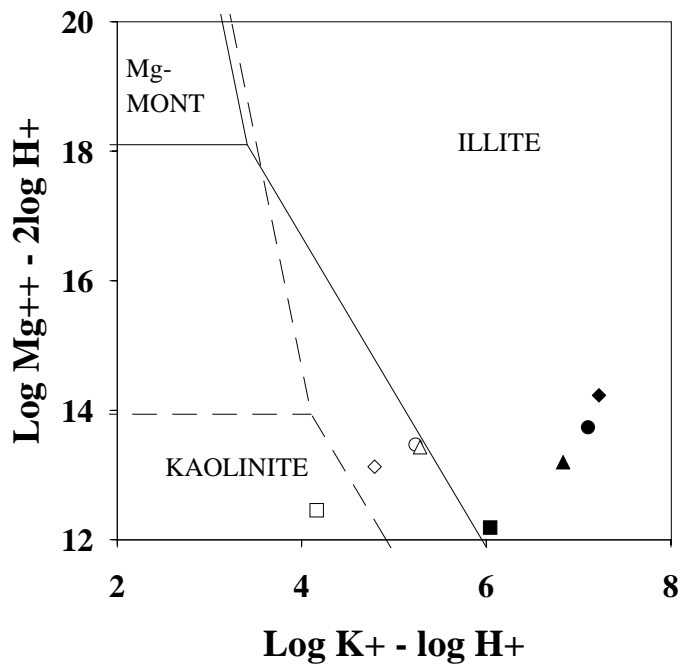
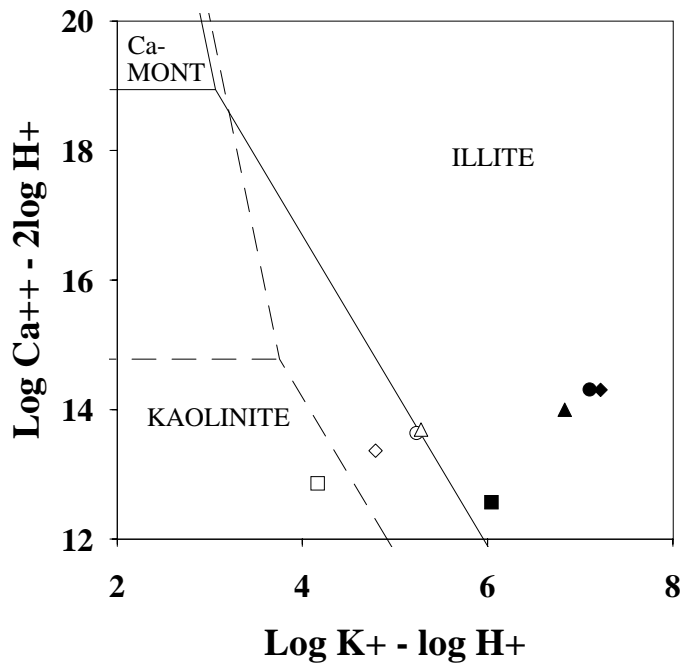


Figure 15. Aqueous activity diagrams for systems $KO-CaO-Al_2O_3-SiO_2-HCl-H_2O$ and $KO-MgO-Al_2O_3-SiO_2-HCl-H_2O$ at $70^\circ C$, 1 bar. Mineral stability boundaries are indicated by dashed lines for $\log H_4SiO_4$ activity = -3.80 , and by continuous lines for $\log H_4SiO_4$ activity = -4.35 . The diagrams are constructed from the data of Helgeson (1969).

Stability boundaries between aluminosilicates were constructed by balancing reactions on aluminium and setting the activity of silica to both the highest and lowest values calculated, i.e., $10^{-3.8}$ (typical of water A), and $10^{-4.35}$ (water B only). The equilibrium constants for the clay mineral reactions at 70°C were evaluated from the data of Helgeson (1969). The variables of ionic activity and pH are used as axes on the diagrams. The speciation results plotted in Figure 4.1 indicate stability with respect to kaolinite. With increasing reaction times a trend towards the stability field of montmorillonite can be seen, which is particularly dominant in the case of water B.

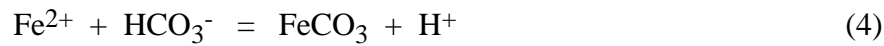
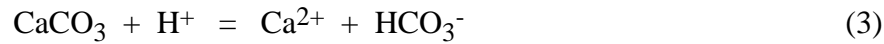
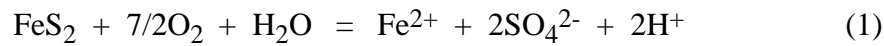
In Figure 4.2, the speciation results for water A, which fall in the field of kaolinite, show a trend of development towards the stability field of illite. All the speciation results of water B, in that case, fall in the stability field of illite and tend to go "deeper" in that field with increasing reaction times.

4.3 ACCESSORY NON-CLAY MINERALS

The total quantitative increase (1.8 meq) of exchangeable calcium ions in the bentonite (calculated based on approximated average concentration increase of 6.0 meq/100 g) is marginally higher than the total amount (0.28 meq) of calcium ions available from the water solution in reacting vessels. This fact, supported by the absence of gypsum and the disappearing trend of calcite indicated by the X-ray diffractograms of reacted samples, leads to the conclusion that gypsum (completely) and calcite (partially) dissolve in bentonite as described by others (Bateman et al. 1991, Wanner et al. 1992, Yui et al. 1992).

Based on the interpretation of the water and bentonite analysis results, a qualitative model can be presented which characterises the dissolution and precipitation reactions of the accessory non-clay minerals and their role during the alteration of MX-80 bentonite:

(A) Oxygen present in water and the bentonite pore space enables the partial oxidation (dissolution) of pyrite (1) and the precipitation of goethite (2). These proton-releasing reactions in pore water promote calcite dissolution (3), which buffers the pH. Some of the reaction-released locally high concentrations of bicarbonate and Fe^{2+} ions re-precipitate in the bentonite in the form of siderite (4), which may indicate the depletion of oxygen.



(B) In the bentonite, the dissolution of calcite and gypsum provides additional calcium ions to those arising from the water, resulting in an acceleration of the sodium-to-calcium exchange process in montmorillonite. (C) Some of the protons released in the pore water by the above reactions (1, 2 and 4) are assumed to exchange sodium in the smectite clay. Evidence to support this assumption is based on: 1) the recorded, lower cation exchange capacity (CEC) values in the parts of bentonite samples close to the interaction-front with water (CEC is calculated only as the sum of exchangeable Ca, Na, Mg and K), and 2) the pH increase in both water types during the experiment. It should be noted, however, that the greater part of the pH increase in the bentonite is believed to arise from calcite dissolution, as pointed out, for example, by Yui et al. (1992).

(D) The microprobe (SEM, EDS) and the stereomicroscope analysis results of reacted bentonite samples provide solid evidence of the partial dissolution of the sample-containing copper capsule and the release into pore water of copper ions. It was found that part of these ions precipitate in the bentonite (probably with some of the carbonate and/or sulphate compounds), while the rest are assumed to enter the smectite clay by replacing sodium, as described, for example, in transport phenomena in bentonite clay with respect to copper (Pusch et al. 1990). It should be noted, however, that during the experiment these processes were found to be restricted to the external zone of the bentonite samples and occurred to the most part (36 month samples) up to a maximum distance of 300 μm from the contact surface with the wall of copper capsules. The remaining bulk part of the carbonate and sulphate compounds (not precipitated in the bentonite) diffused into the water.

It may be assumed that the alteration from sodium to calcium montmorillonite will continue as long as the calcite content in bentonite is not fully depleted (Wanner et al. 1992). Based on the above-described accessory mineral reactions, it seems that in the case of calcite- and sulphide-bearing bentonites such as Volclay MX-80, the sodium-to-calcium exchange in smectite is promoted as long as the oxidation reaction of pyrite continues. In addition, the negatively charged smectite

clay surface has a higher affinity for calcium than to potassium ions (Hall 1987), and calcium is typically more abundant than potassium in (Finnish) groundwaters. Thus the formation of illite, which is predominantly dependent on the presence of potassium ions and their interlayer fixation in montmorillonite, is expected to be further suppressed.

4.4 MASS-BALANCE CALCULATIONS

4.4.1 Sulphate release mechanism

The oxidation of pyrite and the dissolution of gypsum are the two major candidate reactions in bentonite which can generate the release of sulphate ions into water. As shown by the general reaction (1) in section 4.3 above, the oxidation of pyrite is dependent on the available quantity of oxygen. In order to examine the validity of each of the two sulphate-releasing dissolution reactions, mass-balance calculations were made in consideration of two end cases:

Interaction in a system closed to oxygen diffusion (anaerobic)

The maximum dissolved oxygen content of the solutions used in the experiment is calculated (based on 0.439 l of water in the cans and approximated dissolved oxygen concentration of 7 mg/l) to be 3.08 mg (9.6×10^{-5} mol). To this value are added 0.22 ml (9.8×10^{-6} mol) of oxygen from air trapped in the bentonite pore-space (calculated based on evaluated 10% porosity of 11 ml compacted bentonite samples). Accordingly the highest oxygen content that may participate in the dissolution reaction of pyrite under such conditions is 1.15×10^{-4} mol (about 0.1 mmol). Participation of such a quantity of oxygen in the general reaction (1) above would enable the dissolution of 0.03 mmol pyrite and, proportionally, the release into the solution of only 0.06 mmol sulphate.

During the experiment, however, the total content of sulphate was found to increase in the water by about 1 mmol (calculated based on sulphate concentration increase of 235 mg/l in both water types), which is greater by about one order of magnitude than the value (0.06 mmol) calculated in the above. Thus, under anaerobic conditions the dissolution reaction of gypsum may be regarded as the dominant sulphate-releasing process. Under such conditions the required amount

of gypsum to dissolve is calculated to be 0.14 g, corresponding to a concentration in bentonite of 0.8 wt.%, which is not unreasonable.

Interaction in a system open to oxygen diffusion (aerobic)

In this case, the oxidation of pyrite may be regarded as the major sulphate release reaction. Calculated based on the stoichiometric relation between the reacting oxygen and produced sulphate in the general reaction (1) above, and according to 1 mmol of sulphate generated during the experiment, the consumed oxygen content would be close to 1.75 mmol, and the amount of pyrite which is required to be oxidised is calculated as 0.04 g. This quantity of pyrite corresponds to a minimum concentration in bentonite of 0.25 wt.%, which is in accordance with the amount of pyrite evaluated from the XRD and microscope analyses of the original, unreacted bentonite material.

4.4.2 Calcite dissolution

Assuming the precipitation of siderite to be minor, the amount of calcite dissolved in the bentonite is calculated from the recorded concentration increase of 160 mg/l carbonate in the water solutions to be 0.116 g (1.2 mmol), which corresponds to a concentration in bentonite of 0.55 wt.%. It should be pointed out that in this calculation the precipitation of copper carbonates and the effects of possibly-existing minor organic substances in the bentonite are ignored. As in the case of pyrite, the calculated concentration level of calcite in bentonite is in accordance with the quantities evaluated from the XRD and microscope analyses.

It should be noted that a correlation between the above calculated quantity of dissolved calcite in bentonite and the amount of protons generated by the oxidation reaction of pyrite is expressed in the stoichiometric relation between the reactions 1 and 3 above, which may further support the validity of the calculation results. Finally, based on the above-described mineralogical processes and mass-balance calculations, a qualitative interpretation of the accessory non-clay mineral reactions in bentonite is presented in Table 4.

Table 4. Accessory non-clay mineral reactions in the MX-80 sodium bentonite with dependency on oxygen availability (assumed).

Reaction	Open	Intermed.	closed
Pyrite dissolution	rapid	slow	limited
Siderite precipitation	minor	minor	limited
Calcite dissolution	rapid	slow	limited
Gypsum dissolution	complete	complete	complete*

* Main sulphate release mechanism in anaerobic conditions.

5 CONCLUSIONS

Regardless of the ionic concentration of reacting water solutions, the cation exchange is an initiative process in the bentonite-groundwater system at intermediate temperatures. The original sodium ions in montmorillonite are weakly held in the clay interlayer position and tend to be replaced by other cations, of which the most prominent is calcium. This is found to be the case even during the interaction of bentonite with the potassium-rich solution. The bulk alteration process in the bentonite occurs in terms of the change of montmorillonite from the sodium- to calcium-rich form. While some evidence is found to indicate the fixation of potassium ions in montmorillonite there are no analytical data to support the formation of illite.

The near field geochemistry predictions imply limited oxidising conditions, which could prevail for some time after sealing of the repository. As described, for example, in studies of natural analogues and their importance for performance assessment (Brandberg et al. 1993), pyrite is expected to act as a redox buffer agent. This is in accordance with the present study results where, in addition to the role of pyrite, calcite dissolution is found to be balancing the pH.

The self-production of calcium ions by MX-80 bentonite is expected to decrease the probability of sodium-to-potassium exchange process in montmorillonite. Thus, under conditions of the Finnish repository concept the montmorillonite-to-illite transformation reaction may be prevented. After reaching equilibrium with the groundwater solution the montmorillonite (calcium-rich) clay will probably remain stable over long periods of time.

Recommendations

The type and relative amount of accessory non-clay minerals in the bentonite are important to verify before starting and during the course of the laboratory study. Interaction experiments conducted under aerobic and anaerobic conditions with both fresh and saline groundwater solutions are suggested. Quantitative modelling of the results would enable determination of the role and significance of non-clay mineral reactions at variable oxidising conditions, and assist in forming a more comprehensive prediction of the near-field geochemical conditions.

Short-term interactions (7 - 30 days) are recommended to be included in the laboratory study, as the results may increase the sensitivity of determining major time-dependent processes in bentonite. It should be noted that when conducting short-term interactions the saturation of samples must be considered. The saturation should be verified prior to the start of the experiment.

Since early 1995 a new bentonite-groundwater interaction experiment, which follows the main guidelines and recommendations given above, has been conducted by the authors in co-operation with the Chemical Technology Laboratory (KET) of the Technical Research Centre of Finland (VTT). During the course of the present laboratory study an attempt will be made also to analyse the bentonite pore-water chemistry in order to examine and verify some of the assumptions made with regard to pore water pH in consideration of reacting various compounds and minerals in the bentonite.

REFERENCES

- Allard, B., Larsson, S. A., Albinsson, J., Tullborg, E. L., Karlsson, M., Andersson, K. & Torstenfelt, B. 1981. Minerals and precipitates in fractures and their effects on the retention of radionuclides in crystalline rocks. In: Near field phenomena in geologic repositories for radioactive waste. Paris: OECD/NEA. Pp. 93 - 100.
- Anderson, D. M. (ed.) 1983. Smectite alteration. Proceedings of a colloquium at State University of New York at Buffalo, May 26 - 27, 1982. Swedish Nuclear Fuel and Waste Management Co., KBS Technical Report TR-83-03. 36 p. ISSN 0348-7504.
- Bateman, K., Entwisle, D.C., Kamp, S. & Savage, D. 1991. Bentonite-groundwater interactions: Results of compression rig experiments. Swiss National Cooperative for the Storage of Radioactive Waste (Nagra), Interner Bericht 91-53 (Technical Report WE/91/21C). 58 p.
- Borchardt, G. 1989. Smectites. In: Minerals in Soil Environments. Edited by J. B. Dixon and S. B. Weed. Soil Science Society of America. USA: Madison, Wisconsin.
- Brandberg, F., Grundfelt, B., Höglund, L. O., Karlsson, F., Skagius, K. & Smellie, J. 1993. Studies of natural analogues and geological systems - their importance to performance assessment. Helsinki: Nuclear Waste Commission of Finnish Power Companies, Report YJT-93-07. 166 p. ISSN 0359-548X.
- Bruno, G., Decarreu, A., Proust, D. & Lajudie, A. 1992. Clay mineral transformations in static hydrothermal conditions within a simulated engineered barrier for nuclear waste disposal. In: A. Meunier (Editor). Clays and Hydrosilicate Gels in Nuclear Fields. Appl. Clay Sci., Vol. 7, pp. 169 - 178.
- Brusewitz, A. M. 1988. Asymmetric zonation of a thick Ordovician K-bentonite bed at Kinnekulle, Sweden. Clays and Clay Minerals, Vol. 36, no. 4, pp. 349 - 353.

Cuevas, J., Medina, J. A. & Leguey, S. 1992. Saponitic clays from the Madrid basin: Accessory-minerals influence in hydrothermal reactivity. In: A. Meunier (Editor). *Clays and Hydrosilicate Gels in Nuclear Fields*. Appl. Clay Sci., Vol. 7, pp. 185 - 199.

Fritz, B. & Kam, M. 1985. Chemical interactions between the bentonite and the natural solutions from the granite near a repository for spent nuclear fuel. Swedish Nuclear Fuel and Waste Management Co., KBS Technical Report TR-85-10. ISSN 0348-7504.

Grim, R. E. & Güven, N. 1978. *Bentonites - Geology, Mineralogy, Properties and Uses*. New York: Elsevier. 256 p.

Güven, N. 1990. Longevity of bentonite as a buffer material in a nuclear-waste repository. *Eng. Geol.*, Vol. 28, pp. 233 - 247.

Hall, P. L. 1987. Clays: their significance, properties, origins and uses. In: M. J. Wilson (Editor). *A Handbook of Determinative Methods in Clay Mineralogy*. New York: Chapman and Hall Publishers. P. 308. ISBN 0-412-00901-3.

Helgeson, H. C. 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *American Journal of Science*, Vol. 267, pp. 729 - 804.

Inoue, A., Watanabe, T., Khyama, N. & Brusewitz, A. M. 1990. Characterization of illitization of smectite in bentonite at Kinnekulle, Sweden. *Clays and Clay Minerals*, Vol. 38, no. 3, pp. 241 - 249.

Inoue, A., Utada, M. & Wakita, K. 1992. Smectite-to-illite conversion in natural hydrothermal systems. *Applied Clay Science*, Vol. 7, pp. 131 - 145.

Johnston, R. M. 1983. The conversion of smectite to illite in hydrothermal systems: A literature review. Atomic Energy of Canada Limited (AECL)-7792. 27 p. ISSN 0067-0367.

Johnston, R. M. & Miller, H. G. 1985. Hydrothermal stability of bentonite-based buffer materials. Atomic Energy of Canada Limited (AECL)-8376. 67 p. ISSN 0067-0367.

Krupka, K. M. & Conca, J. L. 1992. Geochemical controls on the compositions of water in the near field and the chemical buffering properties of bentonite. In: Performance Assessment Center for Engineered Barrier (PACE) Program FY1991 Report. Richland, Washington: Battelle, Pacific Northwest Laboratories. 57 p.

Lampén, P. & Snellman, M. 1993. Summary report on groundwater chemistry. Helsinki: Nuclear Waste Commission of Finnish Power Companies, Report YJT-93-14. 162 p. ISSN 0359-548X.

Melamed, A., Pitkänen, P. Olin, M., Muurinen, A. & Snellman, M. 1992. Interaction of water and compacted sodium-bentonite in simulated nuclear waste disposal conditions. In: C. G. Sombret (Editor). Scientific Basis for Nuclear Waste Management XV (Mater. Res. Soc. Proc., Pittsburgh, PA, 1992), Vol. 257, pp. 557 - 566.

Melamed, A. & Pitkänen, P. 1994. Water - compacted Na-bentonite interaction in simulated nuclear fuel disposal conditions: The role of accessory minerals. In: A. Barkatt & R. A. Van Konynenburg (Editors). Scientific Basis for Nuclear Waste Management XVII. (Mater. Res. Soc. Proc., Pittsburgh, PA, 1994), Vol. 333, pp. 919 - 924. ISSN 0275-0112.

Müller-Vonmoos, M., Kahr, G., Bucher, F. & Madsen, F. T. 1990. Investigation of Kinnekulle K-bentonite aimed at assessing the long-term stability of bentonites under repository conditions. Eng. Geol., Vol. 28, pp. 269 - 280.

Pirhonen, V. 1986. Stability of bentonite in spent fuel repository conditions. TVO/KPA - Turvallisuus ja tekniikka, Work report 86-04. 66 p.

Pitkänen, P., Snellman, M. & Leino-Forsman, H. 1992. Modelling of water-rock interaction at TVO investigation sites - summary report. Helsinki: Nuclear Waste Commission of Finnish Power Companies, Report YJT-92-30. 71 p. ISSN 0359-548X.

Plummer, L. N., Jones, B. F. & Truesdell, A. H. 1976. WATEQF--A FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibria of natural waters. U.S. Geological Survey Water-Resources Investigations Report 76-13. 61 p.

Pusch, R. 1978. Highly compacted Na bentonite as buffer substance. Swedish Nuclear Fuel and Waste Management Co., KBS Technical Report TR-74. 42 p.

Pusch, R. 1983. Stability of deep-sited smectite minerals in crystalline rock - chemical aspects. Swedish Nuclear Fuel and Waste Management Co., KBS Technical Report TR-83-16. ISSN 0348-7504.

Pusch, R. & Karnland, O. 1988a. Hydrothermal effects on montmorillonite. A preliminary study. Swedish Nuclear Fuel and Waste Management Co., SKB Technical Report TR-88-15. 64 p. ISSN 0284-3757.

Pusch, R. & Karnland, O. 1988b. Geological evidence of smectite longevity. The Sardinian and Gotland cases. Swedish Nuclear Fuel and Waste Management Co., SKB Technical Report TR-88-26. ISSN 0284-3757

Pusch, R. & Güven N. 1990. Electron microscopic examination of hydrothermally treated bentonite clay. Eng. Geol., Vol. 28, pp. 303 - 314.

Pusch, R. & Karnland, O. 1990. Preliminary report on longevity of montmorillonite clay under repository-related conditions. Swedish Nuclear Fuel and Waste Management Co., SKB Technical Report TR-90-44. 47 p. ISSN 0284-3757.

Pusch, R., Karnland, O. & Muurinen, A., 1990. Transport and microstructural phenomena in bentonite clay with respect to the behaviour and influence of Na, Cu and U. Helsinki: Nuclear Waste Commission of Finnish Power Companies, Report YJT-90-06. 92 p. ISSN-0359-548X.

Velde, B. & Brusewitz, A. M., 1982. Metasomatic and non-metasomatic low grade metamorphism of Ordovician meta-bentonites in Sweden. Geochim. et Cosmoc. Acta, Vol. 46, pp. 447 - 452.

Vieno, T., 1994. Safety analysis of disposal of spent nuclear fuel. Espoo: Technical Research Centre of Finland, VTT Publications 177. 262 p. ISBN 951-38-4415-3.

Wanner, H., Wersin, P. & Sierro, N. 1992. Thermodynamic modelling of bentonite-groundwater interaction and implications for near field chemistry in a repository for spent fuel. Swedish Nuclear Fuel and Waste Management Co., SKB Technical Report 92-37. 28 p. ISSN 0284-3757.

Whitney, G. 1992. Dioctahedral smectite reactions at elevated temperatures: Effects of K-availability, Na/K ratio and ionic strength. In: A. Meunier (Editor). Clays and Hydrosilicate Gels in Nuclear Field. Appl. Clay Sci., Vol. 7, pp. 97 - 112.

Wilson, M. J. 1987. X-ray powder diffraction methods. In: M. J. Wilson (Editor), A Handbook of Determinative Methods in Clay Mineralogy. New York: Chapman and Hall Publishers. 308 p. ISBN 0-412-00901-3.

Yui, M. et al. 1992. Modelling of chemical buffering effect of engineered barriers for groundwater in geological isolation system of high-level radioactive waste (in Japanese). PNC TN 8410 92-162. Extracted data from the report in English.