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Thermodynamic modelling of bentonite-groundwater interaction and implications for near field chemistry in a repository for spent fuel.

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THERMODYNAMIC MODELLING OF BENTONITE-GROUNDWATER
INTERACTION AND IMPLICATIONS FOR NEAR FIELD CHEMISTRY
IN A REPOSITORY FOR SPENT FUEL

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Thermodynamic Modelling of Bentonite-Groundwater Interaction and Implications for Near Field Chemistry in a Repository for Spent Fuel

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Keywords: bentonite, ion-exchange, near-field, geochemistry

Abstract

Predictions of near field geochemistry are made using a thermodynamic model for bentonite/groundwater interaction. This model is a refinement and extension of the model developed by the senior author. It is based on recent experiments performed at high solid/water ratio and adapted to the Swedish type of HLW repository design. Thus, from the obtained experimental results on solution composition, the model includes chemical reactions resulting from both the impurities and the main clay fraction within the bentonite. Ion exchange reactions are treated both with and without the contribution of edge sites. Due to its thermodynamic basis, the model exhibits prediction capability over a wide range of conditions in terms of solid/water ratio.

The modelling of repository conditions implies, due to the lack of experimental information, simplifications with regard to thermodynamic properties of the bentonite. This mainly involves the non-consideration of the temperature effect and of the acid/base properties of the solid. Nevertheless, our results yield insight into important processes affecting porewater chemistry. Thus, the model suggests that proton exchange reactions may exert a strong control on calcite dissolution within highly compacted bentonite. Estimations of chemical changes over time in the bentonite were done on the basis of a mixing tank model. These results indicate transformation of Na-bentonite to Ca-bentonite over time. The extent of this process, however, critically depends on the amount of carbonate present in the bentonite.

Abstract (Swedish)

Prediktioner av närområdets geokemi har gjorts med en modell, vilken beskriver interaktionen mellan bentonit och grundvatten. Denna modellen är en utökning och förbättring av en modell utvecklad av huvudförfattaren. Den är baserad på experiment utförda med höga fast fas/vatten förhållanden och är anpassad till den svenska designen för slutförvar för använt bränsle. Modellen innefattar både kemiska reaktioner från föroreningar, såväl som från lerfraktionen. Jonbytesreaktionerna behandlas både med och utan bidrag från "kant"-positionerna. Tack vare att modellen är termodynamiskt baserad, kan den prediktera i ett stort spann av förutsättningar i fråga om fast fas/vatten förhållanden.

Modelleringen av förvarsförhållanden innebär, på grund av den begränsade experimentella informationen, förenklingar av bentonitens termodynamiska egenskaper. Detta innefattar huvudsakligen försummandet av temperatur effekter och syra/bas egenskaperna hos den fasta fasen. Likväl, indikerar modellen att protonutbytesreaktionen kan ha stor påverkan på kalcit upplösningen i den högkompakterade bentoniten. Uppskattningar av kemiska förändringar i bentoniten som en funktion av tiden har gjorts med en tank reaktor modell. Resultaten visar en övergång från Na-smektit till Ca-smektit. Omfattningen av denna process beror emellertid starkt av mängden karbonat i bentoniten .

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1 Introduction

Bentonite is envisaged as backfill material in repositories for radioactive waste, mainly because of its favorable physical properties. These include its swelling behavior and its effectiveness as a barrier for the migration of hazardous material (SKB Annual Report 1989; Projekt Gewähr, 1985). In the Swedish design of the final repository for spent fuel, highly compacted sodium bentonite is used as buffer material around the fuel-containing copper canisters in the vertically orientated emplacement holes (Figure 1). The backfill material in the tunnels is characterized by a mixture of bentonite and sand. The extent of the retardation process in the near field requires information on porewater composition in highly compacted bentonite. However, the possible chemical and temperature variation of bentonite over time has consequences on the porewater composition and on physical properties of the solid media. In particular, a possible transformation of Na-bentonite to Ca-bentonite through ion exchange leads to a drastic decrease in its swelling capacity and thus to a significant increase in permeability (Madsen and Müller-Vonmoos, 1988; Pusch et al., 1991). In addition, increase in temperature can, under certain conditions, induce illitization which results in the formation of a K-rich bentonite (Pusch, 1985; Pusch and Karland, 1988; Müller-Vonmoos and Kahr, 1985).

So far very few quantitative attempts have been made to model the geochemical behavior of highly compacted bentonite under conditions relevant for repository sites (Wanner, 1986; Grambow et al., 1986). This, in part, is due to the lack of experimental data simulating repository conditions, e.g., high bentonite/water ratios.

In this work we present a thermodynamic model for bentonite/groundwater interaction based on recent experiments (Werme, 1992) which were performed at high bentonite/water ratios at room temperature. This approach, which represents an extension of the model developed by Wanner (1986), allows characterization of porewater chemistry in compacted sodium bentonite. It must be emphasized that this thermodynamic model takes into account solution and surface interactions of the clay fraction and of the main impurities and therefore, in principle, can be applied to any bentonite-water system. The model is limited, however, by the information obtained from the experimental data. This mainly regards the lack of information concerning the surface properties of the clay fraction which precludes a detailed treatment of the surface reactions and thus leads to a simplified approach. Both treatments regarding surface reactions of clays are explained in the next section. Furthermore, the temperature effect cannot be considered in this work due to the lack of experimental information. In spite of these simplifications, the model can be used, for informative purposes, to extrapolate to near field conditions over long time periods. This is done under the assumption that the near field behaves like a mixing tank. The

limits of this approach and open questions are discussed. Finally, additional important experimental data needed for predicting near field geochemistry are summarized.

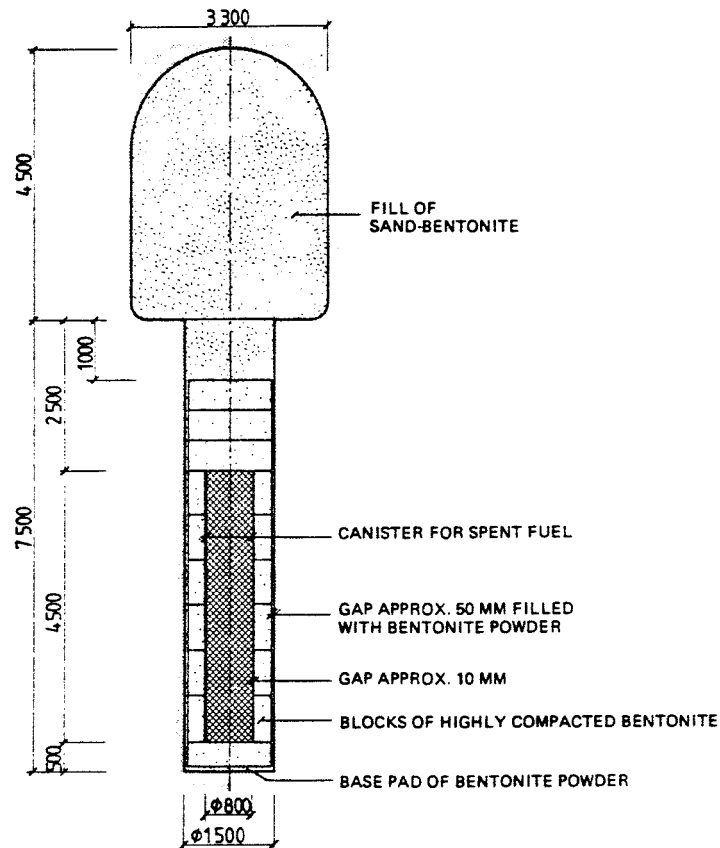


Figure 1: Waste emplacement geometry of Swedish repository (dimensions given in mm). This figure is taken from SKB Annual Report 1989.

2 Basis for bentonite model

2.1 Experimental data

Experimental data on the interaction of bentonite and water were made available by SKB (Werme, 1992). In these experiments four samples of untreated Wyoming bentonite (MX-80) (Table 1) were reacted with water, two with deionized water (DI) and two with Allard water (Swedish type granitic groundwater, cf. Table 1) at a very high solid to water ratio (1400

g/dm³). Subsequently, two samples of each reacted and filtered solution were analyzed for the main constituents Ca²⁺, Na⁺, Mg²⁺, SO₄²⁻, Cl⁻, alkalinity (Alk), and pH (Table 1). The charge balance shows agreement within 10% except for the experimental run 58/59 which shows a difference of 15%. All the obtained concentrations indicate a significant change in water composition upon reaction with bentonite for both deionized and Allard water samples. However, no major difference between these two reacted sample types is observed. This result yields insight into an important chemical property of bentonite, namely ion exchange. In fact, this result indicates that the ion exchange reactions are not significantly affected by initial solution composition but are induced by dissolution of impurities in the bentonite. In all cases a significant increase in Na⁺, pH, Alk, and SO₄²⁻ concentrations is noted. Ca²⁺ shows variable concentration, but is generally below the one occurring in Allard water (Table 1).

Speciation calculation of the solution, performed with the code MIN_SURF (Berner, 1986; Sierro, 1992), an extended version of the MINEQL computer code (Schweingruber, 1982; 1984), indicate saturated to slightly oversaturated conditions with respect to calcite equilibrium. This result is in agreement with the mineralogical composition of the MX-80 bentonite which contains impurities of carbonate and quartz (see Table 2). The speciation calculation indicates oversaturation with respect to dolomite. This is in agreement with previous studies (e.g., Lippmann, 1973) which show that dolomite precipitation is kinetically inhibited at room temperature. Significant concentrations of sulfate are present (~75 meq/dm³) which arise from the dissolution of impurities. These consist of traces of sulfate phases. Dissolution of pyrite cannot account for the increase in dissolved sulfate, as can be deduced from pyrite oxidation experiments reported by Nicholson et al. (1990). Chloride is of less importance since it is present at similar concentrations as found for unreacted Allard water. In summary, the results of the interaction of compacted Na-bentonite with two different types of water indicate calcite equilibrium and dissolution of the sulfate and chloride salts.

Table 1 also shows results of the interaction of soda-treated bentonite with both deionized and Allard water. Here charge balance computation indicates a considerable spread in the data (2 to 20% difference between total cation and anion concentrations). As might be expected, the previous addition of soda results in higher alkalinity, i.e., total carbonate concentration, compared to the untreated samples. Furthermore, increase of the solid/water ratio (samples no. 64/65, 66) results in even higher sodium, carbonate and pH. In addition, chloride concentrations show a ten-fold increase with regard to untreated samples. On the other hand, SO₄²⁻, Mg²⁺, and Ca²⁺ are found in similar concentrations as those found for the untreated bentonite samples.

Table 1

Experimental data of solution composition after reaction of Na-bentonite with water, solid/water = 1.4 g/cm³, except for exp. no. 64-66 (see first column). Values correspond to total concentration in solution in M (mol/dm³), except Alk (eq/dm³). These data were provided by Werme (1992).

Exp. water	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	Alk	pH
MX-80							
56 DI	1.09E-01	1.50E-04		1.49E-03	4.27E-02	1.20E-02	9.19
57	9.13E-02	1.50E-04		1.55E-03	3.64E-02	8.67E-03	9.19
62 DI	9.57E-02	1.00E-04		1.72E-03	4.06E-02	5.00E-03	9.10
63	6.96E-02	1.00E-04		1.24E-03	2.92E-02	3.67E-03	8.86
58 Allard	1.09E-01	3.99E-04	4.12E-06	2.00E-03	3.64E-02	7.67E-03	9.45
59	7.83E-02	4.99E-04		1.66E-03	2.92E-02	3.33E-03	9.25
60 Allard	9.13E-02	1.00E-04	4.12E-05	1.92E-03	3.54E-02	7.33E-03	9.21
61	8.70E-02	1.00E-04	2.06E-05	1.55E-03	2.92E-02	5.67E-03	9.29
soda-treated							
50 DI	2.00E-01	1.75E-04	9.45E-05	1.66E-02	2.29E-02	1.43E-01	9.87
51	2.17E-01		1.61E-04	1.66E-02	2.29E-02	1.67E-01	9.93
52 DI	1.91E-01	1.00E-04	7.00E-05	1.55E-02	2.08E-02	1.50E-01	9.87
53	2.17E-01			1.49E-02	2.08E-02	1.57E-01	9.97
54 Allard	1.87E-01			1.55E-02	1.98E-02	1.27E-01	9.91
55	1.96E-01			1.61E-02	1.98E-02	1.33E-01	9.98
67 Allard	2.35E-01	7.50E-05	1.24E-05	1.63E-02	2.19E-02	1.37E-01	9.89
68	2.00E-01	1.50E-04	8.65E-05	1.92E-02	2.29E-02	1.53E-01	9.88
64 DI, 1.6	3.96E-01	7.50E-05	1.24E-05	3.66E-02	4.58E-02	1.83E-01	10.05
65	3.96E-01	1.00E-04	3.94E-05	3.66E-02	4.89E-02	1.97E-01	9.6
66 DI, 1.8	6.96E-01			5.92E-03	5.95E-02	2.27E-01	11.71
Allard water	2.26 E-03	4.64E-04	1.9E-04	1.48E-03	1.0E-04	1.80E-03	8.1

Speciation calculations of the solutions resulting from the experiments with the soda-treated bentonite samples indicate oversaturation conditions (10-15 times) with respect to calcite, contrary to the untreated samples. This result is somewhat unexpected in view of the relatively fast precipitation kinetics of calcite (e.g., Busenberg and Plummer, 1986). Oversaturated conditions with respect to the thermodynamic stable mineral phase can arise from (1) the formation of very

fine particles, and (2) the formation of thermodynamically metastable mineral phase (e.g., Morse and Casey, 1988). In the case of carbonates, the formation of thermodynamically metastable solid solutions under a variety of solution conditions at low temperature is a commonly known process (Lippmann, 1973; Morse and Casey, 1988; Jacobsen and Postma, 1989; Wersin et al., 1989). Based on this information, we suggest, for the soda-treated bentonite system, the formation of some form of calcium carbonate solid solution controlling Ca^{2+} solubility. We are aware that this explanation is somewhat arbitrary and cannot be used in a quantitative way in the bentonite model due to the scarcity of the experimental information. With respect to SO_4^{2-} , the soda-treated samples indicate similar behavior compared to the untreated samples in terms of dissolution of sulfate impurities. The noted increase in sodium, carbonate, pH, and chloride concentration is viewed as a result from the preceding soda-treatment of the bentonite.

Table 2

Data for Na-bentonite (MX-80) required for bentonite model.

Property	Value	Reference
Cation exchange capacity (CEC) ¹	76.4 meq/100g	1, 2
Exchangeable Na ¹	62.4 meq/100g	2
Exchangeable Mg ¹	3.0 meq/100g	
Exchangeable Ca ^{1,2}	7.4 meq/100g	
Total carbonate (CaCO_3)	1.4 g/100g	2
Total Quartz (SiO_2)	~ 10 g/100g	1
density (highly compacted)	1.70 g/cm ³	3
density (highly compacted, water saturated)	2.07 g/cm ³	3
porewater/bentonite ratio	0.38 cm ³ /cm ³	4

¹ refers to 100g of oven-dried material

² value for exchangeable Ca could be subject to systematic error because of presence of calcite (Couture, 1985).References: 1: van Olphen and Fripiat (1979), 2: Müller-Vonmoos and Kahr (1983), 3: McKinley (1984), 4: Projekt Gewähr (1985)

2.2 Thermodynamic description of ion exchange

2.2.1 Concept of cation exchange capacity

Bentonite consists primarily of montmorillonite, a member of the smectite group. Figure 2 illustrates the schematic mineral structure of montmorillonite consisting of silicate layers in which each layer is formed by a tetrahedral-octahedral-tetrahedral unit. These layers are stacked, separated by water interlayers of different sizes. Isomorphous substitution, mainly of Al^{3+} for Si^{4+} , leads to a permanently negative charge in the layer which is compensated externally by cations. In contact with water the surface cations are exchangeable, and consequently the cation exchange capacity (CEC) is a measure of the permanent negative layer charge.

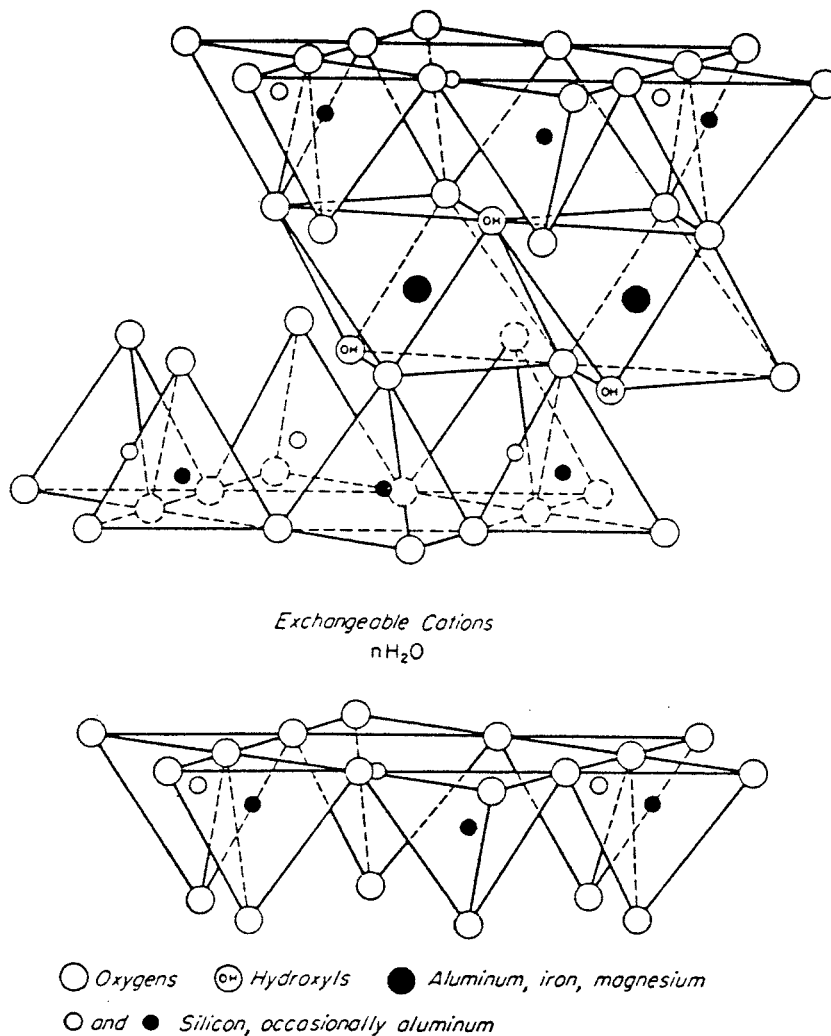


Figure 2: Diagrammatic sketch of the structure of montmorillonite (taken from Grim and Kulbicki, 1961)

2.2.2 Ion exchange behavior in the layer

The cation exchange reaction describing the stoichiometric displacement of, e.g., Na⁺ by Ca²⁺ is:



$$\text{where } K = \frac{[\text{CaX}_2] [\text{Na}^+]^2}{[\text{NaX}]^2 [\text{Ca}^{2+}]} \quad (2)$$

X is a layer surface site, [] refers to the concentration of the sorbed species NaX, CaX₂ and the solution species Na⁺, Ca²⁺. K is the *conditional equilibrium constant*, valid for a specific composition at the surface and ionic strength. The *thermodynamic equilibrium constant*, K^o, for this reaction is:

$$K^o = \frac{\{ \text{CaX}_2 \} \{ \text{Na}^+ \}^2}{\{ \text{NaX} \}^2 \{ \text{Ca}^{2+} \}} \quad (3)$$

where {i} stands for activity of species i which is related to eq. (2) by

$$K^o = K \frac{f_{\text{CaX}_2} f_{\text{Na}^+}^2}{f_{\text{NaX}}^2 f_{\text{Ca}^{2+}}} \quad (4)$$

where f_i is the activity coefficient of species i.¹ Experimental data on ion exchange in Wyoming montmorillonite (Gast, 1971; Sposito et al., 1983) has shown that ion exchange of the major exchangeable cations (Na⁺, Ca²⁺, Mg²⁺) follows ideal behavior if the change in surface composition is relatively small. Thus, under these conditions, K may be considered independent of compositional change of the bentonite surface layers and therefore eq.(4) simplifies to:

$$K^o = K \frac{f_{\text{Na}^+}^2}{f_{\text{Ca}^{2+}}} \quad (5)$$

The activity coefficients, f_{Ca²⁺}, f_{Na⁺}, depend, among others, on the ionic strength I of the solution and may be calculated, for the ionic strengths relevant in this report, by the Debye-Hückel expression:

¹ This approach implicitly treats all involved species as solution species (cf. Wanner, 1986).

$$\log f_i = - \frac{z^2 A \sqrt{I}}{1 + B a_0 \sqrt{I}} \quad (6)$$

where z is the valence of the ion, and A and B are empirical constants dependent on temperature. At 25 °C, $A = 0.51$ and $B a_0 = 1.5$ (Biedermann et al., 1982).

2.2.3 *Influence of edge charge*

So far, only ion exchange arising from the layer charge has been considered, where displacement by the proton is negligible at $\text{pH} > 4$ (Sposito, 1983; Fletcher and Sposito, 1989). However, the edge surface, which consists of hydrolyzed AlOH and SiOH functional groups, also carries charges which depend on pH and can be positive or negative (White and Zelazny, 1988). In the pH range of interest in this work, i.e. $8 < \text{pH} < 11$, the net charge at the edge surface is negative and is considered to constitute 10 to 15% of the total of montmorillonite surface charge (Fletcher and Sposito, 1989). Cations, including the proton, compete for these negatively charged edge sites. The simplest thermodynamic description of this ion exchange considers the cationic displacement at one edge site (Fletcher and Sposito, 1989). Thus, the reaction for the stoichiometric displacement of sodium by the proton is



where E stands for edge surface site, and the thermodynamic description is similar to the one derived for the ion exchange at the layer surface.

A more rigorous approach considers two functional groups at the edge surface, namely =AlOH and =SiOH, and treats them according to the surface complex formation theory (Zysset, 1992) in which the charge effect due to the difference in the electrical potential between the surface and the solution is taken into account. Unfortunately, there is no published experimental information available on acid-base properties of bentonite for $\text{pH} > 9$, i.e., at conditions relevant for our system. However, preliminary, unpublished surface titration experiments (Charlet, 1992) suggest strong increase in negative charge at $\text{pH} > 9.5$.

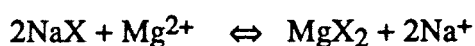
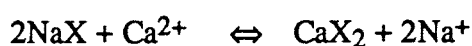
It is important to emphasize that inclusion of the edge charge requires information on the acid/base behavior of the montmorillonite surface which cannot be extracted from the present experimental data. In this report we therefore treat the ion exchange equilibria in bentonite using the approach outlined in eqs. (1)-(4). Hence, neglecting the edge contribution, we assume

one exchangeable site X^- on the surface and derive ion exchange equilibria from the experimental data for the untreated Na-bentonite samples and from CEC data (van Olphen and Fripiat, 1979; Müller-Vonmoos and Kahr, 1983). However, for comparison, we include the contribution of edge charge by using the simplified description given in eq. (5) and the equilibrium constants obtained from the literature (Fletcher and Sposito, 1989). Thus, we test, at least in a preliminary way, the results obtained from the simplified approach. Finally, the lack of experimental data in terms of acid/base behavior, i.e. surface titration data, precludes, at present, the incorporation of a surface complexation approach into the bentonite model.

3 Derivation and application of the bentonite model

3.1 Derivation of the ion exchange constants

The thermodynamic bentonite model is derived on the basis of the experimental results with the untreated Na-bentonite (section 2.1) and the relevant ion exchange reactions derived thereof for montmorillonite (section 2.2). Thus, we consider cation exchange involving Na^+ , Mg^{2+} , and Ca^{2+} . K^+ was not analyzed in Werme's experiments, and since its effect on porewater chemistry is not of importance in the present model (cf. Wanner, 1986), we have not included this cation in the ion exchange mechanisms. Therefore, the cation exchange reactions are:



The equilibrium constants for cation exchange are derived from the relationships given in eqs. (2) and (5) by means of the following: The concentrations of the solution species at equilibrium are obtained from the speciation calculation of the solution. The concentrations of the sorbed species NaX and MgX_2 at equilibrium are obtained from the initial quantities of exchangeable ions in bentonite, available for 1 dm^3 of porewater, as given in Table 2, minus the respective concentration measured in solution. On the other hand, CaX_2 is derived indirectly because the presence of calcite does not allow the same calculation. Thus, CaX_2 at equilibrium is calculated from the relation:

$$[CaX_2] = 1/2 * ([X]_t - [NaX] - 2[MgX_2])$$

where $[X]_t$ is the total concentration of X and is set equal to the CEC.

The constants derived for each of the four experimental runs for the Na-Ca exchange are given in Table 3.

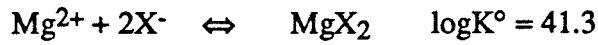
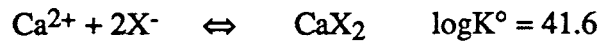
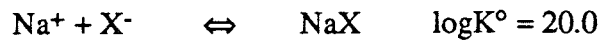
Table 3

Conditional equilibrium constants, K , and thermodynamic equilibrium constants, K° , for cation exchange derived from experimental data (untreated MX-80); for explanations see text.

Exp.no	$K_{\text{Na-Ca}}$	$K_{\text{Na-Mg}}$
56/57	1.40	no data
62/63	1.37	no data
58/59 ¹	0.80	2.05
60/61	1.43	1.11
K_{average}	1.40 ± 0.10	1.11
K°	1.63 ± 0.10	1.34

¹ This data is discarded (see text).

There is a good agreement between the obtained values except for one set of experiments (no. 58/59). Moreover, this set of data indicates (1) poor agreement in charge balance and (2) oversaturated conditions with respect to calcite contrary to the other ones. Therefore, we discard the experimental set no. 58/59 and select the average value of the equilibrium constants obtained from the other 3 sets of data (Table 3). The equilibrium constant for Na-Mg is taken from the data set 60/61 due to the lack of further experimental information (Table 3). Therefore, the estimated error is relatively large, but fortunately Mg only has a minor influence on bentonite geochemistry, as is indicated by our results and other work (Sposito et al., 1983; Wanner, 1986). The final thermodynamic equilibrium constants used in our model are the formation constants of the sorbed species NaX, CaX₂, and MgX₂. The formation constant of NaX is set arbitrarily to 10²⁰, according to e.g., Wanner (1986); Fletcher and Sposito (1989). On this basis, the constants are calculated as formation constants.



If we want to include the contribution of edge sites to ion exchange equilibria, we are bound to rely on literature data because of the lack of surface titration data (see section 2.2) for our bentonite system. Thus, we include the data given by Fletcher and Sposito (1989) for clay-electrolyte interactions, who used a simple description of the edge surface outlined in the previous section. In our case the relevant reactions are



Again, we emphasize that this is a simplified treatment of edge sites which assumes only one negatively charged site and ignores surface charge effects. A further refinement of the edge site contributions is not possible to date in view of the lack of acid/base data for the bentonite surface.

3.2 *Thermodynamic treatment of impurities*

On the basis of solution data (section 2.1) and mineralogical information on MX-80 bentonite, we model the chemical reactions involving impurities for both untreated and soda-treated experiments. In the case of the experiments with untreated Na-bentonite, the following thermodynamic constraints are set:

(1) Calcite equilibrium.

(2) **Quartz equilibrium.** This is assumed on the basis of mineralogical analysis for Wyoming bentonite MX-80 (van Olphen and Fripiat, 1979; Müller-Vonmoos and Kahr, 1983) which shows 10% of quartz impurities.

(3) **No dolomite equilibrium.** Mg mobility is attributed entirely to ion exchange reactions within the clay-fraction.

(4) **Dissolution of all calcium sulfate.** Thus all SO_4^{2-} is accounted for by this proposed process.

(5) **Dissolution of all sodium chloride.** This accounts for occurrence of minor amounts of Cl^- .

(6) **No dissolution of the clay fraction.** This assumption is based on thermodynamic stability calculations on montmorillonite (Zysset, 1992) which indicate low Al and Si concentrations ($< 10^{-6}$ M) under the pH conditions relevant for the bentonite-groundwater system, i.e. $8 < \text{pH} < 11$.

In the case of the experiments with soda-treated Na-bentonite, we include the thermodynamic constraints (2), (3), (4), (5), and (6). Furthermore, we assume equilibrium with respect to a CaCO_3 mineral phase showing ten-fold higher solubility compared to calcite (cf. section 2.1).

3.3 *Testing the bentonite model*

3.3.1 *Testing for experiments with untreated bentonite*

Our thermodynamic model for bentonite is based on ion exchange properties (section 2.3) of the bentonite and on the treatment of the impurities (section 2.4). The first test of this model consists of its application to the experimental data for untreated bentonite. The model is executed with the aid of the computer code MIN_SURF (Berner, 1986, Sierro, 1992) which is an extended version of the computer code MINEQL (Schweingruber, 1982; 1984) containing a revised data base into which the derived ion exchange equilibria are inserted. In a first run, we consider only layer exchange sites, neglecting edge contribution. Thus, we enter the initial conditions, i.e., initial total concentrations, $C_{0,t}$ marked as subscript 0, of exchangeable cations Na, Mg, Ca:

$$\begin{aligned}
[\text{Na}]_{0,t} &= [\text{NaX}]_0 + [\text{NaCl}]_0 + [\text{Na}]_{\text{gr},t} \\
[\text{Ca}]_{0,t} &= [\text{CaX}_2]_0 + [\text{CaSO}_4]_0 + [\text{Ca}]_{\text{gr},t} \\
[\text{Mg}]_{0,t} &= [\text{MgX}_2]_0 + [\text{Mg}]_{\text{gr},t}
\end{aligned}$$

$[\text{NaX}]_0$ and $[\text{MgX}_2]_0$ are derived from Table 2 and $[\text{CaX}_2]_0$ is calculated as explained above; $[\text{NaCl}]_0$, $[\text{CaSO}_4]_0$ take the dissolution of the chloride and sulfate impurities into account and correspond to the measured concentrations of chloride and sulfate, respectively; $[i]_{\text{gr},t}$ stands for the total dissolved concentration of component i in the groundwater (Allard water). Moreover, for the remaining components we add the initial conditions:

$$\begin{aligned}
[\text{X}]_{0,t} &= \text{CEC} \\
[\text{CO}_3]_{0,t} &= [\text{CO}_3]_{\text{gr},t} \\
[\text{H}]_{0,t} &= [\text{H}]_{\text{gr},t} \\
[\text{SO}_4]_{0,t} &= [\text{CaSO}_4]_0 + [\text{SO}_4]_{\text{gr},t} \\
[\text{Cl}]_{0,t} &= [\text{NaCl}]_0 + [\text{Cl}]_{\text{gr},t}
\end{aligned}$$

Finally, we fix the following activities:

$$\begin{aligned}
\{\text{CaCO}_3(\text{s})\} &= 1 && \text{Calcite equilibrium} \\
\{\text{SiO}_2(\text{s})\} &= 1 && \text{Quartz equilibrium} \\
p(\text{CO}_2) &= 10^{-3.5} \text{ atm}
\end{aligned}$$

Table 4 shows the results of the computation (indicated by layer model) by the MIN_SURF code, in comparison with the experimental results. Relatively good agreement for the main components between the two results is noted, especially considering the uncertainty of the experimental data as derived from the charge balance.

In a second stage we include edge sites as explained in section 3.1. The initial conditions are modified only by the addition of one edge component E^- which is set to 15% of CEC (Fletcher and Sposito, 1989). Thus, we assume that, at initial conditions, the negative edge charge is neutralized by protons. Table 4 shows the results of this computation (indicated by edge model) which also indicates relatively good agreement with the experimental data. Compared to the output of the layer model, the edge model shows similar agreement with measured concentrations in terms of the main exchangeable cations Na^+ and Ca^{2+} . This is rather encouraging, since the edge model is based on previous experimental data (Fletcher and Sposito, 1989)

which were obtained under entirely different conditions with regard to pH and solid/water ratio. In view of this, further experimental information on edge charge characterization at high solid/water ratios may yield even better predictions of bentonite-water equilibria.

3.3.2 *Testing for experiments with soda-treated bentonite*

A further test of the model is to apply it to soda-treated samples. It should be emphasized that the initial conditions cannot be reproduced, since the details of treatment, such as the added Na_2CO_3 quantity and its effect on surface composition, are not known. Therefore, we test different plausible initial conditions.

First we assume that soda treatment resulted in the saturation of exchangeable sites with Na^+ . The added base is assumed to have been removed by CaCO_3 precipitation. Consequently, changes in initial conditions compared to the untreated experiments only involve $[\text{Na}]_{t,0}$ which is equal to CEC (therefore $[\text{CaX}_2]$ and $[\text{MgX}_2]$ are zero). The model calculation, under these assumptions, leads to systematic underestimation of sodium and calcium in solution by a factor of 2 to 3 and, by an even a larger extent, to an underestimation of the alkalinity. The inclusion of edge sites according to the above procedure does not significantly affect this result. In view of the poor agreement between the modelled and experimental results, we conclude that the soda-treatment results in a higher total sodium concentration in the bentonite than that corresponding to the cation exchange capacity, and also in higher initial alkalinity.

Therefore, in a second approach, the excess of sodium and carbonate is taken into account by assuming an initial presence of Na_2CO_3 in bentonite which upon further reaction with water is redissolved. From the solution analyses, a rough estimation of the amount of possibly dissolved soda can be made. Under these assumptions we estimate the following initial conditions: $[\text{Na}]_0 = \text{CEC} + 2[\text{Na}_2\text{CO}_3]$, and $[\text{CO}_3]_t = [\text{Na}_2\text{CO}_3]$, where $[\text{Na}_2\text{CO}_3] \approx 0.1$ M. All other input parameters are identical to the previous case. The results of these calculations are shown in Table 4. It should be noted that the thermodynamic model derived predicts the solution composition of a different bentonite system fairly well.

Table 4

Comparison between experimental data and modelled data for bentonite solution. The values given in the lines marked "experimental" are average values of the two runs, cf. Table 1; they refer to total concentration in solution in M, except Alk (eq/dm³). For all calculations pCO₂ = 10^{-3.5} atm. Layer model: assuming only one layer site for ion exchange; Edge model: assuming two sites according to Fletcher and Sposito (1989).

Exp.	exp./model	Na ⁺	Ca ²⁺	Mg ²⁺	Alk	pH
untreated						
56/57	experimental	1.0E-1	1.5E-4		1.0E-2	9.2
	layer model	9.0E-2	1.1E-4		7.0E-3	9.0
	edge model	8.9E-2	1.2E-4		6.4E-3	9.0
62/63	experimental	8.3E-2	1.0E-4		4.3E-3	9.0
	layer model	8.2E-2	8.2E-5		8.0E-3	8.8
	edge model	8.2E-2	1.0E-4		7.1E-3	8.9
60/61	experimental	8.9E-2	1.0E-4	3.1E-5	6.5E-3	9.2
	layer model	7.7E-2	7.0E-5	2.0E-5	8.7E-3	9.0
	edge model	7.5E-2	7.8E-5	2.0E-5	8.0E-3	9.0
soda-treated¹						
50/51	experimental	2.1E-1	1.7E-4	1.3E-4	1.6E-1	9.9
	layer model	2.7E-1	7.3E-5	1.3E-6	1.6E-1	9.8
	edge model	1.9E-1	8.0E-5	7.3E-7	1.1E-1	9.7
52/53	experimental	2.0E-1	1.0E-4	7.5E-5	1.5E-1	9.9
	layer model	2.7E-1	7.2E-5	1.3E-6	1.7E-1	9.8
	edge model	1.9E-1	7.9E-5	7.2E-7	1.1E-1	9.7
64/65	experimental	4.0E-1	8.8E-5	2.6E-5	1.9E-1	10.1
	layer model	3.1E-1	8.3E-5	1.5E-6	1.5E-1	9.8
	edge model	2.4E-1	1.0E-4	8.4E-7	8.8E-2	9.6
Snellman's (1984) data						
90 days	experimental	1.0E-2	3.0E-5	1.9E-5	7.9E-3	9.1
	layer model	7.9E-3	4.3E-5	7.8E-6	4.5E-3	8.9
	edge model	1.0E-4	2.3E-5	5.5E-6	7.4E-3	9.1

¹ modelled values have been corrected for excess of Na₂CO₃ (see text)

The inclusion of the edge model under the same assumptions (Table 4) also indicates good agreement with experimental data. Furthermore, as noted for the untreated samples, the prediction of Na⁺ and Ca²⁺ concentrations is slightly superior compared to the layer model.

3.3.3 *Testing for the experiments of Snellman (1984)*

For further verification of the bentonite model we test it against earlier experiments (Snellman, 1984) performed with the same material but at a much lower solid/water ratio (0.27 vs. 1400 g/dm³). Table 4 shows the analyzed solution concentrations and the corresponding ones obtained from model calculations performed using the same initial conditions as for the untreated samples and assuming only ion exchange in the layers. This indicates that this simple bentonite model also predicts Na-bentonite/water equilibria at low solid/water ratios fairly well. It is noteworthy to mention that the bentonite model of Wanner (1986), which was based on this set of experiments (Snellman, 1984) and on a similar thermodynamic approach, displays slightly different characteristics in terms of ion exchange equilibria. This concerns mainly Na-Ca exchange where Wanner (1986) derived a slightly higher equilibrium constant, 2.4 vs. 1.6 for logK^{*}. A close comparison of both derivations reveals that this difference can be explained in terms of the slightly different CEC used (73 vs. 76.4 meq/100g) which compensates for the difference in K^{*} and thus does not significantly affect the calculations. Thus, the validity of Wanner's model extrapolated to higher bentonite/water is supported by this work.

3.3.4 *Comparison with other literature data*

Another point to be made regards our results on Na-Ca exchange in the light of data in the soil science literature. The equilibrium constant for displacement of Na⁺ by Ca²⁺ for Na-montmorillonite is reported in the range of 1 to 5.7 (Bruggenwert and Kamphorst, 1982) which is lower than the one derived here (15.8). This difference is probably due to the much lower solid/water ratio, resulting, for example in a higher CEC (90-100meq/100g) (van Olphen and Fripiat, 1979; Zysset, 1992). However, this difference may also reflect the usually lower pH conditions at which the experiments were performed compared to the ones presented here. In fact, at high pH the contribution of edge sites to negative charge increases and, thus, the assumption of only one charged site produces an increase in the ion exchange constant. This is supported by the fact that even our crude edge model yields a slightly better prediction of bentonite-water equilibria for the experimental systems studied. Nevertheless, both our simplified models appear to be robust for a fairly large range of conditions, and thus we consider that their application to near field conditions is justified.

4 Extrapolation to repository conditions

4.1 Prediction of porewater composition

As seen in Figure 1 the buffer material around each canister consists of highly compacted bentonite. Table 2 shows that 100 g of highly compacted bentonite takes up 21.8 g of water. Thus, roughly 21.8 ml are in contact with 76.4 meq of ion exchange sites. The resulting total CEC is 3.50 eq per dm³ of porewater. The experiments upon which our model is based were conducted at only slightly more diluted conditions (1.07 eq/dm³). In addition, we have seen that our model can be used for a large range of solid/water ratios and of initial compositions. Thus, extrapolation to chemical conditions in the near field is relatively straightforward. In this calculation, we react Allard water (composition given in Table 1) with highly compacted sodium bentonite at quartz and calcite saturation for a closed system. Thus, we model this process according to the procedure outlined in the previous section.

In the first approach we neglect the effects caused by edge charge. We now treat carbonate equilibria in a closed system. Otherwise the same initial conditions are entered as for the modelling of the experiments with untreated bentonite of Werme (1992). This also holds for the treatment of the impurities in bentonite (cf. section 2.4). The first row of Table 5 gives the results of the prediction of porewater composition using the layer model. It is noteworthy to mention that dissolution of CaSO₄ and also of NaCl in the bentonite is assumed to lead to a total depletion of these compounds and removal from the system once the porewater has been exchanged by fresh groundwater (see section 4.2.2).

In the second approach we include edge charge according to our edge model. The results of this calculation are given in the first row of Table 6. The predicted porewater composition is significantly altered compared to the previous model which is contrary to the results obtained for bentonite-water interactions at lower solid/water ratio (cf. Table 4). This specifically regards acid/base equilibria where the edge model predicts, e.g., a considerable drop in pH. Thus, according to the model, proton exchange reactions involving edge sites, E⁻, at very high solid/water ratios, lead to a displacement of the proton by other cations: $z\text{HE} + \text{M}^{z+} \rightarrow \text{ME}_z + z\text{H}^+$, where M stands for Na, Ca, or Mg. Furthermore, this edge charge-driven process leads to the dissolution of much more calcite compared to the model where edge charge is neglected (0.37 M vs. 10⁻³ M calcite). However, it must be emphasized that, in view of the lack of necessary experimental information on acid/base properties of highly compacted bentonite, the effect of edge charge can only be evaluated qualitatively.

4.2 *Long term extrapolations: Mixing tank model*

4.2.1 *Derivation of the mixing tank model*

Once the Na-bentonite buffer material is saturated with the surrounding water, slow transport through this material occurs. Consequently, porewater chemistry and composition of the bentonite are slowly changing. This, in turn, will affect the ion exchange properties of bentonite. Specifically, the progressive displacement of Na^+ by Ca^{2+} will alter the physical properties of the clay, especially in terms of its swelling capacity. Therefore, quantitative assessment of the long-term behavior of bentonite at near field conditions is important.

We used a very simple approach, the mixing tank model, to estimate the effect of time on bentonite chemistry. In this model, the groundwater flowing past the repository is assumed to mix completely with the near field water. Furthermore, the composition of porewater is considered to be uniform throughout the near field. In the mixing tank concept the time required to completely exchange the porewater is viewed as one water exchange cycle. A simple estimation of timescales for one water exchange cycle can be made from the hydraulic conductivity of clay (10^{-11} m/s), the thickness of the bentonite wall around the canister (0.35 m), and, for conservative purposes, a hydraulic gradient of 0.1 (e.g., Pusch and Karnland, 1988). The resulting time of 13'800 years thus serves as rough estimate of the time required for replacing the bentonite porewater completely with fresh groundwater. After each water exchange cycle the composition of bentonite will be altered. Fresh groundwater will equilibrate with bentonite after each exchange cycle. Since the amount of exchangeable sites in the bentonite is assumed to remain constant with time, this change affects the relative proportion of exchangeable cations within the bentonite. Quartz and calcite are considered to dissolve according to their solubility product. The total amount of carbonate available in bentonite is derived from mineralogical analysis (Table 2) to be 0.61 mol/dm^3 .

Table 5

Predicted porewater composition of some major species on basis of mixing tank model. Concentrations in M, Alk in eq/dm³. Layer model.

cycle	NaX	CaX ₂	Na ⁺	Ca ²⁺	Alk	pH	CaCO ₃
0	2.63E+0	3.68E-1	2.11E-1	1.02E-4	3.88E-3	9.09	1.03E-3
1	2.60E+0	3.82E-1	2.74E-2	1.40E-6	2.80E-2	10.47	1.44E-2
10	2.38E+0	4.94E-1	2.33E-2	1.54E-6	2.33E-2	10.44	1.22E-1
20	2.16E+0	5.98E-1	2.04E-2	1.69E-6	1.99E-2	10.41	2.22E-1
30	1.98E+0	6.89E-1	1.82E-2	1.83E-6	1.74E-2	10.38	3.08E-1
40	1.82E+0	7.68E-1	1.65E-2	1.97E-6	1.54E-2	10.35	3.83E-1
50	1.67E+0	8.39E-1	1.51E-2	2.12E-6	1.38E-2	10.32	4.49E-1
60	1.54E+0	9.03E-1	1.40E-2	2.27E-6	1.24E-2	10.30	5.08E-1
70	1.42E+0	9.60E-1	1.30E-2	2.43E-6	1.16E-2	10.27	5.61E-1
80	1.31E+0	1.01E+0	1.21E-2	2.59E-6	1.07E-2	10.25	6.09E-1
81	1.30E+0	1.02E+0	1.20E-2	2.61E-6	1.06E-2	10.24	6.14E-1
82	1.30E+0	1.02E+0	3.67E-3	2.18E-7	1.90E-3	8.19	-
90	1.29E+0	1.02E+0	3.57E-3	2.10E-7	1.90E-3	8.19	-
100	1.27E+0	1.03E+0	3.57E-3	2.15E-7	1.90E-3	8.19	-
140	1.22E+0	1.05E+0	3.57E-3	2.39E-7	1.90E-3	8.19	-
180	1.17E+0	1.06E+0	3.58E-3	2.66E-7	1.90E-3	8.19	-

Table 6

Predicted porewater composition of some major species on basis of mixing tank model. Concentrations in M, Alk in eq/dm³. Edge model.

cycle	NaX	CaX ₂	NaE	CaE ₂	HE	Na ⁺	Ca ²⁺	Alk	pH	CaCO ₃
0	2.32E+0	5.22E-1	7.88E-2	2.23E-1	1.14E-3	3.99E-1	6.65E-4	2.33E-1	6.24	3.79E-1
1	2.30E+0	5.32E-1	7.75E-2	2.24E-1	1.65E-6	2.25E-2	1.63E-6	2.24E-2	10.31	3.90E-1
10	2.13E+0	6.17E-1	6.73E-2	2.29E-1	1.34E-6	1.99E-2	1.71E-6	1.93E-2	10.40	4.77E-1
20	1.96E+0	7.01E-1	5.86E-2	2.34E-1	1.38E-6	1.80E-2	1.85E-6	1.68E-2	10.37	5.60E-1
27	1.85E+0	7.55E-1	5.36E-2	2.36E-1	1.41E-6	1.68E-2	1.94E-6	1.60E-2	10.35	6.16E-1
28	1.85E+0	7.55E-1	5.36E-2	2.36E-1	1.43E-4	3.64E-3	7.84E-8	2.00E-3	9.01	-
30	1.84E+0	7.56E-1	5.35E-2	2.36E-1	2.94E-4	3.62E-3	7.79E-8	1.94E-3	8.70	-
50	1.82E+0	7.66E-1	5.24E-2	2.36E-1	7.50E-4	3.62E-3	8.08E-8	1.91E-3	8.29	-
100	1.75E+0	7.92E-1	4.93E-2	2.38E-1	8.85E-4	3.63E-3	9.03E-8	1.90E-3	8.19	-
140	1.70E+0	8.09E-1	4.79E-2	2.38E-1	8.65E-4	3.63E-3	9.87E-8	1.90E-3	8.18	-
180	1.64E+0	8.28E-1	4.59E-2	2.39E-1	8.30E-4	3.64E-3	1.08E-7	1.90E-3	8.18	-

4.2.2 Results of the mixing tank model

Long-term calculations on the basis of the mixing tank model were done by using the code MIN_SURF as subroutine and taking into account the altered distribution of exchangeable cations in the bentonite for each new input entry. Thus, the first input, which is set according to the previously outlined procedure (section 3.1), provides the equilibrium condition before the first exchange cycle. Then the code calculates the equilibrium of the new distribution in the bentonite in contact with fresh groundwater. This exchange procedure is repeated 180 times.

The results of these calculations, for the layer model, are listed in Table 5 and illustrated in Figures 3 and 4. With regard to exchangeable ions, Mg shows an insignificant change across exchange cycles.

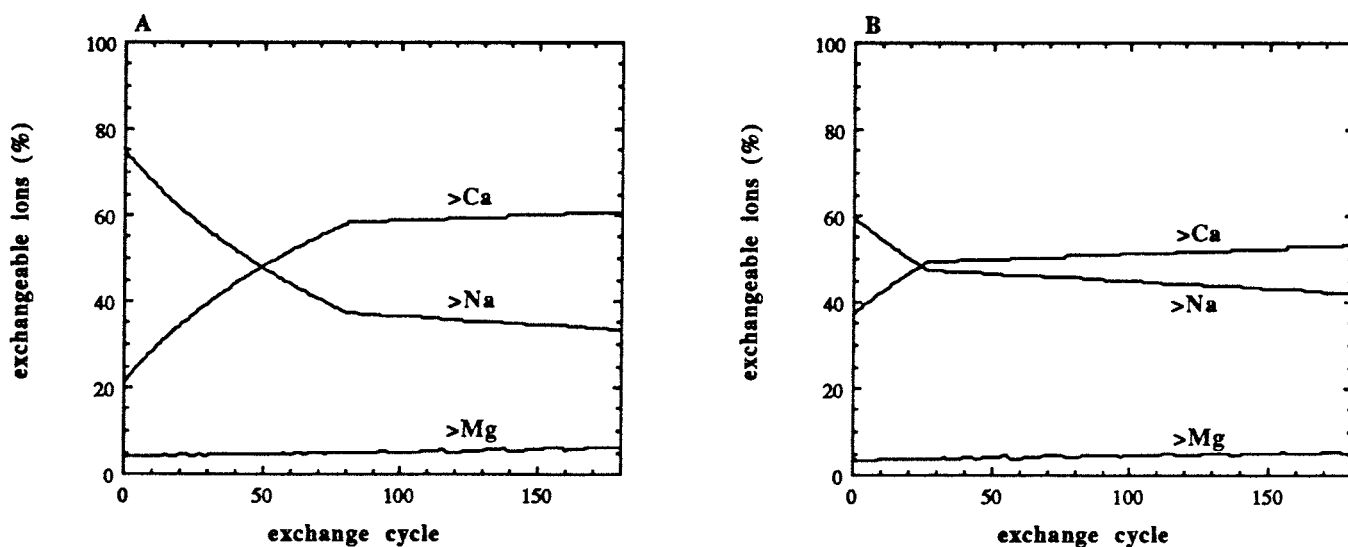


Figure 3: Prediction of composition of bentonite in terms of sorbed exchangeable ions as a function of exchange cycles according to the mixing tank model. A: layer model B: edge model.

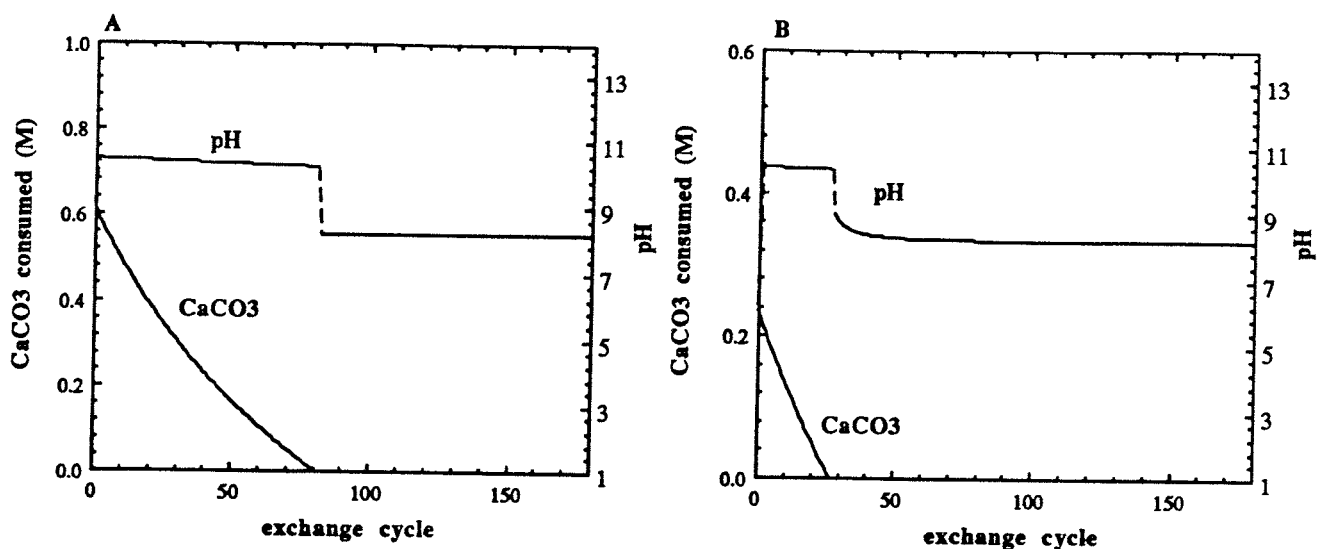
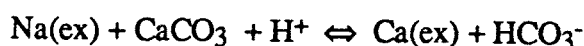


Figure 4: Prediction of pH and consumed calcite in bentonite as a function of exchange cycles according to the mixing tank model. A: layer model. B: edge model.

The pH is around 10.5 after the first exchange cycle, corresponding to calcite equilibrium in a closed system. The CaSO_4 present in the fresh bentonite, responsible for keeping the pH at 9, has been dissolved before the first exchange cycle. An important aspect involves the observed transformation of Na-bentonite to a Ca-rich bentonite which arises from the combined effect of ionic exchange and calcite dissolution. This process can be presented by following reaction:



Thus, calcite dissolution provides a continuous source of calcium available to the clay surface. However, this process results in the slow exhaustion of the carbonate pool. In the layer model this occurs after 81 cycles and induces a drastic change in the chemical composition of the porewater. As a consequence, a drop in pH of the porewater to groundwater conditions occurs (Table 5; Figure 4A) and further enrichment of Ca in bentonite proceeds at a much slower rate. The model predicts that this change occurs at a Ca/Na ratio of around 3/2 (Figure 3A). Thus, in the case of relatively poorly mineralized groundwater, the transformation of bentonite is critically dependent on the amount of available carbonate present in bentonite.

Table 6 and Figures 3B and 4B show the results of the same type of calculation but using the edge model. A similar trend is noted in spite of the difference in porewater predicted for initial bentonite-water equilibrium (cf. cycle 0). Thus, according to the model, proton exchange reactions at edge sites do not affect porewater chemistry significantly once the proton has been displaced the exchangeable cations (Na^+ , Ca^{2+}). However, the total consumption of calcite in the bentonite occurs much earlier (27 exchange cycles) due to the much higher dissolution of this impurity during the first equilibration process. This leaves a bentonite with a 1/1 ratio of Na to Ca which after depletion of the carbonate pool shows very slow transformation in agreement with the previous model. In summary, both models indicate transformation of bentonite to a Ca-richer type, but the timescales regarding the extent of this process differ significantly.

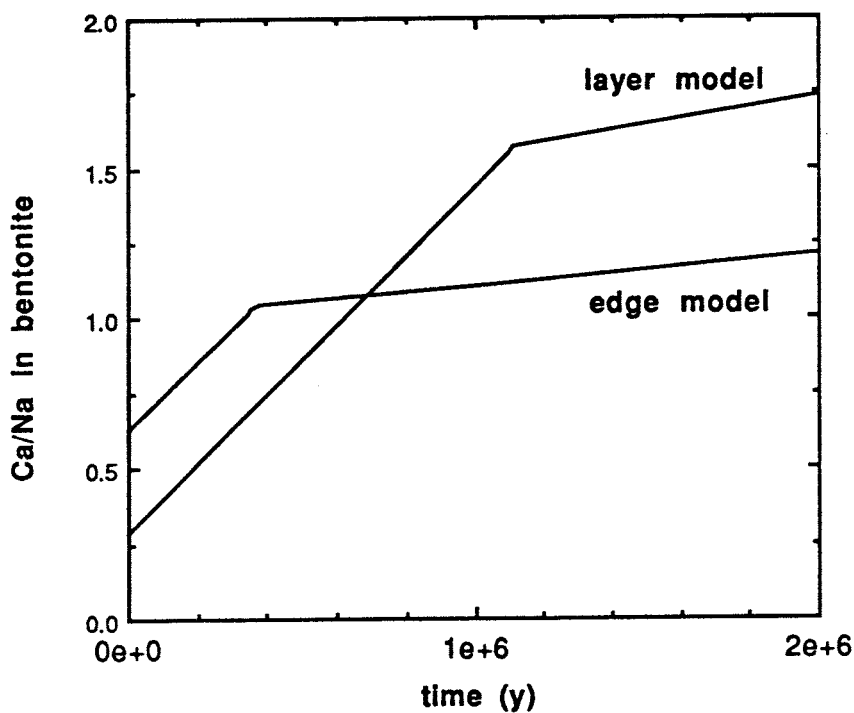


Figure 5: Variation of Ca/Na ratio in highly compacted bentonite over time (years) according to mixing tank model assuming a time of 13'800 years for one water exchange cycle (see text).

Figure 5 illustrates the transformation in bentonite as a function of time. In this presentation water exchange cycles are converted to the time scale, according to the estimation given in section 4.2.1. Thus, a significant increase of the Ca/Na ratio in bentonite is predicted by both ion exchange models over long time scales. We would like to emphasize, however, that a better es-

timation of timescales of the transformation process would require to include transport by ion diffusion into our model.

Our results indicate that Ca-bentonite is thermodynamically more stable than Na-bentonite in contact with such type of groundwater. Moreover, as Wanner (1986) has pointed out, geochemical data on natural systems, such as bentonite-containing aquifers, suggest the importance of combined calcite dissolution and ion exchange reactions in the clays.

4.3 *Open questions*

As discussed in the sections above, our long-term model predictions involve a number of simplifications with respect to the chemical processes occurring in the near field. In our view, the following key parameters affect the uncertainty of the predictions of bentonite chemistry.

Thermodynamic data: With regard to the ion exchange data, the effect of edge charge on ion exchange reactions, e.g., proton exchange, may be of importance under high pH conditions. Our preliminary and comparatively crude treatment of edge charge suggests a significant effect of the increased charge on proton release, thus inducing increased carbonate consumption. Thus, a more refined approach for the highly compacted bentonite system would allow a better assessment of the surface charge. In addition, the question of the possible formation of a carbonate solid solution, as mentioned in the last paragraph of section 2.1, cannot be answered on the basis of currently available data. This problem should be kept in mind when designing future studies.

Redox conditions: The characterization of bentonite impurities, other than those considered in this work, could yield further insight. Thus, the analysis of the redox couples in the iron and sulfur system would give information in terms of redox behavior, a critical parameter for understanding radionuclide mobility in the near field porewater.

Temperature dependence: Experimental data at higher temperature, reflecting more closely the repository conditions, are essential to determine the effect of temperature on ion exchange constants but also to estimate the temperature effects on mineral transformation within the clay fraction.

Mineral transformation: Apart from the transformation of Na-bentonite to a Ca-rich bentonite, other alteration mechanisms, such as illitization of the smectite fraction, may be of im-

portance at increased temperature. Such transformations are expected to alter the chemical and physical properties of the near field significantly (Pusch and Karnland, 1988) and therefore should be taken into consideration.

Transport properties: With regard to solute transport in the bentonite, different numerical approximations for the diffusion process could be inserted into the model by using appropriate boundary conditions. This would provide a critical test to the mixing tank assumption.

5 Summary and Conclusions

The focus of this work was to develop a model which provides a thermodynamic assessment of chemical reactions in the near field and allows predictions of the chemical behavior of highly compacted bentonite over long time periods. The basis for the thermodynamic assessment is the experimental information (Werme, 1992) on the interaction of Wyoming bentonite and water at high solid/water ratios. From the experimental results on solution composition and from previous analysis of the solid fraction, the following assumptions with regard to impurities in this type of bentonite are made: (1) calcite equilibrium, (2) quartz equilibrium, (3) the dissolution of sulfate and chloride is attributed to the presence of traces of CaSO_4 and NaCl . The main montmorillonite fraction is assumed to promote ion exchange reactions according to its cation exchange capacity (CEC). Furthermore, in view of the possible contribution of edge charge to ion exchange, we consider two different cases. In the first one, we consider ion exchange reactions to take place exclusively in the montmorillonite layer. In the second one, we include edge charge for the ion exchange process by applying previous experimental information reported by Fletcher and Sposito (1989). The combination of the treatment of impurities and ion exchange in montmorillonite provides the core of the thermodynamic model which is inserted into the computer code MIN_SURF.

MIN_SURF calculations indicate that the model predictions are in good agreement with experimental results of Werme (1992). This is true for both treatments of ion exchange used, although the inclusion of edge sites generally yields a slightly better agreement. In addition, the application of these two types of models to experimental conditions of lower solid/water ratios (Snellman, 1984) reveal good agreement between modelled and experimental results. This indicates the robustness of both types of models over a large range of composition.

We apply our thermodynamic model to conditions expected in the near field, i.e., highly compacted bentonite in equilibrium with groundwater. In view of the lack of experimental data, we neglect the influence of temperature. Contrary to results obtained from modelling bentonite/water equilibria described above, significant differences in water composition are predicted depending on the treatment of ion exchange. In the case of neglectance of edge charge, relatively high pH conditions and low amounts of calcite dissolution are predicted, whereas the opposite is predicted from the model which includes edge charge. This difference is due to the contribution of proton exchange reactions at edge sites, predicted by the edge model, leading to release of H^+ .

The evolution of chemical processes of highly compacted Na-bentonite with time is estimated under the assumption that the near field behaves like a mixing tank. In this concept bentonite porewater is completely exchanged by fresh groundwater during one water exchange cycle. Applying the concept of a mixing tank, our thermodynamic model is run for up to 180 water exchange cycles. The results of these calculations indicate a progressive change in bentonite composition with time leading to an enrichment of exchangeable Ca and to a simultaneous decrease in exchangeable Na in the bentonite. The transformation rate, however, strongly depends on the amount of $CaCO_3$ available in the bentonite. Once this carbonate pool is depleted, the conversion of Na- to Ca-bentonite proceeds at a much lower rate. Both types of ion exchange treatments show this overall trend. However, results obtained from the model which includes edge charge suggest that the Na-Ca transformation is less extensive over time.

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