



TECHNICAL REPORT 01-08

Porewater chemistry in compacted re-saturated MX-80 bentonite: Physico-chemical characterisation and geochemical modelling

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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

PREFACE

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

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ABSTRACT

Bentonites of various types are being investigated in many countries as backfill materials in high-level radioactive waste disposal concepts. Being able to understand the chemistry of the porewater in compacted bentonite, and the factors which influence it, is critical to the synthesis of sorption data bases and to predicting radionuclide solubilities, and hence to repository safety studies. However, quantification of the water chemistry in compacted bentonite is difficult because reliable samples for chemical analysis cannot be obtained even by squeezing at exceedingly high pressures.

In this report concepts are developed which are somewhat different from those used in previously published works on bentonite porewater. Considerations of the swelling properties of montmorillonite led to the proposition that there were, generally speaking, three types of water associated with re-saturated compacted bentonite. The water defined as the porewater is only a small fraction of the total. The porewater volume present in re-saturated bentonites having different initial dry densities was quantified using Cl^- "through diffusion" data.

Highly compacted bentonite is considered to function as an efficient semi-permeable membrane so that re-saturation involves predominantly the movement of water molecules and not solute molecules. This implies that the composition of the external saturating aqueous phase is a second order effect. Consequently Cl^- concentrations in the porewater could be calculated from the deduced porewater volume values and the measured Cl^- inventory.

The pH of the porewater of a compacted bentonite is an extremely important parameter because of its influence on radionuclide solubility and sorption. Arguments are presented in support of the thesis that the initial pH is fixed by the high buffering capacity afforded by the amphoteric $\equiv\text{SOH}$ sites. The pH of the porewater depends directly on the speciation of these sites i.e. the proportions of sites present as $\equiv\text{SOH}$, $\equiv\text{SOH}_2^+$ and $\equiv\text{SO}^-$. In the report it is explained how this speciation is determined by the preparation process in the "as received" powder.

As a consequence of the high cation exchange capacity of montmorillonite, the large mass of montmorillonite in relation to the small porewater volumes in a highly compacted re-saturated bentonite, the major ion composition in the porewater will be controlled by the montmorillonite and the other solid phases present and will be very strongly buffered.

The above considerations are used in conjunction with detailed physico-chemical characterisation studies on MX-80 (Appendix) to calculate initial porewater compositions in compacted bentonites.

For the MX-80 material specified, the porewaters calculated for initial dry densities between 1200 and 1600 kg m^{-3} had relatively high ionic strengths (0.3 to 0.33 M), similar cation concentrations and a pH equal to 8.0. The porewaters changed from being Na_2SO_4 rich at 1200 kg m^{-3} to a $\text{NaCl}/\text{Na}_2\text{SO}_4$ type water at 1600 kg m^{-3} .

ZUSAMMENFASSUNG

In vielen Ländern werden verschiedene Bentonite als Verfüllmaterial für Endlager hochaktiver radioaktiver Abfälle untersucht. Das Verständnis der Porenwasserchemie des kompaktierten Bentonits und die Kenntnis deren Einflussfaktoren sind sowohl für die Synthese von Sorptionsdatenbasen als auch zur Vorhersage der Radionuklidlöslichkeiten entscheidend und folglich auch für Sicherheitsstudien eines Endlagers. Die Quantifizierung der Wasserchemie in kompaktiertem Bentonit ist jedoch schwierig, da man selbst bei äusserst hohen Drücken keine verlässlichen Wasserproben für eine chemische Analyse erhält.

Im vorliegenden Bericht werden Konzepte vorgestellt, die sich von bereits veröffentlichten Arbeiten über Bentonit Porenwasser unterscheiden. Aufgrund des Quellvermögens von Montmorillonit geht man von 3 Arten verschiedener Wässer aus, die in wiederaufgesättigten kompaktierten Bentonit vorkommen können. Das als Porenwasser definierte Wasser macht dabei nur einen kleinen Anteil aus. Das Volumen des Porenwassers in wiederaufgesättigten Bentoniten mit unterschiedlichen Trockendichten, wurde mit Hilfe von Cl^- Diffusionsversuchen ("through diffusion") ermittelt.

Man betrachtet einen in hoher Masse kompaktierten Bentonit als eine wirksame semi-permeable Membran, so dass die Wiederauf sättigung vorwiegend über die Bewegung von Wassermolekülen und nicht über gelöste Moleküle stattfindet. Dies bedeutet, dass die Zusammensetzung der wässrigen Phase eine untergeordnete Rolle spielt. Folglich können Cl^- Konzentrationen im Porenwasser über das abgeleitete Porenwasservolumen und das Cl^- Inventar berechnet werden.

Der pH Wert des Porenwassers eines kompaktierten Bentonits übt einen entscheidenden Einfluss auf die Löslichkeit und Sorption von Radionukliden aus.

Im vorliegenden Bericht wird die Annahme diskutiert, dass der initiale pH Wert durch die hohe Pufferkapazität der amphoteren $\equiv\text{SOH}$ Gruppen bestimmt wird. Der pH Wert des Porenwassers hängt direkt mit der Speziation der amphoteren $\equiv\text{SOH}$ Gruppen zusammen, die sowohl als $\equiv\text{SOH}$, $\equiv\text{SOH}_2^+$ und $\equiv\text{SO}^-$ Gruppen vorliegen können. Im vorliegenden Bericht wird ferner darauf eingegangen, inwiefern der Aufbereitungsprozess die Speziation der amphoteren Gruppen im unbehandelten Bentonitmaterial beeinflusst.

Infolge der hohen Kationenaustauschkapazität des Montmorillonits und der kleinen Porenwasservolumina im Verhältnis zur grossen Masse eines kompaktierten und wiederaufgesättigten Bentonits wird deutlich, dass die chemische Zusammensetzung des Porenwassers vom Montmorillonit und anderen mineralischen Phasen bestimmt und gepuffert wird.

Die oben gemachten Überlegungen zur Berechnung der initiale Porenwasserzusammensetzungen in kompaktiertem Bentonit sind in Verbindung mit detaillierten physiko-chemischen Untersuchungen an MX-80 zu bewerten (siehe Anhang).

Für das untersuchte MX-80 Material wurden Porenwasserzusammensetzungen für verschiedene Trockendichten berechnet (1200 und 1600 kg m^{-3}). Sie zeigten eine relativ hohe Ionenstärke (0.3 bis 0.33 M), eine ähnlich hohe Kationenkonzentration und einen pH Wert von 8.0. Die Zusammensetzung der Porenwässer änderte sich von einem Na_2SO_4 -haltigen Wasser (bei einer Trockendichte von 1200 kg m^{-3}) auf ein $\text{NaCl}/\text{Na}_2\text{SO}_4$ -haltiges Wasser (bei 1600 kg m^{-3}).

RÉSUMÉ

Des bentonites de différents types sont étudiées dans plusieurs pays en tant que matériel de remplissage pour les futurs dépôts de déchets nucléaires de haute activité. Être capable de comprendre la chimie de l'eau des pores dans la bentonite compactée et les facteurs qui l'influencent est essentiel pour la création de bases de données de sorption et pour la prédiction de la solubilité des radionucléides et donc par voie de conséquence pour les études de sûreté des dépôts. Néanmoins, la connaissance quantitative de la chimie aqueuse dans la bentonite compactée est difficile car des échantillons fiables pour les analyses chimiques ne peuvent pas être obtenus même à des pressions excessivement hautes.

Dans ce rapport sont développés des concepts différents de ceux utilisés dans des travaux publiés antérieurement sur l'eau des pores de la bentonite. Des considérations sur la capacité à enfler de la montmorillonite ont mené à la proposition qu'il y avait trois types d'eau associées avec la bentonite compactée et re-saturée. L'eau définie comme l'eau des pores représente seulement une petite fraction du total. Le volume présent dans la bentonite re-saturée ayant des taux de dessèchement initiaux différents a été quantifié en utilisant des données de diffusion de Cl^- à travers le matériau.

Le fonctionnement de la bentonite hautement compactée est considérée comme étant similaire à celui d'une membrane semi-perméable efficace de telle manière qu'une re-saturation implique de façon prédominante le mouvement des molécules d'eau et non des molécules dissoutes. Ceci implique que la composition de la phase aqueuse externe saturée est un effet du second ordre. En conséquence, les concentrations de Cl^- dans les eaux de pore pourraient être calculées en utilisant les valeurs déduites du volume de l'eau de pore et l'inventaire mesuré de Cl^- .

Le pH d'une eau de pore de bentonite est un paramètre extrêmement important. Les arguments présentés supportent la thèse que le pH initial est fixé dans le matériau compact par la haute capacité de tampon fournie par les sites $\equiv\text{SOH}$ amphotères. Le pH de l'eau de pore dépend directement de l'état de ces sites, c'est à dire de la proportion de sites présents en tant que $\equiv\text{SOH}$, $\equiv\text{SOH}_2^+$ et $\equiv\text{SO}^-$. Dans le rapport, il est expliqué comment cet état est déterminé dans la poudre brute par le procédé de production.

Comme conséquence de la grande capacité d'échange de cation de la montmorillonite, de la grande masse de la montmorillonite et des petits volumes d'eau de pore dans la bentonite hautement compactée et re-saturée, la composition des ions majeurs dans l'eau de pore sera contrôlée par la montmorillonite et les autres phases solides présentes et sera très fortement tamponnée.

Les considérations ci-dessus sont utilisées en conjonction avec des études de caractérisation physico-chimiques sur MX-80 présentées en Appendice pour calculer la composition initiale des eaux de pore dans les bentonites compactées.

Pour le matériel MX-80 spécifié, les eaux de pore calculées pour des densités initiales sèches entre 1200 et 1600 kg m^{-3} ont des forces ioniques relativement élevées (0.3 à 0.33 M), des concentrations de cations similaires et un pH égal à 8.0. Les eaux de pore passent d'une eau riche en Na_2SO_4 à 1200 kg m^{-3} à une eau de type $\text{NaCl}/\text{Na}_2\text{SO}_4$ à 1600 kg m^{-3} .

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1 INTRODUCTION

In almost all countries with a high-level radioactive waste management programme, bentonite, in the form of dry compacted blocks and/or compacted granulates, will be used as a backfill material. During re-saturation with groundwater the bentonite swells and seals against the emplacement tunnels. The very low transmissivity to water movement and good sorption characteristics make compacted bentonite an extremely effective near-field diffusion barrier to the movement of radionuclides.

Despite many years of study, general agreement on the composition of the porewater in a re-saturated compacted bentonite has remained somewhat elusive. Particularly important in this context is the system pH because of its critical influence on the solubilities and sorption of many safety relevant elements. The reason for this lack of agreement is a relatively simple one. Direct water composition measurements are exceedingly difficult to perform. Many hundreds to thousands of bar are required to extract even small volumes of water from highly compacted bentonite samples re-saturated under confined conditions. In addition, such exceedingly high pressures may well modify the water chemistry. (See for example MUURINEN & LEHIKONEN, 1999.)

Consequently, the majority of proposals put forward for compacted bentonite porewater compositions have been based on data from batch or squeezing tests on bentonite powder or granules carried out at low solid-to-liquid (S:L) ratios compared with the compacted material, coupled with modelling studies. Over the past fifteen years or so, there have been a number of publications on this topic e.g. WANNER (1986a,b), WANNER et al. (1992), CURTI (1993), WIELAND et al. (1994), SNELLMAN (1994); OHE & TSUKOMOTO (1997), MUURINEN & LEHIKONEN (1997, 1999), BRUNO et al. (1999), PUSCH et al. (1999).

The procedures adopted in all of these studies are similar to those first proposed by Wanner and co-authors. Characteristics of the approach are that all of the porosity in the dry compacted state is considered to be occupied by the porewater, external groundwaters are equilibrated with the bentonite in some initially defined state ("mixing tank" approach), the P_{CO_2} is taken to be constant, or to have an initial value in a closed system, and the calculated porewater compositions (initial, and the temporal variations) are a function of the re-saturating external groundwater composition (WIELAND et al., 1994, BRUNO et al., 1999; CURTI & WERSIN, 2002).

As far as performance assessment studies for high-level waste repositories are concerned, the ability to give a chemically well founded porewater composition for compacted bentonite is essential. It is a pre-requisite for predicting near-field

solubilities, developing sorption data bases and also for assessing the influence of long term groundwater-bentonite interactions. Further, an understanding of the porewater chemistry, and the factors which influence it, might be a first step in explaining (apparent) differences between batch sorption values and those extracted from diffusion tests (e.g. MIYAHARA et al., 1991, OSCARSON et al., 1994, BRADBURY & BAEYENS, 2002).

A methodology based on physico-chemical characterisation and geochemical modelling, previously developed for determining porewater chemistries in tight low porosity/permeability argillaceous sedimentary rocks (BRADBURY & BAEYENS, 1998), has been applied to compacted bentonite. However, the results from the physico-chemical characterisation procedure, important though they are for calculating a bentonite porewater, are not the main subject here. Consequently, a description of the experimental procedures, data and the derivation of model parameters are documented separately in the Appendix. The main focus of this work is on how to apply these data in the special case of a highly compacted bentonite re-saturated under confined conditions. Before this is addressed some characteristics of compacted bentonite relevant to the calculations need to be considered.

Note that in order to avoid unnecessary repetition in the following text, "bentonite" will refer to the compacted form, unless otherwise stated, and when porewaters are discussed in connection with bentonite it is assumed that re-saturation has occurred under constant volume conditions.

2 PRELIMINARY CONSIDERATIONS

2.1 Montmorillonite

Bentonites contain large quantities of montmorillonite (65 to 90 wt.%) and consequently its properties are largely determined by this clay mineral (see for example GRAUER, 1986).

The generally accepted structure of montmorillonite is a unit made of an alumina octahedral sheet sandwiched between two silica tetrahedral sheets, Figure 1. The tetrahedral-octahedral-tetrahedral (TOT) layers have dimensions in the a and b directions of the order of 1000 nm and combine together, one above the another, in the c direction to form platelets. The thickness of these platelets are only a few individual montmorillonite layers. Larger clay particles are formed from stacks of these platelets (GRIM, 1953) in which the number of platelets in each stack varies from 3-5 in Na-montmorillonite to 10-20 (and more) for a Ca-montmorillonite (PUSCH et al., 1990).

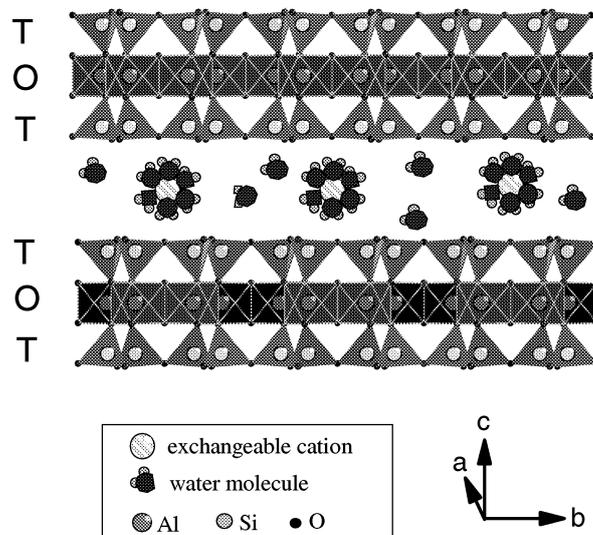


Figure 1: Schematic representation of the montmorillonite structure.

Water, and other polar molecules can enter between the unit layers causing expansion in the c direction (interlayer swelling). The c-axis lattice parameter is ~ 0.96 nm in the absence of any polar molecules in the interlayer. The interlayers in montmorillonite tend to take up water "layer-wise" and each monolayer of water increases the c-spacing by ~ 0.25 nm (KEREN & SHAINBERG, 1975; NEWMAN, 1987). In bentonite there are between 1 and 4 monolayers of

H₂O in the interlayer space after re-saturation, depending on the initial dry density.

The total surface area of montmorillonites is very large, $\sim 7.5 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$, and most of this area lies in the interlayer region. For comparison, the external specific surface area is only $\sim 3 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$.

Substitution of trivalent Al for tetravalent Si and divalent cations (e.g. Mg, Fe) for trivalent Al in the montmorillonite structure leads to a permanent negative lattice charge which is compensated by the preferential sorption of cations on the layer surfaces. In aqueous systems these cations can exchange with those in solution, see section 2.4.1.

In addition to the cation exchange sites, another site type exists on the edges of the montmorillonite structural units. These "edge" sites are amphoteric, see section 2.4.2, and, as will be shown later, the properties of both site types play an important role in determining the porewater chemistry in bentonite.

2.2 Swelling

One of the most widely studied properties of bentonite is its tendency to swell in contact with a source of water. When the bentonite is in a dry, highly compacted form, high swelling pressures result if re-saturation occurs under confining conditions. Basically, there are two processes which lead to the generation of swelling pressures.

The first, which can produce pressures of thousands of bar, is associated with the re-hydration of the interlayer cations and is the main mechanism at close separation of the montmorillonite unit layers. In this region water appears to be taken up in successive monolayers. After about 3-4 monolayers of water have entered between the unit montmorillonite layers i.e. at interlayer separation distances $>1 \text{ nm}$, hydration effects becomes less important and electrical double layer repulsion becomes the major swelling mechanism. Here the swelling pressures may be several tens of bar. (See for example VAN OLPHEN, 1963).

As an example of the consequences of swelling, consider a bentonite with a dry density of 1600 kg m^{-3} , a moisture content of $\sim 10 \text{ wt.}\%$ and a porosity of $\sim 35 \text{ vol.}\%$ (interpolated from the data in Table 3, Chapter 3). This macroscopic pore volume is essentially full of air since most of moisture content is in the interlayer region in the hydration shells associated with the cations and corresponds to a layer of water between one and two molecules thick. If this system re-saturates under constant volume conditions, a simple calculation, based on the increase in the interlayer distance, indicates that the swelling resulting from the uptake of

two to three additional water layers in the interlayer region is sufficient to fill the available porosity. Thus, with an increase of water content from the initial value of ~10 wt.% to ~30 wt.%, the swelling fills virtually all of the initial air filled macro porosity and converts it into interlayer space.

The above processes are reflected in swelling pressure versus dry density measurements such as those illustrated in Figure 2. Up to an initial dry density of ~1600 kg m⁻³ the swelling due to the re-hydration of the interlayer cations can be accommodated essentially in the initial pore volume. The swelling pressures arise predominantly from electrical double layer repulsion and are correspondingly relatively weak. For initial dry densities >1600 kg m⁻³, the available macro porosities can no longer take up all of the swelling caused by the re-hydration of the interlayer cations and hence the swelling pressures generated rise rapidly with increasing dry density. The swelling pressure in this region is predominantly due to interlayer cation re-hydration.

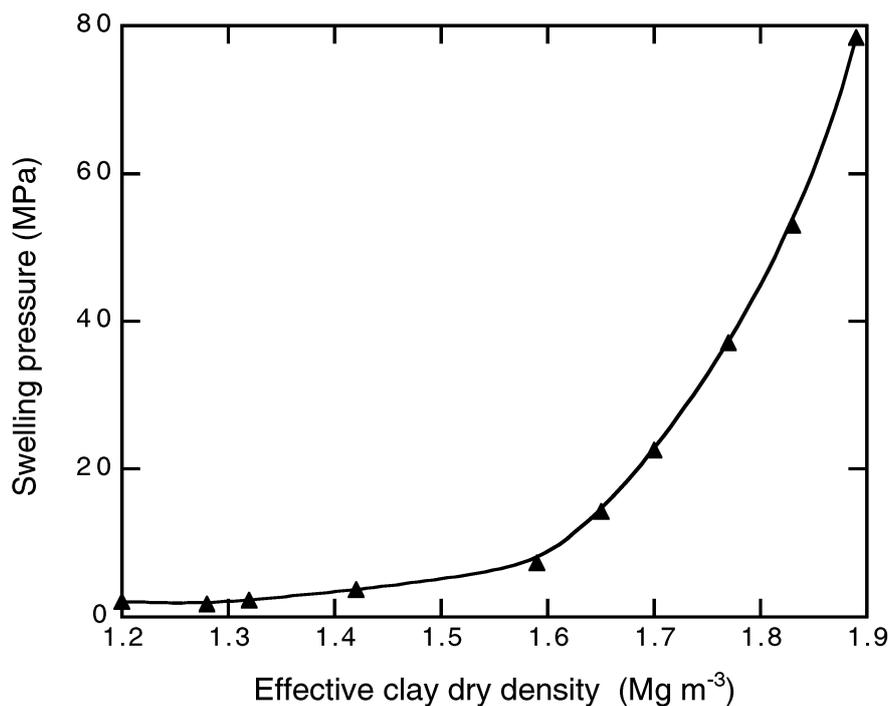


Figure 2: Swelling pressure of MX-80 bentonite as a function of dry density. (Taken from PUSCH, 1980).

2.3 Bentonite as a semi permeable membrane

The possible influences of the composition of the re-saturating fluid is an important consideration in the development of procedures for defining a porewater for bentonite. Bentonite may be used as a backfill material in host

rock formations such as granites and argillaceous rocks, where groundwater chemistries are significantly different.

One of the main premises in the approach proposed here is that highly compacted bentonite can function as an efficient semi-permeable membrane (see Chapter 10 in HORSEMAN et al., 1996). This implies that the re-saturation of bentonite involves predominantly the movement of water molecules and not solute molecules. Thus, to a first approximation, the composition of the external saturating aqueous phase is a second order effect which will have little influence on the initial bentonite porewater composition. Also, as discussed further in section 2.4, the very small porewater volumes and the large masses of montmorillonite and other minerals involved, imply that the bentonite will condition the porewater.

Figure 3 is reproduced from the work of KARNLAND (1997, Figure 2-7) and shows the swelling pressure plotted against the initial MX-80 dry density as a function of the composition of the re-saturating solution. If the external fluid has a significant influence on the porewater chemistry, then a corresponding effect on the swelling would be expected. (The modelling work of KARNLAND (1997) has assumed this to be the case.) However, if bentonite is functioning as a semi-permeable membrane, virtually no influence of re-saturating fluid composition would be expected.

The data plotted in Figure 3 show that the effect of solutions containing up to 3.5 wt.% NaCl on the swelling pressure is certainly not large. Indeed, most of the measured values fall mainly within the scatter band of the measurements made using pure water as the re-saturating fluid.

DIXON (2000), recently reviewed the role of salinity on the development of swelling pressure in bentonite buffer and backfill materials. He concluded that provided the initial dry densities were greater than 900 kg m^{-3} , the swelling pressures developed are unaffected for groundwater salinities up to $\sim 75 \text{ g L}^{-1}$. Even brines appear to have little or no influence for initial dry densities $>1500 \text{ kg m}^{-3}$.

In contrast to the interpretation of KARNLAND (1997), the above results could be taken as being indicative of bentonite behaving as a semi-permeable membrane during re-saturation and that the effectiveness of the membrane is a function of the initial density. At low dry densities ($< 900 \text{ kg m}^{-3}$), where the membrane efficiency is much less than 100 %, the external fluid composition may, above a certain concentration, have an influence. However, at high densities and membrane efficiencies approaching 100 %, the re-saturating fluid composition plays little or no role.

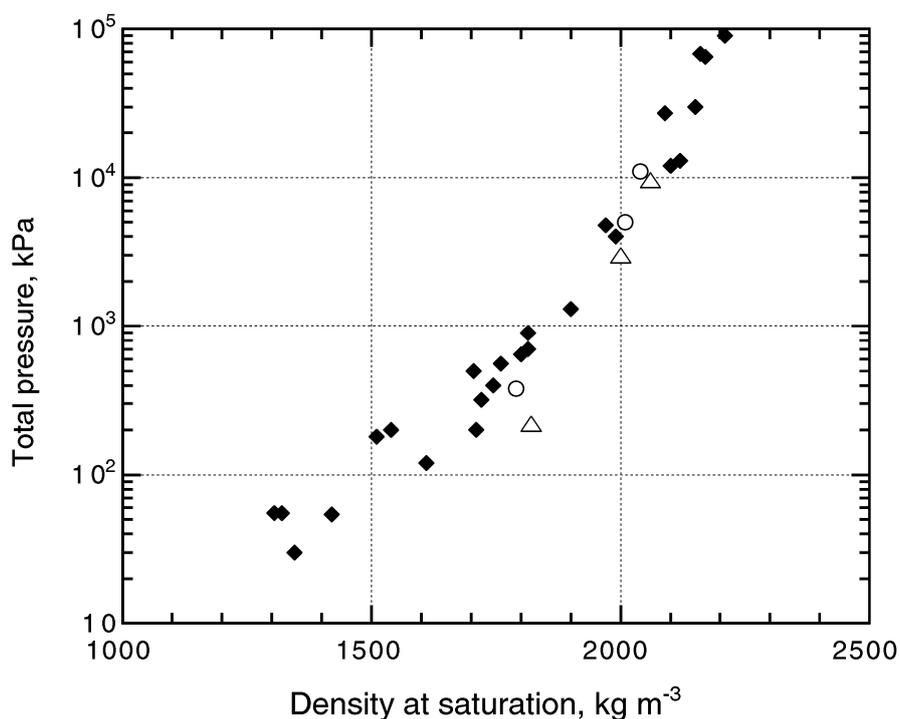


Figure 3: Swelling pressure versus dry density as a function of re-saturating solutions (◆) pure water; (○) 0.5 % NaCl solution; (△) 3.5 % NaCl solution. (Taken from KARNLAND, 1997).

2.4 "Ion pool" in bentonite

2.4.1 Exchangeable cations

The surfaces of montmorillonite clay platelets carry a permanent negative charge arising from isomorphous substitution of lattice cations by cations of a lower valency. Charge neutrality is maintained by the presence of an excess of cations in solution held electrostatically in close proximity around the outside of the Si-Al-Si clay units. Since the areas within the interlayer space are predominant, the compensating cations reside mainly there. The electrostatically bound cations, which constitute the electrical double layer, can undergo stoichiometric exchange with the cations in solution (GRIM 1953, VAN OLPHEN, 1963). The total permanent negative charge of a clay mineral is defined as the cation exchange capacity (CEC). The exchange capacities of montmorillonites are high, $\sim 1 \text{ Eq. kg}^{-1}$, and since the MX-80 bentonite contains $\sim 75 \text{ wt.}\%$ montmorillonite, this implies that its exchange capacity is also significant.

In bentonite there are large masses of montmorillonite and only small volumes of porewater (see section 2.2 and Chapter 3) and hence the ion capacities of

the solids are massively greater than those in the aqueous phase. The consequence of this is that montmorillonite and the other solid phases, through the cation loadings on the clay and solubility considerations respectively, will determine the composition of the porewater. In addition, the high exchange capacity of the montmorillonite component acts as a powerful buffer for the composition of the porewater.

2.4.2 Amphoteric surface edge sites

There is a second category of reactive sites associated with montmorillonite which are perceived as being surface hydroxyl groups ($\equiv\text{SOH}$) situated along the edges of the clay platelets, "edge" or "broken bond" sites. (See for example BOLT & VAN RIEMSDIJK, 1987) These sites have a capacity of $\sim 10\%$ of the CEC and can protonate and deprotonate so that the concentrations of neutral, protonated and deprotonated edge sites ($\equiv\text{SOH}$, $\equiv\text{SOH}_2^+$, $\equiv\text{SO}^-$ respectively) change as a function of pH as shown for example in Figure 4. Using a similar argument to the one given above for the cation exchange sites, the hydroxyl groups can potentially function as a powerful pH buffer.

For completeness, $\equiv\text{SOH}$ site types, capacities and protolysis constants for montmorillonite are given in Table 1. These values were obtained from the analyses of batch titration experiments (BAEYENS & BRADBURY, 1997, BRADBURY & BAEYENS, 1997) i.e. on dispersed systems. In compacted bentonite the spacings between the edges of clay stacks may become very small resulting in the overlap of electrical double layers ("double layer water" see Chapter 3). The implications of this for the protolysis behaviour of the $\equiv\text{SOH}$ edge sites is not clear, but could influence their amphoteric characteristics.

Table 1: Summary of site types, site capacities, and protolysis constants for conditioned Na-montmorillonite. ($\equiv S^{W1}OH$, $\equiv S^{W2}OH$ denote the two weak site types which can protonate and de-protonate in the model of BRADBURY & BAEYENS, 1997).

Site types:	Site capacities:	
$\equiv S^{W1}OH$	$4.0 \times 10^{-2} \text{ mol kg}^{-1}$	
$\equiv S^{W2}OH$	$4.0 \times 10^{-2} \text{ mol kg}^{-1}$	
Surface complexation reaction	Mass action equation	$\log K_{\text{int}}$
$\equiv S^{W1}OH + H^+ \leftrightarrow \equiv S^{W1}OH_2^+$	$K_{\text{int}(+)} = \frac{[\equiv S^{W1}OH_2^+]}{[\equiv S^{W1}OH] \cdot (H^+)}$	4.5
$\equiv S^{W1}OH \leftrightarrow \equiv S^{W1}O^- + H^+$	$K_{\text{int}(-)} = \frac{[\equiv S^{W1}O^-] \cdot (H^+)}{[\equiv S^{W1}OH]}$	-7.9
$\equiv S^{W2}OH + H^+ \leftrightarrow \equiv S^{W2}OH_2^+$	$K_{\text{int}(+)} = \frac{[\equiv S^{W2}OH_2^+]}{[\equiv S^{W2}OH] \cdot (H^+)}$	6.0
$\equiv S^{W2}OH \leftrightarrow \equiv S^{W2}O^- + H^+$	$K_{\text{int}(-)} = \frac{[\equiv S^{W2}O^-] \cdot (H^+)}{[\equiv S^{W2}OH]}$	-10.5

Note: [] are concentrations; () are activities

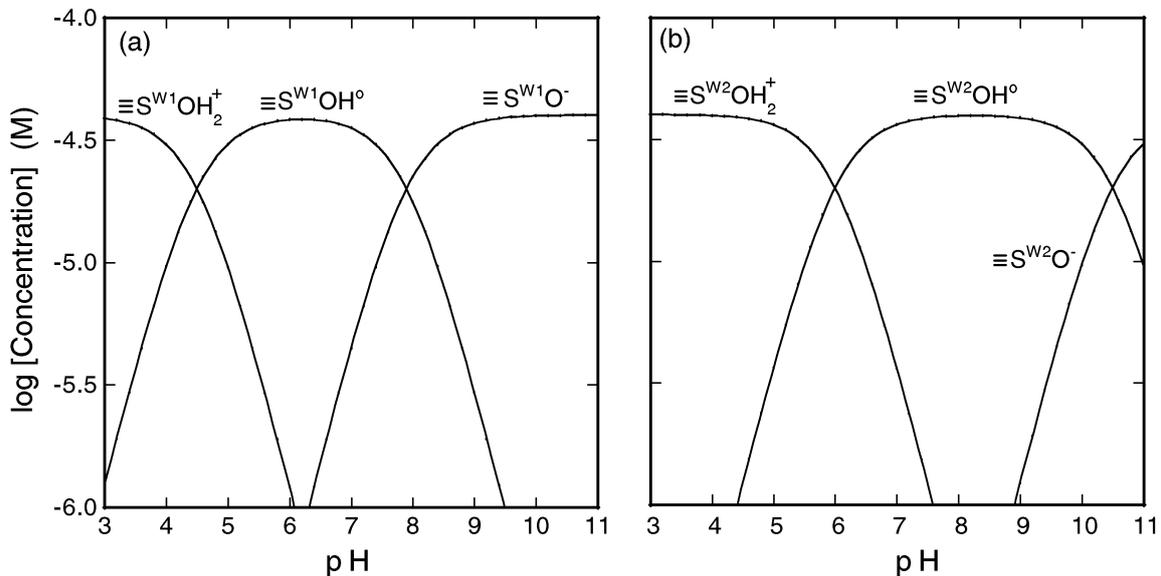


Figure 4: Calculated surface speciation of the two protolysis sites for conditioned Na-montmorillonite as a function of pH in 0.1 M NaClO₄. S:L = 1 g L⁻¹. (a) $\equiv S^{W1}OH$, (b) $\equiv S^{W2}OH$ (BRADBURY & BAEYENS, 1997).

3 "WATER" IN BENTONITE AND POROSITIES

The "nature" of the water in bentonite and how it is distributed throughout the microstructure, and indeed, what the microstructure is, have been the subject of many investigations and much speculation over the last few decades. Although the different views on these topics vary in detail, there is a broad consensus that, in general, three types of water can be distinguished.

When bentonite (dry density $> 1200 \text{ kg m}^{-3}$) re-saturates under constant volume conditions, most of the water which is taken up resides in the interlayer space between the individual TOT montmorillonite units, "interlayer water". Depending on the initial density, and the nature of the exchangeable cations, the interlayer water is probably only a few monolayers thick and, because of its more structured nature, probably has different properties from free water (see for example NEWMAN, 1987). The rest of the re-saturating water volume can be described as "external water" and this can be viewed as being of two types. Part will be in the electrical double layers associated with the external surfaces of the clay stacks, "double layer water". Where the stack surfaces are close together the double layers will overlap and be truncated. In such cases the inter-stack external surface spacings will be of the same order as that between the TOT layers. The remaining fraction of water can be regarded as "free water". The free water may exist as interconnected thin films on the outside of the clay stacks, when the stack separation is large enough, and also as films surrounding the other mineral grains in the bentonite. (In the reference MX-80 bentonite, $>25 \text{ wt.}\%$ consists of quartz and feldspar, Table A1).

A schematic picture of water in bentonite is given in Figure 5. The term bentonite porewater is used in this report to refer to the free water present as interconnected thin films on the outside of some of the montmorillonite stacks and other mineral grains. Although it is clear from theoretical considerations that the volumes of free water are only a small fraction of the total volumes of water needed to re-saturate bentonites, see for example Figure 10 in PUSCH et al. (1990), no direct experimental data exist as to the values of this free water volume as a function of the initial bentonite dry density.

In the simple schematic representation shown in Figure 1, the interlayer spaces in bentonite are very narrow, probably $< 1 \text{ nm}$ (BOLT, 1979). Further, in regions where the individual montmorillonite stacks are in close proximity, strong double layer overlap will occur. Under these circumstances it is reasonable to assume that anion exclusion effects will be so large that it is highly unlikely that anions can move through these regions (BOLT & DE HAAN, 1982) which contain virtually all of the water taken up by the bentonite upon re-saturation. However, Cl^- anions do move relatively readily through compacted bentonite since diffusion

coefficients have been measured in through-diffusion tests (see for example MUURINEN et al., 1987).

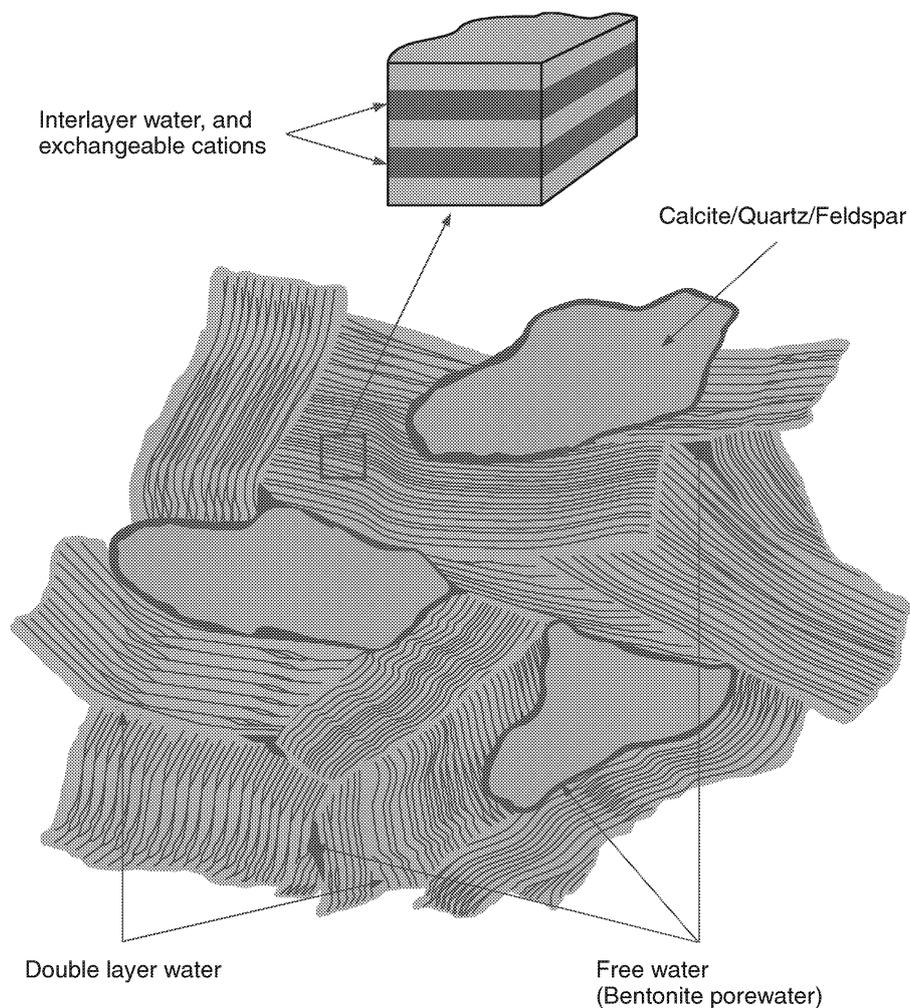


Figure 5: Schematic representation of “interlayer water”, “double layer water” and “free water” in compacted bentonite.

If the chloride anions cannot move through the interlayer and overlapping double layers regions, then it is reasonable to propose that the interconnected thin films of water on the outside of the clay stacks and the other mineral grains, see Figure 5, must be providing the diffusion pathways. Therefore, the hypothesis put forward is that the pore volume associated with the transport of Cl^- (and other anions) is the "free-water volume" and that this "free water" is the porewater in a bentonite. As an example, the through-diffusion results for Cl^- reported by MUURINEN et al. (1987) are considered in Table 2, and these data

were used to produce estimates for the porewater volumes per kg of bentonite as a function of dry density.

From Table 2 it can be readily appreciated that the porewater volume in bentonite is only a small fraction of the dry compacted pore volume and that its value decreases with increasing compaction. This implies that the porewater chemistry in a compacted bentonite will depend on the initial dry density.

Table 2: Data from $^{36}\text{Cl}^-$ through-diffusion measurements in compacted MX-80 bentonite (MUURINEN et al., 1987), and estimates for the porewater volumes per kg as a function of dry density.

dry density (kg m^{-3})	effective diffusion coefficient, D_e , of Cl^- ($\text{m}^2 \text{s}^{-1}$)	Cl^- through-diffusion porosity (vol. fraction)	bentonite porewater volume (L kg^{-1})
1200	1.1×10^{-11}	0.06	0.050
1500	2.8×10^{-12}	0.03	0.020
1800	2.0×10^{-13}	0.004	0.0022
2100	8.5×10^{-14}	0.003	0.0014

4 POREWATER CHEMISTRY CALCULATIONS IN MX-80 BENTONITE

The source material for compacted bentonite is a powder which has undergone an industrial scale preparation procedure. The physico-chemical properties of the powdered material will not change upon compactation and therefore will be the same in both forms. The physico-chemical characteristics of the powder can thus be directly applied to the compacted bentonite.

In some previous work a physico-chemical characterisation technique, coupled with geochemical modelling, was developed to enable the porewater composition in very tight clay rich argillaceous rocks to be calculated (BRADBURY & BAEYENS, 1998). Briefly, the technique is based on aqueous extractions and major cation displacement experiments which yield cation occupancies on the clay minerals and a consistent set of selectivity coefficients. The saturated solid phases present and inventories together with the above, constitute the basic data set required to calculate a porewater chemistry. The characterisation procedure was applied here to the MX-80 bentonite powder and the results are described in detail in the Appendix.

Although these data are extensive, they are still not sufficient to fully define the bentonite – water system. Two further quantities, in addition to those already available, need to be fixed. For bentonite systems it turns out that the two most readily quantifiable ones are the pH (P_{CO_2}) and the chloride concentration.

In the following, the moist bentonite powder is first considered so that the state of the amphoteric $\equiv\text{SOH}$ sites can be defined. It is important to know the initial state of these sites since they determine the pH of the porewater in the closed compacted bentonite system as will be described later.

4.1 MX-80 Powder

In almost all bentonite porewater calculations reported in the open literature, the pH is derived from some sort of assumption regarding the system P_{CO_2} . Equilibrium with air P_{CO_2} , $10^{-3.5}$ bar (e.g. WANNER, 1986a,b), or a closed system (PUSCH et al. 1999; BRUNO et al. 1999) are two of the most common situations considered. The amphoteric $\equiv\text{SOH}$ edge sites are also often included. However, for an open bentonite system at a fixed P_{CO_2} and calcite saturation such sites have no influence on the pH. In a closed system, however, they play a decisive role in determining the pH. However, the pH calculated depends sensitively on the initial state assumed for these sites i.e. the proportions of sites present as $\equiv\text{SOH}$, $\equiv\text{SOH}_2^+$, and $\equiv\text{SO}^-$. The latter point is hardly ever discussed, let alone any justification given regarding the initial state assumed.

The approach adopted here first considers the industrial process used to produce the "as received" bentonite powder. Once the raw bentonite is removed from the deposit and throughout the time it is stored on the surface, it is exposed to atmospheric conditions (rain, air). At some point, the raw wetted bentonite is processed further on a production line in which the clay sequentially passes through slicers, roll crushers, rotary dryers, mill cyclones and sieves before being stored again, in powdered form ($<100\ \mu\text{m}$), prior to transport. The water content of the powdered bentonite at this stage has been reduced to somewhere between 8 and 12 wt.%. The process is illustrated in Figure 6.

The preparation procedure has conditioned the powdered bentonite to be in equilibrium with air. This has a number of implications. First, any readily oxidisable minerals e.g. finely divided pyrite, will have been oxidised. Secondly, the cation occupancy data presented in the Appendix are those associated with this atmosphere conditioned powdered bentonite. Thirdly, and probably most significant of all, the pH in the moist bentonite powder will be that determined by carbonate/sulphate mineral equilibration at air P_{CO_2} i.e. $10^{-3.5}$ bar. The consequence is that the amphoteric hydroxy groups at the edges of montmorillonite platelets will have been conditioned to a state reflecting this equilibrium. Further, there is no reason to believe that any subsequent compaction of the powdered bentonite should alter the protolysis state of these sites.

The hypothesis put forward here is that the bentonite porewater will be buffered to a pH reflecting the protonation/deprotonation state of the $\equiv\text{SOH}$ sites since the masses of montmorillonite are large and the volumes of free water small, as discussed in section 2.4 and Chapter 3.

However, in order to calculate this pH for a solution in equilibrium with the air equilibrated bentonite powder, a Cl^- concentration needs to be specified. Only the Cl^- inventory of $1.35 \times 10^{-3}\ \text{mol kg}^{-1}$ is known, Table A2. The question then becomes whether or not a good, chemically plausible estimate of the Cl^- concentration can be made.

If a Cl^- concentration is assumed, then a unique pH corresponding to each Cl^- concentration can be calculated for the solution/air equilibrated bentonite powder system. Such calculations were carried out using the geochemical code MINSORB (BRADBURY & BAEYENS, 1997) together with the Nagra/PSI thermodynamic data base compilations from PEARSON & BERNER (1991) and PEARSON et al. (1992).

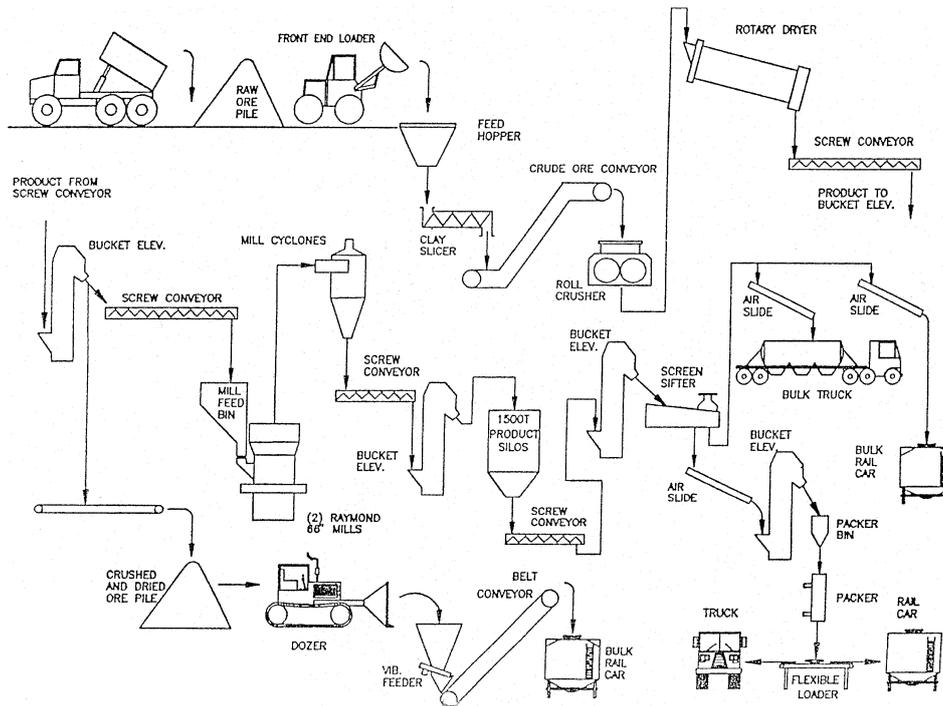


Figure 6: Schematic diagramme of the processing procedures used to produce the "as received" MX-80 bentonite powder.

The volumes of "free water" per kg of bentonite required to produce the Cl^- concentrations used in the calculations for a Cl^- inventory of $1.35 \times 10^{-3} \text{ mol kg}^{-1}$ are given in Table 3.

Table 3: pH values calculated at different solid to "free water" volume ratios for MX-80 powder with a Cl^- inventory of $1.35 \times 10^{-3} \text{ mol kg}^{-1}$. ($\text{PCO}_2 = 10^{-3.5} \text{ bar}$)

"free water" vol./bentonite ratio (L kg^{-1})	Cl^- concentration (M)	calculated pH
0.001	1.35	7.27
0.008	1.69×10^{-1}	7.96
0.016	8.44×10^{-2}	8.03
0.03	4.50×10^{-2}	8.05
0.05	2.70×10^{-2}	8.06
0.1	1.35×10^{-2}	8.08

For free water contents of the bentonite powder varying from 10^{-1} L kg^{-1} to 10^{-3} L kg^{-1} , the pH range covered is 8.1 to 7.3 respectively. In the following an attempt is made to bound the free water volume in an MX-80 bentonite powder.

Normally, the as received bentonite powder has a total water content of ~ 10 wt.% i.e. 10^{-1} L kg^{-1} . If all of this water were "free water" then this would correspond to a system pH of ~ 8.1 , see Table 3. But it is known that this water is predominantly in the interlayer region and that the interlayers take up water approximately "monolayer-wise", see Figure 7. For the MX-80 bentonite, with a total surface area of $\sim 562 \times 10^3$ m 2 kg^{-1} (Table A2), a monolayer of water in the interlayer region corresponds to $\sim 7 \times 10^{-2}$ L kg^{-1} so that a maximum of $\sim 3 \times 10^{-2}$ L kg^{-1} can be considered as "free water". The Cl^- concentration corresponding to this would be 4.5×10^{-2} M and the calculated pH = 8.05.

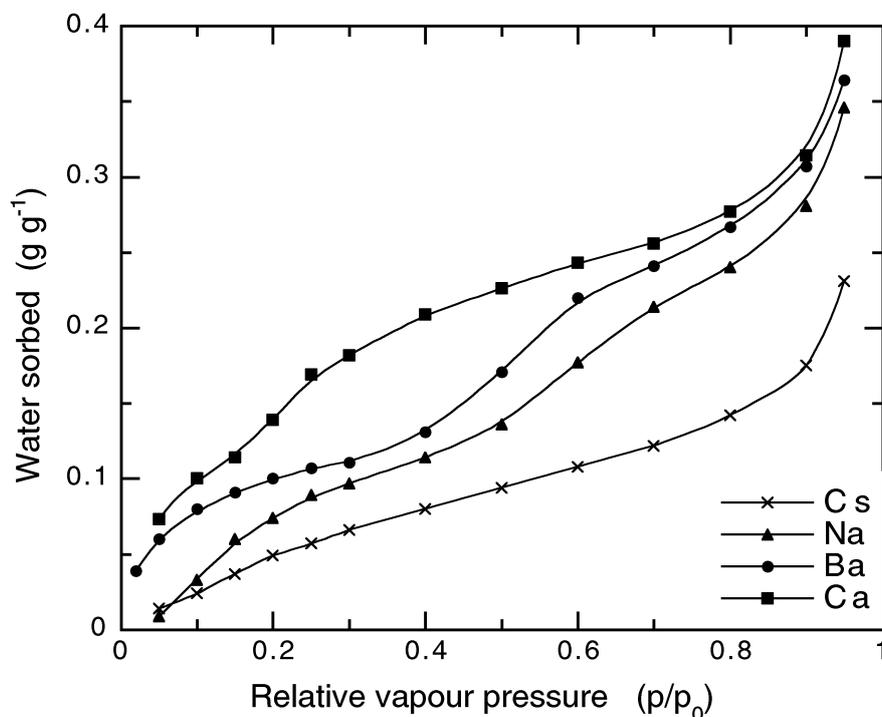


Figure 7: Up-take of water "monolayer-wise" on Cs-, Na-, Ba- and Ca-montmorillonites. (Taken from NEWMAN, 1987.)

As far as this geochemical modelling approach is concerned, the absolute limiting case is a monolayer of free water over the external surfaces. At any lower coverage conventional chemical considerations are likely to break down, and the connection between water chemistry and cation occupancies and the protolysis of the edge sites (central to the approach proposed) is lost. Thus, if the external specific surface area of MX-80 powder is taken to be $\sim 31 \times 10^3$ m 2 kg^{-1} , Table A3, a monolayer of water coverage corresponds to a

volume of $7.8 \times 10^{-3} \text{ L kg}^{-1}$, which yields a Cl^- concentration of $\sim 0.17 \text{ M}$ and a calculated pH of 7.96, Table 3.

Thus, in the range from an external monolayer of free water to a total water content of 10 wt.%, the powdered bentonite/equilibrium solution system pH only varies between 8.05 and 7.96. On this basis a pH of 8 is selected. The state of the $\equiv\text{SOH}$ sites in the powdered material will correspond to this pH.

4.2 Calculated initial porewater compositions in compacted bentonite as a function of the dry density

The initial cation loadings (Table A8) and the state of the $\equiv\text{SOH}$ sites on the MX-80 powder in an open system in equilibrium with air are given in Table 4.

Table 4: Initial cation loadings and state of the amphoteric $\equiv\text{SOH}$ sites on MX-80 bentonite powder in equilibrium with air.

Exchangeable cations and $\equiv\text{SOH}$ sites	Concentration (mol kg^{-1})
Na-mont.	6.68×10^{-1}
K-mont.	1.3×10^{-2}
Mg-mont.	2.0×10^{-2}
Ca-mont.	3.3×10^{-2}
$\equiv\text{S}^{\text{W1}}\text{OH}$	1.3×10^{-2}
$\equiv\text{S}^{\text{W1}}\text{OH}_2^+$	4.2×10^{-6}
$\equiv\text{S}^{\text{W1}}\text{O}^-$	1.7×10^{-2}
$\equiv\text{S}^{\text{W2}}\text{OH}$	3.0×10^{-2}
$\equiv\text{S}^{\text{W2}}\text{OH}_2^+$	9.4×10^{-5}
$\equiv\text{S}^{\text{W2}}\text{O}^-$	3.0×10^{-4}

Note: The charge on the $\equiv\text{SOH}_2^+$ and $\equiv\text{SO}^-$ sites are compensated by outer sphere complexes which have not been included in the modelling.

In the compacted system the loadings and condition of the $\equiv\text{SOH}$ sites are taken to be the same as in the as received powder. However, the compacted system is treated as being closed, which is a reasonable assumption for the calculation of the initial porewater composition. The implication is then that the solid phase will determine the chemistry of the porewater because of the very high solid to liquid ratio and the absence of air.

A mass balance approach to modelling the porewater chemistry in compacted bentonite was adopted. Such an approach automatically takes into account the buffering effects of the exchangeable cations and the amphoteric $\equiv\text{SOH}$ sites. (Neither the pH nor the P_{CO_2} are fixed in the calculations.) From the values given in Table 4, the mass balance inventories can readily be calculated at any chosen initial dry density.

In the calculations it is assumed that there is saturation with respect to calcite, gypsum, celestite, fluorite and quartz. The chloride concentration is fixed over the Cl^- inventory, section A 2.2.2, and the free water volume at any given dry density, Table 2. The concentrations of K, Mg and Ca are determined over the cation exchange equations given in the Appendix, section A 2.4.1.

A further constraint on the system is the mineral inventories e.g. calcite and gypsum, Tables A1 and A2. Clearly, the results from the calculations must be checked to ensure that the quantity of any mineral phase dissolved is less than the quantity originally present.

Definition of the system in the above manner allows unique porewater chemistries to be calculated at different initial dry densities using any appropriate speciation code and thermodynamic data base.

Table 5 summarises the calculated compositions of MX-80 porewaters as a function of the initial dry density. In terms of ionic strength (I.S.) and cation concentrations, the porewaters calculated for dry densities from 1200 to 1600 kg m^{-3} are very similar. However, the porewater composition changes from a Na_2SO_4 water at 1200 kg m^{-3} to a $\text{NaCl}/\text{Na}_2\text{SO}_4$ water at 1600 kg m^{-3} .

Table 5: Compacted MX-80 porewater compositions calculated for a closed system as a function of the initial dry compacted density.

Dry density (kg m ⁻³)	1200	1300	1400	1500	1600
log P _{CO₂} (bar)	-3.38	-3.39	-3.41	-3.43	-3.48
pH	8.0	8.0	8.0	8.0	8.0
I.S. (M)	0.295	0.300	0.306	0.314	0.327
<u>Concentration (M)</u>					
Na	2.20 x 10 ⁻¹	2.26 x 10 ⁻¹	2.33 x 10 ⁻¹	2.43 x 10 ⁻¹	2.61 x 10 ⁻¹
K	1.13 x 10 ⁻³	1.15 x 10 ⁻³	1.19 x 10 ⁻³	1.23 x 10 ⁻³	1.32 x 10 ⁻³
Mg	6.12 x 10 ⁻³	6.37 x 10 ⁻³	6.68 x 10 ⁻³	7.06 x 10 ⁻³	7.69 x 10 ⁻³
Ca	9.01 x 10 ⁻³	9.07 x 10 ⁻³	9.21 x 10 ⁻³	9.47 x 10 ⁻³	1.01 x 10 ⁻²
Sr	7.90 x 10 ⁻⁵	7.96 x 10 ⁻⁵	8.08 x 10 ⁻⁵	8.31 x 10 ⁻⁵	8.87 x 10 ⁻⁵
Cl	2.70 x 10 ⁻²	3.46 x 10 ⁻²	4.74 x 10 ⁻²	6.75 x 10 ⁻²	1.08 x 10 ⁻¹
SO ₄	1.12 x 10 ⁻¹	1.11 x 10 ⁻¹	1.09 x 10 ⁻¹	1.04 x 10 ⁻¹	9.45 x 10 ⁻²
C _{inorg.}	9.66 x 10 ⁻⁴	9.54 x 10 ⁻⁴	9.25 x 10 ⁻⁴	8.80 x 10 ⁻⁴	7.79 x 10 ⁻⁴
F	2.27 x 10 ⁻⁴	2.26 x 10 ⁻⁴	2.24 x 10 ⁻⁴	2.19 x 10 ⁻⁴	2.08 x 10 ⁻⁴
Si	1.83 x 10 ⁻⁴				

5 SUMMARY

The results of this study showed that there are a number of important factors which have an influence on the porewater chemistry in compacted bentonite: cation loadings on the montmorillonite component, chloride inventory, solubility limiting phases and the air conditioning of the source powder (fixing the state of the amphoteric $\equiv\text{SOH}$ sites).

Consideration of the swelling behaviour of compacted bentonite led to a picture of the types of water present in the re-saturated material. The proposal put forward was that the bentonite porewater is the "free water" existing as interconnected thin films on the outside surfaces of some of the montmorillonite stacks and other mineral grains. The volumes of this "free water" are very low compared with those required to saturate the bentonite and are a strong function of the initial dry density. Values were deduced from Cl^- through diffusion tests. Further, arguments were brought to indicate that highly compacted and constrained bentonite functions as an efficient semi-permeable membrane. Thus the re-saturation of bentonite involves predominantly the movement of water molecules and not solute molecules.

In bentonite there are large masses of montmorillonite and only small volumes of porewater. Thus montmorillonite and the other solid phases present will determine the composition of the porewater since the ion capacities of the solids are massively greater than those in the aqueous phase. The high exchange capacity and amphoteric $\equiv\text{SOH}$ "edge" or "broken bond" sites in montmorillonite act as powerful buffers for the chemistry of the porewater.

Mineralogical and physico-chemical measurements enabled the MX-80 bentonite samples to be thoroughly characterised in terms of chloride and sulphate inventories, solubility limiting phases, cation exchange capacity and fractional cation occupancies. Selectivity coefficients for Ca-Na, K-Na and Mg-Na were obtained with the aid of these results (Appendix).

However, in addition to the data from the characterisation studies, two further key variables had to be quantified in order to calculate a porewater in bentonite. These were the chloride concentration and the pH (or P_{CO_2}).

From an examination of the procedures used to produce the powder for the manufacture of compacted bentonite blocks and granulates, it was concluded that the "as received" material had been atmosphere conditioned i.e. the bentonite powder was in equilibrium with air P_{CO_2} ($10^{-3.5}$ bar). An important consequence of this is that the amphoteric surface hydroxy groups were conditioned to the pH of the solution with which the bentonite powder was last in equilibrium. (The best estimate for the initial value of this pH was 8.0.)

Compaction would not influence the state of the amphoteric edge sites and they are considered to act as a powerful pH buffer and in turn condition the bentonite porewater in a closed system. The Cl^- concentration as a function of initial dry density was fixed over the Cl^- inventory in bentonite ($1.35 \times 10^{-3} \text{ mol kg}^{-1}$) and the porosity values deduced from Cl^- through diffusion tests.

For compacted dry densities between 1200 and 1600 kg m^{-3} , the calculated bentonite porewaters had relatively high ionic strengths (0.30 to 0.33 M) and were saturated with calcite, gypsum, celestite, quartz and fluorite at a pH of 8.0 . The cation concentrations were very similar, but the porewater composition changed from a Na_2SO_4 water at 1200 kg m^{-3} to a $\text{NaCl}/\text{Na}_2\text{SO}_4$ water at 1600 kg m^{-3} .

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APPENDIX

In the Appendix the results of a physico-chemical characterisation study of MX-80 are presented. The mineralogy and important physico-chemical parameters are given. A description of the experimental work carried out on a sample of MX-80 bentonite, which enabled data such as chloride and sulphate inventories, cation occupancies and selectivity coefficients to be quantified, is presented.

A 1 MINERALOGY AND PHYSICO-CHEMICAL CHARACTERISTICS

The MX-80 Na-Bentonite (Wyoming, USA) was obtained from Bentonit International GmbH, D-41 Duisburg-Meiderich. Samples of the "as received" powdered MX-80 were heated to constant weight in an oven at 105 °C. The water content was determined to be 7.1 wt.%.

MÜLLER-VONMOOS & KAHR (1982, 1983) have characterized the MX-80 bentonite and have carried out a mineralogical analysis which is reproduced in Table A1. In this analysis ~2 wt.% of the material remained as "unidentified".

Table A1: Mineralogical composition of MX-80 bentonite. The compositions are expressed in wt.% of oven-dried MX-80.

Mineral	wt.%
Montmorillonite	75
Kaolinite	<1
Mica	<1
Quartz	15.2
Feldspar	5-8
Calcite	0.7
Siderite	0.7
Pyrite	0.3
Organic carbon	0.4

Total and amorphous iron(hydr)oxide, chloride and sulphate inventories are given in Table A2.

Table A2: Iron(hydr)oxide content, and Cl⁻ and SO₄²⁻ inventories.

Other constituents	(mmol kg ⁻¹)	References
amorphous iron (hydr)oxide	10.6 ± 0.4	this work
total iron (hydr)oxide	25.9 ± 0.7	
NaCl	1.35 ± 0.1	this work
	1.04 ± 0.2	WANNER et al. (1992)
CaSO ₄	23.5 ± 0.9	this work
	26.6 ± 4.2	WANNER et al. (1992)

Some relevant characteristics of MX-80 are summarised in Table A3 for completeness.

Table A3: Lattice density and surface areas of MX-80.

Physical property	Data values	Source reference
Lattice density (kg m ⁻³)	2755	MÜLLER-VONMOOS & KAHR (1983)
N ₂ BET specific surface area (m ² g ⁻¹)	30 31.3	KRUSE (1992) BRADBURY & BAEYENS (1998a)
Ethylene glycol total surface area (m ² g ⁻¹)	562	MÜLLER-VONMOOS & KAHR (1983)

A 2 DERIVATION OF BASIC PARAMETERS REQUIRED FOR THE CALCULATION OF THE POREWATER CHEMISTRY

A 2.1 Analytical methods

Aqueous concentrations of Na, K, Mg, Ca, Sr, S and Si were determined by plasma-emission spectroscopy (Applied Research Laboratory ARL 3410D ICP-OES).

The anions F⁻, Cl⁻ and SO₄²⁻ were analysed using a Dionex DX 500 ion chromatograph. Alkalinity measurements were made on a Metrohm Titroprocessor 670.

It was estimated that the maximum analytical errors were ±10% for the major ions in all of the above measurements.

pH measurements were taken on a WTW Microprocessor 535 pH meter using an Orion 8103 Ross combination pH electrode.

The O₂ content in the atmosphere controlled glove boxes was measured on line with a gas analyser supplied by Teledyne, and was generally below 2 ppm.

A 2.2 Extraction tests

A 2.2.1 General

Two types of ion extraction experiments were performed in inert atmosphere glove boxes. A first series consisted of an aqueous extraction in which powdered bentonite was shaken end-over-end with de-ionised and de-gassed water at a series of S:L ratios for 28 days. (Similar tests on argillaceous rocks

indicated that times of this order were sufficient for equilibration, BRADBURY & BAEYENS, 1998b) After centrifugation (96000 *g* max.) the supernatant solutions were analysed. One of the main aims of these experiments was to determine the Cl⁻ and SO₄²⁻ inventories of MX-80 bentonite.

A second series of extractions in nickel-ethylenediamine (Ni-en) solutions were carried out in an analogous manner. Ni-en is a powerful high selective complex which displaces all exchangeable cations from the clay minerals into solution (PEIGNEUR, 1976; MAES & CREMERS, 1986). These experiments provided cation exchange capacity and cation occupancy data for the bentonite. In addition, selectivity coefficients for the K-Na, Mg-Na- and Ca-Na equilibria were deduced from these data and the aqueous extraction results, see section A2.3.

A 2.2.2 Aqueous extraction tests

The results from aqueous extraction tests after 28 day equilibration times at three different S:L ratios are summarised in Table A4.

Table A4: Aqueous extraction data for MX-80 at different S:L ratios after 28 days equilibration time.

S:L ratio (g L ⁻¹)	18.6	27.9	37.2
pH	10.1	10.1	10.0
<u>Concentration (M)</u>			
Na	4.33 x 10 ⁻³	5.45 x 10 ⁻³	6.27 x 10 ⁻³
K	2.5 x 10 ⁻⁵	3.5 x 10 ⁻⁵	4.1 x 10 ⁻⁵
Mg	9.0 x 10 ⁻⁶	1.1 x 10 ⁻⁵	1.1 x 10 ⁻⁵
Ca	1.3 x 10 ⁻⁵	1.8 x 10 ⁻⁵	1.9 x 10 ⁻⁵
Sr	1.5 x 10 ⁻⁷	1.7 x 10 ⁻⁷	3.0 x 10 ⁻⁷
F ⁻	2.6 x 10 ⁻⁵	3.6 x 10 ⁻⁵	4.5 x 10 ⁻⁵
Cl ⁻	2.7 x 10 ⁻⁵	3.7 x 10 ⁻⁵	4.7 x 10 ⁻⁵
SO ₄ ²⁻	4.2 x 10 ⁻⁴	6.8 x 10 ⁻⁴	8.7 x 10 ⁻⁴
Alkalinity (Eq. L ⁻¹)	3.44 x 10 ⁻³	4.06 x 10 ⁻³	4.66 x 10 ⁻³
Σ Cations (Eq. L ⁻¹)	4.40 x 10 ⁻³	5.54 x 10 ⁻³	6.37 x 10 ⁻³
Σ Anions (Eq. L ⁻¹)	4.33 x 10 ⁻³	5.49 x 10 ⁻³	6.49 x 10 ⁻³
Si (M)	3.7 x 10 ⁻⁴	4.8 x 10 ⁻⁴	4.8 x 10 ⁻⁴

The charge balance of the aqueous extracts are generally better than $\pm 2\%$. The Cl^- and SO_4^{2-} data, expressed as inventories in mmol kg^{-1} oven dried material, are given for each S:L ratio in Table A5.

Table A5: Chloride and sulphate inventories of MX-80 obtained from the aqueous extraction tests.

S:L ratio (g L ⁻¹)	#Cl ⁻ inventory (mmol kg ⁻¹)	SO ₄ ²⁻ inventory (mmol kg ⁻¹)
18.6	1.45	22.6
27.9	1.33	24.4
37.2	1.26	23.4

#There appears to be a trend in the Cl⁻ inventory data which is currently not understood.

The Cl⁻ and SO₄²⁻ inventories in the bentonite have mean values of 1.35 ± 0.1 and 23.5 ± 0.9 mmol kg^{-1} , respectively. These inventories are in good agreement with the data reported by WANNER et al. (1992), see Table A2.

A 2.2.3 NিকেথিলেনডIAMINE extraction tests

The high selectivity Ni-en complex was prepared by slowly adding ethylenediamine (en) to a Ni(NO₃)₂ solution to obtain a stock solution containing 0.2 M Ni and 0.6 M en. The pH of this solution was adjusted to a value of 8.0 using HNO₃ Titrisol™ solutions.

Solutions containing between 2×10^{-1} M and 5×10^{-3} M Ni-en were prepared from the stock solution and added to 8, 4, 2, 1, 0.5 and 0.25 g lots of the "as received" MX-80, pre-weighed into polypropylene centrifuge tubes, to give S:L ratios of 213, 106, 53, 27, 14 and 6.7 g L⁻¹ respectively, corrected for initial water contents. The added equivalents of Ni-en in each experiment were approximately a factor of 2.5 greater than the exchange capacity to ensure complete displacement of all exchangeable cations. The tubes were closed, shaken end-over-end for 3 days, centrifuged and the supernatant solution analysed. The tests were carried out in triplicate/quadruplicate.

When the Ni-en solution contacts the bentonite, the cations on the clay mineral components are almost immediately displaced into solution (PLEYSIER et al., 1986). Such a process is much more rapid than solid phase dissolution reactions, see for example WOLLAST (1990); DREYBRODT et al. (1996). Consequently, the extent of mineral dissolution is reduced via the common ion

effect. Thus at high S:L ratios especially, the concentrations of cations displaced from the clay minerals dominate the solution compositions.

The cation concentrations measured in the Ni-en extraction solutions are expressed in meq kg⁻¹, Table A6.

Table A6: Ni-en extraction results for Na, K, Mg, Ca and Sr.

S:L ratio (g L ⁻¹)	Na (meq kg ⁻¹)	K (meq kg ⁻¹)	Mg (meq kg ⁻¹)	Ca (meq kg ⁻¹)	Sr (meq kg ⁻¹)	pH
213	700	12.0	39	104	3.0	8.0
	691	12.3	39	103	3.1	8.0
	705	11.6	38	105	3.0	8.0
	694	12.3	39	105	3.0	8.0
106	703	11.8	36	109	3.1	8.2
	695	11.3	36	108	3.1	8.2
	700	11.4	37	109	3.2	8.2
	700	11.5	36	108	3.1	8.2
53	633	12.1	41	140	3.3	8.0
	650	-	42	143	3.3	8.0
	643	-	41	139	3.3	8.0
27	683	12.4	43	168	3.5	8.2
	716	12.3	44	170	3.6	8.2
	682	15.2	44	168	3.5	8.2
14	674	14.1	44	194	3.8	8.4
	652	13.6	44	190	4.0	8.4
	664	-	41	181	3.7	8.5
6.7	591	13.3	39	189	3.5	8.7
	645	16.6	42	206	3.7	8.7
	561	15.5	36	182	3.3	8.8
mean (s dev)	669 (40)	12.9 (1.6)	40 (3)		3.4 (0.3)	

- no reliable measurement

Within the experimental error of the measurements, the data in Table A6 indicate that for Na, K, Mg and Sr there are no significant trends in the quantities of displaced cations with the S:L ratio. The individual measurements generally agree to better than $\pm 5\%$. For these elements, mean values, together with their standard deviations, are included in Table A6. In the case of Ca however, there is a clear trend in the data with S:L ratio and this observation will be discussed below.

A 2.3 Estimates of cation occupancies

In order to calculate a bentonite porewater composition, the fractional cation occupancies of Na, K, Mg and Ca need to be determined for the "as received" material. These cation occupancies can be derived from the Ni-en extraction data, Table A6, and the $\text{Cl}^-/\text{SO}_4^{2-}$ inventory measurements, Table A5.

Na occupancy

From the Ni-en extraction results (Table A6), the average Na extracted from the MX-80 bentonite samples was $669 \pm 40 \text{ meq kg}^{-1}$. This quantity is made up of the Na displaced from the exchange sites of the montmorillonite and the Na present in the porewater associated with the Cl^- inventory (1.35 meq kg^{-1}). Hence the Na occupancy on the clay minerals is the difference between these two values i.e. $668 \pm 40 \text{ meq kg}^{-1}$.

K occupancy

The calculated quantity of K displaced from MX-80 is relatively constant over the range of S:L ratios investigated. Since no salts are associated with this element, the occupancy of K on MX-80 is taken to be $13 \pm 2 \text{ meq kg}^{-1}$.

Mg occupancy

The Mg extracted in meq kg^{-1} at the different S:L ratios remains essentially constant with an average value of $40 \pm 3 \text{ meq kg}^{-1}$ (Table A6). This is taken to represent the Mg loading on the clay.

Ca occupancy

The situation for Ca is different from Mg in that the system contains additional Ca sources, gypsum and calcite, which can contribute to the total measured concentration. The total quantities of Ca and S (as SO_4^{2-}) extracted in the Ni-en experiments are given in Table A7.

The amounts of S (as SO_4^{2-}) released in all of the experiments remains essentially constant. This is interpreted to signify that a constant quantity of gypsum per kg of MX-80 goes into solution at the different S:L ratios. The SO_4^{2-} is accompanied by an equivalent quantity of Ca. Calcium concentrations measured in each of the individual Ni-en tests, corrected for the dissolved gypsum, are plotted in Figure A1.

Although the sequential development of the data sets cannot be explained in detail, the general trends can be semi quantitatively interpreted in terms of a Ca contribution from the dissolution of calcite. At S:L ratios somewhere below 100 g L^{-1} , the quantities of Ca in solution arising from gypsum dissolution and from the montmorillonite are not sufficient to effectively suppress calcite

dissolution by the common ion effect. As the S:L ratio increases, the quantities of Ca displaced from montmorillonite and from gypsum dissolution become the dominant contributors to the total Ca in solution i.e. at high enough S:L ratios dissolution of calcite becomes minimal. From the plot in Figure A1 this condition appears to have been reached at a S:L ratio of around 100 g L⁻¹. The continuous line drawn through the measured Ca concentrations at S:L ratios of 106 and 213 g L⁻¹ and the origin is taken to be representative of the Ca displaced from the montmorillonite. The slope of the solid line yields a value of 33 mmol Ca kg⁻¹.

Table A7: Ni-en extraction results for Ca and S.

S:L ratio (g L ⁻¹)	Ca (total) (meq kg ⁻¹)	S (as SO ₄ ²⁻) (meq kg ⁻¹)
213	104	39
	103	37
	105	37
	105	38
10.6	109	43
	108	40
	109	41
	108	41
53	140	34
	143	36
	139	35
27	168	38
	170	39
	168	35
14	194	36
	190	35
	181	34
6.7	189	33
	206	35
	182	28

Sr occupancy

Sr occupancies on the montmorillonite are calculated over the Sr-Na selectivity coefficient assuming celestite saturation in the compacted bentonite system (see section A 3).

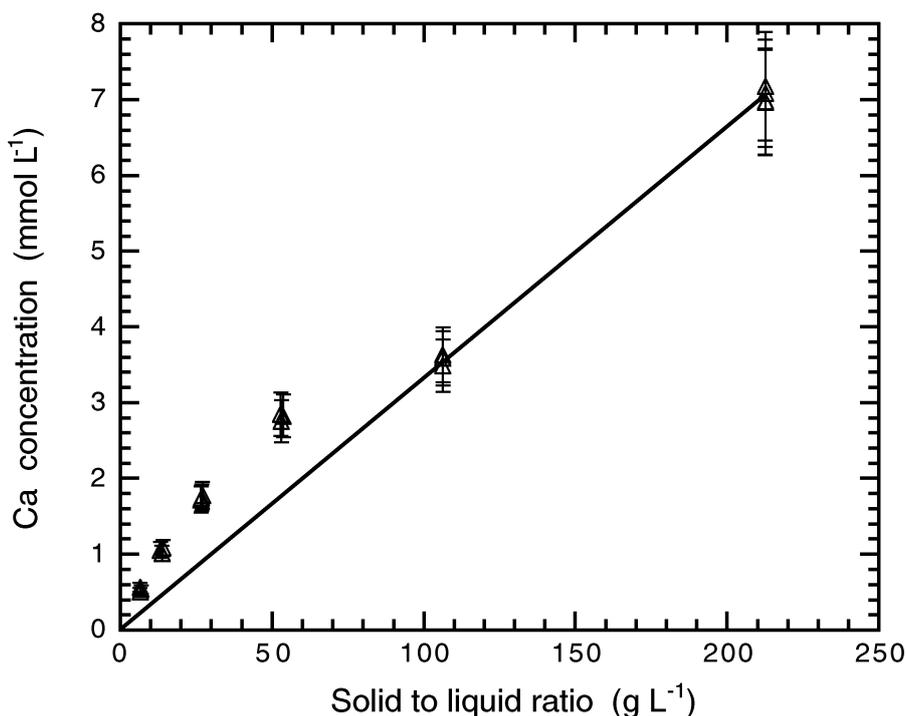


Figure A1: Ca concentration (corrected for CaSO_4 dissolution) in the Ni-en extracts as function of S:L ratio.

Summary of cation occupancies on MX-80

The cation occupancies and equivalent fraction occupancies (N_B values) deduced for the "as received" MX-80 bentonite powder are summarised in Table A8. The equivalent fraction occupancies are defined as:

$$N_B = \frac{\text{Quantity of cation B on the permanent charge sites of the clay minerals (meq kg}^{-1}\text{)}}{\text{CEC (meq kg}^{-1}\text{)}} \quad (\text{A1})$$

where $B = \text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}$ or Sr^{2+} .

The cation exchange capacity is taken to be the sum of the individual occupancies and yields a value of $787 \pm 48 \text{ meq kg}^{-1}$. This value is in good agreement with the CEC data from MÜLLER-VONMOOS & KAHR (1983) on MX-80 bentonite. These authors obtained CEC values between $767 - 780 \text{ meq kg}^{-1}$ using the ammonium acetate method ($\text{pH} = 7$). The cation occupancies for Na, Mg and K given in MÜLLER-VONMOOS & KAHR (1983) are generally lower than the data given in Table A8, i.e. 624 meq kg^{-1} for Na, 30 meq kg^{-1} for Mg and 2 meq kg^{-1} for K. The datum for Ca is slightly higher i.e. 74 meq kg^{-1} .

Table A8: Summary of the cation occupancies and fraction occupancies on MX-80 bentonite.

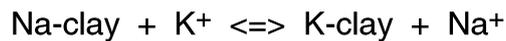
Cation	Cation occupancy (meq kg ⁻¹)	Fractional occupancy (N _B values)
Na	668 ± 40	0.85 ± 0.05
K	13 ± 2	0.017 ± 0.003
Mg	40 ± 3	0.051 ± 0.004
Ca	66 ± 3	0.084 ± 0.004
Sr [#]		
Σ Cations	787 ± 48	

[#] The Sr occupancy is calculated (see section A3.3).

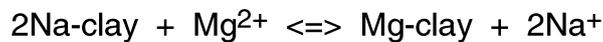
A 2.4 Selectivity coefficients

A 2.4.1 General

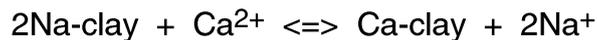
Selectivity coefficients, K_c , for K, Mg, and Ca are calculated here with respect to Na for the MX-80 system. Na was chosen as the reference cation since it is the most abundant cation present. The exchange reactions, and the associated mass action equations defining the selectivity coefficients according to the GAINES & THOMAS (1953) convention, are given below:



$${}_{\text{Na}}^{\text{K}}K_c = \frac{N_{\text{K}}}{N_{\text{Na}}} \cdot \frac{a_{\text{Na}}}{a_{\text{K}}} \quad (\text{A2})$$



$${}_{\text{Na}}^{\text{Mg}}K_c = \frac{N_{\text{Mg}}}{N_{\text{Na}}^2} \cdot \frac{a_{\text{Na}}^2}{a_{\text{Mg}}} \quad (\text{A3})$$



$${}_{\text{Na}}^{\text{Ca}}K_c = \frac{N_{\text{Ca}}}{N_{\text{Na}}^2} \cdot \frac{a_{\text{Na}}^2}{a_{\text{Ca}}} \quad (\text{A4})$$

where "a" represents solution activities and N_{Na} , N_{K} , N_{Mg} and N_{Ca} are equivalent fractional cation occupancies.

As can be seen from the above mass action relations, the quantities required to calculate the selectivity coefficients are the same in each case i.e. the appropriate aqueous cation activities and fractional cation occupancies on the solid. The important data here are the results from the aqueous extraction tests, Table A4, and the in situ cation occupancies given in Table A8.

A 2.4.2 Cation occupancies on the MX-80 in the aqueous extraction tests

When de-ionised water is contacted with the MX-80 samples, mineral dissolution and exchange reactions occur modifying the original cation occupancies on the montmorillonite given in Table A8. For Na and K it is relatively straightforward to calculate the new occupancies, but for Ca and Mg the presence of dissolving minerals has to be taken into consideration. In the following, the results from the test carried out at a S:L ratio of 18.6 g L⁻¹ are used to illustrate the method.

Na occupancies on MX-80

The Na in the aqueous extract originates from two sources; the exchangeable Na on the montmorillonite and the NaCl inventory. The measured Na concentration in the aqueous extract is 4.33 x 10⁻³ M (Table A4), which correspond to 233 meq kg⁻¹. The quantity of Na present as NaCl is 1.35 meq kg⁻¹ (see Table A2) and thus 232 meq kg⁻¹ are displaced from the montmorillonite. Since the original Na occupancy was 668 meq kg⁻¹ (Table A8), the new occupancy in the aqueous extract must be 436 meq kg⁻¹ or $N_{Na} = 0.554$.

K occupancies on MX-80

The exchangeable K on the montmorillonite was assumed to be the only source of this element and therefore the quantity remaining on the solid in the aqueous extraction experiment is simply determined from mass balance considerations. The measured K concentration in the aqueous extract is 2.5 x 10⁻⁵ M which corresponds to 1.34 meq kg⁻¹. The K occupancy in the aqueous extract is thus 12 meq kg⁻¹ or $N_K = 0.015$.

Mg and Ca occupancies on MX-80

The calculation for bivalent cations occupancies cannot be carried out in the same manner since solid phases containing one of these elements are dissolving. Instead, it is noted that the relation

$$N_{Na} + N_K + N_{Mg} + N_{Ca} \sim 1 \quad (A5)$$

must be valid.

Since the Na and K occupancies in the aqueous extracts have been calculated (see above), the sum of the fractional occupancies of Mg and Ca can be found i.e. $N_{Mg} + N_{Ca} = 0.431$.

In order to calculate the N_{Mg} and N_{Ca} values, the selectivity coefficient for the Ca-Mg exchange is required. This parameter was not measured in this study and the well established literature K_c (Ca-Mg) value of 1.2 (BRUGGENWERT & KAMPHORST, 1982, SPOSITO & FLETCHER, 1985) was taken i.e.,

$${}_{Mg}^{Ca}K_c = \frac{N_{Ca}}{N_{Mg}} \cdot \frac{a_{Mg}}{a_{Ca}} = 1.2 \quad (A6)$$

From the Ca^{2+}/Mg^{2+} cation activity ratio in the aqueous extract, Table A4, and the relation: $N_{Mg} + N_{Ca} = 0.431$, the Mg and Ca equivalent fractional occupancies can be calculated from Eqn. A6. These values are 0.176 and 0.255 for Mg and Ca respectively.

H occupancies on MX-80

The H^+ - Na^+ selectivity coefficient for smectites is approximately unity (GILBERT & LAUDELOUT, 1965). Consequently, proton exchange on the permanent charge sites is not expected to be a significant process at the pH values relevant to this study.

A 2.4.3 Calculation of selectivity coefficients for K-Na, Mg-Na, and Ca-Na exchange equilibria

The fractional cation occupancies calculated in section A 2.4.2 can be used together with the concentrations of Na, K, Mg, and Ca measured in the aqueous extraction experiments, expressed in terms of cation activities, to calculate selectivity coefficients from Eqns. A2 to A4. The values for ${}_{Na}^K K_c$, ${}_{Na}^{Mg} K_c$ and ${}_{Na}^{Ca} K_c$ are summarised in Table A9.

From the mass action relations (Eqns. A2 to A4) it can be readily appreciated that the uncertainty in K_c depends upon the errors in the respective fractional occupancies, N_B values, and the aqueous concentrations. The error estimates given in Table A8 were used for the former and an error of $\pm 10\%$ for the latter, section A 2.1. The maximum uncertainties in selectivity coefficients calculated on this basis are included with the K_c values in Table A9. Note that the selectivity coefficient for Mg-Na exchange was calculated from the Ca-Na value determined here over a literature value for Ca-Mg exchange, Eqn. A6. The fractional uncertainty in the Mg-Na values was taken to be the same as that for the Ca-Na selectivities.

Table A9: Selectivity coefficients for K-Na, Mg-Na and Ca-Na exchange equilibria on MX-80 corrected to zero ionic strength (I.S. = 0).

Selectivity coefficients (I.S. = 0)	S:L ratio 18.6 g L ⁻¹	S:L ratio 27.9 g L ⁻¹	S:L ratio 37.2 g L ⁻¹	Mean values
$K_{Na}K_c$	4.6 ± 1.9	3.9 ± 1.6	3.6 ± 1.5	4.0 ± 1.6
$Mg_{Na}K_c$	2.2 ± 1.1	2.0 ± 1.0	2.3 ± 1.2	2.2 ± 1.1
$Ca_{Na}K_c$	2.6 ± 1.2	2.4 ± 1.1	2.7 ± 1.3	2.6 ± 1.2

Note: The selectivity coefficient of Sr with respect to Na was taken to be the same as the Ca-Na value in the calculations presented in Chapter 4.

The calculated selectivity coefficients for the different S:L ratios are not significantly different from one another and are compatible with literature values, $K_{Na}K_c = 2 - 5$; $Ca_{Na}K_c = 2 - 4$ (BRUGGENWERT & KAMPHORST, 1982, SPOSITO et al., 1983a,b).

A 3 INVENTORIES AND SATURATED SOLID PHASES

A 3.1 Chloride and sulphate Inventories

From the aqueous extraction tests (see section A.2.2.2) the inventories of Cl⁻ and SO₄²⁻ were obtained and yielded values of 1.35 x 10⁻³ and 23.5 x 10⁻³ mol kg⁻¹ respectively.

A 3.2 Iron (hydr)oxide and pyrite determinations

Iron (hydr)oxides are often important minor mineral components in many natural systems and are not usually detectable by standard mineralogical procedures. The oxalate extraction method for amorphous iron (SCHWERTMANN 1964) and the dithionite-citrate-bicarbonate extraction procedure for total iron (MEHRA & JACKSON, 1960) were applied to MX-80 bentonite. The results from three separate extraction experiments are summarised in Table A10. The data show that approximately 40% of the ~28 mmol kg⁻¹ total extractable iron is in the amorphous form.

A severe acid extraction of MX-80 in 1 M HNO₃ at a S:L ratio of 10 g L⁻¹ with end-over-end shaking for 24 hours yielded an elemental sulphur content of ~73 mmol kg⁻¹. Aqueous extraction tests, section A 2.2.2, carried out in glove

boxes gave consistent SO_4^{2-} results interpreted in terms of an inventory of gypsum of $23.5 \text{ mmol kg}^{-1}$. Assuming that the dominant sources of sulphur are pyrite and gypsum, and that both have been completely dissolved in the severe acid extraction, this would imply that the pyrite content in the MX-80 is $24.8 \text{ mmol kg}^{-1}$, or $\sim 0.3 \text{ wt.}\%$. This value is in excellent agreement with the determination of MÜLLER-VONMOOS & KAHR (1983), Table A1.

Table A10: Results from extraction measurements for amorphous iron using oxalate (pH = 3), and total iron, using dithionate (pH = 7), on MX-80 bentonite.

Sample	Amorphous iron (mmol kg^{-1})	Total iron (mmol kg^{-1})
1	10.9	27.3
2	11.6	28.7
3	11.6	27.4

A 3.3 Saturated phases

The mineralogical analysis indicates the presence of calcite and quartz. In addition, gypsum is considered to be present as the source of sulphate in the system. (Note that the sulphate inventory of $23.5 \text{ mmol kg}^{-1}$ corresponds to a gypsum content in the bentonite of $\sim 0.3 \text{ wt.}\%$ which would not normally be detectable by standard mineralogical analytical procedures.) The aqueous extraction data show that F^- is present. These considerations lead to the proposal that the solution in equilibrium with MX-80 bentonite powder is saturated with respect to calcite, gypsum, fluorite and quartz.

In the Ni-en displacement tests, see Table A6, $\sim 1.7 \pm 0.15 \times 10^{-3} \text{ mol kg}^{-1}$ of Sr was released at all S:L ratios. The origin of this Sr is unclear. Some is certainly displaced from the montmorillonite, but Sr could also be present as a separate solid phase or as a solid solution or as a combination of all these. Preliminary calculations indicated that there was sufficient Sr in the system to ensure celestite (SrSO_4) saturation in compacted bentonite systems, even taking into account exchange on the clay. Consequently, in the calculations presented in Chapter 4, celestite saturation was assumed and the Sr exchange on the clay calculated over the Na-Sr selectivity coefficient. In this context it should be noted that the occupancy of Sr represents less than 1% of the overall CEC indicating that Sr makes only a second order contribution to the porewater composition.

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