



TECHNICAL REPORT 95-04

A Quantitative Mechanistic Description of Ni, Zn and Ca Sorption on Na-Montmorillonite

Part I: Physico-Chemical Characterisation and Titration Measurements

July 1995

B. Baeyens, M.H. Bradbury

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PREFACE

The Laboratory for Waste Management 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 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.

FOREWORD

This report is the first in a series of three, which together describe experimental investigations and modelling studies on the sorption of radionuclides by Na-montmorillonite. The aim of this work was to identify sorption mechanisms, develop mass action based models and determine the associated parameter values. In Part I the conditioning (purifying) procedures applied to the source material (SWy-1 Na-montmorillonite) are given together with characterisation and titration results. Sorption edge and isotherm data for Ni, Zn and Ca are presented in Part II. In a final report, Part III, an overall model was developed to describe the acid/base and sorption behaviour on Na-montmorillonite.

VORWORT

Der vorliegende Bericht ist der erste aus einer Reihe von drei Berichten, die insgesamt die experimentellen Untersuchungen und Modellrechnungen zur Sorption von Radionuklidern auf Na-Montmorillonit beschreiben. Ziel dieser Arbeit ist neben der Abklärung von Sorptionsmechanismen die Entwicklung von auf Massenwirkungsgesetzen basierenden Modellen und die Bestimmung der dazugehörigen Parameter. In Teil I werden Konditioniermethoden vorgestellt, mit Hilfe derer das Ausgangsmaterial (SWy-1 Na-Montmorillonit) aufgearbeitet wurde. Daneben werden Analysendaten und Ergebnisse der Titrations vorgestellt. Teil II behandelt die pH-abhängige Sorption und Sorptionsisotherme von Ni, Zn und Ca. In Teil III wird abschliessend ein umfassendes Modell vorgestellt, welches neben dem Säure/Base-Verhalten der Oberflächengruppen auch die Sorptionseigenschaften von Na-Montmorillonit beschreibt.

PRÉFACE

Ce rapport est le premier d'une série de trois rapports qui décrivent les travaux expérimentaux et le développement d'une modélisation concernant la sorption de radionucléides par la montmorillonite sodique conditionnée. Le travail présenté ici se focalise sur l'identification des mécanismes de sorption, le développement d'un modèle et la détermination des paramètres associés. Dans le premier rapport on décrit un procédé de conditionnement du matériel de base, la montmorillonite sodique (SWy-1), et, les données de caractérisation et de titration. Dans le deuxième rapport, les seuils de sorption et les isothermes de sorption qui ont été déterminés pour le Ni, le Zn et le Ca sont décrits. Dans le troisième rapport, un modèle est présenté qui reflète uniquement le comportement acide/base des sites de surface et la sorption sur la montmorillonite sodique conditionnée.

ABSTRACT

The work presented in this report is primarily concerned with characterisation studies and titration measurements on conditioned Na-montmorillonite.

The starting material, SWy-1 Na-montmorillonite (Crook County, Wyoming, USA), contains background metal impurities, soluble salts and sparingly soluble minerals which can influence titration and sorption measurements and thereby lead to difficulties in the interpretation of the data. A conditioning procedure is described which yielded a purified clay material in the homo-ionic sodium form with a particle size $< 0.5 \mu\text{m}$. This so-called conditioned Na-montmorillonite was thoroughly physico-chemically characterised before carrying out batch titration measurements on suspensions in 0.1 and 0.5 M NaClO_4 . The reasons for choosing a batch method, coupled with back titration of the supernatant solutions, instead of a continuous procedure, are fully discussed. Chemical analyses data for the supernatant solutions are presented in detail. The influence of background impurities, not removed by the conditioning, and cation exchange processes on the form of the titration curves were investigated. Net Na-montmorillonite titration curves at two different ionic strengths were derived which are considered to reflect only the acid/base behaviour of $\equiv\text{SOH}$ type surface sites. The acid end point in the titration data was used to estimate an $\equiv\text{SOH}$ site capacity of 0.08 moles per kg conditioned Na-montmorillonite.

ZUSAMMENFASSUNG

Die in diesem Bericht dokumentierten Arbeiten beziehen sich vor allem auf Charakterisierungsstudien und Titrationsmessungen an konditioniertem Na-Montmorillonit.

Das verwendete Ausgangsmaterial, SWy-1 Na-Montmorillonit (Crook County, Wyoming, USA), enthält Spuren von Metallverunreinigungen, löslichen Salzen und schwerlöslichen Mineralien, welche die Titrations- und Sorptionsmessungen beeinträchtigen und zu Schwierigkeiten bei der Auswertung der experimentellen Daten führen können. Ein Konditionierungsverfahren wird beschrieben, aus dem ein gereinigtes Tonmaterial in der Na-Form mit einer Teilchengröße von $< 0.5 \mu\text{m}$ resultiert. Der so "konditionierte" Na-Montmorillonit wurde mittels physikalisch-chemischer Methoden eingehend charakterisiert. Anschliessend wurden Batch-Titrationsmessungen mit Suspensionen in 0.1 und 0.5 M NaClO_4 durchgeführt. Die Kriterien für die Wahl eines Batch-Verfahrens mit Rücktitration der überstehenden Lösungen statt eines kontinuierlichen Titrationsprozesses werden diskutiert und begründet. Die Daten aus der chemischen Analyse der überstehenden Lösungen werden ebenfalls präsentiert. Der Effekt von Verunreinigungen, die durch die Konditionierung nicht entfernt werden konnten, und von Kationenaustauschprozessen auf die Form der Titrationskurven wurde ausführlich untersucht. Aus den experimentellen Daten konnten Netto-Titrationskurven für Na-Montmorillonit bei zwei verschiedenen Ionenstärken abgeleitet werden. Es wird angenommen, dass die Kurven nur das Säure-Base-Verhalten der $\equiv\text{SOH}$ -Oberflächengruppen wiedergeben. Die $\equiv\text{SOH}$ -Gesamtkonzentration wurde aus dem Säure-Endpunkt der Titrationsdaten auf 0.08 Mol pro kg konditionierten Na-Montmorillonit abgeschätzt.

RÉSUMÉ

Le travail présenté dans ce rapport est consacré avant tout à la caractérisation et aux mesures de titration sur de la montmorillonite sodique conditionnée.

Le matériel de base, la montmorillonite sodique SWy-1 (Crook County, Wyoming, USA) contient des impuretés métalliques, des sels solubles et des minéraux peu solubles qui peuvent influencer les mesures de titration et de sorption, et ainsi provoquer des difficultés à l'interprétation des données. On décrit un procédé de conditionnement qui fournit une argile purifiée sous la forme sodique homo-ionique avec une taille des particules inférieure à 0.5 μm . Cette montmorillonite sodique conditionnée a été caractérisée sur les plans physique et chimique avant d'être soumise à des mesures de titration de suspensions en solution NaClO_4 0.1 et 0.5 M. On discute amplement des raisons pour lesquelles on a choisi une méthode en batch, couplée à la titration inverse des solutions surnageantes, en lieu et place d'une procédure continue. Les données des analyses chimiques des solutions surnageantes sont présentées en détail. On a étudié l'influence, sur la forme des courbes de titration, des impuretés non éliminées par le conditionnement, ainsi que des processus d'échange cationique. On en a tiré des courbes de titration nettes de la montmorillonite sodique pour deux niveaux de force ionique. On pense qu'elles reflètent uniquement le comportement acide/base des sites de surface du type $\equiv\text{SOH}$. L'extrémité acide des données de titration a permis d'estimer la capacité du site $\equiv\text{SOH}$ à 0.08 moles par kg de montmorillonite sodique conditionnée.

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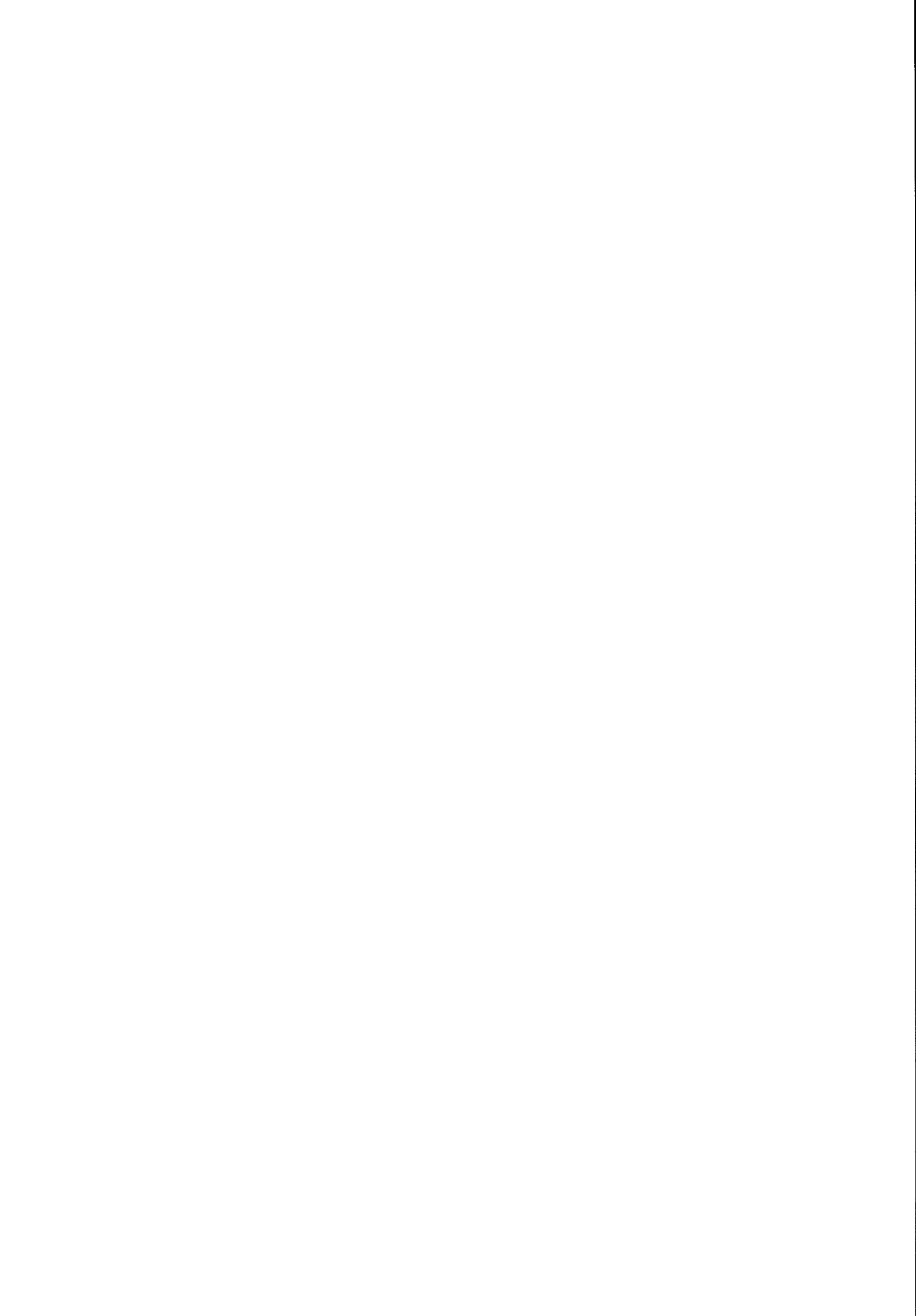
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1 INTRODUCTION

1.1 General

For some time now there has been a growing conviction within the radioactive waste management community that continuing to characterise sorption solely in terms of empirical parameters and relations such as distribution ratios and Freundlich isotherm equations, is becoming increasingly unsatisfactory for a wide variety of reasons. The consequences of such an approach, which are at the same time the reasons for the dissatisfaction, are:

- (a) Sorption data are only strictly applicable for the experimental conditions under which they were measured.
- (b) Large amounts of data and fitting parameters are necessary for an empirical description of sorption under all realistically conceivable conditions.
- (c) Even with very large data bases, only interpolation procedures are valid. Extrapolation to other conditions (and particularly to other systems) may be highly questionable.

Furthermore, an empirical approach does not generally lead to an increase in understanding of sorption processes and certainly does not lead to any predictive capabilities.

The implication of the above is not that the existing, large sorption data bases should be abandoned. Rather, the aim is to point out that an additional approach, based on an understanding of sorption mechanisms and the development of model descriptions, is required. We believe that there is a real need to develop models with a predictive capacity and also to provide a sound scientific basis for justifying and defending sorption values in data bases used in repository performance assessment studies.

Thermodynamic sorption models, based on cation exchange (see for example GAINES & THOMAS 1953; BOLT 1982; SHAVIV & MATTIGOD 1985; FLETCHER & SPOSITO 1989) and surface complexation mechanisms (STUMM & MORGAN 1981; SCHINDLER 1981; MOREL et al. 1981; SPOSITO

1983, 1984; WESTALL 1986; VAN RIEMSDIJK et al. 1986, 1987; STUMM 1987; DAVIS & KENT 1990), have been available for some time. They have been refined and improved to such an extent that they are now widely accepted (e.g. DZOMBAK & MOREL 1990). The former mechanism has been used predominantly to describe sorption processes on clay minerals whereas the latter has been mainly applied to relatively simple, pure, single oxide systems. Though the potential for using such models to interpret and predict sorption data in natural systems has been recognised, it is currently unclear whether, and to what extent, they can be used for complex mineral assemblages and water chemistries. General concepts as to how thermodynamic models can be applied to natural mineral/groundwater systems are lacking, as are experimental methodologies and techniques for obtaining intrinsic complexation constants.

1.2 Background

Clay minerals such as kaolinite, illite, chlorite and montmorillonite generally form at least one of the more important mineral components in crystalline and sedimentary rock formations as far as sorption is concerned. For this reason we decided to study one of the above clay mineral and use it as a test material to develop experimental and modelling procedures. Because of the importance of bentonite as a backfill material in the Swiss concept for a high level waste repository, Na-montmorillonite was selected.

The sorption of many radionuclides, particularly as a function of pH, is strongly dependent on the amphoteric nature of hydroxyl surface functional groups ($\equiv\text{SOH}$) at broken bonds and edge sites on clay minerals (SPOSITO 1984). The proton sorption/desorption behaviour of these $\equiv\text{SOH}$ type sites is generally described by intrinsic surface protonation and deprotonation constants respectively, which are usually deduced from potentiometric titration studies on suspensions (SCHINDLER & KAMBER 1968; STUMM et al. 1970; DAVIS et al. 1978; HUANG 1981). In essence, a titration plot is a proton adsorption/desorption isotherm for the $\equiv\text{SOH}$ sites. A quantitative understanding of the acid/base behaviour of surface binding sites is critical for any model description of sorption processes since protons are always competitive with radionuclides for the available sorption sites.

In principle, sorbent titration curves are easy to generate. However, to produce a titration curve which reflects only the amphoteric behaviour of the $\equiv\text{SOH}$ type sites on clay mineral surfaces is fraught with difficulties. A major part of this paper is devoted to a detailed description of the experimental procedures and quantification of competitive H^+ consuming processes which have to be taken into account in order to generate a true surface site titration curve for Na-montmorillonite. In addition, efforts were directed towards characterising the clay as fully as possible in terms of its mineralogical composition, amorphous and total iron contents, background metal impurities, cation exchange capacity and N_2 -BET surface area. Aqueous phase compositions in equilibrium with Na-montmorillonite (primarily as a function of pH) were measured throughout the investigation. This detailed characterisation work was not only critical for the understanding and interpretation of the titration data but also provided a sound data base for the subsequent sorption and modelling studies.

2 PREPARATION OF MATERIALS AND SOLUTIONS

2.1 General

SWy-1 Na-montmorillonite (Crook County, Wyoming, USA)¹ was purchased from the Source Clay Minerals Repository (University of Missouri-Columbia). Since the aims of the experimental program were to try to identify sorption mechanisms, to interpret the data in terms of corresponding thermodynamic sorption models and, wherever possible, to measure the associated constants, the initial question was whether these aims could be achieved by working directly with the SWy-1 Na-montmorillonite. Even for a relatively pure clay system such as this, it became very clear at an early stage that this was not possible. There were too many variables and unknown factors which could influence the experimental results and hence the interpretation and subsequent analysis. The consequence of this was that the clay-solution system had to be made experimentally simpler (conditioned) in such a way that the physico-chemical characteristics of the mineral phases (essentially the binding sites) remained unaffected. Checks on cation exchange capacities, surface areas, metal background inventories and water chemistries before and after conditioning can be used to make judgements as to whether the rock system is being significantly changed or not (see Chapter 3).

The basic philosophy here was to attempt to characterise and understand the simplified system first, and then, using this understanding as a basis, increase the complexity in a stepwise systematic manner until the natural system was reached. In this way important processes could be identified along the way and any necessary additional measurements made.

2.2 Electrolyte Purification

The concentrations of NaClO₄ electrolyte solutions used in this work ranged between 0.001 and 1.0 M and were prepared from Merck "pro analysis" grade chemicals. With a total heavy metal content of $\sim 5 \times 10^{-4}$ wt.%, this grade of chemical is normally considered to be pure enough for most laboratory experiments. However, when relatively small quantities of sorbent are contacted repeatedly with relatively large volumes of concentrated solutions

¹ The "as received" Crook County Na-montmorillonite is referred to in this, and following reports, as SWy-1 Na-montmorillonite.

(up to 1 M), as is the case in the conditioning procedure for SWy-1 Na-montmorillonite (see section 2.3), even low levels of heavy metal impurities may become critically important. During the conditioning process, there was the distinct possibility that the clay was being inadvertently loaded up with heavy metals. The frequent solution changes inherent in the procedure could be acting, in effect, like a pump for the sorption of the solution background impurities onto the solid. If this effect were to remain undetected then the heavy metal impurities would be competing with, and influencing the sorption behaviour of, the radionuclides being studied. Thus the interpretation and modelling of experimental data could be questionable and may even be falsified by the heavy metal occupancies of the sorption sites.

As a result of these considerations, all solutions prepared from the Merck chemicals were further purified. In principle the method uses the sorption (surface complexation) properties of Al_2O_3 to scavenge the cation impurities from the solutions. A slurry of Aldrich high purity (99.99%), high surface area Al_2O_3 (~ 7 gram in 80 ml of 1 M NaClO_4) was loaded into a thoroughly washed Visking dialysis bag (Medicall Int., London) and sealed. One such bag was shaken together with 1 litre of 1 M NaClO_4 at a pH between 7 and 8. In order to estimate the times required for the background heavy metal scavenging process to be completed and to measure the sort of reduction factors which might be expected, preliminary experiments were carried out with solutions labelled with ^{45}Ca , ^{85}Sr , ^{63}Ni , ^{60}Co and ^{210}Pb . A 1-2 day shaking time was generally required and reduction factors of between 10 and 100 were achieved for the heavy metal impurities. A typical ICP-AES analysis of a 1 M NaClO_4 solution after treatment with Al_2O_3 is given in Table 1. These Al_2O_3 prepared solutions were then diluted as required using high purity de-ionised water.

2.3 Conditioning of SWy-1 Na-montmorillonite

The basic aim of conditioning the SWy-1 Na-montmorillonite was to simplify the clay-water chemistry. This would enable us to carry out the subsequent acid/base titration and sorption experiments under a range of well defined and constant conditions thus reducing the uncertainties in the interpretation of experimental data.

Table 1: Background impurities in a 1 M NaClO₄ solution after treatment with Al₂O₃

Element	Concentration (M)
K	1.1 x 10 ⁻⁴
Mg	1.0 x 10 ⁻⁶
Ca	2.0 x 10 ⁻⁶
Sr	3.3 x 10 ⁻⁷
Ba	2.0 x 10 ⁻⁷
Al	1.0 x 10 ⁻⁶
Si	1.3 x 10 ⁻⁶
Mn	1.0 x 10 ⁻⁶
Ni	1.0 x 10 ⁻⁷

Concentrations of Fe ($< 3 \times 10^{-7}$ M) and Zn ($< 4 \times 10^{-7}$ M) were below reliable detection limits (see section 4.2). Concentrations of the elements P (10^{-7} M), Se (6×10^{-8} M), Pb (2×10^{-8} M), Cu (3×10^{-8} M), Co (2×10^{-8} M) and Cd (4×10^{-9} M) were below the ICP-AES detection limits which are given in brackets.

The conditioning procedure described below was designed to achieve the following:

- (1) To remove any and all soluble salts, and soluble minerals such as bivalent cation carbonates and sulphates.
- (2) To convert the montmorillonite into the homo-ionic Na form and to collect the $< 0.5 \mu\text{m}$ size fraction.
- (3) To equilibrate the conditioned Na-montmorillonite with a symmetric 1:1 electrolyte, such as NaClO₄, at any chosen ionic strength.

Montmorillonite has a significant cation exchange capacity (see section 3.5), and converting it to the homo-ionic Na form enabled the effect of exchange reactions to be better quantified as a function of ionic strength and pH in titration and sorption experiments. "Washing out" salts and minerals allowed the Na form to be wholly maintained under different experimental conditions. Also, the water chemistry was greatly simplified as a result of this procedure.

Finally, there were no longer solid phases present which could buffer in acid/base titration tests and deliver different quantities of cations and anions into solution as a function of pH. (The latter could produce variable competitive effects in radionuclide sorption experiments.) If, in addition, experiments are carried out under CO₂ free conditions i.e. in a controlled inert atmosphere glove box, then only hydrolysis reactions will be influencing the radionuclide speciation as a function of pH. Not having to include inorganic ligands such as carbonates, sulphates, etc. in the modelling automatically removed a number of degrees of uncertainty from the calculations.

The experimental methods used for conditioning SWy-1 Na-montmorillonite follow similar procedures to those outlined by MAES & CREMERS (1973). They are given in some detail below because they represent an important step in the overall procedure for obtaining titration curves and sorption data on Na-montmorillonite.

2.3.1 Conversion to the Homo-Ionic Na-Form

Five litres of 1 M NaClO₄ solution, purified as described in section 2.2, were added to approximately 120 grams of SWy-1 Na-montmorillonite and shaken for ~ 3 hours. The clay suspension was then allowed to flocculate before decanting the supernatant solution. This procedure was repeated three times which was sufficient to remove any soluble salts and to convert the clay into the homo-ionic Na form.

2.3.2 Separation of the < 0.5 µm Clay Fraction

The next phase was a purification procedure designed to obtain a suspension containing the < 0.5 µm Na-montmorillonite fraction. The flocculated Na-montmorillonite suspension (~ 1-2 litres) was separated into twelve 250 ml centrifuge bottles which were then filled with de-ionised water and shaken for 15 minutes. The dilution of the NaClO₄ solution led to the peptisation of the Na-montmorillonite. Following this procedure the suspensions were centrifuged (7 minutes at 600 g max.) so that the fraction smaller than 0.5 µm remaining in the suspension could be decanted and collected in a large container. This fine clay fraction was then immediately flocculated with 1 M NaClO₄ solutions to minimise hydrolysis of the clay. This "washing" procedure was repeated about 10 times. The yield of this process was ~ 50% so that the

resulting clay batch of about 10 litres, contained approximately 6 gram litre⁻¹ of Na-montmorillonite in ~ 0.2 M NaClO₄.

2.3.3 Acid Treatment

The washing process with de-ionised water may have led to some hydrolysis of the clay with the formation of hydroxy-aluminium compounds. Following the treatment used by MAES & CREMERS (1973) the fine clay suspension was acidified with HNO₃ to pH 3.5 - 4 and shaking for 30 minutes. Subsequently, 250 ml lots were centrifuged (~ 5 minutes at 600 g max.), the supernatant decanted off and the clay re-suspended and neutralised by adding 1 M NaClO₄ to give a suspension at pH ~ 7. The resulting 2 - 3 litre stock Na-montmorillonite suspension, which contained ~ 20 gram litre⁻¹ clay at neutral pH, was stored at 4 °C in the dark to minimise microbial growth. Such clay stock suspensions were never kept longer than 6 months.

2.3.4 Conditioning to 0.1 M NaClO₄

Large dialysis bags (~ 35 mm diameter) were washed thoroughly with de-ionised water and filled with approximately 75 ml of the stock Na-montmorillonite suspensions. The bags were sealed such that an air pocket was trapped within the now rigid bag. This air pocket was important since it allowed the free flow of liquid and solid within the bag and thus promoted good mixing during end-over-end shaking through the movement of the gas pocket from one end to the other.

Four of such bags were placed in a 1 litre container which was then filled with an 0.1 M solution of NaClO₄. Again a small air gap was left to promote good mixing within the liquid phase and the containers were shaken end-over-end. The 0.1 M NaClO₄ solution was changed about three times per day and this procedure was continued until the electrical conductivity of the conditioned Na-montmorillonite equilibrium solution was equal to that of the original 0.1 M NaClO₄. About ten exchange cycles were normally required. (The use of dialysis bags facilitated solution exchanges within the container without loss of material.)

Finally, the conditioned Na-montmorillonite suspensions were diluted to ~ 10 gram litre⁻¹ with the equilibrium solution and stored in the dark at 4 °C. The exact clay content of each batch was determined by weighing and evaporation to constant weight (over-night heating at 105 °C). Salt corrections were made by treating 0.1 M NaClO₄ solutions simultaneously in the same manner.

3 PHYSICO-CHEMICAL CHARACTERISATION OF CONDITIONED Na-MONTMORILLONITE

After completion of the conditioning procedure, the equilibrium solution was analysed and the Na-montmorillonite was characterised in terms of its mineralogy, N₂-BET surface area and cation exchange capacity. In addition Fe-extractions were performed to determine the levels of amorphous and "total Fe" present as well as acid extractions to quantify the background impurity content. The SWy-1 Na-montmorillonite was characterised in a similar manner.

3.1 Water Chemistry

Six individual samples of conditioned Na-montmorillonite suspension (Solid to Liquid (S:L) ratio = 8 gram litre⁻¹) in 0.1 M NaClO₄ were centrifuged (1 hour at 95,000 g max.) and the supernatants were sent for analysis. The results are presented in Table 2.

Table 2: Chemical analysis of the liquid phase of 0.1 M NaClO₄ conditioned Na-montmorillonite (pH = 7)

Element	Concentration (M)
K	$1.9 \pm 0.1 \times 10^{-5}$
Mg	$1.0 \pm 0.1 \times 10^{-5}$
Ca	$6.4 \pm 1.1 \times 10^{-6}$
Sr	$4.2 \pm 0.5 \times 10^{-8}$
Ba	$5.4 \pm 0.1 \times 10^{-7}$
Mn	$1.6 \pm 0.1 \times 10^{-7}$
Si	$5.4 \pm 0.3 \times 10^{-5}$

Below reliable detection limits (see section 4.2): Al ($< 3 \times 10^{-7}$ M), Fe ($< 3 \times 10^{-7}$ M) and Zn ($< 4 \times 10^{-7}$ M). Below given ICP-AES detection limits: Rb ($< 2 \times 10^{-8}$ M); Cs ($< 4 \times 10^{-8}$ M); Se ($< 6 \times 10^{-8}$ M); Co ($< 2 \times 10^{-8}$ M); Ni ($< 3 \times 10^{-8}$ M) and Cd ($< 4 \times 10^{-9}$ M)

Calculations carried out using the geochemical code MINEQL (WESTALL et al. 1976) with the thermodynamic data base compilation from PEARSON &

BERNER (1991) and PEARSON et al. (1992) at air P_{CO_2} showed that the cation concentrations given in the above table were below those corresponding to saturation for any common solid phases such as (hydr)oxides and carbonates. Thus, there do not appear to be any remaining solid phases present controlling aqueous cation concentrations. (However, see section 5.4.2 and 5.4.3 where Si, Al and Fe are discussed in detail.)

3.2 Mineralogical Analysis

Mineralogical analyses results for SWy-1 and conditioned Na-montmorillonite are given in Table 3.

Only the minerals reported in Table 3 could be detected by X-ray diffraction methods. The numbers reported for quartz, feldspars and carbonates are absolute values. The numbers reported for clay minerals have been determined by quantitative XRD analysis of the clay fraction ($< 2 \mu\text{m}$), which only yields the relative proportions among the clay minerals. Therefore, these relative numbers have been recalculated on the basis,

$$\Sigma [\text{clay minerals}] = 100 \text{ wt.\%} - \text{wt.\% quartz} - \text{wt.\% feldspars} - \text{wt.\% carbonates}$$

Table 3: Mineralogical analyses results for SWy-1 Na-montmorillonite and conditioned Na-montmorillonite in wt.% (MAZUREK 1994)

Mineral	SWy-1 Na-montmorillonite	Conditioned Na-montmorillonite
Quartz	~ 5	~ 1
Albite	< 1	< 1
K-Feldspar	< 1	< 1
Calcite	~ 2.5	< 0.5
Dolomite	< 0.5	< 0.5
Illite	~ 1	~ 1
Montmorillonite	91	97
Kaolinite/Chlorite	< 1	< 1

"< values" indicate detection limits.

3.3 Iron Extractions

Iron (hydr)oxides are often important minor mineral components in many natural systems which are not usually detectable by standard mineralogical procedures. In view of this, and because iron (hydr)oxides can be significant sinks for many radionuclides, the oxalate extraction method for amorphous iron (SCHWERTMANN 1964) and the dithionate-citrate-bicarbonate extraction procedure for total iron (MEHRA & JACKSON 1960) were applied to suspensions of both conditioned and SWy-1 Na-montmorillonite. The results from five separate extraction experiments are summarised in Table 4. The data show that approximately 50% of the $\sim 13 \text{ mmol kg}^{-1}$ total extractable iron is in the amorphous form. Also, by comparing the results for SWy-1 and conditioned Na-montmorillonite it can be readily seen that the conditioning procedures have neither removed nor generated any additional iron (hydr)oxides.

Table 4: Results from extraction measurements for amorphous iron, using oxalate (pH = 3), and total iron, using dithionate (pH = 7), on SWy-1 and conditioned Na-montmorillonite

Sample	Amorphous iron (mmol kg^{-1})	Total iron (mmol kg^{-1})
Conditioned Na-montmorillonite	7.6 ± 0.8	14 ± 1
SWy-1 Na-montmorillonite	6.2 ± 1.1	13 ± 1

3.4 Acid Extraction Data

Severe acid extractions (pH ~ 0.5) were carried out on conditioned and SWy-1 Na-montmorillonite. For each clay material two series of six batches at a S:L ratio of $6.25 \text{ gram litre}^{-1}$ were end-over-end shaken in 0.5 M HNO_3 Titrisol solutions for 1 day. Samples were centrifuged and the supernatant solutions were analysed by ICP-AES. The results of the extraction tests for SWy-1 and conditioned Na-montmorillonite are summarised in Table 5 where mean values are expressed in mmol kg^{-1} . The reproducibility of the chemical

analyses was in all cases better than $\pm 10\%$. Elements such as Co, Ni, Cu, Cd and Pb were below the detection limits for ICP-AES.

Table 5: Results of severe acid extractions on SWy-1 and conditioned Na-montmorillonite. Equilibration time = 1 day. S:L ratio = 6.25 gram litre⁻¹

Element	Quantity extracted from SWy-1 Na-montmorillonite (mmol kg ⁻¹)	Quantity extracted from conditioned Na-montmorillonite (mmol kg ⁻¹)
K	15	1.9
Mg	110	11
Ca	270	1.1
Sr	3.4	0.05
Ba	0.2	0.04
Al	34	41
Si	68	58
S	15	0.4
Mn	1.6	0.4
Fe	14	11
Zn	0.8	0.8

Such a severe acid extraction will desorb all exchangeable cations on the clay and dissolve the calcite and dolomite present (see Table 3). Also, partial dissolution of the clay minerals and other phases present cannot be avoided.

In general we can see that conditioning has considerably reduced the levels of K and the alkaline earth cations. In the conditioned Na-montmorillonite calcite and dolomite have been removed and the level of Ca remaining probably corresponds to the exchangeable quantity on the clay. This corresponds to a Ca inventory of 1.1 mmol kg⁻¹. Similar conclusions cannot be drawn for Mg since this element is present within the lattice of the clay and would be released by dissolution under these conditions.

The levels of Al and Si are similar for both materials and most likely arise through quartz and clay mineral dissolution. The Fe contents are also the

same and are consistent with the total Fe extraction results in the previous section.

The origin of sulphur (as sulphate) in the system is unknown, but conditioning has reduced the quantities available by a factor of ~ 40. Mn levels were also reduced by conditioning, yielding an inventory of ~ 0.4 mmol kg⁻¹. It is significant that the Zn levels for the conditioned and SWy-1 Na-montmorillonite are approximately the same. The Zn inventory in both cases is ~ 0.8 mmol kg⁻¹.

These acid extractions results will be discussed further and compared with chemical analysis data from titration measurements in Chapter 5.

3.5 Cation Exchange Capacity Measurements

The cation exchange capacity (CEC) of the conditioned Na-montmorillonite was determined using the ²²Na isotopic dilution method. Five ml aliquots of suspension, containing a known wt.% of Na-montmorillonite in 0.1M NaClO₄, were pipetted into dialysis bags and each bag dialysed separately in a large container with 120 ml de-ionised water. This procedure diluted the Na concentration to 0.004 M.

The dialysis bags were removed, wiped off, and transferred to 50 ml containers. The clay was then equilibrated with 25 ml of an 0.001 M NaClO₄ solution which contained a ²²Na radiotracer and equilibrated for 1 day by end-over-end shaking. CEC values were obtained from the changes in activities between the initial and equilibrium solutions. Finally, the equilibrium pH was measured.

A summary of the Na-CEC measurements obtained on the various clay batches is given in Table 6. The mean value of 46 independent measurements yield a CEC of 870 ± 35 meq per kg conditioned Na-montmorillonite.

Table 6: Summary of clay suspension weight determinations and Na-CEC measurements of various conditioned Na-montmorillonite batches

Clay Batch Nr	Date	Weight % ⁽ⁱ⁾ (gram litre ⁻¹)	No of analysis	Na-CEC (meq kg ⁻¹)	pH
1	March 92	10.0	6	874 ±33	6.1
2	March 92	8.0	4	933 ±56	6.4
3	April 92	10.3	2	843 ±20	6.1
4	May 92	11.7	3	839 ±10	6.5
5	July 92	6.7	3	833 ±12	6.3
6	Sept. 92	9.4	3	872 ±22	6.7
7	Oct. 92	10.3	6	844 ±10	6.6
8	Jan. 93	8.3	4	829 ±32	6.1
10	June 93	11.5	3	828 ±15	6.5
11	Feb. 94	8.1	4	878 ±16	6.8
12	April 94	8.0	4	892 ±18	6.7
13	July 94	8.3	4	885 ±12	6.7

(i) Errors in weight determinations were less than 1% in all cases.

In order to carry out similar CEC measurements on SWy-1 Na-montmorillonite it was first necessary to remove any soluble salts or sparingly soluble minerals and convert the clay to the Na-form. This was achieved by weighing 0.5 gram quantities of the SWy-1 material into dialysis bags and adding ~ 70 ml of 0.1 M NaClO₄. Each sealed dialysis bag was then shaken for ~ 3 hours with approximately 1 litre of 0.1 M NaClO₄ at neutral pH. This procedure was repeated 5 times after which the clay suspensions were dialysed to reduce the background electrolyte concentration to 10⁻³ M. The ²²Na isotopic dilution method, as described above, yielded a CEC value for SWy-1 Na-montmorillonite of 600 ± 35 meq kg⁻¹ at pH=6.5.

3.6 N₂-BET Surface Area Measurements

The N₂-BET surface areas (see for example GREGG & SING 1982) of SWy-1 and conditioned Na-montmorillonites were determined from multi-point adsorption isotherms using a Micromeritics Gemini 2360 surface area analyser. Samples were normally degassed for 2 hours at 200 °C prior to measurements. The as received SWy-1 Na-montmorillonite powder had a surface area of $\sim 25 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$.

In the case of conditioned Na-montmorillonite the suspensions were first dialysed (see section 2.3.4) to reduce the NaClO₄ concentration to $\sim 10^{-5} \text{ M}$ and then freeze-dried. The N₂-BET surface area of samples prepared in this way was $\sim 35 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$.

4 EXPERIMENTAL TECHNIQUES

4.1 Electrode Calibration

Titration experiments on Na-montmorillonite were carried out in solutions of NaClO₄ at two ionic strengths, $I = 0.1$ M and 0.5 M. At each of these ionic strengths Orion combination electrodes were calibrated against known hydrogen ion concentrations. Solutions containing 10^{-2} , 10^{-3} and 10^{-4} M acid or base were made up using Merck Titrisol HNO₃ or NaOH analytical grade reagents.

A minor but important point is that activity coefficients need to be known in order to calculate the proton concentrations in solutions where NaOH at known concentrations has been added to establish the pH. The ion activity product of water can be written as,

$$a_{\text{H}} \cdot a_{\text{OH}} = 10^{-14.0} \quad [1]$$

where a_{H} and a_{OH} are the activities of H⁺ and OH⁻ ions respectively. This equation can be re-expressed in terms of [H⁺] and [OH⁻] concentrations, to give :

$$\log [\text{H}^+] = -14.0 - \log [\text{OH}^-] - \log \gamma_{\text{H}} - \log \gamma_{\text{OH}} \quad [2]$$

where $\gamma_{\text{H}} (= \gamma_{\text{OH}})$ is the proton (hydroxyl) activity coefficient calculated using the Davies equation (DAVIES 1962),

$$\log \gamma_i = -0.511 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) \quad [3]$$

where z_i is the charge and I the ionic strength.

As an illustration, two calibration curves of measured electrode potentials against the logarithm of (fixed) proton concentrations are given for ionic strengths of 0.1 and 0.5 M in Figure 1. The associated regression equations, which are of course electrode and ionic strength specific, were used in conjunction with the Davies equation to convert measured mV readings to

proton activities. This procedure was used throughout this work and applies to all pH values given.

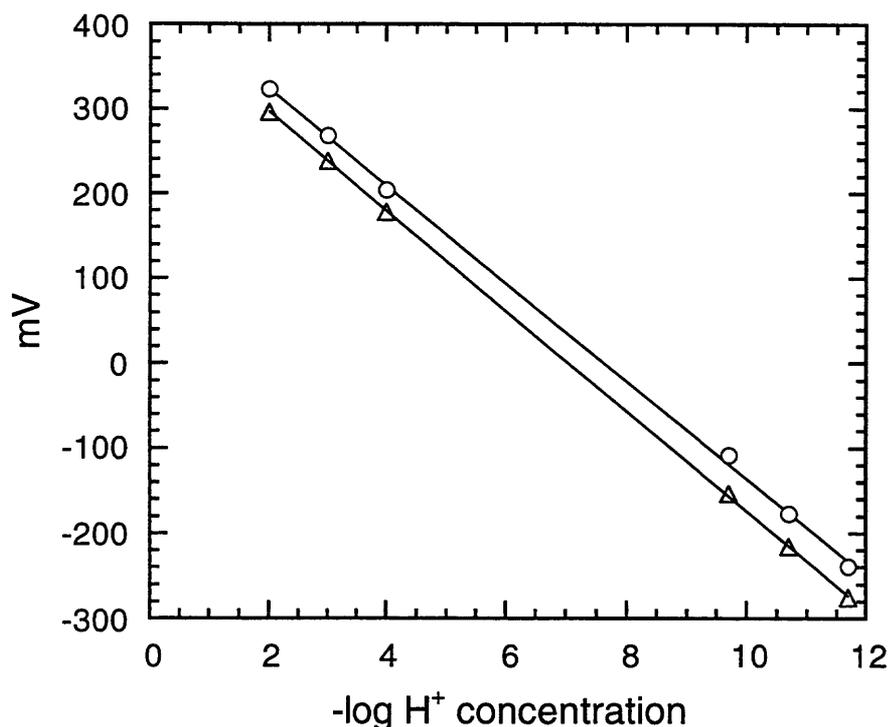


Figure 1: An example of pH calibration curves for 0.1 M and 0.5 M NaClO₄ solutions
 $I = 0.1 \text{ M } (\Delta): mV = 411.8 - 58.0 \times (-\log H^+)$
 $I = 0.5 \text{ M } (O): mV = 437.9 - 57.3 \times (-\log H^+)$

4.2 Determination of Reliable Detection Limits for ICP-AES

Stock solutions were prepared for each of the elements Al, Fe, Mn and Zn at concentrations of 20 ppm in 0.1 M NaClO₄ solutions. These were then accurately diluted to yield a range of different solutions for each particular element with concentrations extending below the given detection limit for the ICP-AES. Sets of solutions for each of the four elements were given for analysis on four separate occasions. The results from this trial were used to determine a "reliable detection limit" for each element and these values are summarised in Table 7.

Table 7: Reliable detection limits of ICP-AES for Al, Fe, Mn and Zn in 0.1 M NaClO₄ solutions

Element	Reliable detection limit	ICP-AES detection limit
Al	$\sim 3 \times 10^{-7}$ M	7×10^{-8} M
Fe	$\sim 3 \times 10^{-7}$ M	2×10^{-8} M
Mn	$\sim 1 \times 10^{-8}$ M	6×10^{-9} M
Zn	$\sim 4 \times 10^{-7}$ M	2×10^{-8} M

As can be seen, the reliable detection limits which emerged from this study are factors of between 5 and 10 higher than the given detection limits for ICP-AES. The reproducibility of the measurements for concentrations above the reliable detection limit was generally better than 10%. However, for concentrations near to the reliable detection limit the error increased, and could be as high as a factor of two in the most extreme cases.

4.3 Colloids

All test samplings were carried out in the glove box after centrifuging at 95,000 g (max) for one hour. Colloidal material in the sampled solutions, arising either from incomplete centrifugation and/or re-suspension of solid during transfer to the glove box, could influence the back titration (section 5.3) and chemical analysis measurements.

In order to test the effectiveness of centrifugation, two sets of experiments were carried out in parallel. In the first, 5 ml suspensions of 0.1 M NaClO₄ conditioned Na-montmorillonite ($9.4 \text{ gram litre}^{-1}$) were added to 30 ml of 0.1 M NaClO₄ solutions set at different pH values between 2 and 12, equilibrated for one day, and then centrifuged in the standard manner before sampling and analysing for Al, Fe, Si, Mn, and Zn. The second experiment was carried out in the same way except that the Na-montmorillonite suspension was confined in dialysis bags (average pore diameter 2.5 nm) and the solutions for analysis were taken from outside the bags. The results are presented in Figure 2. As can be seen, the analyses in the two cases are in good agreement over the whole pH range measured, leading to the conclusion that the centrifugation conditions were effective.

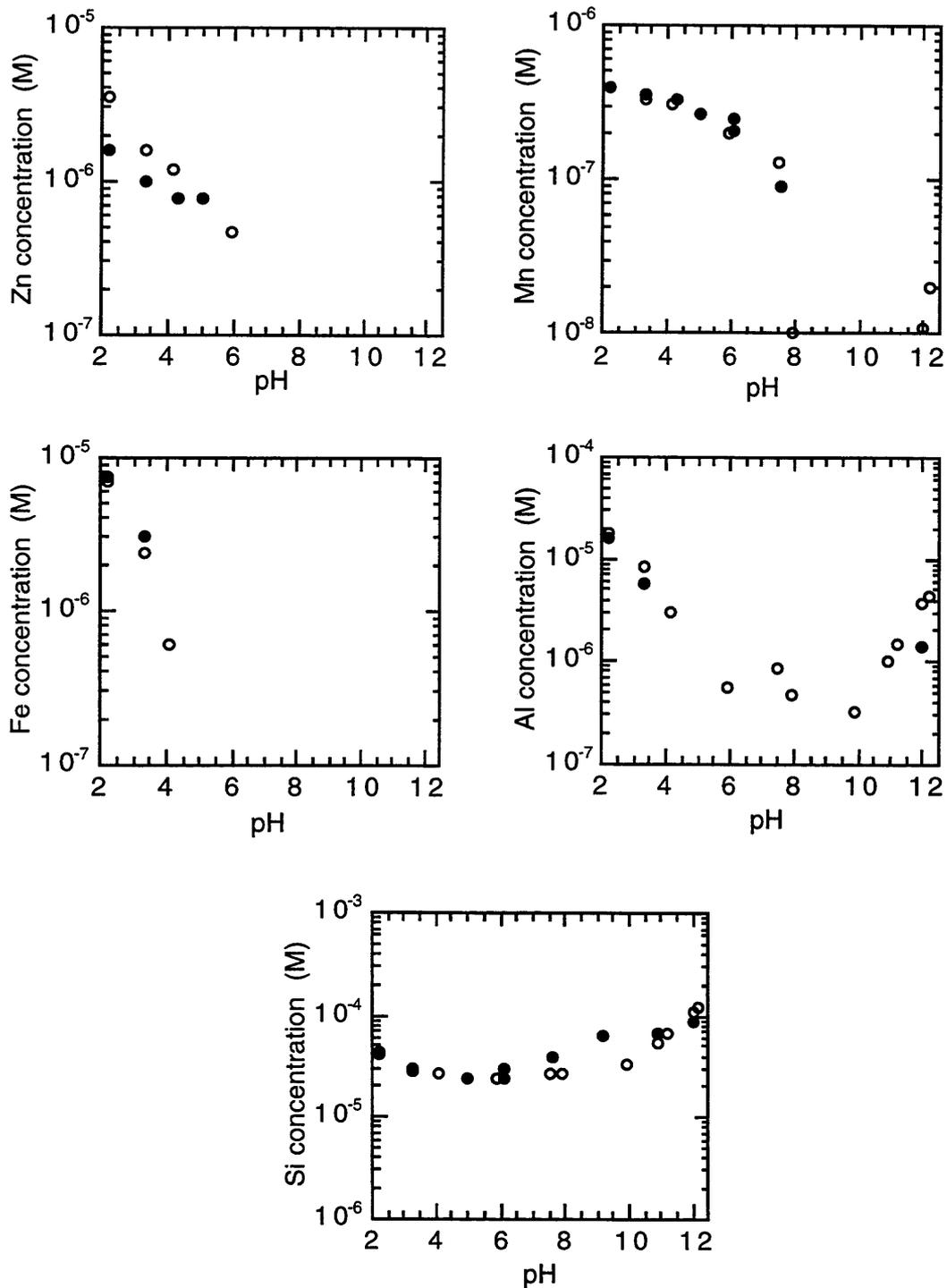


Figure 2: Comparison of measured background concentrations of Zn, Mn, Fe, Al and Si as a function of pH using centrifugation (O) and dialysis bags (●) as phase separation techniques. ($\text{NaClO}_4 = 0.1 \text{ M}$, S:L ratio = $1.34 \text{ gram litre}^{-1}$.)

5 TITRATION EXPERIMENTS ON CONDITIONED Na-MONTMORILLONITE

5.1 Background

Potentiometric titration data for a solid phase in a simple background electrolyte can, at least in theory, be interpreted to yield site capacities and intrinsic surface protonation and deprotonation constants for amphoteric $\equiv\text{SOH}$ type surface sites (JAMES & PARKS 1982; SCHINDLER & STUMM 1987; HIEMSTRA et al. 1987; LÖVGREN et al. 1990; HAYES et al. 1991; HIEMSTRA & VAN RIEMSDIJK 1991). However, in practice the interpretation of such titration curves can be quite difficult.

In the majority of cases suspensions are continuously titrated over a relatively short period of time (hours) to produce a curve of pH versus the quantities of acid or base added. For some systems fast titrations are even recommended (e.g. hydrous ferric oxides, DZOMBAK & MOREL 1990). A second titration curve, over the same pH range for the background electrolyte alone, is subtracted to yield a net titration curve for the solid phase. The latter is taken to reflect the protonation/deprotonation behaviour of the solid surface sites (see for example the work of BEENE et al. 1991 on illites). We will show in the following section that such fast continuous titration methods are not suitable for Na-montmorillonite.

The implicit assumption in the continuous titration approach is, of course, that the amphoteric behaviour of the $\equiv\text{SOH}$ type surface sites is the only significant proton consuming/releasing mechanism responsible for the form of the titration curve. SCHULTHESS & SPARKS (1986, 1987, 1988), amongst others, have pointed out that the normal continuous titration methods ignore H^+/OH^- consumption arising from other sources, principally the dissolution of the solid phase. All solids are soluble to some extent, particularly at extreme pH values. Strictly speaking, in order to obtain a net titration curve for any solid, its solubilisation has to be taken into account and in particular the variation with pH. This variation with pH can significantly influence the form of the titration curves (SCHULTHESS & SPARKS 1986).

The above authors describe a back titration method as a means of overcoming this problem. The supernatant solution from each batch titration is back titrated

to a common end point and provides the reference solution in each test. The quantities of acid (or base) required are subtracted from the original quantities of base (or acid) added to yield the net quantity consumed by the surface.

However, the back titration procedure is not a complete solution to the problem. Inherent in the method are a number of assumptions and uncertainties which are difficult to quantify.

The first major assumption is that any H^+ (or OH^-) consuming dissolution processes are balanced by equivalent processes, with the same consumption of OH^- (or H^+), during the back titration and that these processes are not kinetically hindered. The static batch titration experiments may run over many days whereas back titrations are normally carried out automatically over a period of a few hours.

At first sight this may appear to be a very restrictive assumption since dissolution kinetics are usually relatively fast whereas precipitation kinetics can be exceedingly slow and this may therefore lead to large differences in the H^+ (OH^-) consumption in the forward and back titrations. However, the assumption here does not imply that the system reaches thermodynamic equilibrium with respect to solid phases, but rather with H^+ (OH^-) consumptions in the aqueous phase. For example, proton consuming dissolution reactions in the forward titration can be balanced by (fast) OH^- consuming hydrolysis reactions in the back titration. Although this may leave the system supersaturated with respect to the stable solid phases, it would not have any influence on the proton balance.

If the solid phase is dissolving during a titration test then this begs the question how and to what extent are amphoteric surface sites being affected by the dissolution. Even for simple pure metal oxide systems the answer to this question is not entirely clear. Site types may remain the same e.g. $\equiv FeOH$ (for iron oxides) or $\equiv AlOH$ (for aluminium oxides) but whether site capacities or the distribution of site sorption affinities remain the same is less clear. For more complex solids, for example clay minerals, where the dissolution of structural elements containing Fe, Al or Si is incongruent, the distribution of site types, their affinities and site capacities could all change. Such effects are likely to be more prominent in very high or very low pH ranges.

For clay minerals with large ion exchange capacities, proton exchange and/or cation exchange, coupled with solid dissolution, could play a significant role in determining the form of the titration curve.

Finally, since titration curves and sorption data will be used to derive parameters for sorption models (BRADBURY & BAEYENS 1995), it is important to know how and to what extent background impurities can influence the measurements and their subsequent interpretation. Also, the "state" of these metal impurities in the system might be an important factor in this context i.e. whether the impurity cations are present mainly as sorbed species, or whether they arise from the dissolution of a solid phase. In order to provide the data necessary to quantify the effects of impurities, aqueous phase analyses were carried out in almost all the tests described in the following chapters.

The points mentioned above will be returned to and discussed in Chapter 6, where attempts will also be made to quantify their overall influences in the light of the results presented in section 5.3.

5.2 The Continuous Titration Technique

Continuous titrations for suspensions are often favoured because they are quick and easy to perform, especially on the automatic titration equipment which is now widely available. However, as mentioned above, this type of titration is not considered to be appropriate for Na-montmorillonite suspensions and we would like to present very briefly some of our earlier measurements to illustrate this point.

Two types of experiments were performed. In the first 40 ml aliquots of suspensions containing ~ 5 gram litre⁻¹ Na-montmorillonite in 0.1 M NaClO₄ were titrated under a N₂ cover gas with acid (base). An automatic titrator (Metrohm Titroprocessor 660) was used in the monotonic mode, delivering 50 μ l aliquots of 0.01M acid (base) every 60 seconds. Immediately upon completion of the first leg of the titration, the suspension was titrated back to the starting pH with base (acid) under exactly the same conditions. The resulting pairs of plots are shown in Figures 3(a) and 3(b). It is clear from both figures that there is hysteresis between the forward and reverse titrations performed in this manner.

In order to determine the influence of titration rate, a second set of tests were carried out under similar conditions to those given above except that the suspensions were first set at pH = 3, or pH = 10, and 50 μ l aliquots of base (acid) were delivered every 5 minutes. Again pronounced hysteresis effects are in evidence in Figure 3(c). A similar picture was found in other titration tests carried out at different acid/base addition rates.

Thus, continuous titration methods did not produce a unique curve but rather sets of curves whose form depended on titration rates, starting pH, length of time at low/high pH values, and whether acid additions or base additions were made. In view of these results continuous titration methods for clay suspensions were abandoned in favour of batch forward titrations coupled with back titration of the supernatant solutions as described in the next section. An additional point concerning the batch titration method is that these experiments were carried out over similar time scales to the subsequent sorption tests.

5.3 The Batch Back Titration Technique

5.3.1 Experimental

Titration experiments on conditioned Na-montmorillonite (section 2.3) were carried out in a batch-wise manner in an inert atmosphere glove box where the partial pressure of CO₂ was $<10^{-5.5}$ bar.

The source clay suspensions used in the titration tests contained ~10 gram Na-montmorillonite per litre of 0.1 M NaClO₄. 25 ml aliquots were pipetted from the strongly stirred suspension into a 50 ml polypropylene centrifuge tube to which a further 15 ml of NaClO₄ solution was added. The concentration of the latter was chosen such that the final concentration of the mixture was either 0.1 or 0.5 M NaClO₄.

Standard acid and base solutions each at concentrations of 0.2 or 0.02 M were made up from Merck Titrisol analytical grade starting solutions in 0.1 (0.5) M NaClO₄.

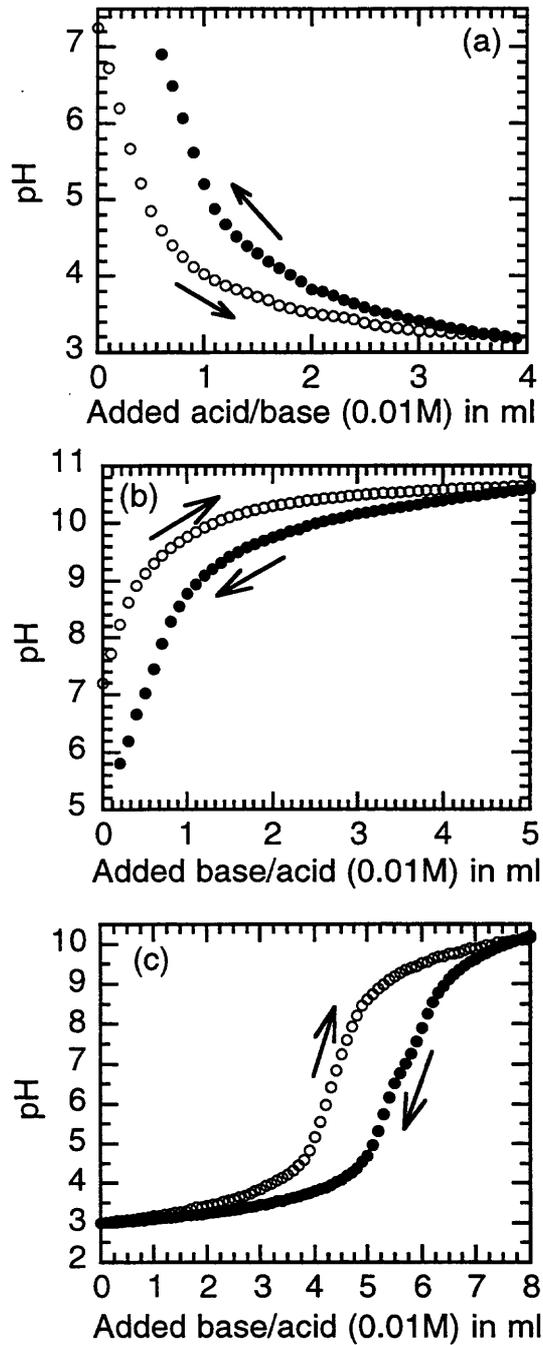


Figure 3. Continuous titration curves for suspensions of conditioned Na-montmorillonite in 0.1 M NaClO₄. (a) Acid followed by base titration. Rate: 50 $\mu\text{l min}^{-1}$; (b) Base followed by acid titration. Rate: 50 $\mu\text{l min}^{-1}$; (c) Base titration starting at pH=3. Acid titration starting at pH=10. Rate: 10 $\mu\text{l min}^{-1}$.

Aliquots of acid or base were taken from the standard solutions and added to the suspensions in the centrifuge tubes to give a series of initial pH values between 2.5 and 11.5. (Preliminary tests had indicated the approximate quantities of acid or base required.) To some samples no acid or base was added and these provided the reference pH values. All centrifuge tubes were tightly capped and shaken end-over-end for 24 hours. One series of samples at $I = 0.5 \text{ M}$ was shaken for 7 days.

After the appropriate shaking time, the closed tubes were transferred out of the glove box, centrifuged for 1 hour at 95,000 g (max) and then returned to the glove box for sampling. Two aliquots of the supernatant solutions were taken; one of 10 ml, for cation analysis, and the other of 25 ml for final pH measurement and subsequent back titration. The back titration were carried out in the glove box with an autotitrating system (Metrohm Titroprocessor 660) set up in the monotonic titration mode i.e. aliquots of acid or base titrant in 0.1 (0.5) M NaClO_4 , were added at ~ 5 minutes intervals until the pH was at least one unit greater or smaller than the pH of the reference samples to which no acid/base had been added. Since in any one series of experiments the start times for the individual batch tests were staggered, there were no significant delays in sampling, measuring the final pH and starting the back titrations.

5.3.2 Batch Back Titration Results

The results from forward and back titration experiments, grouped according to ionic strength, S:L ratio and equilibration time, are presented in Tables 8 to 11. The "Total H^+ (OH^-) consumed" columns represents the quantities of H^+ (OH^-) consumed by all processes not accounted for in the back titration measurements.

As will be shown in Chapter 6, reactions other than those involving amphoteric $\equiv\text{SOH}$ type surface sites can make significant contributions to the H^+ (OH^-) balance depending on the pH and ionic strength. In order to be able to generate a true solid titration curve these processes have to be identified and quantified. However, before this can be carried out an understanding of the system chemistry as a function of pH is required. In the following sections we therefore present and discuss first the chemical analyses results from supernatant solutions from the batch titration tests.

Table 8: Results of batch titration measurements on conditioned Na-montmorillonite at 0.5 M NaClO₄. Equilibration time: 1 day; S:L ratio: 5.9 gram litre⁻¹.

Data point	Added ACID (μmol) ^a	BASE used in back titration (μmol) ^b	Total H ⁺ consumed (μmol)	Total H ⁺ consumed (mmol kg ⁻¹) ^c	pH
A2	2	0.33	1.67	7.1	6.6
A3	4	0.40	3.60	15.3	6.3
A4	6	0.45	5.55	23.5	5.9
A5	10	1.07	8.93	37.8	5.0
A6	14	2.64	11.36	48.1	4.3
A7	18	5.59	12.41	52.6	4.0
A8	22	7.49	14.51	61.5	3.9
A9	26	10.62	15.38	65.2	3.8
Data point	Added BASE (μmol) ^a	ACID used in back titration (μmol) ^b	Total OH ⁻ consumed (μmol)	Total OH ⁻ consumed (mmol kg ⁻¹) ^c	pH
A10	1	0.06	0.94	4.0	7.1
A11	2	0.30	1.70	7.2	7.5
A12	4	0.54	3.46	14.7	8.0
A13	6	0.84	5.16	21.9	8.2
A14	10	2.43	7.57	32.1	9.1
A15	14	3.61	10.39	44.0	9.4
A16	18	6.69	11.31	47.9	9.8
A17	20	8.61	11.39	48.3	9.9
A18	30	14.34	15.66	66.4	10.2
A19	34	17.92	16.08	68.1	10.4

a) Quantities of acid/base added to 40 ml of suspension.

b) Quantities of acid/base added to supernatant solutions normalised to 40 ml.

c) The actual amount of conditioned Na-montmorillonite in each test was 2.36×10^{-4} kg

Table 9: Results of batch titration measurements on conditioned Na-montmorillonite in 0.5 M NaClO₄ solutions. Equilibration time = 1 day. S:L ratio = 6.35 gram litre⁻¹.

Data point	Added ACID (μmol) ^a	BASE used in back titration (μmol) ^b	Total H ⁺ consumed (μmol)	Total H ⁺ consumed (mmol kg ⁻¹) ^c	pH
B1	50	24.1	25.9	102.0	3.3
B2	100	77.3	22.7	89.4	2.8
B3	150	121.1	28.9	113.8	2.6
B4	200	174.2	25.8	101.6	2.5
Data point	Added BASE (μmol) ^a	ACID used in back titration (μmol) ^b	Total OH ⁻ consumed (μmol)	Total OH ⁻ consumed (mmol kg ⁻¹) ^c	pH
B5	50	27.5	22.5	88.6	10.7
B6	100	78.3	21.7	85.4	11.1
B7	150	117.5	32.5	128.0	11.4
B8	200	171.7	28.3	111.4	11.5

a) Quantities of acid or base added to 40 ml of suspension.

b) Quantities of acid or base added to supernatant solutions normalised to 40 ml

c) The actual amount of conditioned Na-montmorillonite in each test was 2.54×10^{-4} kg

Table 10: Results of batch titration measurements on conditioned Na-montmorillonite in 0.5 M NaClO₄ solutions. Equilibration time = 7 day. S:L ratio = 6.35 gram litre⁻¹.

Data point	Added ACID (μmol) ^a	BASE used in back titration (μmol) ^b	Total H ⁺ consumed (μmol)	Total H ⁺ consumed (mmol kg ⁻¹) ^c	pH
C1	5	0.20	4.80	18.9	6.7
C2	10	0.28	9.72	38.3	6.4
C3	20	2.66	17.34	68.3	4.4
C4	50	25.9	24.1	94.9	3.4
C5	200	158.9	41.1	161.8	2.6
Data point	Added BASE (μmol) ^a	ACID used in back titration (μmol) ^b	Total OH ⁻ consumed (μmol)	Total OH ⁻ consumed (mmol kg ⁻¹) ^c	pH
C6	5	0.69	4.31	17.0	7.9
C7	10	1.80	8.20	32.3	8.8
C8	20	6.51	13.49	53.1	9.5
C9	50	27.2	22.8	89.8	10.4
C10	200	161.4	38.6	152.0	11.4

a) Quantities of acid or base added to 40 ml of suspension.

b) Quantities of acid or base added to supernatant solutions normalised to 40 ml

c) The actual amount of conditioned Na-montmorillonite in each test was 2.54×10^{-4} kg

Table 11: Results of batch and back titration measurements on conditioned Na-montmorillonite in 0.1 M NaClO₄ solutions. Equilibration time = 1 day. S:L ratio = 6.35 gram litre⁻¹

Data point	Added ACID (μmol) ^a	BASE used in back titration (μmol) ^b	Total H ⁺ consumed (μmol)	Total H ⁺ consumed (mmol kg ⁻¹) ^c	pH
D2	2	0.01	1.99	7.8	7.8
D3	5	0.38	4.62	18.2	6.9
D4	10	0.68	9.32	36.7	6.1
D5	15	0.91	14.09	55.5	5.3
D6	20	2.30	17.70	69.7	4.4
D7	30	6.68	23.32	91.8	4.0
D8	30	4.72	25.28	99.5	4.0

Data point	Added BASE (μmol) ^a	ACID used in back titration (μmol) ^b	Total OH ⁻ consumed (μmol)	Total OH ⁻ consumed (mmol kg ⁻¹) ^c	pH
D9	2	0.10	1.90	7.5	7.9
D10	5	0.91	4.09	16.1	8.9
D11	10	2.18	7.89	31.1	9.4
D12	15	5.87	9.13	35.9	9.9
D13	20	9.38	10.62	41.8	10.1
D14	30	17.73	12.27	48.3	10.2
D15	30	17.64	12.36	48.7	10.2

a) Quantities of acid or base added to 40 ml of suspension.

b) Quantities of acid or base added to supernatant solutions normalised to 40 ml

c) The actual amount of conditioned Na-montmorillonite in each test was 2.54×10^{-4} kg

5.3.3 Results from Chemical Analyses of Supernatant Solutions from Batch Titration Experiments

The analyses results for the supernatant solutions from the batch titration experiments, Tables 12 to 15, show clearly that elements such as Fe, Al, Si, Zn, Mn, Mg, and Ca were being leached from the conditioned Na-montmorillonite.

As described in Chapter 2, extensive efforts were employed to purify the Na-montmorillonite and only solutions with very low levels of impurities were used in the experiments. It was therefore somewhat surprising to see that some elements were present at relatively high levels and that there was a strong variation with pH. These analytical results indicate that it is exceedingly difficult to achieve a totally "clean" system, and that there will always be background impurity cations present. However, it should not be forgotten that at pH values less than 3 and greater than 11, clay minerals tend to hydrolyse releasing elements such as Al, Si, Fe and Mg into solution (BRINKMAN 1982). (It is less likely that Zn, Mn and Ca are released by this process since they are not generally part of the clay mineral structure). Thus clay mineral hydrolysis may be contributing to the concentrations of the above four cations and therefore the levels measured in the pH ranges < 3 and > 11 may be overestimating the quantities actually available.

The data sets for Ca, Mg, Mn, Zn, Si, Al and Fe measured at a NaClO_4 concentration of 0.5 M after 1 and 7 day equilibration times, are presented graphically in Figures 4(a) to 4(g).

Table 12: Chemical analyses results (M) of the supernatant solutions from batch titration experiments with conditioned Na-montmorillonite at 0.5 M NaClO₄.

S:L ratio = 5.9 gram litre⁻¹. Equilibration time = 1 day.

Data point	pH	Mg	Ca	Si	Al	Fe	Mn	Zn
A8	3.9	2.8E-5	8.4E-6	8.8E-5	1.0E-5	1.3E-6	1.6E-6	2.5E-6
A5	5.0	2.4E-5	7.5E-6	5.8E-5	5.6E-7	< rdl*	1.9E-6	1.4E-6
A2	6.6	1.9E-5	4.6E-6	6.6E-5	4.1E-7	< rdl	6.3E-7	< rdl
A10	7.1	2.1E-5	5.9E-6	7.9E-5	7.0E-7	< rdl	2.7E-7	< rdl
A11	7.5	2.1E-5	6.2E-6	7.7E-5	6.3E-7	< rdl	2.0E-7	< rdl
A1	7.6	1.9E-5	4.6E-6	7.0E-5	< rdl	< rdl	5.2E-7	< rdl
A14	9.1	8.4E-6	4.7E-6	4.9E-5	4.1E-7	< rdl	< rdl	< rdl
A17	9.9	3.9E-6	4.8E-6	1.2E-4	< rdl	< rdl	< rdl	< rdl

* <rdl: Below reliable detection limit, see section 4.2

Table 13: Chemical analyses results (M) of the supernatant solutions from batch titration experiments with conditioned Na-montmorillonite at 0.5 M NaClO₄.

S:L ratio = 6.35 gram litre⁻¹. Equilibration time = 1 day.

Data point	pH	Mg	Ca	Si	Al	Fe	Mn	Zn
B4	2.5	5.3E-5	1.0E-5	1.4E-4	9.1E-5	2.6E-5	2.6E-6	7.0E-6
B3	2.6	5.0E-5	9.9E-6	1.3E-4	8.1E-5	2.2E-5	2.6E-6	5.6E-6
B2	2.8	4.6E-5	1.1E-5	1.1E-4	6.4E-5	1.5E-5	2.5E-6	6.5E-6
B1	3.3	4.9E-5	1.4E-5	1.9E-4	8.6E-5	1.3E-5	2.5E-6	5.6E-6
B5	10.7	1.6E-6	3.0E-6	2.1E-4	3.7E-6	4.9E-7	< rdl*	< rdl
B6	11.1	5.1E-7	1.8E-6	3.0E-4	< rdl	< rdl	< rdl	< rdl
B7	11.4	8.6E-7	1.9E-6	3.8E-4	2.2E-6	3.2E-7	< rdl	< rdl
B8	11.5		2.0E-6	5.6E-4	5.2E-5	7.2E-6	4.2E-8	< rdl

* < rdl: Below reliable detection limit, see section 4.2.

Table 14: Chemical analyses results (M) of the supernatant solutions from batch titration experiments with conditioned Na-montmorillonite at 0.5 M NaClO₄.

S:L ratio = 6.35 gram litre⁻¹. Equilibration time = 7 days.

Data point	pH	Mg	Ca	Si	Al	Fe	Mn	Zn
C5	2.6	7.3E-5	1.5E-5	3.4E-4	1.6E-4	3.5E-5	2.8E-6	8.2E-6
C4	3.4	5.8E-5	1.0E-5	2.0E-4	5.7E-5	6.4E-6	2.6E-6	4.5E-6
C3	4.4	4.6E-5	9.5E-6	1.4E-4	1.9E-6	3.0E-7	2.4E-6	2.0E-6
C2	6.4	3.7E-5	7.2E-6	1.2E-4		< rdl*	1.6E-6	< rdl
C1	6.7	3.3E-5	7.4E-6	9.9E-5	4.4E-7	< rdl	1.1E-6	< rdl
C6	7.9	2.2E-5	6.1E-6	8.5E-5	4.1E-7	< rdl	6.6E-8	< rdl
C7	8.8	1.4E-5	5.2E-6	1.0E-4	7.4E-7	< rdl	< rdl	< rdl
C8	9.5	8.4E-6	5.9E-6	2.0E-4	1.2E-6	< rdl	1.5E-8	< rdl
C9	10.4	1.9E-6	3.9E-6	3.7E-4	5.9E-6	7.2E-7	< rdl	< rdl
C10	11.4	4.6E-7	1.5E-6	7.9E-4	1.3E-5	2.1E-6	< rdl	< rdl

* < rdl: Below reliable detection limit, see section 4.2

Table 15: Chemical analyses results (M) of the supernatant solutions from batch titration experiments with conditioned Na-montmorillonite at 0.1 M NaClO₄.

S:L ratio = 6.35 gram litre⁻¹. Equilibration time = 1 day.

Data point	pH	Mg	Ca	Si	Al	Fe	Mn	Zn
D7	4.0	2.6E-5	6.2E-6	1.1E-4	4.1E-6	1.5E-6	1.6E-6	2.2E-6
D6	4.4	2.3E-5	6.5E-6	1.0E-4	2.7E-6	5.3E-7	1.5E-6	1.7E-6
D3	6.9	1.7E-5	4.3E-6	8.8E-5	8.2E-7	< rdl*	5.6E-7	5.7E-7
D1	7.8	1.5E-5	4.4E-6	1.0E-4	1.1E-6	< rdl	1.9E-7	< rdl
D9	7.9	1.4E-5	4.9E-6	8.5E-5	9.2E-7	< rdl	8.7E-8	< rdl
D11	9.4	5.8E-6	4.1E-6	7.1E-5	8.2E-7	< rdl	< rdl	< rdl
D12	9.9	3.1E-6	4.2E-6	9.0E-5	1.5E-6	< rdl	< rdl	< rdl
D14	10.2	1.1E-6	2.1E-6	1.4E-4	1.4E-6	< rdl	< rdl	< rdl

* < rdl: Below reliable detection limit, see section 4.2

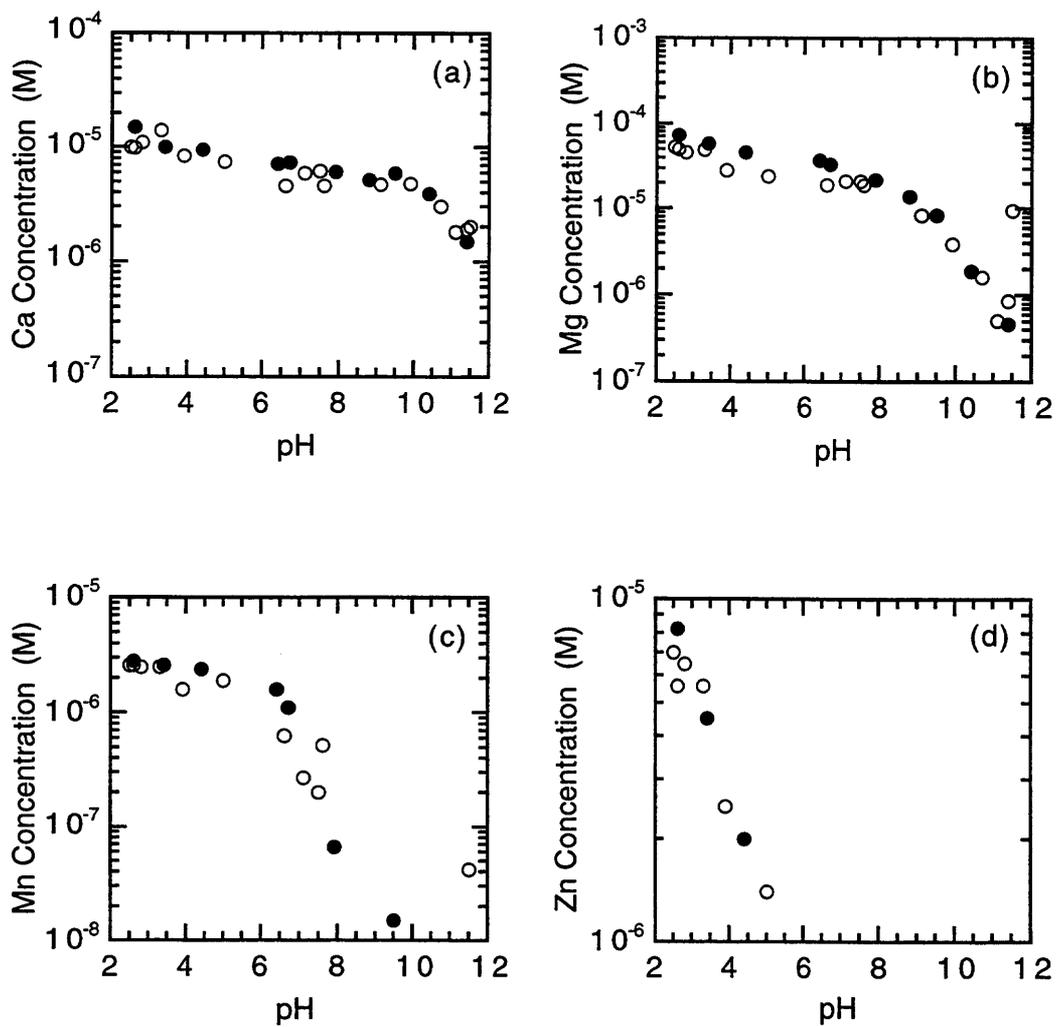


Figure 4: (a) to (d): Cation concentrations in batch titration tests after one (O) and seven (●) days. NaClO_4 concentration = 0.5 M.

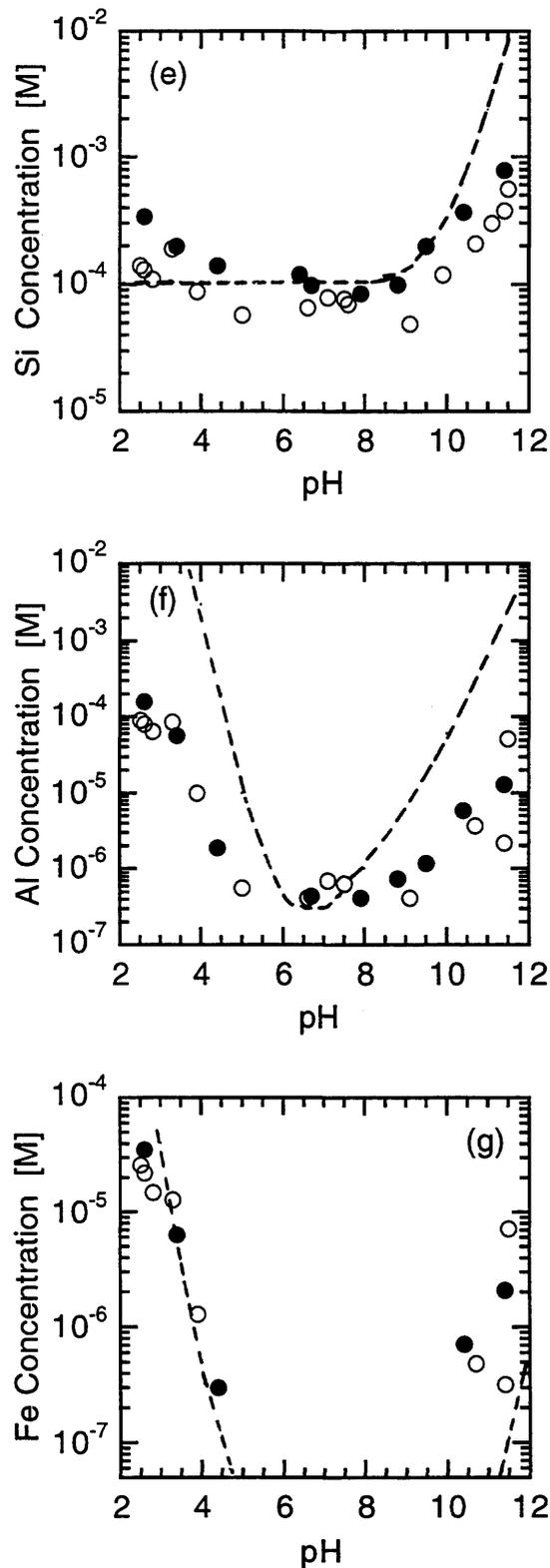


Figure 4: (e) to (g): Cation concentrations in batch titration tests after one (○) and seven (●) days. NaClO₄ concentration = 0.5 M. (The broken lines are the calculated solubilities for quartz, α -Al(OH)₃ (gibbsite) and amorphous ferric oxide in (e), (f) and (g) respectively.)

5.4 Discussion of Analytical Results

5.4.1 Ca, Mg, Mn and Zn

The Ca, Mg and Mn analysis results are given in Figures 4(a), 4(b) and 4(c) respectively. In the pH range up to ~ 10 for Ca, up to ~ 8 for Mg and up to ~ 6 for Mn, the individual data sets indicate no significant variations with pH. Also, measurements after 1 and 7 days are approximately the same over most of the pH range. Taking into consideration the conditioning process, the associated analytical results, the acid extraction data and the above observations, we would conclude that it is highly unlikely that the Ca, Mg and Mn aqueous concentrations arise from, or are controlled by, solid phases. Rather, the above behaviour is entirely consistent with cations which are present at fixed inventories in the conditioned Na-montmorillonite. That is to say, they exist predominantly as sorbed cations on the clay mineral. (At very low pH values clay minerals become unstable, and the rise in Mg concentration at pH ~ 3.5 is most probably due to the release of isomorphically substituted Mg into solution.)

The predominant aqueous species for Ca, Mg and Mn, over most of the pH range considered, is the bivalent cation (see for example BAES & MESMER 1976). For such cations the dominant sorption mechanism at low pH values is cation exchange (see BRUGGENWERT & KAMPHORST 1982). However, in high ionic strength solutions, such as the 0.5 M NaClO₄ used here, exchange reactions for bivalent cations are effectively blocked by the high Na concentrations. Indeed, any bivalent cations sorbed onto the surface by cation exchange are displaced from the solid into solution. The consequence of this argument is that the plateau regions at low pH values exhibited by all three cations in Figures 4 (a)-(c) reflect the inventories of Ca, Mg and Mn respectively. A simple calculation yields estimates of the inventories on conditioned Na-montmorillonite of 3 - 6 mmol kg⁻¹ Mg, 1 - 2 mmol kg⁻¹ Ca and 0.3 - 0.6 mmol kg⁻¹ Mn. The scatter in the aqueous concentration measurements does not allow more exact values to be determined. The inventories for the above 3 cations deduced from the severe acid extraction tests (section 3.4) lie within the ranges given above.

At pH values greater than ~ 10, ~ 8 and ~ 6 for Ca, Mg and Mn respectively the aqueous concentrations begin to decline. In all three cases we interpret this behaviour as being due to sorption via the formation of surface complexes with surface complexation constants increasing in the order Ca, Mg, Mn. Although the evidence presented here for this interpretation is somewhat circumstantial, we will return to this topic in the subsequent sorption and modelling reports where substantiating evidence will be presented. In addition, the influence of background impurities such as Mn (and Zn, see below) and omnipresent major components of natural waters such as Ca and Mg, on radionuclide sorption behaviour, will be analysed and discussed in detail.

The behaviour of Zn differs from that of Ca, Mg and Mn in that it does not exhibit a plateau region at low pH values, Figure 4(d). This is interpreted as being due to strong sorption via surface complexation which is already significant at pH = 3. Some preliminary sorption measurements using carrier free ^{65}Zn at initial activity levels corresponding to very low tracer additions ($< 10^{-9}$ M) tended to confirm this interpretation (Experimental details are given in Part II, BAEYENS & BRADBURY 1995.) A plot of these sorption measurements is given in Figure 5.

An estimate of the Zn inventory made from the aqueous concentration measurements at pH < 3 in an 0.5 M NaClO_4 solution yielded values between 0.9 and 1.3 mmol kg^{-1} . The inventory estimated from the severe acid extraction measurements (0.8 mmol kg^{-1}) is in agreement with the above data.

Because Ca, Mg, Mn and Zn are present at such relatively low levels in comparison with the site capacity of conditioned Na-montmorillonite (see section 7.5), and because their source is not a separate solid phase (see section 6.2), we conclude that these cations have little or no influence on the proton balances calculated from the forward and back titration measurements.

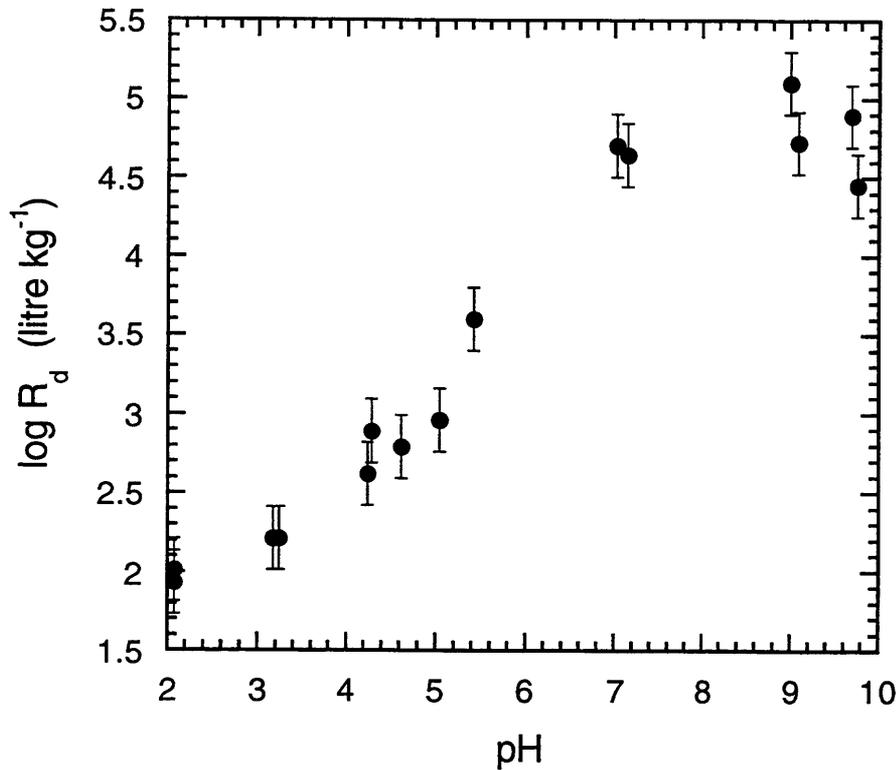
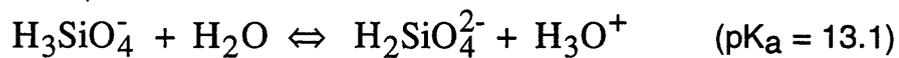


Figure 5: Preliminary sorption edge for Zn on conditioned Na-montmorillonite at 0.1 M NaClO₄ concentration

5.4.2 Si

The measured aqueous concentrations of Si, together with the calculated values assuming saturation with respect to quartz (dashed line), are given in Figure 4(e). (The thermodynamic data were taken from the compilation of PEARSON & BERNER 1991.) Mineralogical analyses of the conditioned Na-montmorillonite indicated that there was ~ 1 wt % quartz still present. The levels of Si in solution are most probably determined by the dissolution of quartz. (Note that at the highest pH values the complete dissolution of 1 wt % quartz corresponds to a Si concentration of ~ 10⁻³ M)

The dissolution of quartz to produce silicic acid (H₄SiO₄), does not, in itself, consume H⁺ or OH⁻ at any pH. In the pH region < 9 silicic acid does not hydrolyse and hence has no influence on the proton balance in titration experiments. However, in the alkaline region (pH > 9) H₄SiO₄ does hydrolyse, consuming hydroxyl ions (or releasing protons) via,



In titration tests with back titration such processes are accounted for, whereas for continuous titration methods they are not. Using the data in Figure 4 and Tables 8-11 it can be shown from mass balance considerations that, excluding OH^- neutralisation, the bulk of the acid needed in the back titrations from pH values above ~ 9.5 is required for the protolysis of H_3SiO_4^- species.

5.4.3 Al and Fe

The data from Tables 12, 13 and 14 for Al and Fe analyses are combined in Figures 4(f) and 4(g) respectively. For both Al and Fe there are no significant differences in the supernatant solution concentrations after 1 and 7 day batch titration times. From pH ~ 4 to ~ 10 the Al aqueous concentrations are essentially constant. (Fe concentrations in this pH range lay below the reliable detection limit.) The form of the plots are completely different from those for Ca, Mg, and Mn suggesting that Al and Fe are not inventory limited.

The dashed lines in the figures are solubility plots for gibbsite and amorphous ferric hydroxide calculated using the thermodynamic data base compilation of PEARSON & BERNER (1991) and PEARSON et al. (1992). However, it should be recognised that there are different forms of "gibbsite" and "ferric hydroxides" and the calculated solubilities given here are only meant to be indicative.

In Figure 4(f) the measured Al concentrations are generally significantly lower than the calculated values, indicating a strong undersaturation with respect to gibbsite. It is possible that dissolution kinetics are playing a role here, however, since the data after 1 and 7 days are essentially the same, we consider this to be unlikely. Rather, the indications are that there is probably too little gibbsite present to maintain saturation. (A step in the conditioning procedure, section 2.3.3, was designed to remove any freshly precipitated $\text{Al}(\text{OH})_3$.) The levels of Al in solution most likely arise from residual $\text{Al}(\text{OH})_3$

remaining after conditioning and also from the hydrolysis of the Na-montmorillonite.

For the calculation of proton balances to produce net titration curves, two important factors concerning the potential influence of Al in the system need to be considered. The first is that at lower pH levels, dissolving gibbsite will bring aluminium into solution, mainly as the trivalent cation, and hence cation exchange reactions will occur. These exchange reactions can influence the proton balance calculations and need to be accounted for, see section 6.2 and 6.3. The second concerns precipitation reactions. In any of the forward titration tests precipitation effects are very unlikely since the starting pH was, without exception, approximately neutral i.e. at the minimum in the curve in Figure 4(f). Thus, any increase or decrease in pH was always in the direction of increasing solubility and there were no indications that solubility limits were ever reached. Thus, precipitation reactions are not occurring and consequently were not influencing proton balance calculations.

At pH values < 5 (and > 10) the experimentally determined Fe data are described reasonably well by the calculated solubility curve for amorphous $\text{Fe}(\text{OH})_3$. The extraction data given in Table 4 show that amorphous iron containing phases are present in the system at a level of $\sim 7.6 \text{ mmol kg}^{-1}$. From a mass balance point of view, there is more than sufficient amorphous Fe present to account for the concentrations measured in solution even at the lowest pH values.

Even though we considered that the aqueous Fe concentrations are determined by an amorphous solid phase, the low pH concentration profile for Fe is somewhat reminiscent of that for Zn. By analogy it may be that trivalent Fe is exhibiting a strong and early pH dependent sorption behaviour. This possibility was investigated by carrying out sorption measurements with trace quantities of carrier free ^{59}Fe . The results are shown in Figure 6.

From the data given in Figure 6 it is clear that the uptake of Fe in the pH range 3 to 7 shows little or no dependence on pH and exhibits a completely different behaviour to that of Zn.

Although the influence of Al and Fe on titration (sorption) measurements is potentially complex, even in this "simplified" conditioned Na-montmorillonite system, we will try to summarise the effects and their relative importance.

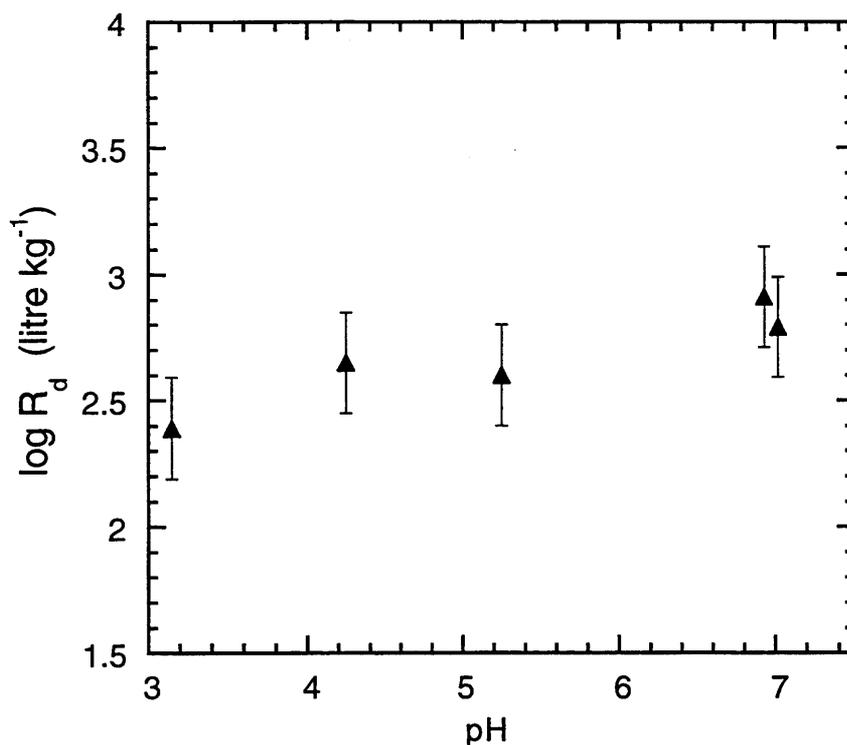


Figure 6. Sorption edge for Fe on conditioned Na-montmorillonite at 0.1 M NaClO_4 concentration

In general, we consider that the arguments given in section 5.1 in support of the back titration method apply to Al and Fe dissolution processes. In particular, precipitation and precipitation kinetics are not of prime importance for proton mass balance calculations since $\text{H}^+(\text{OH}^-)$ consuming dissolution reactions in the forward titration are balanced by fast aqueous phase $\text{OH}^-(\text{H}^+)$ consuming hydrolysis/protolysis reactions in the back titration (see also above discussion for Si). Therefore, there is no significant direct influence of Al/Fe dissolution reactions on the titration results.

For Al and Fe it is unlikely that highly surface active fresh amorphous precipitates were being formed which could have influenced the titration behaviour. (A similar conclusion was also reached by WANNER et al. (1994)

in their titration measurements on Na-montmorillonite.) Starting pH values were always neutral (minimum Al/Fe solubilities) and any increase or decrease in pH was in the direction of increasing solubility. Also the data strongly suggested that the system always remained undersaturated with respect to Al.

When (hydr)oxides of iron are present they may make a contribution to titration results via their own amphoteric surface sites. If we make the conservative assumption that the whole of the iron present in conditioned Na-montmorillonite (14 mmol kg^{-1}) is in the form of hydrous ferric oxide with a site density of $0.2 \text{ mmol /mmol Fe}$ (DZOMBAK & MOREL 1990), this constitutes 2.8 mmoles sites per kg. This is only ~ 3.5 % of the estimated sites available from Na-montmorillonite (80 mmoles sites per kg, Chapter 7). Consequently, we conclude that the iron containing solid phases do not have a direct influence on the titration measurements.

An indirect effect on titration experiments of Al/Fe entering the aqueous phase, particularly at lower pH where the trivalent cation species dominates, arises from cation exchange reactions. The influence of this process is significant and will be discussed separately and quantified in the following chapter.

6 THE INFLUENCE OF PROTON EXCHANGE AND CATION EXCHANGE ON TITRATION MEASUREMENTS

It is well known that clay minerals, particularly at low and high pH values, dissolve incongruently releasing structural elements such as Fe, Al, Si, and Mg (MAY et al. 1986; BRADY & WALTHER 1989; STUMM & WIELAND 1990; WIELAND & STUMM 1992). The released elements may, depending on the local conditions, precipitate as secondary minerals e.g. Al and Fe (hydr)oxides. The effects of dissolution/precipitation reactions occurring simultaneously with titration and sorption measurements were assessed in the previous chapter. In this chapter the effects of other processes, primarily proton exchange and dissolution coupled with cation exchange, on Na-montmorillonite titration experiments will be addressed.

6.1 Proton Exchange on the Fixed Charge Sites

For a homo-ionic Na clay mineral in a simple background electrolyte such as NaClO₄ at a fixed ionic strength, proton exchange reactions can be written as:



Following GAINES & THOMAS (1953) the selectivity coefficient is defined by:

$$K_{\text{Na}}^{\text{H}} = \frac{N_{\text{H}}}{N_{\text{Na}}} \cdot \frac{a_{\text{Na}^+}}{a_{\text{H}^+}} \quad [5]$$

where "a" indicates aqueous activities, and N_{Na} and N_{H} are the equivalent fractions of Na⁺ and H⁺ respectively occupying the exchange sites on the clay.

Let us consider the actual titration conditions used in the case of conditioned Na-montmorillonite and the likelihood of protons exchanging with Na⁺ as well as undergoing acid/base reactions with the surface sites. The selectivity of H⁺ with respect to Na⁺ is close to unity and constant for a montmorillonite clay i.e. $K_{\text{Na}}^{\text{H}}=1$ (GILBERT & LAUDELOUT 1965; FOSCOLOS & BARSHAD 1969). Since the clay mineral begins to undergo hydrolysis at pH < 3, we take this

value as being a likely lower bound for pH. Substituting $a_{\text{H}} = 10^{-3}$ and $a_{\text{Na}} = 10^{-1.11}$ for an 0.1 M NaClO_4 solution into equation 5 gives,

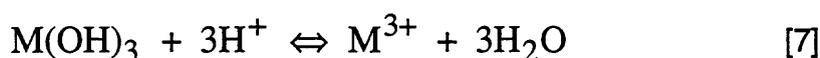
$$N_{\text{H}} = 1 \cdot N_{\text{Na}} \cdot \frac{10^{-3}}{10^{-1.11}} \quad [6]$$

In almost all conceivable practical cases N_{Na} will have a value close to unity in systems where the NaClO_4 concentration is greater than or equal to 0.1 M. Hence, from equation 6, the calculated value of N_{H} is $\sim 1.3 \times 10^{-2}$. Taking a CEC for Na-montmorillonite of 870 meq kg^{-1} (section 3.5), and the calculated proton fractional occupancy of $\sim 1.3 \times 10^{-2}$ implies that $870 \times 1.3 \cdot 10^{-2}$ or ~ 11 meq of protons per kg have exchanged with Na on the clay due to cation exchange. If we use the $\equiv\text{SOH}$ site density of 80 mmol kg^{-1} , estimated later in Chapter 7, and assume all sites to be protonated at $\text{pH} = 3$, then the total proton consumption is 91 mmol kg^{-1} , i.e. the contribution from H^+ - Na^+ exchange is $\sim 10\%$. For titrations carried out down to $\text{pH} = 2$ the situation is considerably worse. The contribution from the $\equiv\text{SOH}$ sites to the total protons consumed remains approximately the same whereas those exchanging with Na^+ would increase by an order of magnitude to 110 mmol kg^{-1} , i.e. $\sim 60\%$ of the total. However, higher background electrolyte concentrations can reduce the influence of proton exchange. For example, at a NaClO_4 concentration of 0.5 M the contribution of proton exchange to the total protons consumed in the above examples would be reduced to $\sim 2\%$ and $\sim 10\%$ at $\text{pH} = 3$ and 2 respectively.

Back titrations of supernatant solutions from batch titration experiments will not compensate for the effects of proton exchange because aqueous and solid phases are separated prior to the back titration. Hence, when the proton mass balance is made, the net proton consumption calculated will include a contribution from proton exchange with Na^+ on the cation exchange sites. In order to reduce this source of error, Na-Montmorillonite suspensions in 0.1 and 0.5 M NaClO_4 were only titrated to $\text{pH} = 4$ and $\text{pH} = 2.5$ respectively. Restricting the end pH to these values reduced the uncertainties arising from proton exchange to negligible levels.

6.2 Dissolution and Cation Exchange Processes at Low pH

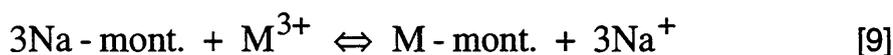
In order to illustrate the influence of cation exchange processes occurring in conjunction with dissolution/precipitation reactions in titration experiments on high exchange capacity solids, consider the following. A homo-ionic Na-montmorillonite at neutral pH, containing a sparingly soluble trivalent hydroxide phase such as $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$, is acidified. As the pH decreases, the solubility of these solids increases. The dissolution process consumes protons:



If this were the end of the reaction sequence all would be well since the back titration would consume three OH^- ions for each $\text{M}(\text{OH})_3$ molecule dissolved, i.e.



Hence the protons consumed by the dissolution reaction would be exactly compensated by the hydroxyls consumed in the back titration. However, when cations are released into solution in the presence of a cation exchange medium, exchange reactions would be expected to occur, i.e.



The trivalent metal cations generated from the dissolution of $\text{M}(\text{OH})_3$ are (partially) removed from solution by cation exchange on the planar sites of the clay and three Na^+ ions are displaced into solution for each exchanged M^{3+} . The extent to which the exchange reaction takes place will depend, amongst other factors, upon pH, the exchange capacity of the solid, the solubility limit of the dissolving phase (or quantity of this phase present) and the aqueous speciation.

The back titration of the supernatant solution from a batch titration experiment in which the above is occurring will not account for the M^{3+} exchanged and therefore the protons consumed in the generation of these ions. The effect of

this will be an overestimation of the proton consumption ascribed to the solid acid/base surface reactions.

However, although trivalent ions such as Al^{3+} and Fe^{3+} generally have high selectivity coefficients with respect to Na^+ , and would therefore be expected to exchange strongly and extensively, the aqueous speciation behaviour is such that the concentration of Al^{3+} and Fe^{3+} decreases extremely rapidly with pH (BAES & MESMER 1976). At pH values above 5 for Al and above 3 for Fe, less positively charged, neutral or negatively charged hydrolysis species are formed and these are highly unlikely to undergo exchange. As a consequence of this, exchange processes will be negligible in neutral to basic solutions and need only be considered at the lowest pH values. Titration curves therefore tend to be skewed towards lower pH values.

In order to estimate the potential effect of the above mechanism on the proton balance in titration measurements as a function of Al/Fe concentration, pH and ionic strength, calculations were carried out to estimate the quantities of trivalent cation sorbed.

For equation 9, a selectivity coefficient for M^{3+} - Na^+ exchange can be defined as,

$$\frac{\text{M}^{3+}}{\text{Na}^+} K_c = \frac{N_{\text{M}^{3+}}}{(N_{\text{Na}^+})^3} \cdot \frac{(a_{\text{Na}^+})^3}{a_{\text{M}^{3+}}} \quad [10]$$

where $a_M = a_{\text{Al}} + a_{\text{Fe}}$

$\text{M}^{3+} = \text{Al}^{3+} + \text{Fe}^{3+}$

$N_M + N_{\text{Na}} = 1$

Aqueous activities of the trivalent cations Al^{3+} and Fe^{3+} were calculated in the acid region of the titration experiments for the corresponding Al/Fe concentration data given in Tables 12 to 15 as a function of ionic strength using MINEQL (WESTALL et al. 1976) and the hydrolysis data for Al and Fe given in PEARSON et al. (1992).

Selectivity coefficient data for Al and Fe are not available for trace metal concentrations at the ionic strengths where we have made measurements. The assumption was made that the exchange behaviour of Al and Fe on Na-montmorillonite is similar to that of trivalent Eu. The Eu selectivity coefficient values given in BRADBURY & BAEYENS (1994) were used to calculate N_M values ($M^{3+} = Al^{3+} + Fe^{3+}$) from which the equivalents of exchanged Al^{3+} plus Fe^{3+} could be estimated as a function of pH and ionic strength. The N_M values are summarised in Tables 16 and 17. According to the interpretation given previously, the proton consumption ascribed to acid/base surface reactions in the acid region will be overestimated by the equivalents of Al^{3+} plus Fe^{3+} exchanged.

The contribution of Fe in the above calculations needs only be taken into account for pH values less than 3 since at higher values the fraction Fe^{3+}/Fe_{TOT} becomes insignificant. Because Al is present at higher concentrations and hydrolysis reactions only become important at pH values above 5, its effect is generally greater than that of Fe. At total concentrations of Al + Fe of $\leq 10^{-6}$ M the influence of cation exchange on the proton balance becomes negligible. The validity of the lowest fractional occupancies given in Tables 16 and 17 (N_M values ≤ 0.005) may be questionable in view of the assumptions used in the calculations. They have been included mainly to illustrate the development of the potential error over the measured range of Fe/Al concentrations. (An N_M value of 0.001 results in a $\sim 1\%$ error in the proton balance, Tables 18 and 19, and therefore has no practical significance.)

The tendency of clays to adsorb Al at low pH values is well known (see for example CREMERS (1972) and references contained therein) and the way in which such reactions can potentially influence titration experiments has been set out here. However, it must be admitted that quantifying the effect constitutes a problem, primarily because reliable selectivity coefficient values for Al and Fe at trace concentrations as a function of ionic strength could not be found. The use of Eu selectivity data is a reasonable assumption but cannot be fully justified. Thus, when considering the data given in Tables 16 and 17, which are used as corrections to the proton balance data (Table 18 and 19 in the following chapter), the intrinsic uncertainties associated with the calculations should not be forgotten.

Table 16: Calculations of the quantities of (Al+Fe) sorbed by cation exchange on Na-montmorillonite during the titration experiments at 0.5 M NaClO₄; log K_C =2.6

Data point	pH	Al conc. (M)	Fe conc. (M)	N _M [‡]	(Al+Fe) sorbed (meq kg ⁻¹)
A2	6.6	4.1E-7	< rdl [#]	-	-
A3*	6.3	4.0E-7	< rdl	-	-
A4	5.9	4.0E-7	< rdl	-	-
A5	5.0	5.6E-7	< rdl	-	-
A6*	4.3	3.0E-6	6.0E-7	0.001	1.2
A7*	4.0	5.0E-6	8.0E-7	0.002	2.1
A8	3.9	1.0E-5	1.3E-6	0.005	4.3
A9*	3.8	1.1E-5	1.4E-6	0.006	5.1
B1	3.3	8.6E-5	1.3E-5	0.040	34.0
B2	2.8	6.4E-5	1.5E-5	0.033	28.1
B3	2.6	8.1E-5	2.2E-5	0.042	35.7
B4	2.5	9.1E-5	2.6E-5	0.048	47.3
C1	6.7	4.4E-7	2.5E-7	-	-
C3	4.4	1.9E-6	2.5E-7	0.001	0.9
C4	3.4	5.7E-5	6.4E-6	0.026	22.1
C5	2.6	1.6E-4	3.5E-5	0.074	62.9

* Concentrations derived from Figures 4e and f

- < rdl: Below reliable detection limits

‡ - N_M values rounded to three decimal places (see text).

Table 17: Calculations of the quantities of (Al+Fe) sorbed by cation exchange on Na-montmorillonite during the titration experiments at $I = 0.1$ M NaClO₄; $\log K_C = 1.6$

Data point	pH	Al conc. (M)	Fe conc. (M)	N _M	Al+Fe sorbed (meq kg ⁻¹)
D2*	7.8	1.0E-6	< rdl	-	-
D3	6.9	8.2E-7	< rdl	-	-
D4*	6.1	1.0E-6	< rdl	-	-
D5*	5.3	5.0E-7	< rdl	-	-
D6	4.4	2.7E-6	5.3E-7	0.021	17.9
D7	4.0	4.1E-6	1.5E-6	0.033	28.1
D8*	4.0	4.0E-6	1.5E-6	0.033	28.1

* Data interpolated from results given in Table 17.

6.3 Dissolution and Sorption Processes at High pH

The form of the titration curve given later in Figure 7, section 7.1, strongly indicates that OH⁻ consuming processes are occurring at pH values greater than 11 in addition to the deprotonation of ≡SOH surface sites since the curve shows no sign of levelling off. The significant increase in the rate of OH⁻ consumption in this pH range (Figure 7) corresponds to the rapid increase in Si, Al and Fe concentrations, see Figures 4(e), (f) and (g) respectively. However, whether these two observations are directly linked is unclear. The solution chemistries of Si, Al and Fe at high pH are uncertain and are probably complicated by the formation of polynuclear species (BAES & MESMER 1976; EIKENBERG 1990). Although sorption reactions of Al and Fe species on ≡SOH type surface sites might be postulated, in analogy with the cation exchange processes occurring in the lower pH regions, section 6.2, there is no direct evidence for this. Therefore, at the present time, we are not in a position to make quantitative estimates of the potential interfering effects occurring at high pH. All we can say is that the effects are likely to lead to increased OH⁻ consumption, i.e. to overestimates for the OH⁻ consumption by ≡SOH sites. Consequently, there is a high degree of uncertainty in the data in Tables 8 - 10 at pH ≥ 11. Values measured in this pH range should be viewed as being less reliable than the other data.

7 TITRATION CURVES, END-POINTS AND SITE CAPACITIES FOR CONDITIONED Na-MONTMORILLONITE.

7.1 Titration Curves for $\equiv\text{SOH}$ Surface Sites on Conditioned Na-Montmorillonite.

The net quantities of protons consumed in the acid titration region for Na-montmorillonite in 0.5 M and 0.1M NaClO_4 electrolyte solutions are presented in Tables 18 and 19 respectively. These values have been produced by combining the data in Tables 8 - 11, forward and back titration measurements, with those in Tables 16 and 17, where estimates for the proton consumption by processes described in the previous chapter are given. By the careful choice of experimental conditions, e.g. see section 6.1, the effects of other potentially disturbing processes were designed out of the experiments, leaving only the "dissolution/cation exchange" mechanism which could not be avoided in the measurements. The values given in Tables 18 and 19 are the corrections resulting from this mechanism.

As a consequence of the results and discussions given in chapters 5 and 6 we believe that the net proton consumption data in Tables 18 and 19 reflect the true levels of protons consumed by the amphoteric $\equiv\text{SOH}$ surface sites of Na-montmorillonite. The complementary half of the data, the base titration results, are as given in Tables 8 - 11 under the heading "Total OH^- consumed (mmol kg^{-1})". A combined plot of all the acid/base titration data is given in Figure 7.

The titration data in Figure 7 will only be discussed in general terms here. In a subsequent report (BRADBURY & BAEYENS 1995), the titration behaviour of Na-montmorillonite will be modelled, and detailed discussions and interpretations of the curves in Figure 7 will be postponed until then.

Table 18: Proton balances from forward and back titration measurements at 0.5 M NaClO₄ with cation exchange corrections.

Data point	pH	Total H ⁺ consumed (mmol kg ⁻¹)	H ⁺ consumed via exchange (mmol kg ⁻¹)	NET H ⁺ consumed (mmol kg ⁻¹)
A2	6.6	7.1	NC	7.1
A3	6.3	15.3	NC	15.3
A4	5.9	23.5	NC	23.5
A5	5.0	37.8	NC	37.8
A6	4.3	48.1	1.2	46.9
A7	4.0	52.6	2.1	50.5
A8	3.9	61.5	4.3	57.2
A9	3.8	65.2	5.1	60.1
B1	3.3	102.0	34.0	68.0
B2	2.8	89.4	28.1	61.3
B3	2.6	113.8	35.7	78.1
B4	2.5	101.6	47.3	54.3
C1	6.7	18.9	NC	18.9
C2	6.4	38.3	NC	38.3
C3	4.4	68.3	0.9	67.4
C4	3.4	94.9	22.1	72.8
C5	2.6	161.8	62.9	98.9

NC = No contribution from cation exchange processes.

Table 19: Proton balances from forward and back titration measurements at 0.1 M NaClO₄ with cation exchange corrections

Data point	pH	Total H ⁺ consumed (mmol kg ⁻¹)	H ⁺ consumed via exchange (mmol kg ⁻¹)	NET H ⁺ consumed (mmol kg ⁻¹)
D2	7.8	7.8	NC	7.8
D3	6.9	18.2	NC	18.2
D4	6.1	36.7	NC	36.7
D5	5.3	55.5	0.8	54.7
D6	4.4	69.7	17.9	51.8
D7	4.0	91.8	28.1	63.7
D8	4.0	99.5	34	65.5

NC = No contribution from cation exchange processes.

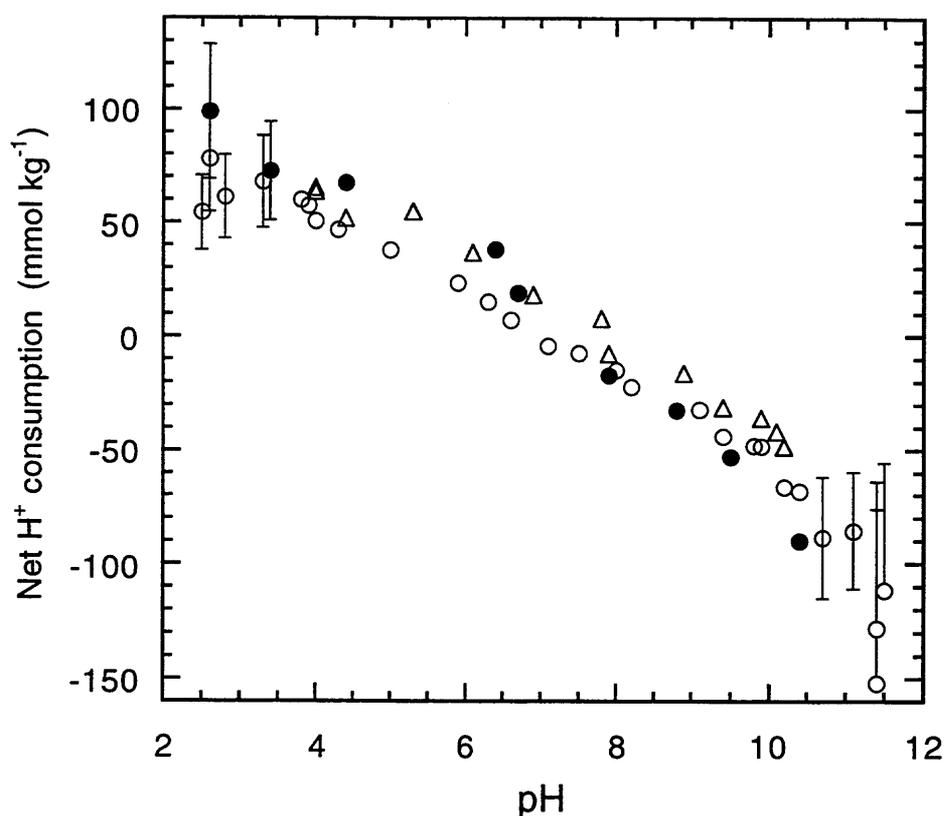


Figure 7: Titration data of conditioned Na-montmorillonite at 0.5 M NaClO₄; 1 day (O); 7 days (●) and at 0.1 M NaClO₄; 1 day (Δ)

7.2 Errors

Despite all the care and precautions taken with the measurements described in the previous chapters, the errors associated with titration data can be potentially quite large, particularly at high and low pH values. For example consider the data given in Figure 8 where the quantities of acid (base) added are plotted as a function of pH together with the net titration curve for conditioned Na-montmorillonite (data from Figure 7, $I = 0.5 \text{ M NaClO}_4$; 1 day). The errors associated with acid/base additions using Eppendorf pipettes are $\leq 1\%$, and the maximum error in the back titration measurements was estimated to be $\sim 5\%$. For most of the data the errors in the quantities of $\text{H}^+(\text{OH}^-)$ consumed are of the order of those in the back titrations. However, for the pH regions < 3.5 and > 10 , the amounts of base (acid) required in the back titrations are close to the quantities of acid (base) added in the forward titrations. This results in the 5% error in the former propagating into an $\sim 30\%$

error in the values for $H^+(OH^-)$ consumed, Tables 9 and 10. In addition, there are the uncertainties in the corrections described and discussed in section 6.3.

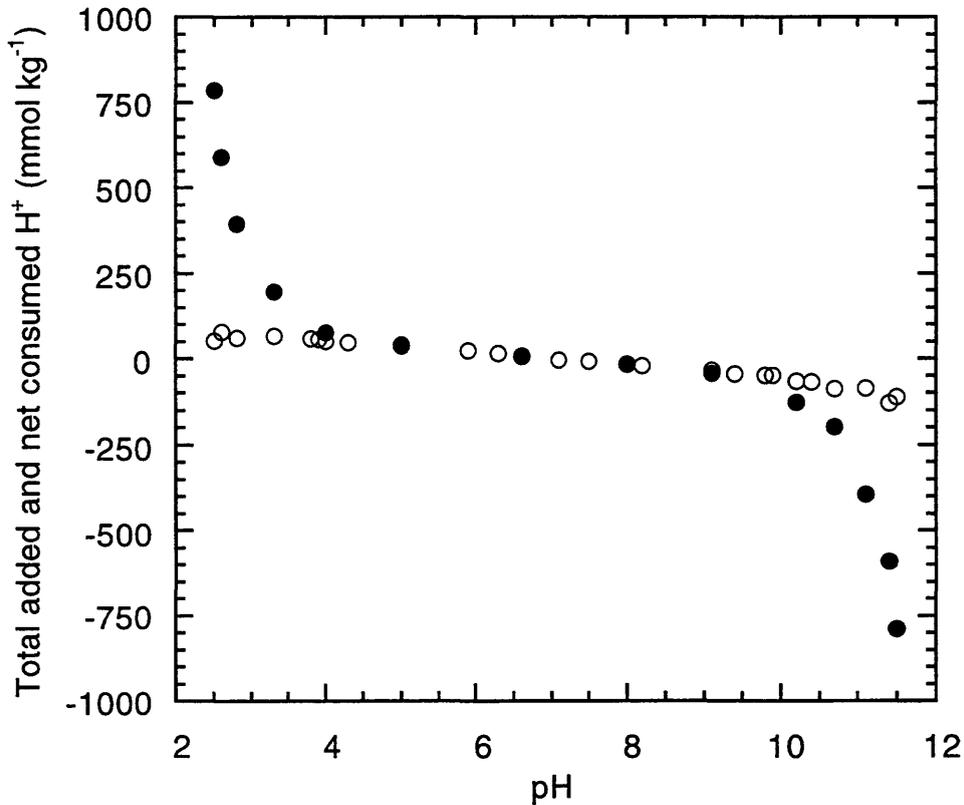


Figure 8: Total added acid/base (●) and corresponding net proton consumption (○) for the titration of conditioned Na-montmorillonite at 0.5 M $NaClO_4$ and 1 day equilibration time

For acid or base additions resulting in pH values in the range 6-8, there were some kinetic effects observed i.e. the system tended to buffer itself back as a function of time to the starting pH of ~ 6.7 . This led to some uncertainty in the value of the pH in the forward titrations.

The titration data plotted in Figure 7 are taken from titration measurements made on different batches of Na-montmorillonite, carried out on different occasions for different times and under different conditions. We would say that the spread in the data in Figure 7 represents a reasonable estimate of the overall uncertainties in the titration values associated with the variables mentioned above.

7.3 Influence of Ionic Strength and Titration Times

Immediately apparent from Figure 7 is that there is little or no difference in the titration plots for background electrolyte concentrations of 0.1 M and 0.5 M NaClO₄, and between titration times of 1 and 7 days. This is in strong contrast to the behaviour observed in metal oxide systems (see for example, HUANG 1981; JAMES & PARKS 1982) where the titration curves measured at different ionic strengths intersect at a common point. The ionic strength independent characteristic observed for Na-montmorillonite is perhaps a first indication that clay minerals and metal oxides do not behave in an analogous manner and therefore that the surface complexation model developed mainly for oxide systems is not directly applicable to clay mineral systems i.e. different model descriptions may be necessary (BRADBURY & BAEYENS 1995).

7.4 Titration End-Points

In theory at least, solid titration curves should exhibit end points in both the acid and base regions. Practically, this is seldom the case. The reasons are numerous. For clay minerals, continuous titration methods have often been applied. As discussed in section 5.1, this technique fails to take into account any effects arising from the dissolution of the solid and also, as shown in the specific case of Na-montmorillonite in section 5.2, the continuous titration results obtained depend on experimental factors such as the time scale over which the titration is carried out, the starting pH, and the direction of the titration.

Even using batch methods with back titration of the supernatant solutions where some of the effects due to dissolution may be taken care of, there are many other processes occurring in parallel with protonation/deprotonation reactions on $\equiv\text{SOH}$ type surface sites. Such processes, which have been discussed in section 5.1 and Chapter 6, are complex and difficult to quantify. All the factors mentioned above would have the effect of smearing out any evidence of an end point, unless they can be taken into account.

In Figure 7, at pH < 4, there is an indication of a plateau in the titration curve which we would tentatively interpret as an end point. The influence of those processes described in section 5.1 and Chapter 6 have been taken into

account in determining the solid titration curve in the acid region. Unfortunately we were not able to analyse the data at the high pH region in a similar manner since the processes occurring there are unclear. Hence the high pH end point is smeared out. All we are able to conclude from the discussion in section 6.3 is that the data above pH ~ 11 are uncertain and overestimate the quantities of base required in the deprotonation of $\equiv\text{SOH}$ sites.

7.5 Estimates of the $\equiv\text{SOH}$ Site Capacity for Na-Montmorillonite

The sorption site capacity of a solid is an important parameter in any surface complex modelling studies and a number of different, often indirect, methods have been proposed and used to measure its value (DAVIS & KENT 1990; DZOMBAK & MOREL 1990 and references therein). If clear end points on the acid (all available $\equiv\text{SOH}$ sites protonated) and base (all available $\equiv\text{SOH}$ sites deprotonated) sides of the titration curve could be established, this would be a more direct means of determining the available site capacity. Even though there are uncertainties we considered the acid side of the titration curve as the most reliable and estimated the end point (indicated in the figure by dotted lines) for the $\equiv\text{SOH}$ site capacity for Na-montmorillonite of 80 mmoles of sites kg^{-1} . This value can be re-expressed as 2.3×10^{-6} moles of sites m^{-2} using the N_2 -BET determined surface area of $35 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$, section 3.6.

8 SUMMARY AND CONCLUSIONS

Commercially available Na-montmorillonite contains significant levels of background impurities and sparingly soluble minerals which influence the titration and sorption properties of the clay suspensions in often unquantifiable ways and which lead to severe difficulties in the interpretation and modelling of data. An experimental procedure was devised to purify the SWy-1 Na-montmorillonite (Crook County, Wyoming) source material and convert it to the homo-ionic Na-form. This conditioning procedure is critical to all the subsequent experiments and was described in detail.

Measurements such as cation exchange capacity, N₂-BET surface area, total and amorphous Fe-oxide content and the aqueous composition of suspensions were carried out to characterise the conditioned Na-montmorillonite. The CEC results showed clearly that there was very good consistency between the different batches used in the investigations.

Continuous potentiometric titration methods for suspensions of Na-montmorillonite, though quick and easy to perform, were shown to exhibit pronounced hysteresis effects and therefore to be unsuitable. Instead, a batch titration technique, coupled with chemical analysis and back titration of the individual supernatant solutions, was chosen. Series of batch titration experiments were carried out in a background electrolyte of NaClO₄ at concentrations of 0.1 and 0.5 M for equilibration times of 1 and 7 days. The effects of proton consuming processes such as dissolution of the clay mineral, H⁺ exchange and Al³⁺/Fe³⁺ exchange on permanent charge sites are described and discussed. Only the latter mechanism could not be designed out of the batch titration tests by the appropriate choice of experimental conditions. However, with the aid of chemical analyses results for the supernatant solutions from titration tests, a quantitative estimate of its influence was made and taken into account.

The end result of these procedures was the production of titration curves which reflected only the acid/base behaviour of the amphoteric ≡SOH surface sites. Within the estimated uncertainty range of the data, the titration curves obtained were independent of ionic strength and equilibration times.

From the end point in the acid region of the titration curve a site capacity for conditioned Na-montmorillonite of ~ 80 mmoles of sites kg^{-1} was estimated (2.3×10^{-6} moles of sites m^{-2}).

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REFERENCES

- BAES, Jr. C.F. & MESMER, R.E. (1976): The hydrolysis of cations. John Wiley & Sons, New York.
- BAEYENS, B. & BRADBURY, M.H. (1995): A quantitative mechanistic description of Zn, Ca and Ni sorption on Na-montmorillonite. Part II: Sorption measurements. PSI Bericht Nr. 95-11. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 95-05, Nagra, Wettingen, Switzerland.
- BEENE, G.M., BRYANT, R. & WILLIAMS, D.J.A. (1991): Electrochemical properties of illites. *J. Colloid Interface Sci.* 147, 358-369.
- BOLT, G.H. (1982): Thermodynamics of cation exchange. In: BOLT, G.H. (ed.): *Soil chemistry B. Physico-chemical models.* Elsevier, Amsterdam, 27-46.
- BRADBURY, M.H. & BAEYENS, B. (1994): Sorption by cation exchange. Incorporation of a cation exchange model into geochemical computer codes. PSI Bericht Nr. 94-07. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 94-11, Nagra, Wettingen, Switzerland. 1994.
- BRADBURY, M.H. & BAEYENS, B. (1995): A quantitative mechanistic description of Zn, Ca and Ni sorption on Na-montmorillonite. Part III: Modelling. PSI Bericht Nr. 95-12. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 95-06, Nagra, Wettingen, Switzerland.
- BRADY, P.V. & WALTHER, J.V. (1989): Controls on silicate dissolution rates in neutral and basic pH solutions at 25 °C. *Geochim. Cosmochim. Acta* 53, 2823-2830.
- BRINKMAN R. (1982): Clay transformations: Aspects of equilibrium and kinetics. In: BOLT, G.H. (ed.): *Soil chemistry B. Physico-chemical models.* Elsevier, Amsterdam, 433-458.

- BRUGGENWERT, M.G.M. & KAMPHORST, A. (1982): Survey of experimental information on cation exchange in soil systems. In: BOLT, G.H. (ed.): Soil chemistry B. Physico-chemical models. Elsevier, Amsterdam, 141-203.
- CREMERS, A. (1972) Chemical and physico-chemical aspects of soil and clay acidity. *Agricultura* Nr. 2.
- DAVIES, C.W. (1962): Ion Association. Butterworths, London.
- DAVIS, J.A. & KENT, D.B. (1990): Surface complexation modelling in aqueous geochemistry. In: HOCELL, Jr. M.F. & WHITE, A.F. (eds.): Mineral-Water Interface Geochemistry 23, 177-260.
- DAVIS, J.A., JAMES, R.O. & LECKIE, J.O. (1978): Surface ionisation and complexation at the oxide/water interface. I. Computation of electrical double layer properties in simple electrolytes. *J. Colloid Interface Sci.* 63, 480-499.
- DZOMBAK, D.A. & MOREL, F.M.M. (1990): Surface complexation modelling. John Wiley & Sons, New York.
- EIKENBERG J. (1990): On the problem of silica solubility at high pH. PSI Bericht Nr. 74. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 90-36, Nagra, Wettingen, Switzerland.
- FLETCHER, P. & SPOSITO, G. (1989): The chemical modelling of clay/electrolyte interactions for montmorillonite. *Clay Minerals* 24, 375-391.
- FOSCOLOS, A.E. & BARSHAD, I. (1969): Equilibrium constants between both freshly prepared and aged H-montmorillonites and chloride salt solutions. *Soil Sci. Soc. Am. Proc.* 33, 242-247.
- GAINES, G.I. & THOMAS, H.C. (1953): Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. *J. Chem. Phys.* 21, 714-718.

- GILBERT M. & LAUDELOUT, H. (1965): Exchange properties of hydrogen ions in clays. *Soil Sci.* 100, 157-162.
- GREGG, S.J. & SING, K.S.W. (1982): Adsorption, surface area and porosity. Academic Press, London.
- HAYES, K.F., REDDEN, G., ELA, W. & LECKIE, J.O. (1991): Surface complexation models: An evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *J. Colloid Interface Sci.* 142, 448-469.
- HIEMSTRA, T., VAN RIEMSDIJK, W.H. & BRUGGENWERT, M.G.M. (1987): Proton adsorption mechanism at the gibbsite and aluminium oxide solid/solution interface. *Netherlands J. Agric. Sci.* 35, 281-293.
- HIEMSTRA, T. & VAN RIEMSDIJK, W.H. (1991): Physical chemical interpretation of primary charging behaviour of metal(hydr)oxides. *Colloids and Surfaces* 59, 7-25.
- HUANG C.P. (1981): The surface acidity of hydrous solids. In: ANDERSON, M.A. & RUBIN, A.J. (eds.): Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Science, Ann Arbor, 183-217.
- JAMES, R.O. & PARKS, G.A. (1982): Characterization of aqueous colloids by their electrical double-layer and intrinsic surface chemical properties. In: MATIJEVIC, E. (ed.): *Surface and Colloid Science* 12, Plenum Press, New York, 119-216.
- LÖVGREN, L., SJÖBERG, S. & SCHINDLER, P.W. (1990): Acid/base reactions and Al(III) complexation at the surface of goethite. *Geochim. Cosmochim. Acta* 54, 1301-1306.
- MAES, A. & CREMERS, A. (1973): Cation-exchange hysteresis in montmorillonite: A pH-dependent effect. *Soil Sci.* 119, 198-202.

- MAY, H.M., KINNIBURGH, D.G., HELMKE, P.A. & JACKSON, M.L. (1986): Aqueous dissolution, solubilities and thermodynamic stabilities of common aluminosilicate clay minerals: Kaolinite and smectites. *Geochim. Cosmochim. Acta* 50, 1667-1677.
- MAZUREK, M. (1994): Personal communication.
- MEHRA, O.P. & JACKSON, M.L. (1960): Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Proc. 7. Nat. Conf. Clays and Clay Minerals*, 317-327.
- MOREL, F.M.M., YEASTED, J.G. & WESTALL, J.C. (1981): Adsorption models: A mathematical analysis in the framework of general equilibrium calculations. In: ANDERSON, M.A. & RUBIN, A.J. (eds.): *Adsorption of inorganics at solid-liquid interfaces*. Ann Arbor Science, Ann Arbor, 263-294.
- PEARSON, JR. F.J., & BERNER, U. (1991): Nagra thermochemical data base I. Core data. Nagra Technical Report NTB 91-17, Nagra, Wettingen, Switzerland.
- PEARSON, JR. F.J., BERNER, U. & HUMMEL, W. (1992): Nagra thermochemical data base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland.
- SCHINDLER, P.W. & KAMBER, H.R. (1968): Die Acidität von Silanolgruppen. *Helv. Chim. Acta* 51, 1781-1786.
- SCHINDLER, P.W. (1981): Surface complexes at the oxide-solution interfaces. In: ANDERSON, M.A. & RUBIN, A.J. (eds.): *Adsorption of inorganics at solid-liquid interfaces*. Ann Arbor Science, Ann Arbor, 1-49.
- SCHINDLER, P.W. & STUMM, W. (1987): The surface chemistry of oxides, hydroxides, and oxide minerals. In: STUMM, W. (ed.) *Aquatic surface chemistry*, John Wiley, New York, 83-110.

- SCHULTHESS, C.P. & SPARKS, D.L. (1986): Back titration technique for proton isotherm modelling of oxide surfaces. *Soil Sci. Soc. Am. J.* 50, 1406-1411.
- SCHULTHESS, C.P. & SPARKS, D.L. (1987): Two-site model for aluminium oxide with mass balanced competitive pH+salt/salt dependent reactions. *Soil Sci. Soc. Am. J.* 51, 1136-1144.
- SCHULTHESS, C.P. & SPARKS, D.L. (1988): A critical assessment of surface adsorption models. *Soil Sci. Soc. Am. J.* 52, 92-97.
- SCHWERTMANN, U. (1964): Differenzierung der Eisenoxide des Bodens durch Extraction mit Ammoniumoxalat-Lösung. *Z. Pflanzenernähr. Düng. Bodenk.* 105, 194-201.
- SHAVIV, S. & MATTIGOD, S.V. (1985): Cation exchange equilibria in soils expressed as cation-ligand complex formation. *Soil Sci. Soc. Am. J.* 49, 569-573.
- SPOSITO, G. (1983): On the surface complexation model of the oxide-aqueous solution interface. *J. Colloid Interface Sci.* 91, 329-340.
- SPOSITO, G. (1984): *The surface chemistry of soils.* Oxford University Press, New York.
- STUMM, W. & MORGAN, J.J. (1981): *Aquatic chemistry* (2nd ed.). John Wiley, New York.
- STUMM, W., HUANG, C.P. & JENKINS, S.R. (1970): Specific chemical interactions affecting the stability of dispersed systems. *Croat. Chem. Acta* 42, 223-244.
- STUMM, W. (1987): *Aquatic surface chemistry.* Wiley Interscience, New York.
- STUMM, W. & WIELAND, E. (1990): Dissolution of oxide and silicate minerals: Rates depend on surface speciation. In: STUMM, W. (ed.) *Aquatic chemical kinetics.* John Wiley & Sons, New York, 367-400.

- VAN RIEMSDIJK, W.H., BOLT, G.H., KOOPAL, L.K. & BLAAKMEER, J. (1986): Electrolyte adsorption on heterogeneous surfaces: Adsorption models. *J. Colloid Interface Sci.* 109, 219-228.
- VAN RIEMSDIJK, W.H., DEWIT, J.C.M., KOOPAL, L.K. & BOLT, G.H. (1987): Metal ion adsorption on heterogeneous surfaces: Adsorption models. *J. Colloid Interface Sci.* 116, 511-522.
- WANNER, H., ALBINSSON, Y., KARNLAND, O., WIELAND, E., WERSIN, P. & CHARLET, L. (1994): The acid/base chemistry of montmorillonite. *Radiochimica Acta* 66/67, 157-162.
- WESTALL, J., ZACHARY, J.L., & MOREL, F. (1976): MINEQL: A computer program for the calculation of chemical equilibrium composition of aqueous systems. Technical Note 18, Dept. of Civil Eng., Massachusetts Institute of Technology, Cambridge, Massachusetts.
- WESTALL, J.C. (1986): Reactions at the oxide-solution interface: Chemical and electrostatic models. In: DAVIS J.A. & HAYES, K.F. (eds.): *Geochemical processes at mineral surfaces*. ACS Symposium Series 323, 54-78.
- WIELAND, E. & STUMM, W. (1992): Dissolution kinetics of kaolinite in acidic aqueous solutions at 25°C. *Geochim. Cosmochim. Acta* 56, 3339-3355.