



PAUL SCHERRER INSTITUT



PSI Bericht Nr. 99-06

August 1999

ISSN 1019-0643

Waste Management Laboratory

Experimental studies of Cs, Sr, Ni, and Eu sorption on Na-illite and the modelling of Cs sorption

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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 planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI Bericht and a Nagra Technical Report.

ABSTRACT

A natural illite (illite du Puy) was purified and converted to the homo-ionic Na-form. The conditioned Na-illite was characterised in terms of its mineralogy, chemical inventory and physico-chemical properties. The structural formula was determined from energy dispersive spectroscopic analyses (SEM/TEM-EDS) and bulk chemistry measurements. A cation exchange capacity of 127 meq kg^{-1} was determined by the ^{22}Na isotope dilution method at neutral pH. The Na-CEC was also measured as a function of pH. The stability of Na-illite as a function of pH in the range ~ 3 to ~ 6 was investigated. At low pH values partial dissolution of the illite occurs releasing the structural elements Al, Si, Mg, and K into solution. The presence of Ca and Sr in solution was interpreted as being due to desorption from cation exchange sites. All of these elements are also present at neutral pH but at considerably lower levels. Such effects cannot be avoided and must be considered in the interpretation of the sorption measurements.

The main focus of the experimental work presented here is on the sorption behaviour of Cs, Sr, Ni and Eu on conditioned Na-illite as a function of NaClO_4 background electrolyte concentration (0.1 and 0.01 M), nuclide concentration and pH in the range ~ 3 to ~ 11 . Sorption edge data (R_d versus pH) and sorption isotherms (quantity of nuclide sorbed versus equilibrium nuclide concentration) are presented for these four elements. Prior to beginning these experiments, sorption kinetics were measured. The broad based pool of sorption measurements generated from this work will provide the source data sets for subsequent modelling.

So far only the Cs sorption measurements have been modelled. A two site cation exchange model was developed to describe the sorption of Cs over the whole range of experimental conditions. The two site types were termed "frayed edge sites" (FES, high affinity/low capacity) and "type II sites" (low affinity/high capacity). Selectivity coefficient values for $\frac{\text{Cs}}{\text{Na}} K_c \{\text{FES}\}$, $\frac{\text{K}}{\text{Na}} K_c \{\text{FES}\}$, $\frac{\text{H}}{\text{Na}} K_c \{\text{FES}\}$ and $\frac{\text{Cs}}{\text{Na}} K_c \{\text{II}\}$ are given for illite together with the corresponding site capacities.

ZUSAMMENFASSUNG

Ein natürlicher Illit (Illite du Puy) wurde gereinigt und in die homo-ionische Na-Form überführt. Der konditionierte Na-Illit wurde hinsichtlich der Mineralogie, des chemischen Inventars und der physikalisch-chemischen Eigenschaften charakterisiert. Die Strukturformel wurde mit Hilfe energiedispersiver spektroskopischer Analysemethoden wie SEM/TEM-EDS und einer chemischen Gesamtanalyse bestimmt. Die Kationenaustauschkapazität wurde mittels ^{22}Na -Isotopenverdünnungsanalyse bei neutralem pH-Wert zu 127 meq kg^{-1} bestimmt. Die Stabilität des Na-Illit in Abhängigkeit des pH-Wertes im Bereich von pH ~ 3 bis ~ 6 wurde untersucht. Bei tiefen pH-Werten tritt eine teilweise Auflösung des Illits unter Freisetzung der Strukturelemente Al, Si, Mg und K auf. Der Nachweis von Ca und Sr in der Lösung wurde auf die Desorption dieser Elemente von den Kationenaustauschplätzen zurückgeführt. Alle diese genannten Elemente sind auch bei neutralem pH-Wert nachweisbar, jedoch in viel geringeren Konzentrationen. Solche Effekte können nicht vermieden werden und müssen bei der Interpretation der Sorptionsmessungen berücksichtigt werden.

Das Hauptaugenmerk der in diesem Bericht vorgestellten experimentellen Arbeiten lag auf dem Sorptionsverhalten von Cs, Sr, Ni und Eu an konditioniertem Na-Illit in Abhängigkeit der NaClO_4 Elektrolytkonzentration (0.1 bis 0.01 M), der Nuklidkonzentration und des pH-Wertes im Bereich von pH ~ 3 bis ~ 11 . Die R_d -Werte aus der pH-abhängigen Sorption und die der Sorptionsisotherme (Menge an sorbiertem Nuklid in Abhängigkeit der Gleichgewichtskonzentration dieses Nuklids) werden für die oben genannten Elemente vorgestellt. Bereits vor diesen Messungen wurden die jeweilige Sorptionskinetik bestimmt. Das umfangreiche Datenmaterial aus diesen Sorptionsmessungen dient als Quelldatensatz für die nachfolgende Modellierung.

Bislang wurden nur die Cs-Sorptionsdaten modelliert. Ein zwei "Sites" Kationenaustauschmodell wurde entwickelt, um das Sorptionsverhalten von Cs innerhalb des gesamten Bereiches der experimentellen Bedingungen zu beschreiben. Die beiden möglichen "Sites" werden "frayed edge sites" (FES, hohe Sorptionsaffinität, geringe Sorptionskapazität) und "type II sites" (geringe Sorptionsaffinität, hohe Sorptionskapazität) genannt. Selektivitätskoeffizienten für ${}_{\text{Na}}^{\text{Cs}} K_c \{ \text{FES} \}$, ${}_{\text{Na}}^{\text{K}} K_c \{ \text{FES} \}$, ${}_{\text{Na}}^{\text{H}} K_c \{ \text{FES} \}$ und ${}_{\text{Na}}^{\text{Cs}} K_c \{ \text{II} \}$ sowie die zugehörigen Sorptionskapazitäten werden für Illit bestimmt.

RÉSUMÉ

Ce travail a consisté à acquérir des données expérimentales sur les propriétés de sorption d'une illite purifiée et conditionnée. Pour cela, une illite naturelle (l'illite du Puy) a été d'abord débarrassée de ces phases accessoires et conditionnée sous forme homo-ionique sodique. Cette illite conditionnée a ensuite été caractérisée en terme de composition minéralogique, d'analyses chimiques globales, de cations échangeables, et de propriétés physico-chimiques (CEC, surface spécifique). La formule structurale de l'illite a ainsi pu être déterminée à partir des analyses X par dispersion d'énergie (SEM/TEM-EDS) et des analyses chimiques globales. Une capacité d'échange cationique du sodium (Na-CEC) de 127 meq kg^{-1} a été déterminée à pH neutre par dilution isotopique (^{22}Na). La CEC du sodium a également été mesurée en fonction du pH. Enfin, en préalable aux expériences de sorption, la stabilité de l'illite sodique a été étudiée en fonction du pH, dans l'intervalle de pH ~ 3 à ~ 6 . A faible pH, l'illite se dissout partiellement libérant ainsi des cations comme Al, Si, Mg et K en solution. Tous ces éléments sont également présents à pH neutre, mais à des concentrations nettement moindres. Le relâchement de Ca et Sr en solution a été interprétée comme étant due à la désorption des sites d'échange cationique alors que Si, Al, Mg et K proviennent réellement de la dissolution de l'argile. Ces processus ne peuvent être évités et doivent donc être pris en compte dans l'interprétation des expériences de sorption.

Le travail expérimental présenté dans ce rapport a permis d'acquérir des données expérimentales cohérentes pour la sorption du Cs, Sr, Ni et de Eu sur l'illite sodique conditionnée, et ce en fonction de la concentration de l'électrolyte NaClO_4 de fond (0.1 et 0.01 M), de la concentration en nucléides et du pH compris dans un intervalle ~ 3 - ~ 11 . Ce rapport présente ainsi pour les 4 éléments mentionnés précédemment la variation du coefficient de distribution R_d en fonction du pH et de la concentration en nucléide (isothermes d'adsorption). Préalablement à ces mesures les cinétiques d'adsorption de ces différents nucléides avaient été mesurées. Ce travail a donc permis de mesurer un vaste ensemble de résultats expérimentaux cohérents et complets qui serviront maintenant de données de base pour la modélisation ultérieure de la rétention sur l'illite.

Finalement, seules les mesures de sorption du Cs ont été à ce jour complètement interprétées et modélisées. Un modèle d'échange cationique sur deux sites a été développé pour décrire l'adsorption du Cs sur toute la gamme des conditions expérimentales employées. Les deux types de sites ont été dénommées "frayed edge sites" (FES, affinité élevée, faible capacité), et site de type II (faible affinité, capacité élevée). Les valeurs des coefficients de sélectivité $\frac{\text{Cs}}{\text{Na}} K_c \{\text{FES}\}$, $\frac{\text{K}}{\text{Na}} K_c \{\text{FES}\}$, $\frac{\text{H}}{\text{Na}} K_c \{\text{FES}\}$ et $\frac{\text{Cs}}{\text{Na}} K_c \{\text{II}\}$ sont données dans ce rapport pour l'illite conjointement aux capacités du site correspondant.

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1 INTRODUCTION

The migration rates of radionuclides released from a nuclear waste repository will be strongly influenced by sorption processes occurring in the host rock formation. Since performance assessment studies require sorption data over a wide range of chemical conditions, knowledge of sorption processes and of the system parameters which influences them, is essential.

Clays are often important mineral components in many rock types and, because of their generally strong radionuclide retention properties, a vast amount of work has been devoted to characterising their sorption properties in the last two decades or so. Most of these data are expressed in terms of empirical parameters/relations and consequently it is difficult to extrapolate the results to different chemical conditions.

In recent years, attempts have been made to develop models that are capable of describing and predicting the sorption of radionuclides on clay minerals over a wide range of conditions. The hypothesis behind many of these studies is that by understanding and being able to model sorption on clay minerals, sorption in natural systems containing significant levels of such minerals can be predicted because they provide the major sinks for radionuclides (the so called "bottom up" approach).

BRADBURY & BAEYENS (1997a) have proposed a sorption model for montmorillonite based on two uptake mechanisms at the water-clay interface i.e. cation exchange and surface complexation. These two mechanisms can occur simultaneously on several sites. Cation exchange is related to the presence of a permanent negative surface charge arising from isomorphous substitutions in the clay mineral lattice (GRIM 1953). Surface complexation is perceived to be a reaction between aqueous metal species and amphoteric $\equiv\text{SOH}$ sites ($\text{S} = \text{Si}$ or Al) existing primarily at the edges of clay mineral platelets (DAVIS & KENT 1990). This and similar models can only be described as "near mechanistic" since microscopic reactions and parameters are derived from macroscopic measurements and not directly determined.

The work reported here extends the characterisation procedures and experimental methodologies developed for montmorillonite (BAEYENS & BRADBURY 1995a; 1995b, 1997) to another important clay mineral, namely illite. The aim was to provide a broad data set for a subsequent modelling exercise again similar to that carried out for montmorillonite. This report focuses on the purification and characterisation procedures and the sorption measurements of Cs, Sr, Ni and Eu on the conditioned Na-illite material.

A two site cation exchange model developed to describe the sorption of Cs over the whole range of experimental conditions is also included.

2 PREPARATION OF MATERIALS AND SOLUTIONS

2.1 Background electrolyte purification

Most of the experiments were performed in a NaClO_4 background electrolyte at various concentrations. During the purification and conditioning procedures of the illite, large quantities of electrolyte solution were required. Since illite is able to effectively sorb trace quantities of aqueous metal species, repeated contact with fresh electrolyte solutions containing impurities could lead to relatively high occupations of the sorption sites by these metal impurities. The effect of such a process on the subsequent sorption measurements is practically impossible to determine. In order to minimise such undesirable effects, the background electrolyte was purified following the same procedures as described by BAEYENS & BRADBURY (1995a).

All the NaClO_4 solutions (0.1 and 0.01 M) were prepared from Fluka "supra-pur" grade chemicals and ultra-pure de-ionised water (resistivity of 18 $\text{M}\Omega$ cm). The purification procedure is based on the effectiveness of Al_2O_3 as a scavenger for trace metals in solution. About 7 grams of Aldrich high purity high surface area Al_2O_3 was loaded into a Visking dialysis bag (Medicall Int., London) which had been previously thoroughly washed with de-ionised water. About 80 ml of a 1 M NaClO_4 solution was added to the bag which was then sealed leaving a small air pocket in order to promote good mixing of the solid and the liquid phases. One bag was shaken in a 1 litre polyethylene container with a 1 M NaClO_4 solution for 1 day. By using labelled solutions BAEYENS & BRADBURY (1995a) estimated that this procedure decreases impurity levels by a factor 10 to 100 depending on the particular metal. The purified 1 M NaClO_4 solutions were diluted to different NaClO_4 concentrations with ultra-pure water. In the following, any reference to NaClO_4 solutions implies the purified solutions unless otherwise stated.

2.2 Conditioning illite du Puy

The source material, illite du Puy, was supplied by the French Commissariat à l'Énergie Atomique, Service for Waste Storage and Disposal Studies (CEA-Saclay). Illite du Puy, first described by GABIS (1958), is present within an 80 m thick Oligocene geological formation. The mineral composition varies vertically from a quasi-pure illite at the top to a much higher kaolinite content at the bottom. As with most natural rock formations, illite du Puy is not completely homogeneous and lateral differences can also be found. Finally, in addition to kaolinite, quartz and well crystallised calcite are present.

As the aim of this study was to work on a single phase illite system, the “as-received” clay was first purified in order to eliminate secondary minerals. However, any purification procedure should not alter the illite. In particular, its surface properties should not be modified as this could lead to changes in the sorption characteristics. Checks on key physico-chemical parameters such as the cation exchange capacity (CEC), as well as electron microscope observations before and after treatment indicated no significant differences.

The basic aim of the purification procedure was to produce a single mineral in equilibrium with a simple background electrolyte.

2.2.1 Preparation of powdered illite

The illite du Puy was provided as decimetre sized rock pieces. Samples were crushed using a Retsch mechanical crusher and then powdered in a Retsch electric mortar. The $< 63 \mu\text{m}$ fraction of the illite powder was separated using a Retsch electric sieve (240 mesh). This $< 63 \mu\text{m}$ illite powder will be referred to as the “as received” illite and represents the starting material for the experiments.

2.2.2 Conversion of illite to the Na-form

Approximately 120 grams of the “as received” illite were added to 2 litres of a 1 M NaClO_4 solution (section 2.1) and shaken end-over-end for about 3 hours. The illite suspension was then allowed to flocculate over night before decanting off the supernatant solution. This procedure was repeated three times which was sufficient to remove any soluble salts and to convert the clay to the homo-ionic Na-form.

2.2.3 Separation of the $< 0.5 \mu\text{m}$ Na-illite fraction

The next step in the purification procedure was to separate out the $< 0.5 \mu\text{m}$ Na-illite fraction. The previously prepared suspension was separated into twelve 250 ml centrifuge bottles which were then filled with de-ionised water, shaken for ~15 minutes in order to allow the illite to peptise and then centrifuged for ~7 minutes at ~600 g max. The Na-illite fraction in the supernatant solution ($< 0.5 \mu\text{m}$) was transferred into a large polyethylene container using a glass U-tube connected to a pump. A fresh 1 M NaClO_4 solution was then immediately added in order to flocculate the fine clay particles and to prevent hydrolysis.

The whole “washing procedure” described above was repeated approximately 20 times giving a yield from this process of ~35 wt.% of peptised illite. The resulting clay batch contained approximately 6 g L^{-1} of Na-illite in ~0.4 M NaClO_4 . This stock suspension was stored in the dark at 4 °C and was kept no longer than 6 months. Batches of ~2 litres at various ionic strength were prepared from the stock suspension for the sorption experiments.

2.2.4 Acid treatment

In the previous washing procedure with de-ionised water it is unavoidable that the illite hydrolyses to some extent, which may result in the precipitation of metal hydroxy compounds. In order to remove such unwanted secondary phases, the procedure described by MAES & CREMERS (1973) was used. Two litres of the stock suspension were taken and acidified to pH ~3.5 with HNO_3 and left for 1 hour. Thereafter, the suspension was centrifuged (7 minutes at 600 g max.), the supernatant liquid decanted off and the clay re-suspended and neutralised in a 1 M NaClO_4 solution.

2.2.5 Conditioning to the NaClO_4 background electrolyte

After the acid treatment, about 75 ml of the Na-illite suspension were placed in large dialysis bags (~35 mm diameter) which had been previously thoroughly washed with de-ionised water. The bags were closed so that a small air pocket was left at the top of the sealed bag. This air pocket promoted good mixing during the shaking stage by allowing a free flow of liquid and solid within the bag.

Four bags were then placed into a 1 litre polyethylene container which was filled with a NaClO_4 solution at the desired concentration, 0.1 or 0.01 M. The container was then shaken end-over-end for a few hours after which the electrical conductivity of the NaClO_4 solution was measured prior to changing it for a fresh solution. This procedure was repeated until the electrical conductivity of the equilibrium solution was equal to that of the original 0.1 M NaClO_4 . (This usually required about 5 cycles.)

Finally, the resulting illite suspensions were collected in a polyethylene container and diluted to 1 litre with the last equilibrium solution. The illite content of the suspension was determined by heating weighed aliquots at 105 °C to constant weight. Salt corrections were made by treating 0.1 or 0.01 M NaClO_4 solutions simultaneously in the same manner.

Conditioned suspensions with between 7 and 14 g L⁻¹ of Na-illite in the desired NaClO₄ solution were obtained in this way. Prior to the sorption experiments these batches were also stored at 4 °C in the dark.

Typical examples of the water chemistries of the last conditioning waters from the preparation of such illite batches are given in Table 1. (For comparison purposes an analysis of a 0.1 M NaClO₄ solution is given.) As can be appreciated from this table the concentrations of background metals are at relatively low levels. The slight differences in composition between the 0.1 and 0.01 M NaClO₄ solutions are most probably due to cation exchange effects. Such analyses provide a good means of checking the consistency and quality of the conditioning process from batch to batch.

Table 1: Chemical analyses (in M) of the last conditioning water from the preparation of conditioned Na-illite in NaClO₄ at 0.1 and 0.01 M, pH~7. (Measurements were carried out by ICP-AES.)

Element	Background electrolyte 0.1 M NaClO ₄	conditioned Na-illite at 0.1 M NaClO ₄	conditioned Na-illite at 0.01 M NaClO ₄
Si	< (7 x 10 ⁻⁷)	3 x 10 ⁻⁵	4 x 10 ⁻⁵
Al	4 x 10 ⁻⁷	3 x 10 ⁻⁶	5 x 10 ⁻⁶
Fe	< (2 x 10 ⁻⁷)	3 x 10 ⁻⁷	< (2 x 10 ⁻⁷)
Mg	10 ⁻⁷	3 x 10 ⁻⁶	2 x 10 ⁻⁶
Mn	< (6 x 10 ⁻⁸)	7 x 10 ⁻⁸	8 x 10 ⁻⁸
K	7 x 10 ⁻⁵	1.5 x 10 ⁻⁵	5 x 10 ⁻⁶
Ca	5 x 10 ⁻⁷	10 ⁻⁵	7 x 10 ⁻⁶
Ba	2 x 10 ⁻⁷	2 x 10 ⁻⁷	< (9 x 10 ⁻⁹)
Zn	< (2 x 10 ⁻⁷)	4 x 10 ⁻⁷	5 x 10 ⁻⁷
Ni	< (5 x 10 ⁻⁷)	< (5 x 10 ⁻⁷)	< (5 x 10 ⁻⁷)
Sr	< (10 ⁻⁸)	5 x 10 ⁻⁸	~10 ⁻⁸
P	< (3 x 10 ⁻⁶)	10 ⁻⁵	10 ⁻⁵
S	< (2 x 10 ⁻⁶)	< (2 x 10 ⁻⁶)	< (2 x 10 ⁻⁶)

The numbers given in the parentheses are "reliable detection limits" which are taken to be 10 times higher than the ICP-AES detection limits.

The elements Pb, Co, Cd, Cu, Rb, Cs, Hg could not be detected and were therefore below the ICP-AES detection limits (< 10⁻⁸ M).

3 PHYSICO-CHEMICAL CHARACTERISATION OF THE CONDITIONED Na-ILLITE

3.1 Mineralogical composition

Both the “as received” illite and conditioned Na-illite samples were sent to the French National Institute for Agronomy Research (INRA), Laboratory for Soil Science (Versailles, France) for mineralogical analyses.

The “as received” illite sample was analysed by X-ray diffraction (XRD) to give an estimate of the initial mineralogical composition and to identify any secondary phases present. The XRD patterns were interpreted using a de-convolution software package (DECOMPXR, France) and yielded an estimate for the initial composition of 74 wt.% illite and kaolinite, ~20 wt.% calcite (with some siderite) and small amounts of quartz (< 5 wt.%). Note that the composition of clay mineral bearing samples cannot be determined with a precision better than a few wt.% using the XRD technique. Since the aim was to obtain an accurate mineralogical characterisation of the conditioned Na-illite, XRD analysis was combined with techniques such as bulk chemical analyses, ethylene-glycol-monoethyl-ether (EGME) surface area measurements, and Fourier Transform Infra-Red (FTIR) spectroscopy .

The conditioned Na-illite was only composed of illite and kaolinite. (Chlorite, smectite and mixed-layer clays were not detected.) Calcite was no longer present at all, as indicated by the absence of the 3.031 and 3.849 Å reflections in the XRD spectrum and the absence of the 1438 and 874 cm⁻¹ bands on the FTIR spectrum. Because reliable quantitative information on the proportions of illite and kaolinite in the sample could not be derived from the XRD data, the proportions of illite and kaolinite were calculated from the bulk chemical analyses assuming an ideal composition for kaolinite of Si₂Al₂O₅(OH)₄. In this manner the clay mineral mixture was calculated to be 93 wt.% illite and 7 wt.% kaolinite.

In addition, de-convolution of the XRD pattern indicated that the interlayer lattice distance of the illite was very close to 1 nm which implies that the illite is pure. The specific surface area measured by the EGME method was 129 m² g⁻¹ which for a grain density of 2.71 g cm⁻³ yielded a mean thickness for the illite crystals of ~5.7 layers, i.e. ~6 nm.

3.2 Structural formula of the illite

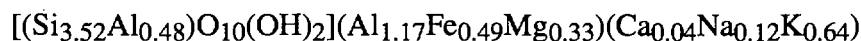
Energy dispersive spectrometric (EDS) measurements were carried out on conditioned Na-illite samples in both the scanning electron microscope (SEM) and the high resolution transmission electron microscope (HRTEM). Such measurements allow mean stoichiometric formulae for the Na-illite to be derived. Table 2 presents the composition of the conditioned Na-illite obtained by EDS together with bulk chemical analyses data. They are compared with structural formulae given by GABIS (1958) and TESSIER (1984) from bulk chemical analyses of the illite du Puy.

The table shows that there is quite good consistency between the measurements for the conditioned Na-illite and for the untreated illites. However, the conditioned Na-illite appears to be slightly richer in Fe, ~0.53 p.f.u. (per formula unit) compared with ~0.33 p.f.u. Such slight differences can be accounted for by the natural variability of illite du Puy and most probably do not result from any effects of the purification procedure.

Table 2: Structural formulae of the conditioned Na-illite obtained by bulk chemical analyses and by EDS compared to the formulae of the illite du Puy obtained by GABIS (1958) and TESSIER (1984).

	<i>Tetrahedral position</i>		<i>Octahedral position</i>			<i>Interlayer</i>		
	Si	Al	Al	Fe	Mg	Ca	Na	K
Bulk	3.47	0.53	1.12	0.43	0.46	0.04	0.12	0.61
EDS	3.52	0.48	1.17	0.49	0.33	0.02	0.02	0.64
Gabis	3.51	0.49	1.23	0.34	0.42	0.09	0.05	0.61
Tessier	3.48	0.52	1.24	0.32	0.38	0.07	0	0.66

The representative structural formula of the conditioned Na-illite deduced from EDS and bulk analyses results is:



This illite is highly substituted in the octahedral site, with significant Fe and Mg. From a pure mineralogical point of view, such a mineral is intermediate between the phengite end-member (also substituted by Fe and Mg in the octahedral site, but in which K is not depleted i.e. K = 2 p.f.u.) and the usual illite end-member, in which the octahedral site is only occupied by Al. Such an illite is usually referred to as ledikite.

Finally, the HRTEM observations confirm the conclusions drawn from the other analyses. The conditioned Na-illite is composed of well crystallised platelets whose size appears to be quite heterogeneous, lying between a few hundreds nm and a few sheet layers. The following figure depicts a typical micrograph of an illite crystal observed by HRTEM in which individual sheet layers can be distinguished.

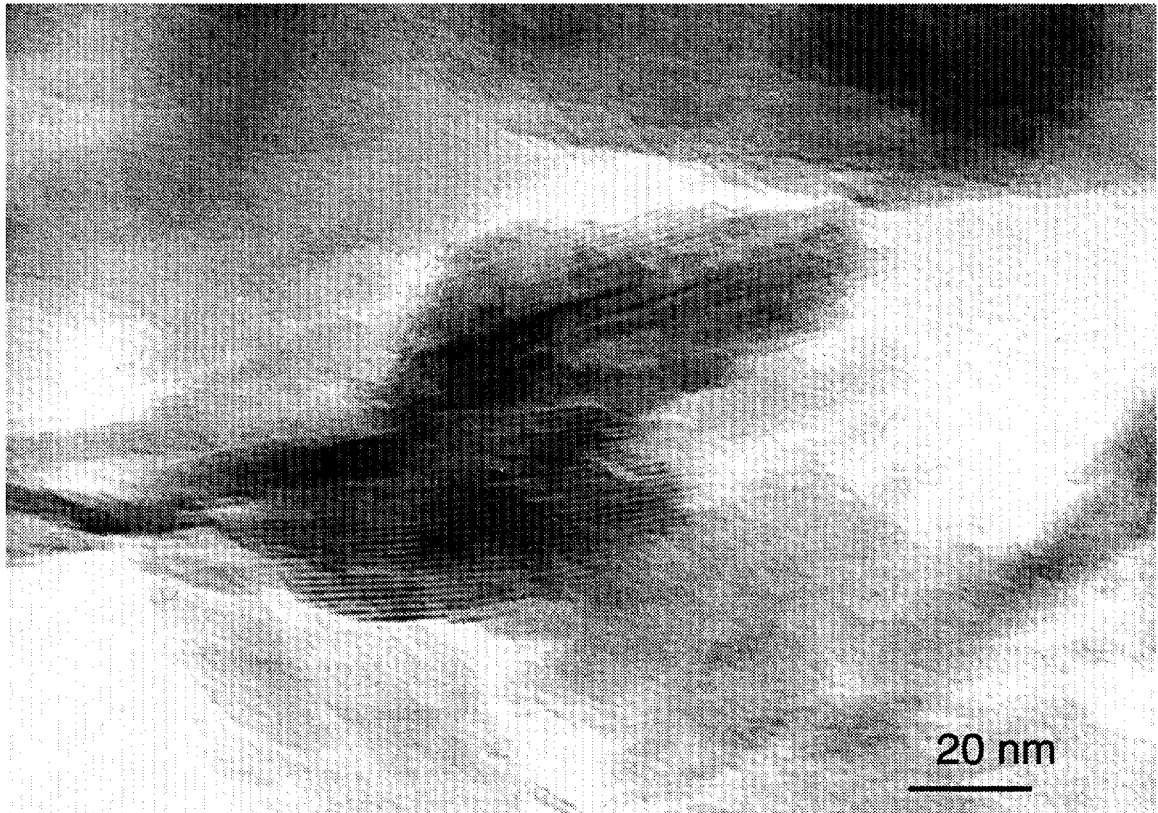


Figure 1: Micrograph obtained by high resolution transmission electron microscope (HRTEM) of illite crystallites from the conditioned Na-illite. The high crystallinity of the conditioned Na-illite is illustrated by the regular stacking sequence of the mineral.

3.3 Surface area measurements

The N₂-BET surface area of the “as received” illite du Puy was determined from multi-point adsorption isotherms using a Micromeritics Gemini 2360 surface area analyser, Table 3. Prior to the measurements samples were degassed for 2 hour at 200 °C.

During the mineralogical characterisation performed by INRA (France), the surface areas of the “as received” and conditioned materials were determined by the EGME method and these values are also included in Table 3. As can be seen the results for the “as received” illite du Puy are in good agreement.

Table 3: N₂-BET and EGME surface areas measurements for illite du Puy and conditioned Na-illite.

Sample	N ₂ -BET (m ² g ⁻¹)	EGME (m ² g ⁻¹)
“as received” illite du Puy	97	95
conditioned Na-illite	-	129

3.4 CEC of conditioned Na-illite

3.4.1 CEC measurements at pH ~7

CEC values often depend on the method used (see for example GRIM 1953). Here CEC values were determined at neutral pH by the ²²Na isotopic dilution method. This technique consists of equilibrating a Na conditioned clay suspension, with a known mass of clay, with a ²²Na labelled NaClO₄ solution. The concentration of the solution was chosen such that the “moles” of Na in solution were approximately equal to the “moles” of Na on the illite surface.

50 ml of the conditioned Na-illite suspension (in 0.1 or 0.01 M NaClO₄) were pipetted into a dialysis bag and placed in a 1 litre container filled with 0.001 M NaClO₄. After several hours end-over-end shaking, the NaClO₄ solution was changed. This procedure was repeated 4 times in order to obtain a conditioned Na-illite suspension in 0.001 M NaClO₄.

10 ml aliquots of the conditioned clay suspension were then equilibrated over at least 3 days with 25 ml of ²²Na labelled 0.001 M NaClO₄ solutions. At the end of this time the samples were centrifuged (95000 g max. for 1 hour), the activity in solution

measured by gamma spectrometry and the pH determined. The CEC values were calculated from the initial and final activities in solution.

As a control on the reproducibility of the conditioning procedure the CEC of each batch of conditioned Na-illite was measured using the ^{22}Na isotopic dilution technique at neutral pH. The results of the Na-CEC determinations for 8 different batches are included in Figure 2 (triangles). The mean Na-CEC obtained for conditioned Na-illite from the above determinations was $127 \pm 12 \text{ meq kg}^{-1}$. This value is within the generally accepted range of Na-CEC values for illite clay minerals, i.e. 100-200 meq kg^{-1} (BROUWER et al. 1983; COMANS et al. 1991). Moreover, the Na-CEC value of 131 meq kg^{-1} already published for illite du Puy (GORGEON 1994) is in excellent agreement with the values measured here.

In addition to the above, the Na-CEC for conditioned Na-illite was measured as a function of time over 21 days, Table 4. The data lie within acceptable variations for CEC determinations.

Table 4 : Evolution of the Na-CEC as a function of time for conditioned Na-illite.

Time (days)	Na-CEC (meq kg^{-1})	pH
3	132	7.1
7	122	7.1
14	112	7.1
21	121	7.1

3.4.2 Na-CEC of illite as a function of pH

The Na-CEC was measured as a function of pH in an 0.009 M background electrolyte of NaClO_4 at a S:L ratio of 14.4 g L^{-1} . The pH was set through additions of HNO_3 solutions to 30 ml of Na-illite suspensions (pH range 2 to 7) before directly labelling with ^{22}Na . Samples were shaken end-over-end for one week and then centrifuged for one hour at 95000 g max. The residual activity of the supernatant solutions was measured by gamma spectrometry together with ^{22}Na standards. Figure 2 shows the data measured in this investigation together with those published by GORGEON (1994) also for illite du Puy.

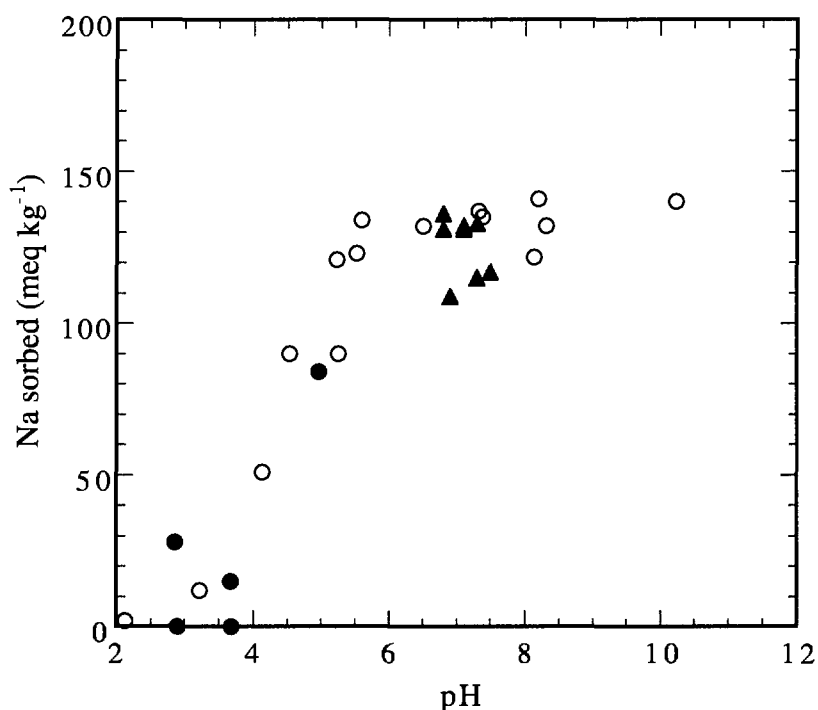


Figure 2: Evolution of the Na-CEC as a function of pH. The closed symbols correspond to data obtained on the conditioned Na-illite in 0.009 M NaClO₄ (●) and 0.001 M NaClO₄ (▲); this study. The open circles are similar measurements made on a Na-illite in 0.02 M NaClO₄ (GORGEON 1994).

Both set of experimental data are in reasonable agreement. In the pH range ~6 to ~2, the CEC measured by the ²²Na isotope dilution technique decreased to near zero. In section 3.8 it will be shown that at pH values below ~6, illite becomes increasingly unstable and partially dissolves. Cations such as Ca and Sr are also desorbed into solution. While it is generally clear that the decrease in the Na-CEC arises from the competitive influence of cations such as Al, K, Mg and Ca released into solution and protons, a quantitative description of the processes involved has not yet been developed.

3.5 Iron extractions

Iron (hydr)oxides are often important minor mineral components in many natural systems which are not usually detectable by standard mineralogical procedures (JENNE 1977). Moreover, the “washing procedures” described in section 2.2.3 could have lead to the formation of metal (hydr)oxides. Since many radionuclides are known to have high affinities for iron (hydr)oxides, the oxalate extraction method (SCHWERTMANN 1964) and the dithionate-citrate-bicarbonate extraction procedure (MEHRA & JACKSON 1960) were applied in order to determine the amorphous and total iron content of the illite suspensions respectively. Both the “as received” illite and the

conditioned Na-illite were studied. Table 5 summarises the results from two independent sets of measurements.

Table 5: Results from extraction measurements for amorphous iron, using oxalate at pH = 3, and total iron, using dithionate at pH = 7, for illite du Puy and the conditioned Na-illite. (Total iron in the Na-illite lattice is ~902 mmol kg⁻¹.)

Sample	Amorphous Fe (mmol kg ⁻¹)	Total Fe (mmol kg ⁻¹)
“as received” illite	5.6 ± 0.4	17.0 ± 1.0
conditioned Na-illite	8.1 ± 0.3	25.4 ± 1.2

The results show that in both cases about one third of the total iron is amorphous. Also it appears that the conditioning procedure has increased the total quantity of iron containing phases in the system. However, it should be realised that in the “as received” case the amount of iron is given per kg for the whole material (including carbonates and quartz) whereas for conditioned illite the value is per kg of clay minerals only. The fraction of clay minerals in the “as received” material is approximately 70 wt.%. If it is assumed that iron phases are taken over with the clay during the conditioning processes described in section 2.2.2 and 2.2.3, and iron contents are compared on a “per unit weight of clay minerals basis”, then it can easily be seen that the values given in Table 5 are effectively the same. Thus little or no iron (hydr)oxides have been generated during the conditioning process.

TESSIER (pers. comm. 1998) claims that the dithionate-citrate-bicarbonate extraction procedure might be aggressive enough to remove iron from the clay lattice, implying that the values for the total iron contents given above should be considered as upper bound values.

Finally, it should be noted that no iron coatings on the illite were observed by HRTEM. Applying arguments similar to those described in BRADBURY & BAEYENS (1999) to the conditioned Na-illite, leads to the conclusion that iron (hydr)oxides at the above levels will have no significant influence on the sorption measurements described in Chapters 4 and 5.

3.6 Severe acid extraction

Severe acid extractions were also performed both on the “as received” and conditioned Na-illite in order to determine trace cation levels. However, it must be remembered that partial dissolution of the clay can occur in such experiments.

For both the “as received” and conditioned illites, 3 ml of HNO₃ “supra-pur” (65%) were added to six 35 ml aliquots of the illite suspensions in 0.1 M NaClO₄ so that the pH was near to zero. Samples were shaken end-over-end for 24 hours, centrifuged for 1 hour at 95000 g max. and then the supernatant solutions were analysed by ICP-AES. The results are summarised in Table 6.

It can be seen that the conditioning procedure strongly reduces the contents of Mn, Ba, P, S, Ca and Sr in particular. For Ca and Sr the reductions are related to the removal of carbonates and the remaining Ca content in the conditioned Na-illite most probably corresponds to exchangeable cations. Similarly, the conditioning procedure has removed S which could originally have been present as minor sulphate phases within the illite du Puy. Finally, the acid extraction data are quite consistent with the Fe extraction results in Table 6.

Table 6: Results from severe acid extraction tests on the “as received” illite du Puy and conditioned Na-illite. Equilibration time = 1 day; S:L ratio = 8.7 g L⁻¹.

Elements	Quantity extracted from the “as received” illite du Puy (mmol kg ⁻¹)	Quantity extracted from conditioned Na-illite (mmol kg ⁻¹)
K	70 (±6)	36 (±1)
Rb	0.2 (±0.01)	0.2 (±0.01)
Si	217 (±8)	210 (±4)
Al	118 (±2)	146 (±2)
Fe	16 (±1)	21 (±1)
Mn	4 (±0.2)	1 (±0.2)
Mg	57 (±3)	39 (±1)
Ca	2350 (±150)	33 (±1)
Sr	1.5 (±0.04)	0.1 (±0.01)
Ba	1.6 (±0.05)	0.1 (±0.01)
Ni	0.02 (±0.05)	0.03 (±0.05)
Cu	0.04 (±0.04)	0.07 (±0.02)
Zn	1 (±1)	0.4 (±0.04)
Pb	0.02 (±0.02)	0.02 (±0.03)
P	47 (±2.4)	13 (±1)
S	9 (±0.4)	1.2 (±0.3)

3.7 Composition of the “equilibrium” solutions in the sorption experiments

During sorption measurements carried out as a function of pH (see Chapters 4 and 5), illite may undergo partial dissolution and metal cations can desorb into solution. Such processes could influence the sorption results and it was therefore deemed important to know the exact composition of the solutions at the end of the experiments (i.e. after 7 days for S:L ratios of ~0.9 and ~2.4 g L⁻¹). A summary of the chemical analyses of the supernatant solutions at two S:L ratios for background electrolyte concentrations of 0.1 M and 0.01 M NaClO₄ after 7 days equilibration time are presented in Tables 7 to 10. These data will be essential in any future interpretations of the sorption data.

Table 7: Chemical analyses of the supernatant solutions after 7 days interaction time between 0.1 M NaClO₄ and conditioned Na-illite; S:L ratio of 0.9 g L⁻¹. (All values given in mol L⁻¹.)

pH	Si	Al	Fe	Mg	K	Ca	Sr	Mn
3.1	7.6E-5	4.3E-5	2.4E-6	1.2E-5	2.0E-5	4.8E-5	1.1E-7	8.2E-7
4.3	4.9E-5	1.7E-5	2.2E-6	7.3E-6	1.6E-5	4.5E-5	1.0E-7	6.4E-7
5.5	3.2E-5	3.3E-6	2.0E-6	4.6E-6	1.6E-5	1.9E-5	6.1E-8	1.6E-7
6.4	2.1E-5	1.7E-6	7.4E-7	2.5E-6	2.2E-5	1.1E-5	4.7E-8	3.9E-7
7.3	3.4E-5	1.9E-6	9.4E-7	2.5E-6	-	1.3E-5	5.9E-8	-
9.3	3.4E-5	7.0E-5	9.4E-7	1.5E-6	6.8E-5	4.9E-6	1.8E-8	-
10.9	5.9E-5	2.4E-5	-	4.4E-7	6.3E-5	2.4E-6	1.3E-8	-

- no reliable measurement

Table 8: Chemical analyses of the supernatant solutions after 7 days interaction time between 0.1 M NaClO₄ and conditioned Na-illite; S:L ratio of 2.4 g L⁻¹. (All values given in mol L⁻¹.)

pH	Si	Al	Fe	Mg	K	Ca	Sr	Mn
3.2	1.7E-4	9.1E-5	5.6E-6	2.8E-5	2.7E-5	1.2E-5	2.7E-7	2.1E-6
4.5	1.0E-4	2.9E-5	2.4E-6	1.4E-5	1.8E-5	1.1E-4	2.6E-7	1.0E-6
5.8	6.0E-5	-	7.6E-7	7.4E-6	1.3E-5	5.2E-5	1.6E-7	2.9E-7
6.6	3.6E-5	2.2E-6	9.2E-7	-	1.5E-5	-	-	5.7E-8
7.3	2.9E-5	9.3E-7	4.0E-7	3.0E-6	-	1.6E-5	6.4E-8	-
9.3	2.5E-5	2.6E-6	2.6E-7	6.8E-7	4.8E-5	9.3E-6	3.0E-8	-
10.9	7.8E-5	3.3E-5	2.9E-7	8.5E-7	5.4E-5	3.5E-6	1.4E-8	-

- no reliable measurement

Table 9: Chemical analyses of the supernatant solutions after 7 days interaction time between 0.01 M NaClO₄ and conditioned Na-illite; S:L ratio of 0.83 g L⁻¹. (All values given in mol L⁻¹.)

pH	Si	Al	Fe	Mg	K	Ca	Sr	Mn
3.2	7.3E-5	1.9E-5	2.2E-6	1.1E-5	1.7E-5	4.6E-5	9.3E-8	6.9E-7
4.4	4.1E-5	2.5E-6	2.7E-7	4.6E-6	7.9E-6	3.1E-5	6.1E-8	3.9E-7
5.7	2.7E-5	7.4E-7	2.2E-7	1.9E-6	5.2E-6	1.9E-5	3.1E-8	5.2E-8
6.7	2.1E-5	6.5E-7	1.6E-7	1.2E-6	5.8E-6	8.1E-6	1.3E-8	4.3E-8
7.7	3.1E-5	1.9E-6	5.1E-7	1.1E-6	-	6.4E-6	1.6E-8	-
9.8	8.1E-5	1.3E-5	2.3E-6	2.1E-6	2.5E-5	5.3E-6	1.3E-8	-
11.0	7.6E-5	3.0E-5	2.0E-6	2.1E-6	2.6E-5	4.8E-6	-	-

- no reliable measurement

Table 10: Chemical analyses of the supernatant solutions after 7 days interaction time between 0.01 M NaClO₄ and conditioned Na-illite; S:L ratio of 2.2 g L⁻¹. (All values given in mol L⁻¹.)

pH	Si	Al	Fe	Mg	K	Ca	Sr	Mn
3.2	1.7E-4	3.4E-5	3.9E-7	3.1E-5	2.5E-5	1.1E-4	2.2E-7	1.7E-6
4.5	9.9E-5	4.5E-6	3.8E-7	1.0E-5	1.3E-5	6.4E-5	1.4E-7	5.6E-7
5.8	6.5E-5	1.8E-6	1.0E-6	3.7E-6	7.7E-6	2.7E-5	5.9E-8	8.0E-8
6.6	4.6E-5	4.6E-6	2.0E-7	1.6E-6	4.7E-6	8.2E-6	1.9E-8	6.8E-9
8.8	4.9E-5	7.1E-6	1.4E-6	2.0E-6	1.3E-5	5.1E-6	-	-
9.7	6.5E-5	2.9E-5	3.1E-6	3.9E-6	1.6E-5	4.4E-6	-	-
11.0	1.6E-4	7.0E-5	8.0E-6	9.0E-6	2.8E-5	3.9E-6	-	9.4E-8

- no reliable measurement

3.8 Illite stability as a function of pH

When sorption measurements are being carried out as a function of pH, the stability of the clay mineral and the aqueous composition become especially important considerations. Any partial dissolution of the clay mineral may be accompanied by the release of competing cations, desorption of bound cations and the precipitation of secondary phases. In addition to those data presented in connection with the sorption measurements in section 3.7, Tables 7 to 10, further illite stability experiments at pH values below 7 were carried out for times up to 60 days.

3.8.1 Experimental procedure and results

Aliquots of Na-illite suspensions in 0.1 and 0.01 M NaClO₄ were diluted in appropriate NaClO₄ solutions to yield two groups of samples: one with a S:L ratio of 2.2 to 2.4 g L⁻¹ and the other with a S:L ratio of 0.83 to 0.9 g L⁻¹. Quadruple sets of samples for each NaClO₄ concentration, S:L ratio and pH combination were set to pH values between ~3 and ~6 by adding 1 M HNO₃ solution and shaking end-over-end for times between 1 and 60 days. After the appropriate time, the samples were centrifuged at 95000 g max. for one hour after which 20 ml aliquots of the supernatant solutions were pipetted out, acidified with 0.5 ml HNO₃ (65% "supra-pur"), diluted to a total volume of 25 ml and sent for ICP-AES analyses. The measured aqueous concentrations of K, Mg, Ca, Sr, Mn, Fe, Al and Si are presented in Tables 11 to 14.

3.8.2 Evolution of the concentrations of K, Mg, Al and Si

In order to illustrate the trends in the evolution of the aqueous concentrations of the structural elements K, Mg, Al and Si, the data at pH ~3 taken from Tables 11 to 14 are graphically presented in Figure 3. Measurements made at higher pH values have not been presented since the behaviour of the above elements is similar to that at pH ~3, but much less pronounced.

The data for Si, Mg and K in Figure 3 exhibit the same trends and show (i) a regular increase in concentration as function of time, (ii) no effect of ionic strength and (iii) a clear effect of S:L ratio. The concentrations of these elements are in all cases higher at the highest S:L ratio. The evolution of the Si, Mg and K concentrations in Figure 3 strongly suggest that all these elements are released into solution through the dissolution of a solid phase.

The behaviour of Al is similar to Si, Mg and K with the exception that there is a clear effect of ionic strength. This would indicate that in addition to dissolution cation exchange reactions are taking place. At low NaClO₄ concentrations Al³⁺ has a greater tendency to undergo exchange reactions than at higher background electrolyte concentrations leading to lower Al concentrations in the former case, see Figure 3.

Table 11: Analyses of supernatant solutions (M) from interaction tests of conditioned Na-illite as a function of pH and time. S:L = 0.9 g L⁻¹ and 0.1 M NaClO₄.

pH	K	Mg	Ca	Sr	Mn	Fe	Al	Si
1 day								
3.1	1.3E-5	6.2E-6	4.7E-5	1.0E-7	6.5E-7	2.5E-6	3.2E-5	3.8E-5
4.2	1.0E-5	4.0E-6	4.6E-5	1.1E-7	4.9E-7	1.1E-6	1.5E-5	2.6E-5
5.0	8.8E-6	2.8E-6	2.2E-5	6.7E-8	1.3E-7	9.2E-7	3.3E-6	1.8E-5
6.1	1.7E-5	4.3E-6	1.1E-5	5.9E-8	7.1E-8	2.8E-6	-	2.5E-5
7 days								
3.1	2.0E-5	1.2E-5	4.8E-5	1.1E-7	8.2E-7	2.4E-6	4.3E-5	7.6E-5
4.3	1.6E-5	7.3E-6	4.5E-5	1.0E-7	6.4E-7	2.2E-6	1.7E-5	4.9E-5
5.5	1.6E-5	4.6E-6	1.9E-5	6.1E-8	1.6E-7	2.0E-6	3.3E-6	3.2E-5
6.4	2.2E-5	2.5E-6	1.1E-5	4.7E-8	3.9E-8	7.4E-7	1.7E-6	2.1E-5
21 days								
3.1	2.0E-5	1.7E-5	4.5E-5	1.0E-7	9.4E-7	2.7E-6	5.2E-5	1.1E-4
4.4	1.2E-5	6.9E-6	4.5E-5	9.7E-8	6.4E-7	3.4E-7	1.2E-5	5.0E-5
5.3	8.9E-6	3.8E-6	2.2E-5	6.6E-8	3.3E-7	2.0E-7	1.5E-6	3.4E-5
6.1	1.1E-5	3.2E-6	1.4E-5	4.7E-8	3.4E-7	-	1.5E-6	2.5E-5
60 days								
3.2	2.5E-5	2.6E-5	5.1E-5	9.7E-8	9.8E-7	3.3E-6	6.9E-5	1.5E-4
4.4	1.4E-5	1.1E-5	4.8E-5	1.1E-7	8.3E-7	1.2E-6	1.1E-5	6.2E-5
5.5	9.2E-6	4.7E-6	2.5E-5	6.7E-8	5.0E-7	3.4E-7	1.2E-6	4.2E-5
6.2	9.2E-6	4.7E-6	1.3E-5	5.1E-8	4.2E-7	1.1E-7	-	3.6E-5

Table 12: Analyses of supernatant solutions (M) from interaction tests of conditioned Na-illite as a function of pH and time. S:L = 2.4 g L⁻¹ and 0.1 M NaClO₄.

pH	K	Mg	Ca	Sr	Mn	Fe	Al	Si
1 day								
2.8	-	1.5E-5	1.2E-4	2.8E-7	1.7E-6	5.0E-6	6.5E-5	8.8E-5
3.8	2.1E-5	8.3E-6	1.1E-4	2.6E-7	9.0E-7	3.9E-6	3.2E-5	6.5E-5
4.6	1.2E-5	4.3E-6	4.9E-5	1.5E-7	2.9E-7	5.4E-7	4.3E-6	3.5E-5
6.1	1.1E-5	4.4E-6	1.5E-5	5.6E-8	5.7E-8	2.2E-6	6.1E-6	3.3E-5
7 days								
3.2	2.7E-5	2.8E-5	1.2E-4	2.7E-7	2.1E-6	5.6E-6	9.1E-5	1.7E-4
4.5	1.8E-5	1.4E-5	1.1E-4	2.6E-7	1.0E-6	2.4E-6	2.9E-5	1.0E-4
5.8	1.3E-5	7.4E-6	5.2E-5	1.6E-7	2.9E-7	7.6E-7	-	6.0E-5
6.6	1.5E-5	-	-	-	5.7E-8	9.2E-7	2.2E-6	3.6E-5
21 days								
3.2	3.1E-5	3.9E-5	1.2E-4	2.7E-7	2.3E-6	5.3E-6	1.1E-4	2.5E-4
4.4	1.7E-5	1.6E-5	1.1E-4	2.5E-7	1.0E-6	9.0E-7	2.0E-5	1.2E-4
5.2	1.4E-5	9.5E-6	4.8E-5	1.5E-7	6.2E-7	3.1E-7	1.8E-6	8.0E-5
6.2	1.1E-5	4.8E-6	1.9E-5	7.9E-8	8.2E-8	5.3E-7	1.8E-6	5.2E-5
60 days								
3.4	4.3E-5	5.8E-5	1.3E-4	2.9E-7	2.6E-6	5.3E-6	1.2E-4	3.4E-4
4.6	2.0E-5	2.4E-5	1.2E-4	2.5E-7	1.8E-6	5.2E-7	1.5E-5	1.5E-4
5.6	2.7E-5	1.4E-5	5.7E-5	1.6E-7	6.6E-7	2.0E-7	2.3E-6	1.0E-4
6.3	1.6E-5	8.6E-6	2.3E-5	-	3.0E-7	2.0E-7	6.5E-7	7.2E-5

Table 13: Analyses of supernatant solutions (M) from interaction tests of conditioned Na-illite as a function of pH and time. S:L = 0.83 g L⁻¹ and 0.01 M NaClO₄.

pH	K	Mg	Ca	Sr	Mn	Fe	Al	Si
1 day								
3.1	1.2E-5	7.7E-6	4.3E-5	8.7E-8	5.3E-7	1.8E-6	1.1E-5	3.8E-5
4.2	1.2E-5	4.4E-6	3.2E-5	6.4E-8	2.6E-7	6.9E-7	5.6E-6	2.9E-5
5.7	6.4E-6	2.7E-6	2.0E-5	4.1E-8	4.6E-8	9.4E-7	3.5E-6	2.2E-5
6.6	7.1E-6	2.4E-6	7.3E-6	-	2.3E-8	1.1E-6	-	2.0E-5
7 days								
3.2	1.7E-5	1.4E-5	4.6E-5	9.3E-8	6.9E-7	2.2E-6	1.9E-5	7.3E-5
4.4	7.9E-6	5.7E-6	3.1E-5	6.1E-8	3.9E-7	2.7E-7	2.5E-6	4.1E-5
5.7	5.2E-6	2.3E-6	1.9E-5	3.1E-8	5.2E-8	2.2E-7	7.4E-7	2.7E-5
6.7	5.8E-6	1.6E-6	8.1E-6	1.3E-8	4.3E-8	1.6E-7	6.5E-7	2.1E-5
21 days								
3.3	1.7E-5	1.8E-5	4.5E-5	9.7E-8	7.6E-7	2.7E-6	2.5E-5	9.3E-5
4.4	1.7E-5	7.4E-6	3.4E-5	6.9E-8	3.7E-7	2.2E-7	2.7E-6	5.2E-5
5.5	9.9E-6	2.3E-6	1.8E-5	3.3E-8	5.7E-8	2.0E-7	-	2.8E-5
6.4	4.2E-6	1.7E-6	8.1E-6	1.6E-8	2.7E-8	2.0E-7	4.2E-7	2.4E-5
60 days								
3.1	2.4E-5	2.5E-5	4.6E-5	1.0E-7	8.1E-7	2.9E-6	3.9E-5	1.3E-4
4.6	1.3E-5	9.8E-6	3.4E-5	7.1E-8	4.6E-7	1.8E-7	3.4E-6	6.9E-5
5.7	7.7E-6	3.4E-6	2.0E-5	4.0E-8	8.9E-8	2.0E-7	9.3E-7	3.9E-5
6.5	7.5E-6	2.0E-6	9.4E-6	2.4E-8	4.1E-8	1.8E-7	2.7E-6	3.2E-5

Table 14: Analyses of supernatant solutions (M) from interaction tests of conditioned Na-illite as a function of pH and time. S:L = 2.2 g L⁻¹ and 0.01 M NaClO₄.

pH	K	Mg	Ca	Sr	Mn	Fe	Al	Si
1 day								
3.1	1.8E-5	1.7E-5	1.0E-4	2.0E-7	1.3E-6	3.3E-6	2.0E-5	9.9E-5
4.2	9.8E-6	7.1E-6	6.1E-5	1.2E-7	4.8E-7	9.4E-7	5.7E-6	6.9E-5
5.2	2.7E-5	1.1E-5	2.8E-5	6.0E-8	1.7E-7	-	-	-
6.3	6.7E-6	2.1E-6	8.6E-6	1.4E-8	2.1E-8	7.6E-7	4.1E-6	3.8E-5
7 days								
3.2	2.5E-5	3.1E-5	1.1E-4	2.2E-7	1.7E-6	3.9E-6	3.4E-5	1.7E-4
4.5	1.3E-5	1.0E-5	6.4E-5	1.4E-7	5.6E-7	3.8E-7	4.5E-6	9.9E-5
5.8	7.7E-6	3.7E-6	2.7E-5	5.9E-8	8.0E-8	1.0E-6	1.8E-6	6.5E-5
6.6	4.7E-6	1.6E-6	8.2E-6	1.9E-8	6.8E-9	2.0E-7	4.6E-6	4.6E-5
21 days								
3.2	3.0E-5	3.9E-5	1.2E-4	2.2E-7	1.8E-6	4.3E-6	4.7E-5	2.3E-4
4.6	1.8E-5	1.2E-5	6.3E-5	1.2E-7	4.9E-7	8.1E-7	4.6E-6	1.2E-4
5.7	1.2E-5	4.2E-6	2.8E-5	5.9E-8	1.6E-7	2.0E-7	6.0E-7	7.3E-5
6.8	7.6E-6	1.7E-6	8.0E-6	1.3E-8	2.7E-8	1.6E-7	6.5E-6	5.3E-5
60 days								
3.3	4.4E-5	5.5E-5	1.2E-4	2.4E-7	2.0E-6	3.7E-6	6.3E-5	3.1E-4
4.7	1.9E-5	1.5E-5	6.1E-5	1.1E-7	4.6E-7	2.0E-7	3.8E-6	1.5E-4
5.7	8.6E-6	5.5E-6	2.7E-5	5.3E-8	2.4E-7	2.0E-7	1.2E-6	8.9E-5
6.7	8.5E-6	1.9E-6	9.1E-6	1.7E-8	1.6E-8	1.8E-7	1.2E-6	6.8E-5

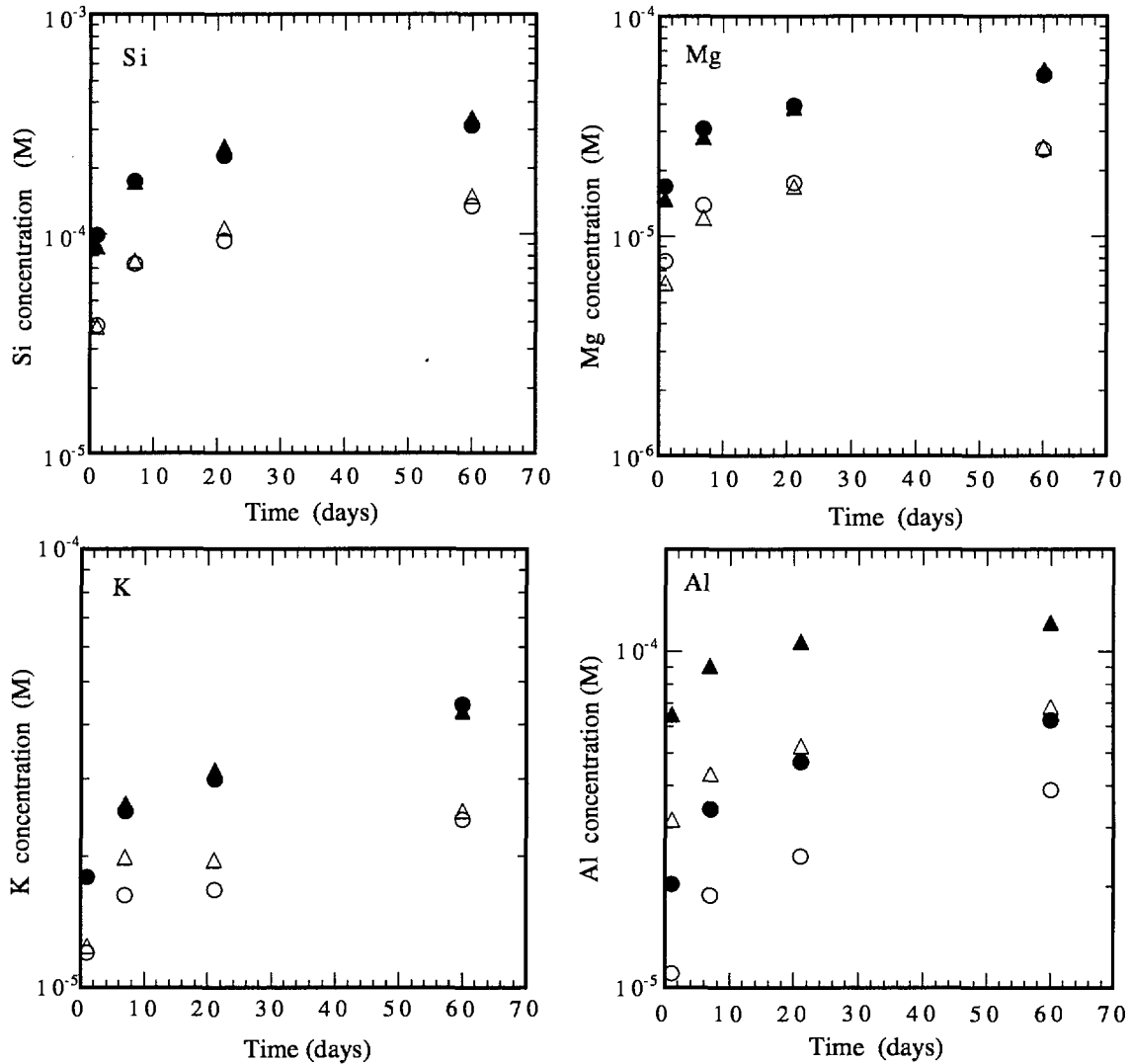


Figure 3: Evolution of Si, Mg, K and Al concentrations in the supernatant solution of suspensions of conditioned Na-illite at pH ~3 as a function of time.

(▲): 0.1 M NaClO₄; 2.4 g L⁻¹.

(△): 0.1 M NaClO₄; 0.9 g L⁻¹.

(●): 0.01 M NaClO₄; 2.2 g L⁻¹.

(○): 0.01 M NaClO₄; 0.83 g L⁻¹.

If the data for Si, Mg and K are plotted as incremental values as a function of time on a logarithmic scale at a given pH, it can be shown that the release rates for all these elements are very similar and do not depend on the S:L ratio. (The measured concentrations at neutral pH are taken as the reference values.). Figure 4 presents a plot of the data obtained for a Na-illite suspension at 0.1 M NaClO₄ at pH ~3 at a S:L ratio 2.4 g L⁻¹ and shows that the rates of release are non-linear and are the same for all three elements. Such a result strongly indicates that Si, Mg and K are being released into solution through the same process. As the only Mg- and K-bearing primary mineral is illite, the source of these elements in solution is interpreted to be the dissolution of the Na-illite. (The release rates for Al are different since this element undergoes cation exchange reactions.)

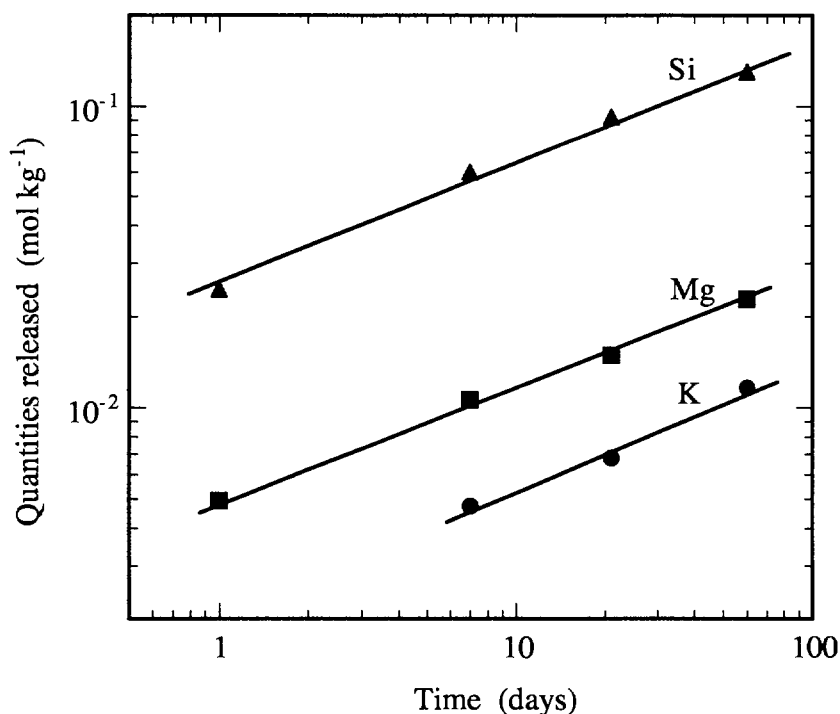


Figure 4: Incremental quantities of Si (▲), Mg (■) and K (●) released into solution as a function of time in a suspension of conditioned Na-illite at 0.1 M NaClO₄, S:L = 2.4 g L⁻¹ and pH~3.2 expressed as mol kg⁻¹. (The reference values at neutral pH were taken from Table 1.)

If it is assumed that Si neither sorbs nor precipitates, this data can be used to estimate an average initial rate of dissolution of illite. (These assumptions are eminently reasonable since Si is in solution as the neutral H₄SiO₄ species, which is highly unlikely to sorb on illite, and the solutions are undersaturated with respect to amorphous silica.) By

considering the composition and surface area of Na-illite, an estimate of the initial dissolution rate at pH ~3 can be made using the relation:

$$V_{\text{diss}} = \frac{\Delta\text{Si}}{N_{\text{Si}} \cdot S \cdot \Delta t} \quad [1]$$

where :

N_{Si} is the number of moles of Si per mol of conditioned Na-illite (mol mol^{-1}),

ΔSi is the amount of Si released into solution (mol kg^{-1}),

S is the surface area of conditioned Na-illite ($\text{m}^2 \text{kg}^{-1}$),

Δt is the time increment (s).

A value of $\sim 4 \times 10^{-14} \text{ mol m}^{-2} \text{ s}^{-1}$ was found which is consistent with previous studies performed on illite in this pH range (see for example the review of NAGY 1995).

Finally, with the information generated above, it is possible to calculate an upper limit for the quantities of clay dissolved in the 7 day sorption experiments. Taking an average molar mass for the conditioned Na-illite of 320 g mol^{-1} , only about 0.1 wt.% of the initial illite is dissolved in the tests at the lowest pH of 3. This amount represents a worst case estimate, and since illite dissolution rates are strongly dependent on pH (see Tables 11 to 14), considerably less illite will dissolve for pH values around neutral.

3.8.3 Evolution of the concentration of Ca and Sr

Figure 5 shows the time dependent concentrations of Ca and Sr for the pH ~3 data sets. The forms of the curves are very similar to one another but the Ca concentrations are a factor of ~500 higher (see also Tables 11 to 14). The behaviour of Ca and Sr differs significantly from the 4 elements discussed previously.

For Ca and Sr there were no kinetic effects at all pH values studied; equilibrium concentrations were attained within one day. There is also no influence of the NaClO_4 background concentration but a clear effect of the S:L ratio is seen. This suggests that Ca and Sr are present as sorbed cations. Note that the conditions at pH ~3 are such that all of the exchangeable Ca and Sr is displaced from the clay and the background Na concentration has little or no influence. The inventories of Ca and Sr calculated from the data measured at pH ~3 are $\sim 5 \times 10^{-2}$ and $\sim 10^{-4} \text{ mol kg}^{-1}$ respectively.

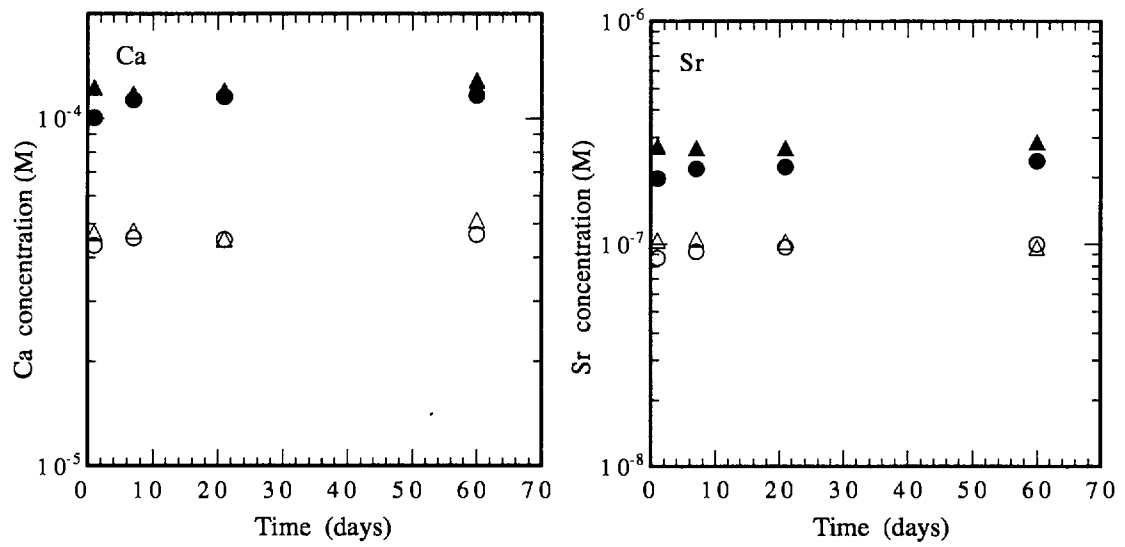


Figure 5: Evolution of Ca and Sr concentrations in the supernatant solution of suspensions of conditioned Na-illite at pH ~3 as a function of time.

(▲): 0.1 M NaClO₄; 2.4 g L⁻¹;

(△): 0.1 M NaClO₄; 0.9 g L⁻¹.

(●): 0.01 M NaClO₄; 2.2 g L⁻¹;

(○): 0.01 M NaClO₄; 0.83 g L⁻¹.

4 SORPTION MEASUREMENTS

The sorption of Cs, Sr, Ni and Eu on the conditioned Na-illite has been measured in controlled N₂ atmosphere glove boxes (CO₂ ~5 ppm and O₂ ~5 ppm) under a wide variety of chemical conditions. In particular, the sorption dependency on pH, ionic strength, radionuclide concentrations and time was systematically investigated. It is not the intention in this report to give any detailed interpretations of the Sr, Ni and Eu results, but such measurements will provide the broad based data sets required for future (quasi)mechanistic sorption modelling on illite (c.f. Ni and Zn sorption modelling on conditioned Na and Ca montmorillonite (BRADBURY & BAEYENS 1997a, 1998). So far only the results from the Cs sorption investigations have been modelled. The measured data, sorption model and calculated sorption curves are discussed separately in Chapter 5.

4.1 Experimental methods

4.1.1 Radiotracers and analytical methods

Source radiotracer solutions of ¹³⁴Cs, ⁸⁵Sr, ⁶³Ni and ¹⁵²Eu were purchased from Amersham International Plc. Each source solution was diluted in ~50 ml of de-ionised water to produce a stock solution having a pH of ~2. The stock solutions were used directly to label the solutions used in the experiments. Labelled solutions were always allowed to stand at least overnight before use in order to ensure equilibrium (wall sorption). Standard labelled solutions were also prepared and were always counted simultaneously with the sample solutions from the batch sorption tests.

Aqueous activities were measured using either a Canberra Packard Tri-Carb 2250 CA liquid scintillation analyser (for ⁶³Ni), or a Canberra Packard Cobra Quantum gamma counter (for ¹³⁴Cs, ⁸⁵Sr and ¹⁵²Eu). Counting times were always chosen to obtain a one sigma (or better) error in the total counts.

4.1.2 Estimation of experimental errors

BAEYENS & BRADBURY (1995b) carried out a formal estimate of the maximum expected error for sorption values determined by similar experimental procedures to those used here. In a worst case, the estimate in log R_d values was ±0.15 log units. Some sorption measurements were repeated several times during the course of this investigation using different illite batches. The error associated with the sorption

measurements was always within ± 0.2 log units for the log of the distribution coefficient. Consequently, an uncertainty of ± 0.2 log units is taken as a conservative estimate and all of the results are given with this error bar. Such an error estimate includes uncertainties from all sources including, for example, wall sorption effects (see BAEYENS & BRADBURY 1995b; LAUBER et al. 1998).

4.1.3 Kinetic experiments

The first step in any series of sorption measurements for a particular radionuclide was to measure the sorption kinetics. The time required to reach an “equilibrium” (steady-state) aqueous activity was then taken as the experimental duration for all of the following sorption tests. In the technique described below the Na-illite is contained in a dialysis bag which allowed samples to be taken as a function of time without having to centrifuge. Experience has shown that this is a better and more convenient method for determining sorption kinetics than preparing a series of batch tests and centrifuging and sampling individual experiments at different time intervals.

25 ml of the conditioned Na-illite suspension were added to 35 ml of 0.1 M NaClO₄ in a thoroughly washed dialysis bag which was then closed. A solution of 0.1 M NaClO₄ containing MOPS buffer (see section 4.1.4) at a concentration of 2×10^{-3} M was prepared at pH = 7.0 in triplicate and labelled with the radionuclide. At time $t = 0$, the bag was placed into a polypropylene flask containing 840 ml of the labelled NaClO₄ solution. In parallel, a blind experiment was conducted in which everything was the same except that the dialysis bag contained no Na-illite. The purpose of this test was to estimate the time required for the equilibration of activities within and without the dialysis bag.

During the experiment, two 4 ml samples of the solution were pipetted out at regular time intervals and their activities measured. Each time a volume of solution was removed, an equal volume of 0.1 M NaClO₄ was added in order to keep the S:L ratio constant. This “dilution effect” was taken into account when calculating distribution ratios.

The experiment with the dialysis bag alone indicated that activities within and without the dialysis bags only needed approximately one hour to equalise. Thus nuclide diffusion rates through the bag wall were very high and consequently had a minimal influence on the sorption kinetic results. The sorption kinetics for Sr were rapid, reaching equilibrium in less than 1 day. For Ni and Eu the kinetics were similar to one another but slower than for Sr. Nevertheless, only ~3 days were required, see for

example Figure 6 and Table 15. Subsequent sorption experiments were shaken for at least 7 days. The sorption kinetics for Cs sorption are treated separately in Chapter 5.

Table 15: Experimental conditions for the Ni sorption kinetic tests on conditioned Na-illite in 0.1 M NaClO₄.

pH	7.0
S:L ratio (g L ⁻¹)	0.3
Buffer	MOPS
Initial Ni concentration (M)	2.8×10^{-9}
Number of data points	12

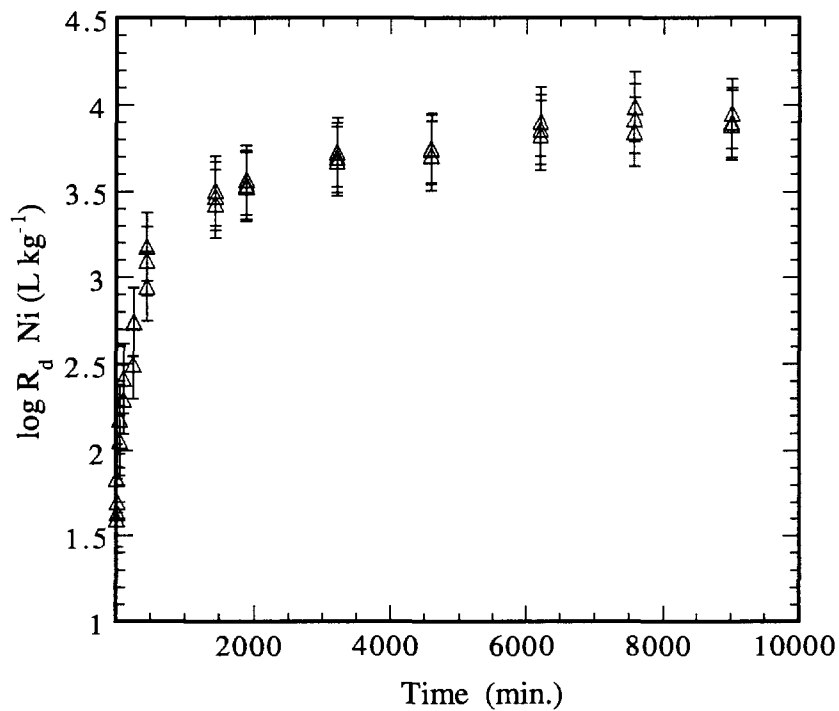


Figure 6: Evolution of $\log R_d$ as a function of time for Ni sorption on conditioned Na-illite.

4.1.4 Sorption measurements as a function of pH

In a second set of experiments sorption was measured at trace radionuclide concentration as a function of pH. "Trace" here means the lowest concentration possible compatible with good counting statistics for the equilibrium activities. (See the tables given later in this chapter for details of individual radionuclides.)

In the pH range 4 to 9 it was necessary to use buffers in order to ensure pH stability during the experiments. The particular buffers were chosen (Table 16) because of their very weak tendencies to complex with metals (PERRIN & DEMPSEY 1974). Experimental tests performed with conditioned Na-montmorillonite (BAEYENS & BRADBURY 1995b) and with conditioned Na-illite (this work) demonstrated that the buffers used did not have any significant effect on sorption. The concentration of buffer in the sorption experiments was always 2×10^{-3} M and the pH was adjusted to the required values with high purity 1 M NaOH or HNO₃.

Table 16: Buffers used in the sorption edge experiments. (Data taken from PERRIN & DEMPSEY 1974.)

Buffer	pK _a	pH range
AA (Acetic Acid)	4.76	4.2 - 5.2
MES (2-(N-morpholino)ethane-sulphonic acid)	6.15	5.7 - 6.7
MOPS (3-(N-morpholino)propanesulphonic acid)	7.20	6.8 - 7.7
TRIS (Tris(hydroxymethyl)aminomethane)	8.06	7.5 - 8.5
CHES (3-(cyclohexyl amino)ethanesulphonic acid)	9.55	9.0 - 10.0

The procedure used was similar for all radionuclides. The NaClO₄ solution (0.1 or 0.01 M) was labelled and left to stand overnight. 5 ml of buffer solution and 25 ml of labelled NaClO₄ were pipetted into a 40 ml polypropylene centrifuge tube. For strongly acidic (pH < 4.2) or alkaline conditions (pH > 8.8), buffers were not used and instead 5 ml of inactive NaClO₄ were added. These operations were performed outside the glove box. The centrifuge tubes were then placed in the glove box after allowing the solutions to degas under vacuum. 5 ml of the conditioned Na-illite suspension were added to each tube which was then closed with a screw cap and shaken end-over-end in the glove box for 7 days. (All experiments were carried out in duplicate.) This was followed by centrifugation (1 hour at 95000 g max.) outside the glove box and sampling for radio assay (two 5 ml aliquots). The final solution pHs were measured in the glove box.

4.1.5 Sorption isotherm experiments

Sorption isotherms (sorption as a function of the equilibrium nuclide concentration) were measured at neutral pH in 0.1 M NaClO₄ solutions buffered by MOPS (concentration of 2 x 10⁻³ M). Solutions with a range of nuclide concentrations were prepared by successively diluting an original 0.1 M NaClO₄ solution containing a high concentration of the nuclide in question (~10⁻³ M of CsCl or Sr(NO₃)₂ or Ni(NO₃)₂ or Eu(NO₃)₃) with 0.1 M NaClO₄. Labelling and the experiment procedures were then essentially the same as those described above except that all experiments were carried out in duplicate at the same pH using MOPS as a buffer.

4.1.6 Presentation of the sorption results

Sorption measurements are often presented in terms of percentage or fraction of the nuclide inventory sorbed as a function of some parameter (pH, time, equilibrium concentration, ionic strength). However, it has been pointed out by several authors that representing data in this way can often be less sensitive than when sorption results are expressed as distribution coefficients, R_d values (see for example JANNASCH et al. 1988; BRADBURY & BAEYENS 1997b). In particular, within the framework of nuclear waste management, the crucial parameter is the aqueous radionuclide concentration and this can be more easily be calculated from the distribution coefficient (BAEYENS & BRADBURY 1997). Consequently, almost all of the following sorption data are presented in terms of the logarithm of the distribution ratio, R_d, defined in the usual manner as :

$$R_d = \frac{C_{\text{init}} - C_{\text{eq}}}{C_{\text{eq}}} \cdot \frac{V}{m} \quad [2]$$

where,

C_{init}: Total (active + inactive) initial aqueous nuclide concentration (M)

C_{eq}: Total (active + inactive) equilibrium aqueous nuclide concentration (M)

V: volume of liquid phase (L)

m: mass of solid phase (kg)

In addition the results are also presented in the form of sorption isotherms i.e. the quantity sorbed per unit mass of solid versus the equilibrium aqueous concentration. In such plots, a gradient of unity is indicative of linear sorption, i.e. R_d is constant as a function of concentration, and a gradient less than unity indicates non-linear sorption behaviour, i.e. R_d decreases with increasing concentration.

4.2 Sr sorption on Na-illite.

Sorption edges for Sr on Na-illite were determined at trace concentrations in 0.1 and 0.01 M NaClO₄. A sorption isotherm was measured at pH = 7 in 0.1 M NaClO₄. The measurements are presented in Figures 7, 8 and 9 and the corresponding experimental conditions are summarised in Tables 17, 18 and 19 respectively. (Note that the sorption kinetics for Sr were rapid and reached equilibrium within 1 day.)

The sorption measurements as a function of pH given in Figures 7 and 8 indicate clearly that the uptake of Sr is a function of the background electrolyte concentration. This can most clearly be appreciated in the pH range 5.5 to 8.5 where R_d increases by almost two orders of magnitude for a change in NaClO₄ concentration from 0.1 to 0.01 M. This is broadly in accord with what would be expected from a cation exchange mechanism. The decrease in sorption values below pH = 5.5 is due to competitive effects from cations released into solution from the illite itself, see section 3.8. The origin of the increase in R_d values above pH ~8.5 is less clear but could be due to Sr undergoing surface complexation reactions (c.f. Ca sorption on Na-montmorillonite in BAEYENS & BADBURY 1995b).

The gradient of the sorption isotherm plot in Figure 9 is near unity, again as would be expected from an uptake mechanism dominated by cation exchange. The measurements cease at a total Sr concentration of $\sim 6 \times 10^{-8}$ M corresponding to the background concentration of inactive Sr in these experiments. (See Tables 7 and 8).

Table 17: Experimental conditions for the Sr sorption edge measurements on conditioned Na-illite in 0.1 M NaClO₄.

Experimental conditions	Series I	Series II
pH range	2.7 - 10.9	5.1 - 8.3
S:L ratio (g L ⁻¹)	1.78	1.78
Buffers	yes	yes
Initial Sr concentration (M)	9.2 x 10 ⁻¹⁰	10 ⁻⁹
Equilibration time (days)	7	7
Number of data points	11	6

Table 18: Experimental conditions for the Sr sorption edge measurements on conditioned Na-illite in 0.01 M NaClO₄.

Experimental conditions	Series I	Series II
pH range	2.7 - 11.1	6.3 - 9.3
S:L ratio (g L ⁻¹)	1.53	1.89
Buffers	yes	yes
Initial Sr concentration (M)	9.9 x 10 ⁻¹⁰	1.1 x 10 ⁻⁹
Equilibration time (days)	7	7
Number of data points	12	4

Table 19: Experimental conditions for the Sr sorption isotherm measurements on conditioned Na-illite in 0.1 M NaClO₄.

pH	7.0
S:L ratio (g L ⁻¹)	1.75
Buffer	MOPS
Equilibration time (days)	7
Number of data points	13

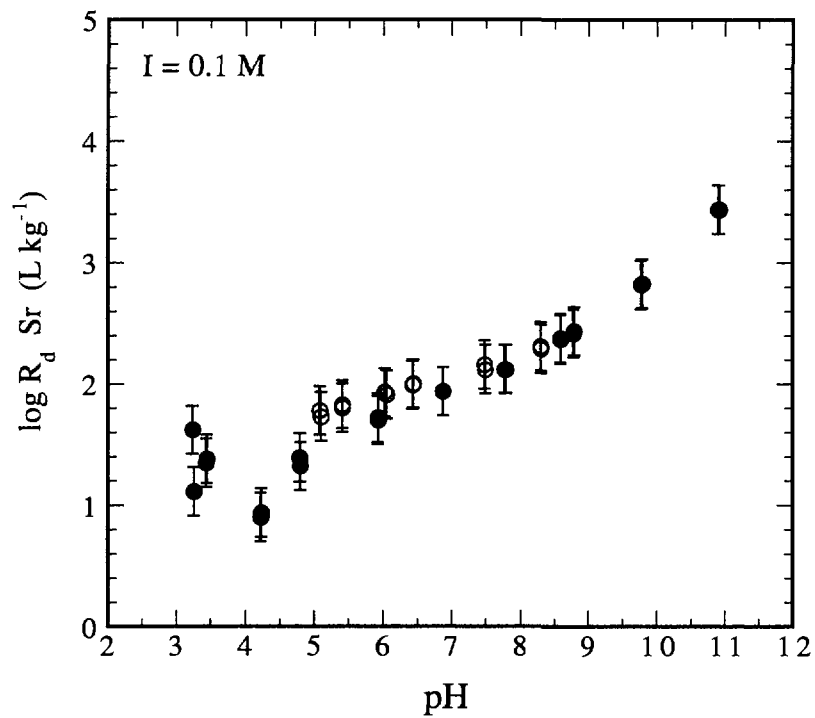


Figure 7: Sr sorption edge measurements in 0.1 M NaClO₄. Series I (full circles). Series II (open circles). See Table 17.

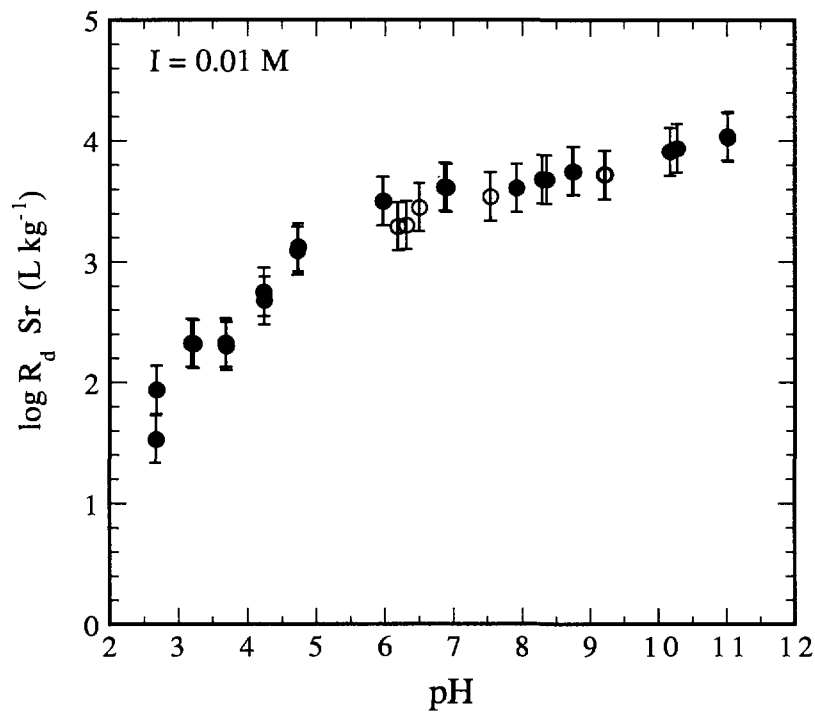


Figure 8: Sr sorption edge measurements in 0.01 M NaClO₄. Series I (full circles). Series II (open circles). See Table 18.

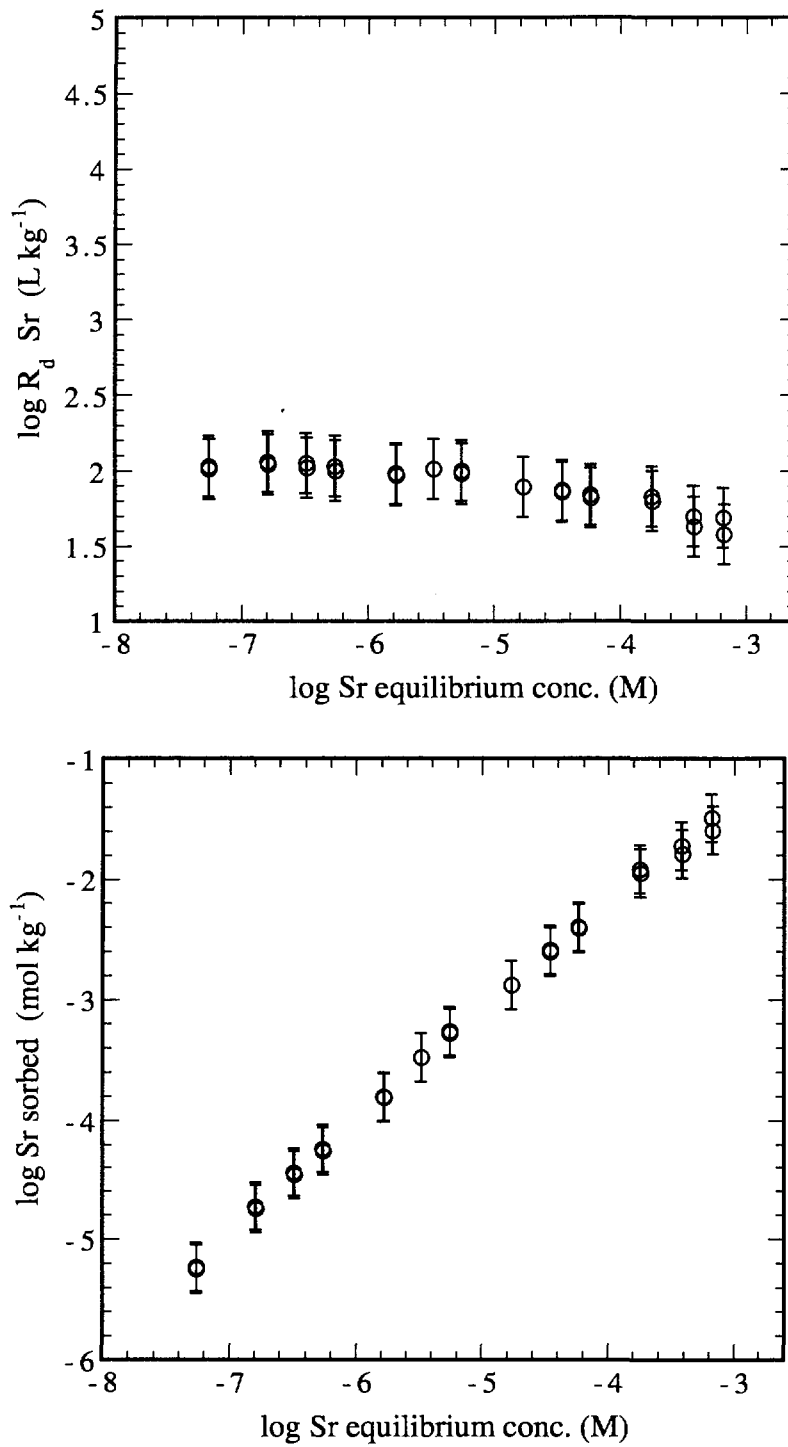


Figure 9: Sr sorption data as a function of equilibrium concentration on conditioned Na-illite in 0.1 M NaClO₄ at pH = 7.0. See Table 19.

4.3 Ni sorption on Na-illite

Sorption edges for Ni on Na-illite were determined at trace concentrations in 0.1 and 0.01 M NaClO₄. A sorption isotherm was measured at pH = 7 and 0.1 M NaClO₄. The measurements are presented in Figures 10, 11 and 12 and the corresponding experimental conditions are summarised in Tables 20, 21 and 22 respectively.

The Ni sorption edge data (Figures 10 and 11) show little or no dependence on electrolyte concentration and the two sets of data virtually overlap. (A slight dependence on NaClO₄ concentration below pH ~6 may be in evidence.) The form of the curves suggests that a surface complexation mechanism is dominating the sorption under the measurement conditions for these two data sets.

Two distinct regions can be identified in the Ni sorption isotherm plot given in Figure 12. At equilibrium Ni concentrations < 10⁻⁷ M the slope is almost unity whereas at higher concentrations the slope decreases to ~0.5, corresponding to Langmuir and Freundlich type behaviour respectively (TRAVIS & ETNIER 1981). At least two sorption site types would be required to model such data or, alternatively, at least two aqueous species sorbing on one site type.

Table 20: Experimental conditions for the Ni sorption edge measurements on conditioned Na-illite in 0.1 M NaClO₄.

Experimental conditions	Series I	Series II
pH range	2.7 - 10.9	2.7 - 10.9
S:L ratio (g L ⁻¹)	2.28	1.78
Buffers	yes	yes
Initial Ni concentration (M)	1.6 x 10 ⁻⁹	1.2 x 10 ⁻⁸
Equilibration time (days)	7	7
Number of data points	12	17

Table 21: Experimental conditions for the Ni sorption edge measurements on conditioned Na-illite in 0.01 M NaClO₄.

Experimental conditions	Series I	Series II
pH range	2.7 - 11.1	6.2 - 9.2
S:L ratio (g L ⁻¹)	1.53	1.89
Buffers	yes	yes
Initial Ni concentration (M)	6.6 x 10 ⁻⁹	6.7 x 10 ⁻⁹
Equilibration time (days)	7	7
Number of data points	12	4

Table 22: Experimental conditions for the Ni sorption isotherm measurements on conditioned Na-illite in 0.1 M NaClO₄.

pH	7.0
S:L ratio (g L ⁻¹)	1.75
Buffer	MOPS
Equilibration time (days)	7
Number of data points	20

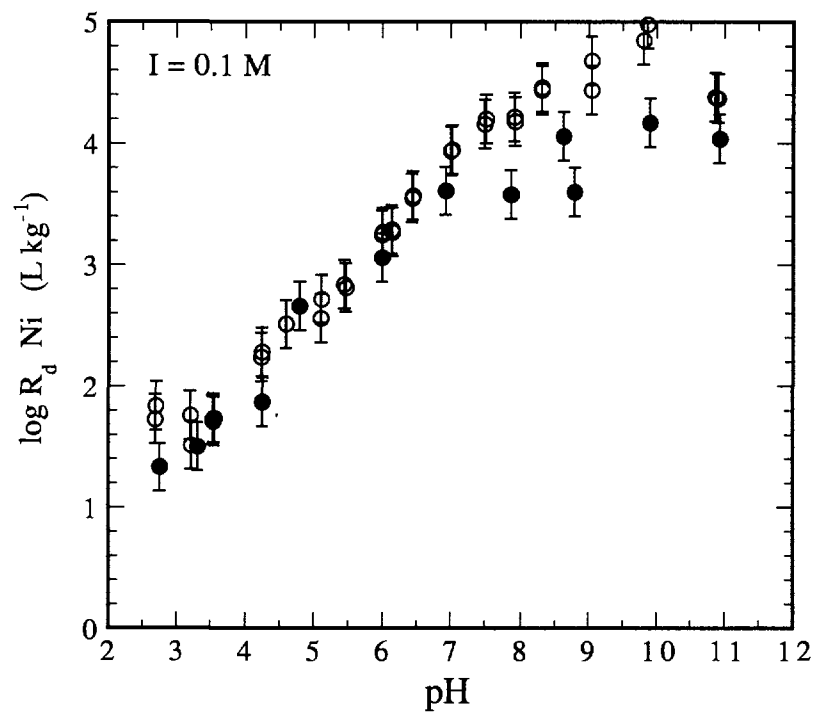


Figure 10: Ni sorption edge measurements in 0.1 M NaClO_4 . Series I (full circles). Series II (open circles). See Table 20.

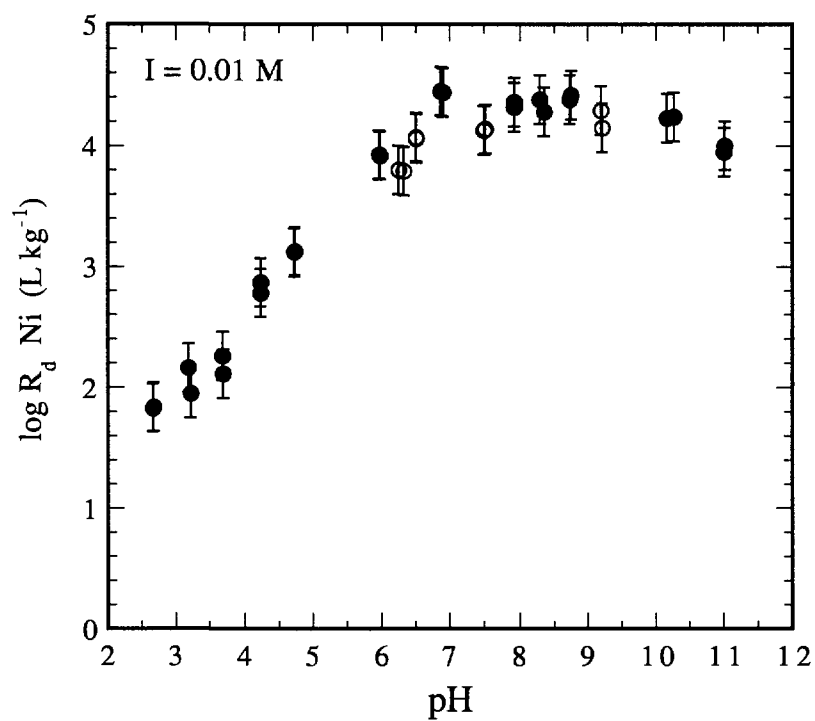


Figure 11: Ni sorption edge measurements in 0.01 M NaClO_4 . Series I (full circles). Series II (open circles). See Table 21.

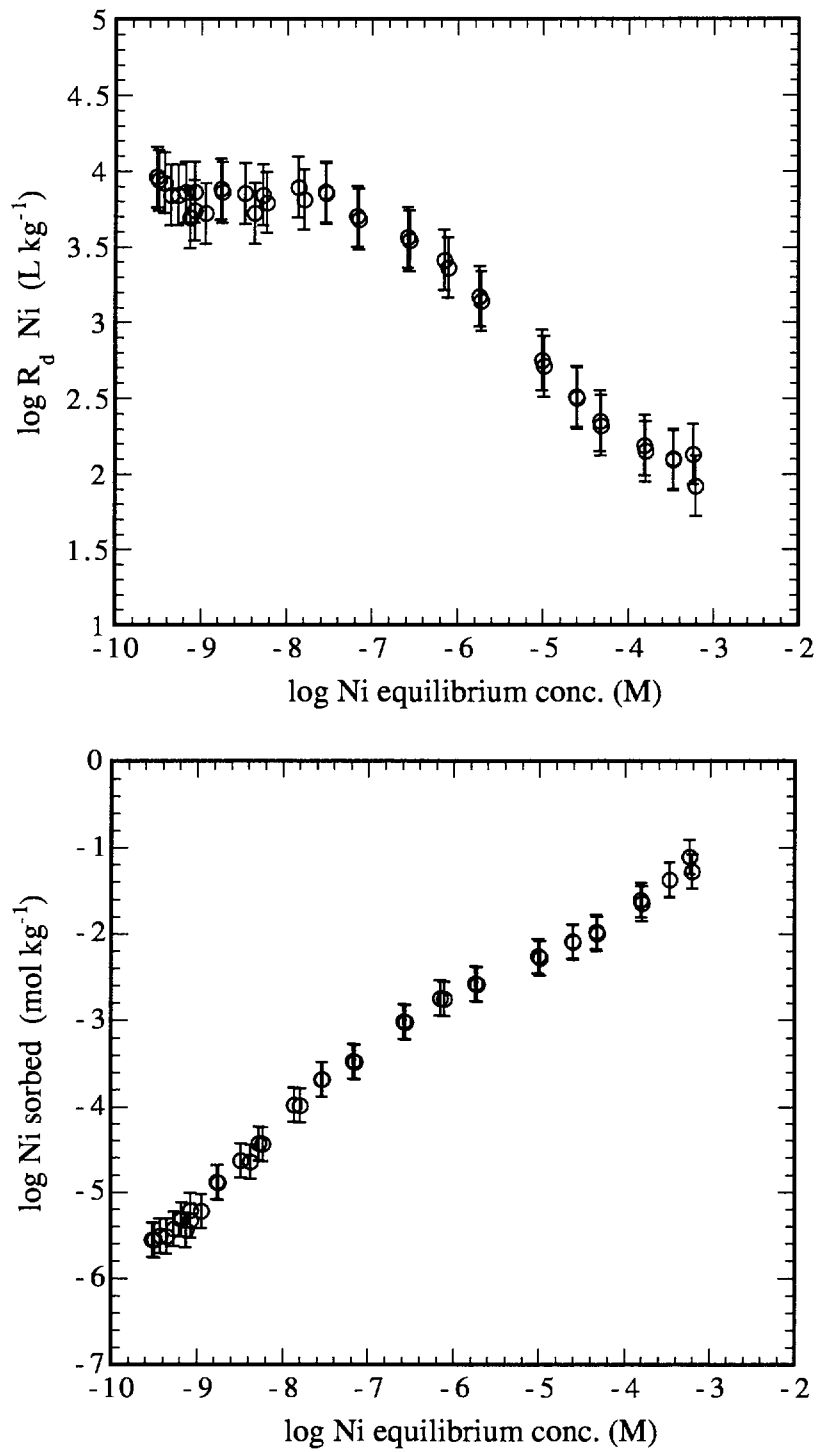


Figure 12: Ni sorption data as a function of equilibrium concentration on conditioned Na-illite in 0.1 M NaClO₄ at pH = 7.0. See Table 22.

4.4 Eu sorption on Na-illite

Sorption edges for Eu on Na-illite were determined at trace concentrations in 0.1 and 0.01 M NaClO₄. A sorption isotherm was measured at pH = 7 in 0.1 M NaClO₄. The measurements are presented in Figures 13, 14 and 15 and the corresponding experimental conditions are summarised in Tables 23, 24 and 25 respectively.

Eu sorbs extremely strongly at pH values above 6 (Figures 13 and 14). On the rising part of the sorption edge a slight dependency on NaClO₄ is apparent. The forms of the two curves would, as in the case of Ni, suggest that the dominant sorption mechanism is likely to be surface complexation. The sorption data measured in the high pH region in 0.1 and 0.01 M NaClO₄ solutions exhibit distinct differences. A decrease in sorption for pH values above ~9 occurs in the lower concentration electrolyte medium whereas the sorption remains virtually constant at 0.1 M NaClO₄. An explanation for this behaviour is not readily apparent.

Similarly to the case of Ni, the Eu isotherm, Figure 15, exhibits a linear sorption region (Eu equilibrium concentrations < 10⁻⁸ M) and a non-linear region with a gradient of ~0.3 at higher concentrations. Such a low gradient indicates that the sorption is highly non-linear.

Table 23: Experimental conditions for the Eu sorption edge measurements on conditioned Na-illite in 0.1 M NaClO₄.

Experimental conditions	Series I	Series II
pH range	2.7 - 10.8	5.1 - 8.3
S:L ratio (g L ⁻¹)	1.78	1.78
Buffers	yes	yes
Initial Eu concentration (M)	2.1 x 10 ⁻⁹	4.3 x 10 ⁻⁹
Equilibration time (days)	7	7
Number of data points	24	6

Table 24: Experimental conditions for the Eu sorption edge measurements on conditioned Na-illite in 0.01 M NaClO₄.

Experimental conditions	Series I
pH range	2.7 - 11.1
S:L ratio (g L ⁻¹)	1.89
Buffers	yes
Initial Eu concentration (M)	3.2 x 10 ⁻⁹
Equilibration time (days)	7
Number of data points	17

Table 25: Experimental conditions for the Eu sorption isotherm measurements on conditioned Na-illite in 0.1 M NaClO₄.

pH	7.0
S:L ratio (g L ⁻¹)	1.75
Buffer	MOPS
Equilibration time (days)	7
Number of data points	20

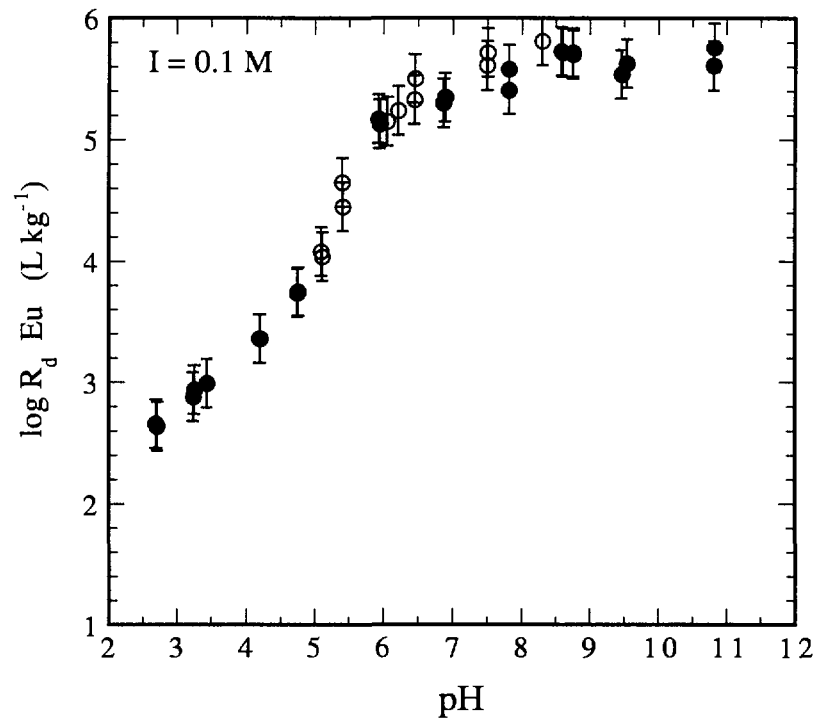


Figure 13: Eu sorption edge measurements in 0.1 M NaClO_4 . Series I (full circles). Series II (open circles). See Table 23.

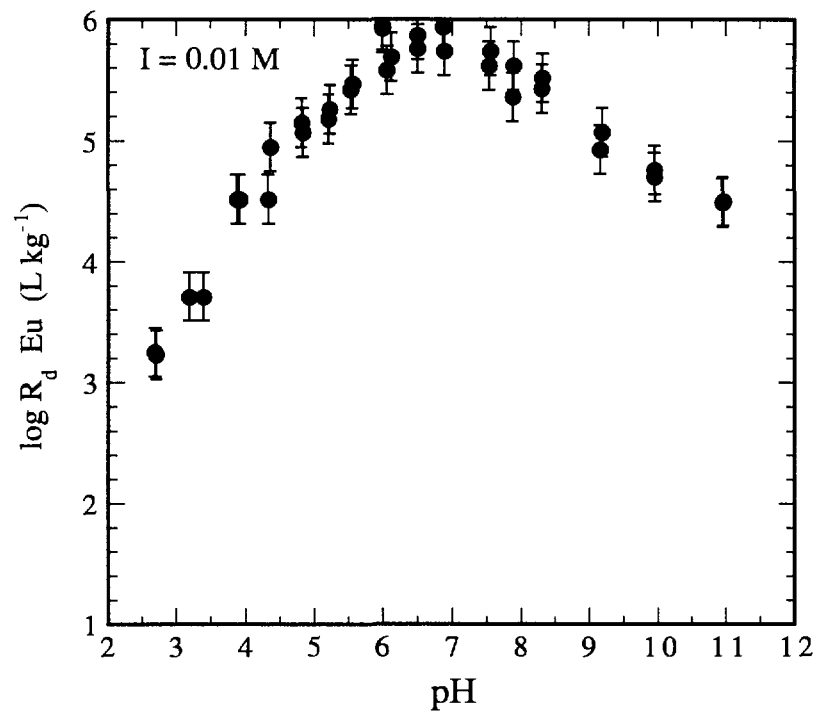


Figure 14: Eu sorption edge measurements in 0.01 M NaClO_4 . See Table 24.

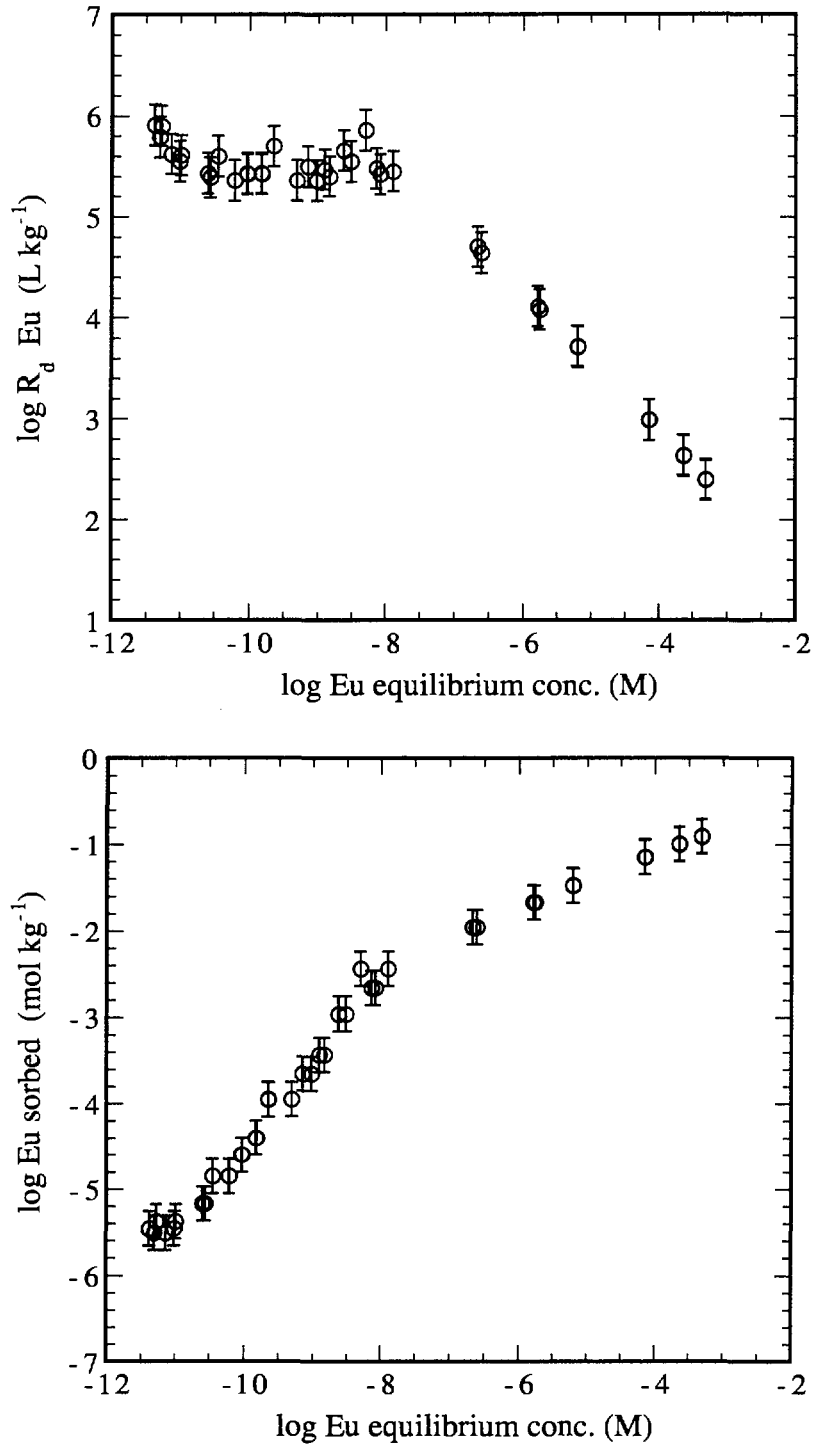


Figure 15: Eu sorption data as a function of equilibrium concentration on conditioned Na-illite in 0.1 M NaClO₄ at pH = 7.0. See Table 25.

5 Cs SORPTION ON Na-ILLITE

The Cs sorption measurements performed as a function pH, ionic strength (NaClO₄ concentration) and equilibrium Cs concentrations have been interpreted in terms of a two site cation exchange model. In contrast to the Sr, Ni and Eu investigations (see previous chapter), the modelling has already been completed for Cs and hence this work will be described in much more detail.

5.1 Background

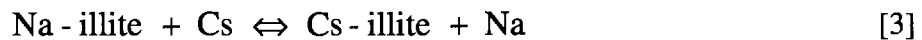
The sorption of Cs has been extensively studied on a wide variety of sorbents reflecting its importance as a safety relevant radionuclide. From the considerable pool of reports about Cs it is possible to select a number of features characterising its uptake by illite. It is well established that Cs sorbs by cation exchange and that the uptake on illite as a function of equilibrium Cs concentration can be non-linear (KOMARNENI 1979; KOMARNENI & ROY 1980; GILLHAM et al. 1980; SHIAO et al. 1981; BAEYENS 1982; TORSTENFELT et al. 1982; BROUWER et al. 1983; GRÜTTER et al. 1986, 1990, 1994; CREMERS et al. 1988; LIESER & STEINKOPF 1989; DE PRETER 1990; DE PRETER et al. 1991; KAUKONEN et al. 1993; WAUTERS et al. 1996a, 1996b, 1996c; STAUNTON & ROUBAUD 1997). Because Cs exists almost exclusively as the monovalent cation in solution, non-linear Freundlich type sorption implies that there are at least two distinct sorption sites for Cs on illite. If two sites are considered then they can be broadly classified into high affinity/low capacity and low affinity/high capacity site types. The former are often referred to as “frayed edge sites” (FES) (see for example JACKSON 1968) and are responsible for the uptake of Cs at low concentrations. There is experimental evidence to indicate that the FES are predominantly accessible to cations with low hydration energies e.g. K, Rb, NH₄ (SAWHNEY 1970, 1972; EBERL 1980) and that these cations, particularly K in natural systems, compete the most effectively with Cs for these sites. Other cations such as Na and H may also compete but only when their concentrations are orders of magnitude greater than Cs. Bivalent cations such as Mg, Ca and Sr with relatively large hydration energies are effectively non-competitive for the FES for steric reasons (SAWHNEY 1972; BROUWER et al. 1983).

The second class of sites are usually associated with the fixed negative charge on the surface of illite arising from isomorphous substitution, “planar sites”. However, recent NMR investigations (KIM & KIRKPATRICK 1997; KIM et al. 1996) of Cs sorbed on illite have identified at least two “Cs chemical environments” at the surface of the illite crystallites. Thus the sorption of Cs could involve up to 3 site types. Indeed, three sites

were required by BROUWER et al. (1983) to describe their Cs sorption measurements on illite.

5.2 Cation exchange modelling

Following on from the information presented above, the sorption behaviour of Cs will be treated as cation exchange occurring on at least two site types with different capacities and affinities. Irrespective of site type the cation exchange reaction of Cs on a Na-illite in a NaClO₄ background electrolyte may be written as:



The selectivity coefficient for the above reaction is defined via a mass action equation according to the convention given in GAINES & THOMAS (1953):

$$K_{\text{Na}}^{\text{Cs}} = \frac{N_{\text{Cs}}}{N_{\text{Na}}} \cdot \frac{a_{\text{Na}}}{a_{\text{Cs}}} \quad [4]$$

a_{Cs} and a_{Na} are the solution activities of cations Cs and Na, respectively. (Since both are monovalent the activity coefficients will be the same and activities ratios can be replaced by concentration ratios.) N_{Cs} and N_{Na} are equivalent fractional occupancies defined as the equivalents of Cs (or Na) sorbed per unit mass divided by the appropriate site capacity, Q , in equivalents per unit mass.

For the sorption of Cs under the condition that $N_{\text{Cs}} \ll 1$, $N_{\text{Na}} \sim 1$, it follows from equation [4] that

$$K_{\text{Na}}^{\text{Cs}} = R_{\text{d}}(\text{Cs}) \cdot (\text{Na}) \cdot \frac{1}{Q} \quad [5]$$

As can be clearly seen from equation [5], Cs sorption on a specific site under constant chemical conditions is proportional to the product of the site capacity and the selectivity coefficient. Also, since selectivity coefficients are deduced from sorption measurements in this work, it is expected that $\log K_{\text{c}}$ values will have approximately the same uncertainty associated with them as $\log R_{\text{d}}$ values i.e. ± 0.2 log units, see section 4.1.2.

Also similar equations can be written for any competitive reactions. In this respect K and H (at low pH values) may be particularly relevant. It is worth noting in this context that selectivity coefficients having common cations measured on the same site type and evaluated for the same site capacity are related. Thus $K_{\text{Na}}^{\text{Cs}}$ on a Na-illite and K_{K}^{Cs} on

a K-illite have been measured under the boundary conditions given above, then the following relation also holds

$$\frac{C_{\text{Cs}}}{C_{\text{Na}}} K_c \cdot \frac{1}{\frac{C_{\text{Cs}}}{K} K_c} = \frac{K}{C_{\text{Na}}} K_c \quad [6]$$

All of the computed curves given later were obtained using the code MINSORB (BRADBURY & BAEYENS 1997a) which is an extended version of the geochemical code MINEQL (WESTALL et al. 1976) containing cation exchange and surface complexation equations. Multi-element sorption on multiple sites can be calculated with this code.

Modelling the sorption behaviour by cation exchange requires a site capacity for each sorption site type being considered and the associated selectivity coefficient. The values of these two parameters are interdependent. Also, when competition is being considered, the selectivity coefficients have to be calculated at the site capacity of the particular site type under consideration in order to achieve an internally consistent parameter set. This is sometimes a problem because although the global cation exchange capacity can be measured relatively easily, individual site capacities are seldom known a priori. Consequently, they are a fitting parameter in the modelling. Hence when different data sets for different nuclides are being analysed, and the same site type is being considered, a site capacity needs to be defined first. Often this cannot be done directly and requires an iterative approach.

5.3 Estimate of the frayed edge site capacity

In certain circumstances it is possible to estimate site capacities. For example, if the Cs sorption isotherm data presented later in section 5.6.2 are plotted as log (Cs sorbed, mol kg⁻¹) against log (equilibrium Cs concentration, M) as illustrated in Figure 16, then a change of slope occurring at a concentration of ~10⁻⁸ M can be identified. At lower concentrations the gradient is approximately unity whereas at higher concentrations the sorption of Cs becomes non-linear and the slope changes to ~0.5.

In terms of the discussion given in section 5.1, the linear part of the plot is interpreted as being the uptake of Cs on the FES followed by a region of lower slope where the uptake on a second site type of lower affinity becomes important. To a first approximation the break in the curve indicates where the FES are becoming saturated and therefore the Cs occupancy on the clay at this point can be used as a first estimate of the site capacity. A value in the range from 0.2 to 0.5 meq kg⁻¹ is obtained in this way from Figure 16.

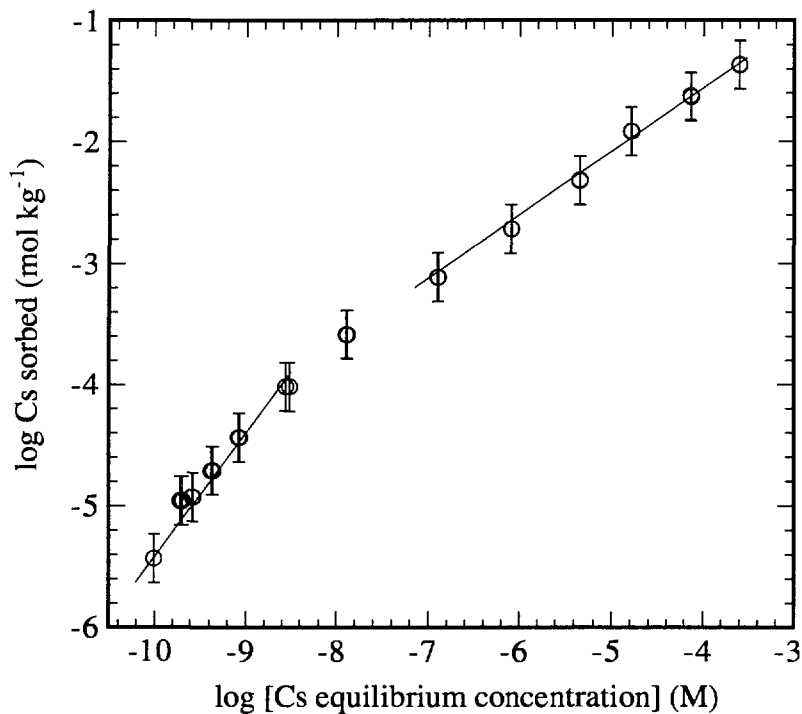


Figure 16: Cs sorption isotherm on conditioned Na-illite (pH = 7, 0.1 M NaClO₄). The break in the curve corresponds approximately to the saturation of the frayed edge sites (see text for details).

This can not only be used as a starting value for modelling the sorption on the FES but also to make estimates of the importance of competitive reactions prior to beginning the modelling using literature values where available. The latter is illustrated in the following section.

5.4 Competing cations

In the vast majority of cases in laboratory experiments and in nature, K is the most common competing cation influencing the sorption of Cs. For this reason, the K concentrations given in Tables 7 to 10 have been extracted and plotted in Figure 17. Even though the K concentration (Figure 17a) is relatively low in the Cs isotherm experiments carried out in 0.1 M NaClO₄ solution at neutral pH, it is nevertheless possible for K to be competing with Cs for the FES and thereby influencing the modelling with respect to the site capacity and selectivity coefficient deduced from the experimental data.

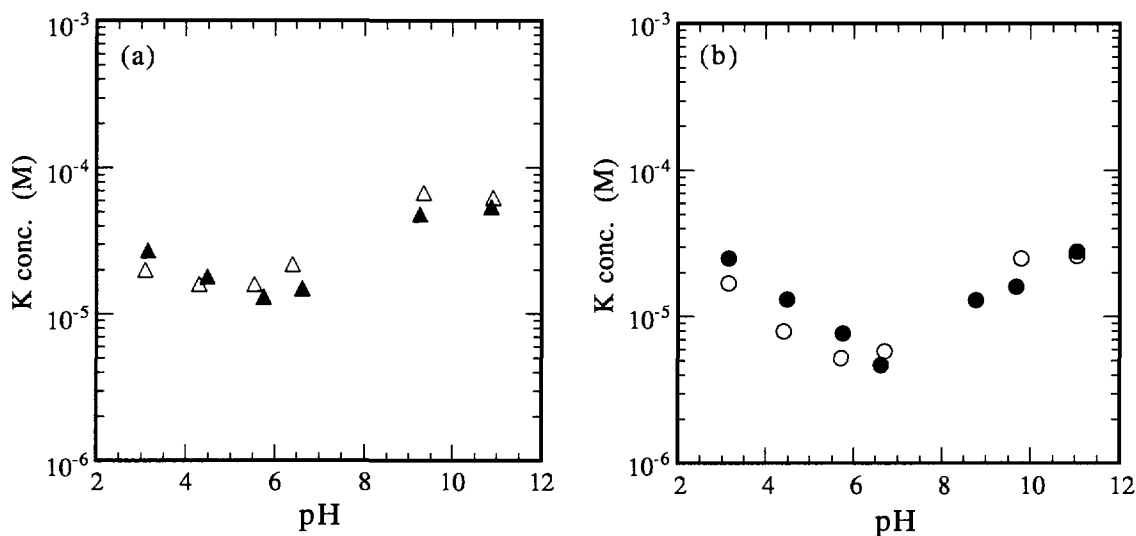


Figure 17: K concentrations in suspensions of conditioned Na-illite as a function of pH for a contact time of 7 days.

(a) 0.1 M NaClO₄: S:L = 2.4 g L⁻¹ (▲); S:L = 0.9 g L⁻¹ (△)

(b) 0.01 M NaClO₄: S:L = 2.2 g L⁻¹ (●); S:L = 0.8 g L⁻¹ (○).

From the fairly extensive study on selectivity coefficient values for illite given in BROUWER et al. (1983) a value of 1.9 for $\log \frac{K}{Na} K_c \{FES\}$ for a FES capacity of 0.5 meq kg⁻¹ can be deduced. These values were also used nearly ten years later by COMANS et al. (1991) and probably represent the best which are currently available. In any event, the FES capacity used in BROUWER et al. (1983) is similar to that estimated here and so their selectivity coefficient is considered sufficiently reliable and appropriate to evaluate the likely competitive influence of K. Simply stated the calculations indicate that for the conditions relevant to the Cs isotherm measurements at 0.1 M NaClO₄, there is effectively no influence of K.

However this is probably not the case for the Cs sorption measurements made on the FES as a function of pH in a 0.01 M NaClO₄ solution. Because of this and because K is the most likely important competitive cation influencing the sorption of Cs at trace concentrations in natural systems, separate experiments on the sorption of Cs on a K conditioned illite were performed with the aim of determining the $\frac{Cs}{K} K_c \{FES\}$ explicitly.

5.5 Determination of the Cs-K selectivity coefficient

The exchange characteristics of the competing cations have to be quantified before the Cs sorption measurements can be modelled. In order to achieve this a purified K-illite clay was produced in a similar way to that described for the Na-illite (Chapter 2) and Cs sorption measured at trace concentrations in 0.01 M KCl as a function of pH. The data are shown in Figure 18 and were fitted using a fixed FES capacity of 0.55 meq kg^{-1} , to be compatible with Cs-Na modelling (see later, sections 5.6.2 and 5.6.3), and $\frac{C_s}{K} K_c \{FES\}$ selectivity coefficient as free parameter. The best fit to the data (continuous line in Figure 18) was achieved with $\log \frac{C_s}{K} K_c \{FES\} = 4.7$. Using the relation given in equation [6], and a value for $\log \frac{C_s}{Na} K_c \{FES\} = 6.95$ (section 5.6.2), and $\frac{C_s}{K} K_c \{FES\} = 4.7$, a $\log \frac{K}{Na} K_c \{FES\}$ value of 2.25 was deduced.

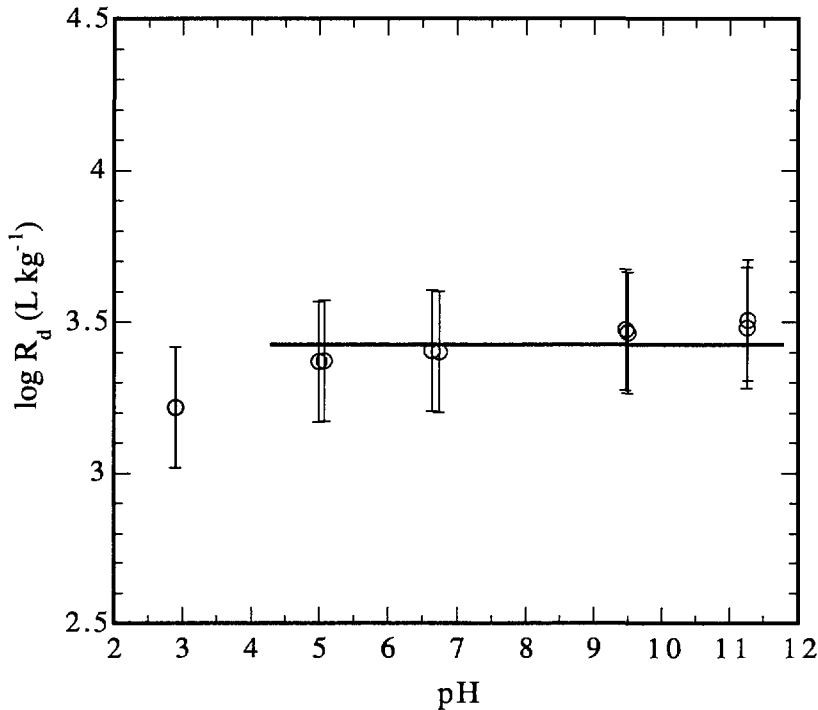


Figure 18: Cs sorption at trace concentration ($< 10^{-8} \text{ M}$) on conditioned K-illite in 0.01 M KCl as a function of pH. A $\frac{C_s}{K} K_c \{FES\} = 4.7 \pm 0.2$ was fitted to the data.

5.6 Experimental results and modelling

In order to avoid unnecessary repetition of figures, the experimental results and their interpretation in terms of a cation exchange model are presented together in this section.

5.6.1 Cs sorption kinetics

The first sets of experiments performed were kinetic tests which indicated the equilibration times required for the subsequent sorption measurements. Over the equilibrium concentration ranges covered in this study ($\sim 10^{-10}$ to $\sim 10^{-4}$ M) Cs sorbs on at least two site types and the kinetics at concentrations towards the extreme ends of the range were thus of interest. In the low concentration region the kinetic tests were set up so that the total Cs concentration used was well below the value required for site saturation (see section 5.3) so that sorption was only occurring on the FES; the initial Cs concentration was 1.6×10^{-8} M. For sorption on the planar sites an initial concentration of 7.4×10^{-4} M was used.

The results from both kinetic experiments are shown in Figure 19. As can be seen, the uptake of Cs on the planar sites was very rapid, reaching completion in a few hours. In contrast, equilibrium sorption values on the FES were only reached after 4 to 5 days. Thus, even in well mixed crushed illite batch tests such as these, it appears that the Cs requires a relatively long time to “find” the high affinity low capacity FES.

In Figure 20 the uptake of Cs on the FES as a function of pH for times between 3 and 60 days are also shown. For pH values in the range 3 to 10 no significant influence on the rate of approach to equilibrium was observed. This was also true for the planar sites. As a consequence of the above results batch sorption tests were shaken for at least 7 days.

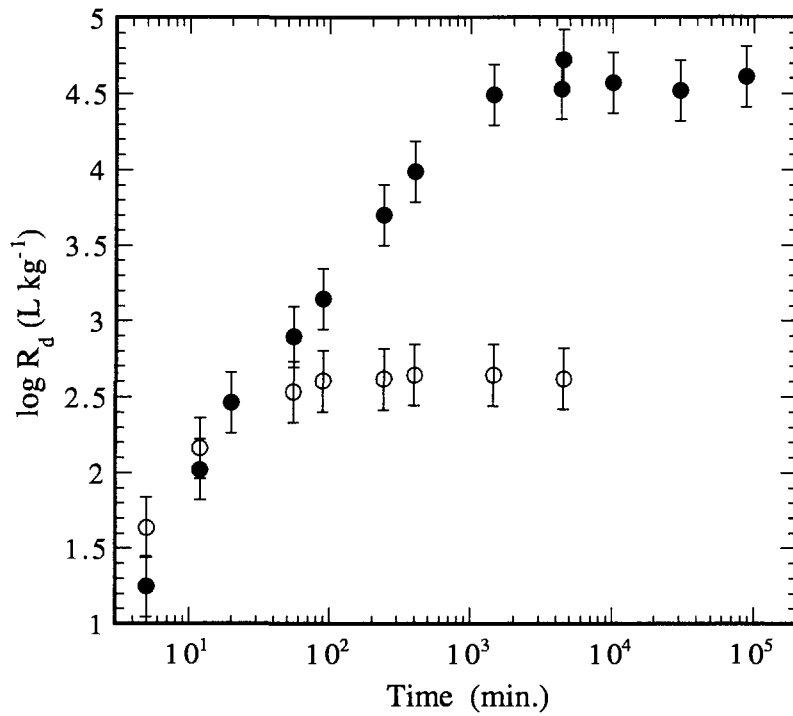


Figure 19: Cs sorption kinetics on the frayed edge sites (●) (initial Cs conc. = 1.6×10^{-8} M) and planar sites (O) (initial Cs conc. = 7.4×10^{-4} M). pH ~7 and 0.1M NaClO₄.

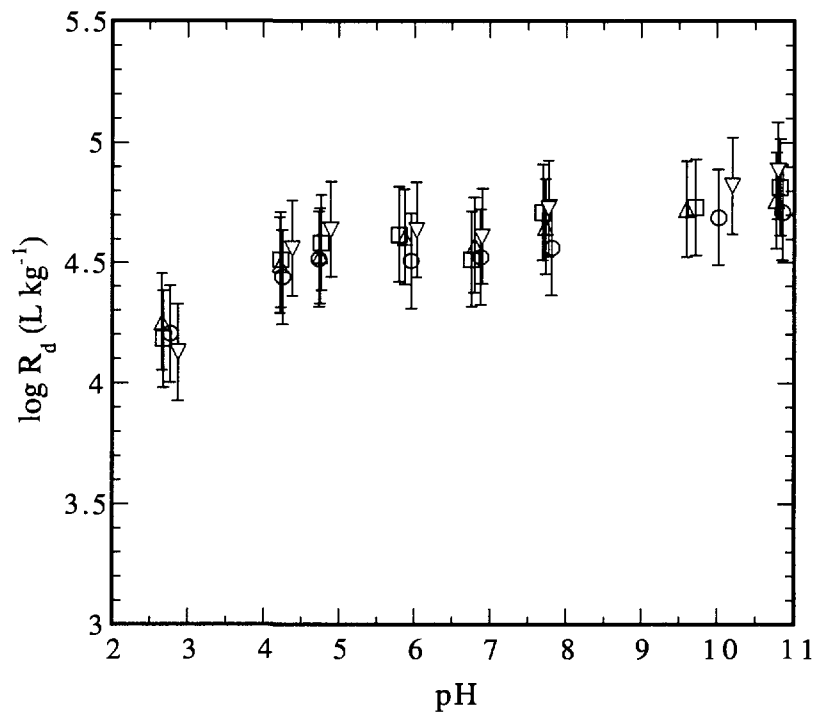


Figure 20: Sorption of Cs on the frayed edge sites as a function of pH and time in 0.1 M NaClO₄. 3 days (O); 7 days (Δ); 21 days (∇); 61 days (□).

5.6.2 Cs sorption isotherm

The sorption of Cs on illite at pH = 7 in a 0.1 M NaClO₄ solution is shown in Figure 21a plotted as R_d against equilibrium Cs concentration. Because of the non-linear sorption behaviour of Cs and the fact that Cs is present in solution as the monovalent cation, it may be stated at the outset that at least four parameters will be necessary to describe the data given in this figure. Of the four parameters required (two site capacities and the corresponding Cs-Na selectivity coefficients) the only information available is an estimate of the FES capacity given above in section 5.3.

The first step in the procedure was to find a FES capacity and $K_c^{Cs/Na}$ selectivity coefficient combination which best fitted the initial high sorption region and reflected the form of the curve (saturation of these sites) using as an initial value the estimated site capacity.

Once these values had been fixed for the first iteration, the next step was to find a similar capacity/selectivity coefficient combination for a second set of sites. The most simple assumption was that these were the planar sites whose capacity is given by the cation exchange capacity of ~127 meq kg⁻¹. This approach however was unsuccessful because the form of the measured curve indicated that site saturation of the second site type was occurring at levels well below the exchange capacity. This second site type was then termed type II sites.

In view of the above a new fitting procedure was carried out with both the type II site capacity and the selectivity coefficient as free parameters. In practice the values that these parameters may have is quite restricted because their combination sets the maximum R_d value, and the capacity sets the concentration range over which site saturation effects determine the form of the curve.

Once values for these four parameters had been estimated, a second round of calculations enabled some "fine tuning" to be carried out to yield the best fit. The calculated contributions to the measured sorption curve from the FES and type II sites are shown as dotted and dashed lines respectively in Figure 21a. (The parameter values are listed in Table 26.) The overall fit to the experimental data is given by the continuous line.

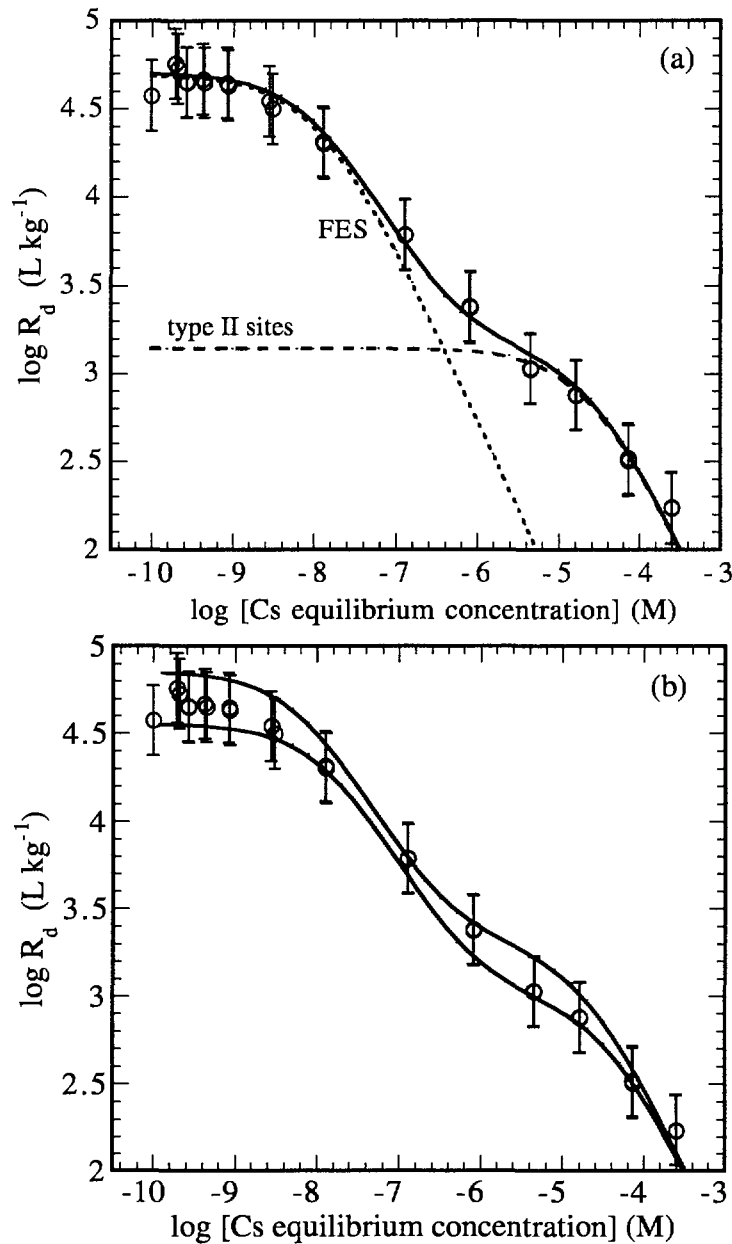


Figure 21: (a) Cs sorption on conditioned Na-illite as a function of concentration in 0.1 M NaClO₄ at pH=7 (open circles). The continuous curve is a fit to the data using the parameter values given in Table 26. The dotted and dashed lines are the contributions made by FES and type II sites respectively to the overall sorption of Cs.

(b) Illustration of the effect of parameter uncertainties on the modelled isotherm curve. The envelope curves were obtained using upper and lower bound values for $K_c^{Cs} \{FES\}$ and $K_c^{Cs} \{II\}$ with an error of ± 0.2 log units.

The type II site capacity, according to the above treatment of the data, is $\sim 35 \text{ meq kg}^{-1}$ which is only $\sim 28\%$ of the available exchange capacity. This implies that there may be a “type III site” capable of taking up Cs at equilibrium concentrations in excess of $3 \times 10^{-4} \text{ M}$. It is worth noting that the existence of a second planar site type associated with the surface negative charge arising from isomorphic substitution is in accord with the NMR results reported for Cs sorbed onto illite by KIM & KIRKPATRICK (1997) and KIM et al. (1996).

The fact that the fit to the data in Figure 21a was good should not be too surprising since four free parameters were available. Nevertheless, the quality of the fits obtained is sensitive to the values chosen. The aim of the approach was to obtain a sorption model for Cs which was as simple as possible and then test it against other data measured under different conditions. A first step in this direction is the modelling of the sorption data presented in next section.

Finally, errors of ± 0.2 log units were estimated for selectivity coefficient values in section 5.2. In order to illustrate the effects which such uncertainties may have on the calculated Cs sorption values, the envelope curves for the shaded region given in Figure 21b were obtained using upper and lower bound values for the ${}_{\text{Na}}^{\text{Cs}} K_c \{ \text{FES} \}$ and ${}_{\text{Na}}^{\text{Cs}} K_c \{ \text{II} \}$ for the frayed edge and type II site capacities, respectively.

5.6.3 Cs sorption as a function of pH and ionic strength

The data measured for the sorption of Cs on the FES (initial Cs conc. $< 10^{-8} \text{ M}$) as a function of pH and NaClO_4 background electrolyte concentration are shown in Figures 22 and 23a,b.

The main features of the data are:

- (i) R_d increases with decreasing NaClO_4 concentration over the range 1 to 0.01 M.
- (ii) At the lowest NaClO_4 concentration of 0.01 M there is a distinct tendency for sorption to decrease at the lower and higher ends of the pH range.
- (iii) The same behaviour at low pH is also evident at the two higher concentrations but is much less apparent.

Cation exchange is normally taken to be pH independent, which does not appear to be the case for the data measured at 0.01 M NaClO_4 in particular. At low background electrolyte concentrations and low pH values competitive effects from the proton and

cations such as K released from the interlayers within the clay, may approach concentration levels significant enough to influence the uptake of Cs on the FES. Inspection of the plots in Figures 22 and 23a would tend to support such an interpretation.

A summary of the selectivity coefficients and frayed edge and type II site capacities is given in Table 26 and the continuous curves given in Figures 23a and 23b were modelled using these parameters. For this set of calculations all parameters in the model were fixed.

The Cs sorption model described here appears to be capable of reproducing the measured sorption values relatively well except for those obtained in 0.01 M NaClO₄ solutions for which no explanation is currently available. However, it must be stated that almost all of the data were required in order to fit selectivity coefficient and site capacity values. Because of this, the general applicability of the model and model parameters deduced needs to be assessed by testing their validity on natural systems in which illite is the dominant sorbent for Cs.

Table 26: Summary of the parameters derived from the modelling of Cs sorption data on illite. The site capacities and the selectivity coefficients for the various exchange reactions are given for the frayed edge sites and for the type II sites.

Site type	Site capacity	Selectivity coefficient values
Frayed edge sites	0.55 meq kg ⁻¹	$\log \frac{Cs}{Na} K_c \{FES\} = 6.95 \pm 0.2$
		$\log \frac{K}{Na} K_c \{FES\} = 2.25 \pm 0.4$
		$\log \frac{H}{Na} K_c \{FES\} = 1.75 \pm 0.2$
Type II sites	35 meq kg ⁻¹	$\log \frac{Cs}{Na} K_c \{II\} = 3.60 \pm 0.2$

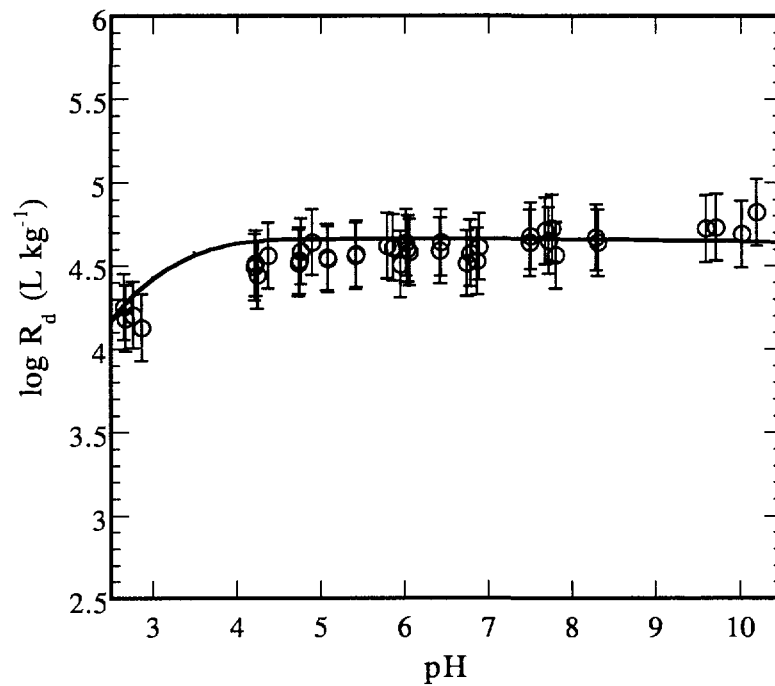


Figure 22: Cs sorption at trace concentration ($< 10^{-8}$ M) on conditioned Na-illite in 0.1 M NaClO_4 as a function of pH. The continuous curve was calculated using ${}_{\text{Na}}^{\text{Cs}}K_c\{\text{FES}\} = 6.95$, ${}_{\text{Na}}^{\text{K}}K_c\{\text{FES}\} = 2.25$ and a fitted value of 1.75 for ${}_{\text{Na}}^{\text{H}}K_c\{\text{FES}\}$

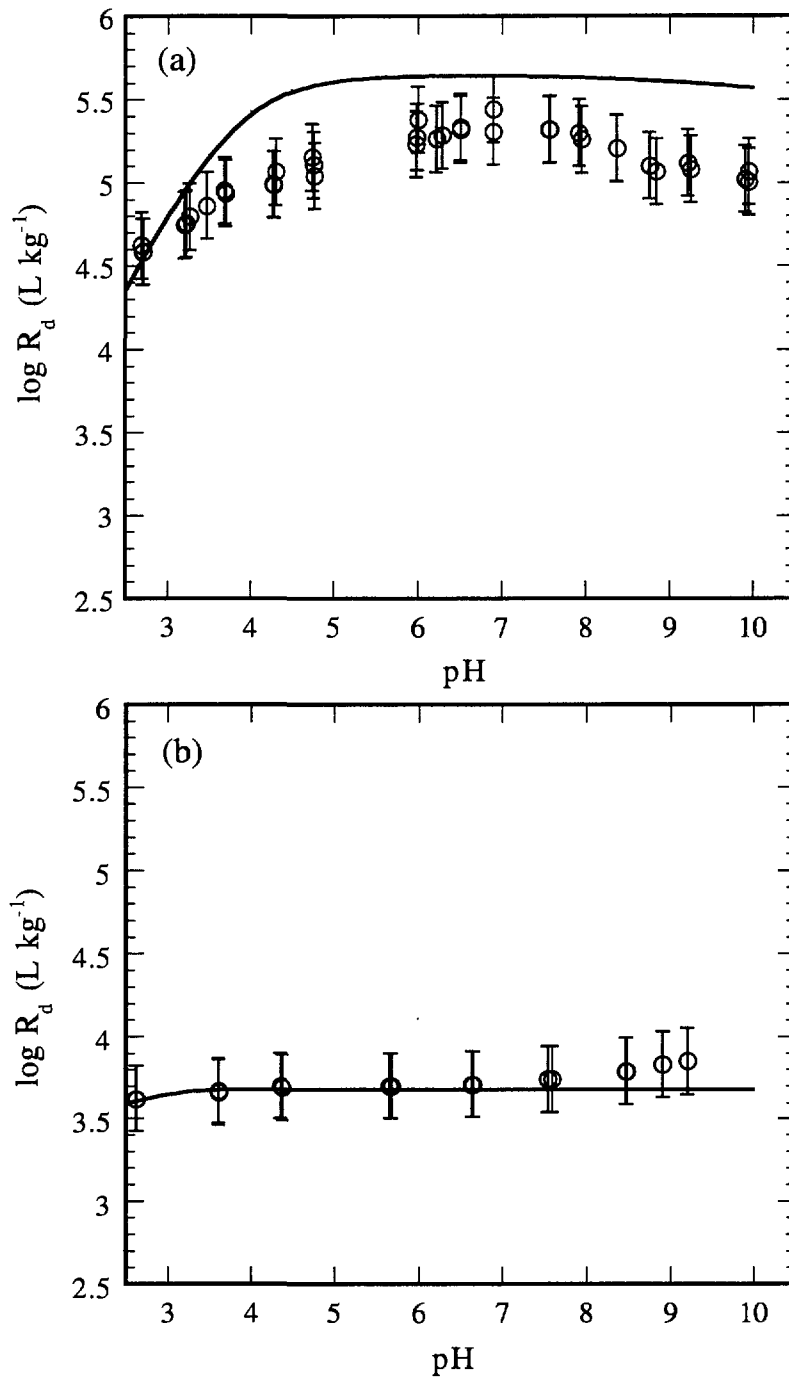


Figure 23: (a) Cs sorption at trace concentration ($< 10^{-8}$ M) on conditioned Na-illite in 0.01 M NaClO_4 as a function of pH. The continuous line is the modelled curve. All parameters fixed (see Table 26).

(b) Cs sorption at trace concentration ($< 10^{-8}$ M) on conditioned Na-illite in 1 M NaClO_4 as a function of pH. The continuous line is the modelled curve. All parameters fixed (see Table 26).

6 SUMMARY

The aim of this work was to extend the sorption and modelling investigations of BAEYENS & BRADBURY (1997) and BRADBURY & BAEYENS (1997a, 1999) on montmorillonite to another clay mineral system. Since this study was a collaboration between PSI and CEA, and considerable work had already been done by the latter organisation on “illite du Puy” (see for example GORGEON 1994), this material was also selected for this study. Illite du Puy is a natural clay mineral with all the associated mineral and chemical complexity. In order to be able to have a chance of understanding sorption processes, and ultimately to develop sorption models, the approach taken by several authors has been to work on well characterised single mineral systems (DZOMBAK & MOREL 1990; GORGEON 1994; BRADBURY & BAEYENS 1997a). Hence the initial effort was focused on purifying and conditioning the “as received” illite du Puy. This was followed by an extensive physico-chemical characterisation programme. Particular attention was paid to ensuring that water chemistry analyses were carried out at all stages of the investigations. It was shown that partial dissolution of the illite can occur with the release of cations such as Al, Si, Mg and K into solution. Also, cations such as Ca and Sr, which are sorbed under the conditions used to prepare the illite, can be released in relatively large quantities if the conditions are changed. Depending on the radionuclide and pH region being considered these effects can have significant influences on the sorption measurements. An important conclusion of this work was therefore that a detailed description of the solution-mineral interaction in laboratory experiments, even in superficially simple systems, is vital.

The second part of the work was devoted to measure the sorption of Cs, Sr, Ni and Eu on purified Na-illite under a wide range of chemical conditions. (These nuclides were chosen to be representative of the alkali, alkali-earth, transition and rare earth/trivalent actinide groups of metals.) In particular, sorption was measured as a function of time, pH, background electrolyte concentration, S:L ratio and nuclide concentration. These detailed measurements will provide the basis data for future (quasi) mechanistic modelling studies on illite.

The Cs sorption edge and isotherm data were modelled in terms of two cation exchange sites termed “frayed edge sites” (high affinity/low capacity) and “type II sites” (low affinity/high capacity). These two sites are predominantly accessible to cations with low hydration energies e.g. K, Rb, NH₄ and these cations, particularly K in natural systems, compete most effectively with Cs. Other cations such as Na and H may also compete but only when their concentrations are orders of magnitude greater than the concentration of Cs. Selectivity coefficient values for $\frac{Cs}{Na} K_c \{FES\}$, $\frac{H}{Na} K_c \{FES\}$,

$\frac{C_s}{N_a} K_c \{FES\}$ and $\frac{C_s}{N_a} K_c \{II\}$ are given for illite together with the corresponding site capacities. Although the Cs sorption model appears to be promising, it is clear that both model and model parameters need to be tested against independent Cs sorption data sets in order to assess its wider applicability.

7 ACKNOWLEDGEMENTS

The first author would like to thank the Waste Management Laboratory for the warm welcome extended to him during his 16 months post doctoral stay at the Paul Scherrer Institut. The constructive critical comments on the manuscript made by Dr. J. Hadermann (PSI) and Dr. I. Hagenlocher (Nagra) are gratefully acknowledged. Gratitude is also expressed to Dr. J. Tits and Dr. E. Wieland for many fruitful discussions. The multitude of chemical analyses contained in this report were carried out by R. Keil. This work was a collaboration between the Waste Management Laboratory, PSI, and the French Commissariat à l'Énergie Atomique (CEA). Partial financial support was provided by Nagra.

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