

Nagra

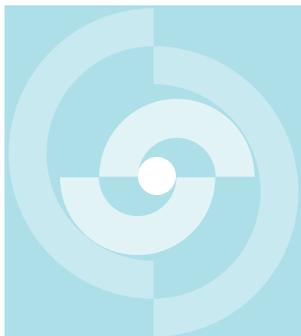
Nationale
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Società cooperativa
nazionale
per l'immagazzinamento
di scorie radioattive



TECHNICAL REPORT 91-06

GRIMSEL TEST SITE

BATCH SORPTION EXPERIMENTS WITH IODINE, BROMINE, STRONTIUM, SODIUM AND CESIUM ON GRIMSEL MYLONITE

S. AKSOYOGLU
C. BAJO
M. MANTOVANI

FEBRUARY 1991

PSI, Würenlingen and Villigen

GRIMSEL TEST SITE / SWITZERLAND
A JOINT RESEARCH PROGRAM BY

- NAGRA — National Cooperative for the Storage of Radioactive Waste, Baden, Switzerland
- BGR — Federal Institute for Geoscience and Natural Resources, Hannover, Federal Republic of Germany
- GSF — Research Centre for Environmental Sciences, Munich, Federal Republic of Germany

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FOREWORD

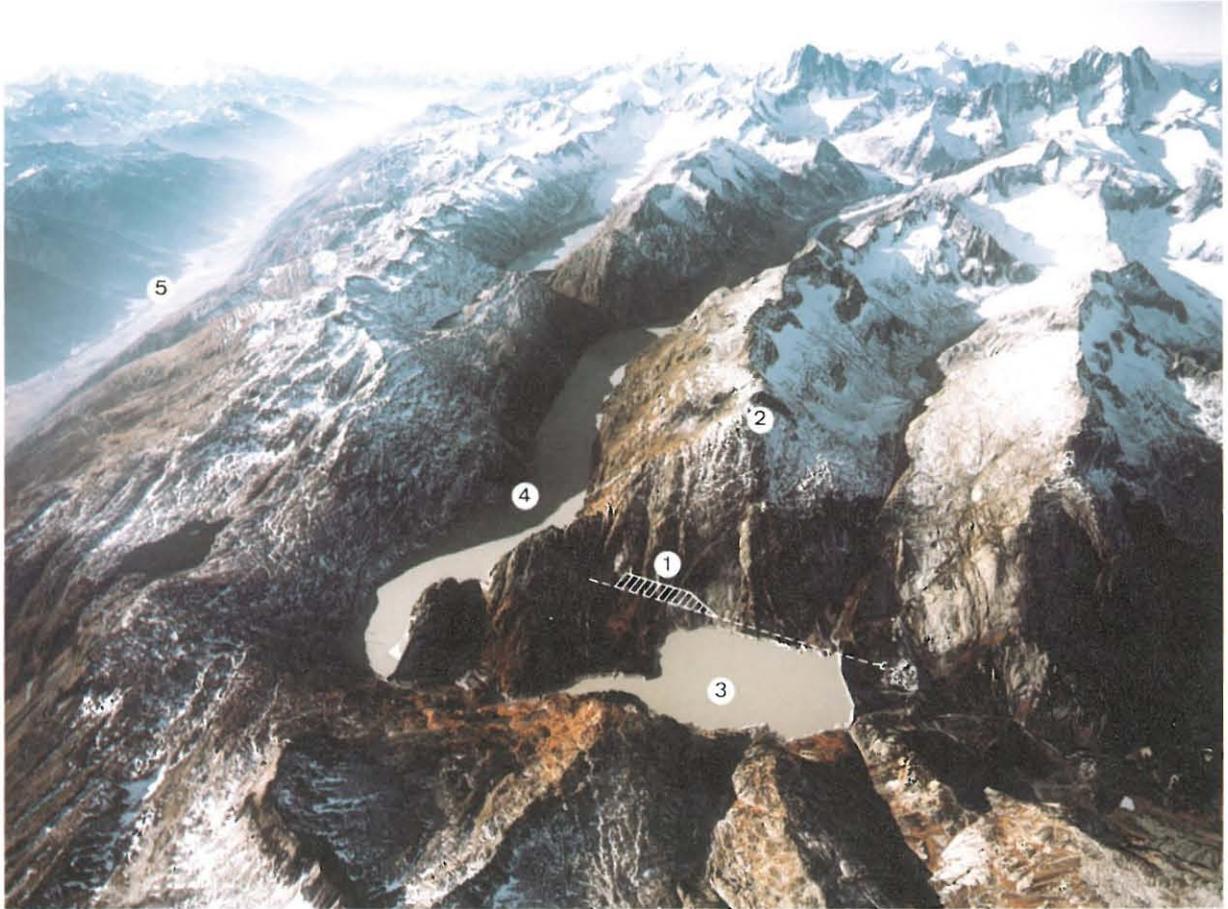
Concepts which foresee the disposal of radioactive waste in geological formations lay great weight on acquiring knowledge of the proposed host rock and the surrounding rock strata. For this reason, Nagra has, since May 1984, been operating the Grimsel Test Site which is situated at a depth of 450 m in the crystalline formation of the Aar Massif. The general objectives of the research being carried out in this system of test tunnels include, in particular

- the build-up of know-how in planning, performing and interpreting underground experiments in different scientific fields and
- the acquisition of practical experience in developing, testing and applying test equipment and measuring techniques.

The Test Site (GTS) is operated by Nagra. On the basis of a German-Swiss cooperation agreement, the various experiments are carried out by Nagra, the Federal Institute for Geoscience and Natural Resources (BGR) and the Research Centre for Environmental Sciences (GSF); the latter two bodies are supported in this venture by the German Federal Ministry for Research and Technology (BMFT).

NTB 85-47 gives an overview of the GTS and a review of the status of the investigation programme as at August 1985.

This report was produced in accordance with the cooperation agreement between the three partners mentioned previously. The authors have presented their own opinions and conclusions, which do not necessarily coincide with those of Nagra, BGR or GSF.



GRIMSEL-GEBIET

Blick nach Westen

- 1 Felslabor
- 2 Juchlistock
- 3 Räterichsbodensee
- 4 Grimselsee
- 5 Rhonetal

GRIMSEL AREA

View looking West

- 1 Test Site
- 2 Juchlistock
- 3 Lake Raeterichsboden
- 4 Lake Grimsel
- 5 Rhone Valley

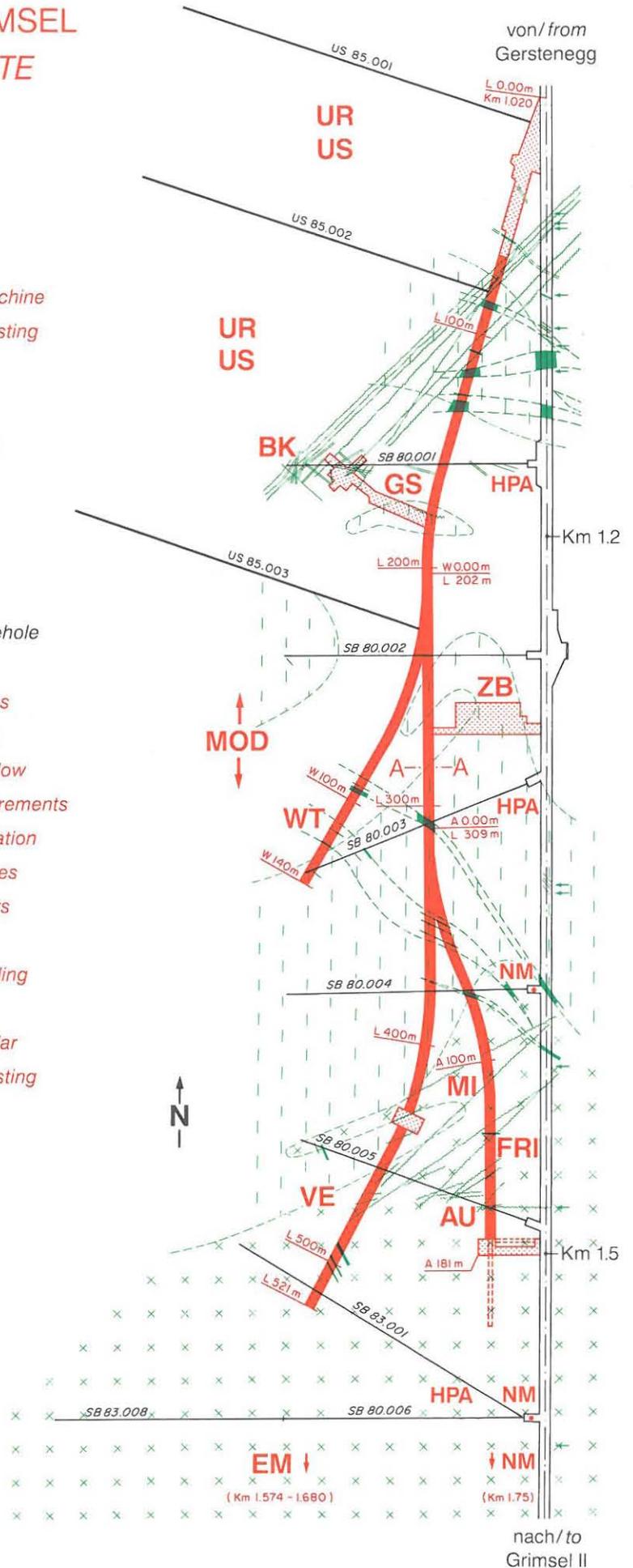
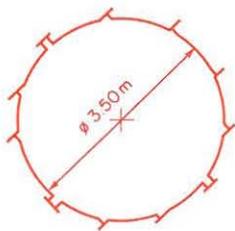
FLG FELSLABOR GRIMSEL
GTS GRIMSEL TEST SITE

Situation



- Zugangsstollen/Access tunnel
- Fräsvortrieb/by tunnel boring machine
- Sprengvortrieb/excavated by blasting
- Zentraler Aaregranit ZAGR
Central Aaregranite CAGR
- Biotitreicher ZAGR
CAGR with high content of biotite
- Grimsel-Granodiorit
Grimsel-Granodiorite
- Scherzone/Shear zone
- Lamprophyr/Lamprophyre
- Wasserzutritt/Water inflow
- Sondierbohrung/Exploratory borehole
- US Bohrung/US borehole
- ZB Zentraler Bereich/Central facilities
- AU Auflockerung/Excavation effects
- BK Bohrlochkranz/Fracture system flow
- EM El.magn. HF-Messungen/-measurements
- FRI Klufftzone/Fracture zone investigation
- GS Gebirgsspannungen/Rock stresses
- HPA Hydr. Parameter/Hydr. parameters
- MI Migration/Migration
- MOD Hydrodyn. Modellierung/H. modeling
- NM Neigungsmesser/Tiltmeters
- UR Untertageradar/Underground radar
- US Seismik/Underground seismic testing
- VE Ventilationstest/Ventilation test
- WT Wärmeversuch/Heat test

A — A Schnitt/Section



Preface

In the framework of its Waste Management Programme, the Paul Scherrer Institute is performing work to increase the understanding of radionuclide transport in the geosphere. These investigations are performed in close cooperation with, and with the financial support of, NAGRA. The present report is issued simultaneously in the PSI and NAGRA NTB report series.

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Abstract

A laboratory support programme has been running in advance of the migration experiments at the Grimsel Test Site (GTS). This report describes the results from batch sorption experiments carried out with iodine, bromine, sodium, strontium and cesium.

Protomylonite surrounding the fracture at the migration site (AU 96) was not available in sufficient amounts, so mylonite from an adjacent fault zone (AU 126) was used for all the laboratory experiments. All the work has been carried out in glove boxes in a nitrogen atmosphere with very low O₂ and CO₂ levels (< 10 ppm). Mylonite was equilibrated with the natural Grimsel groundwater (NGW) prior to sorption experiments. The first series of sorption experiments were carried out without shaking (to avoid creating fresh surfaces). This caused sedimentation of the mylonite and led to slow kinetics. In the later experiments therefore, gentle, continuous agitation was used.

No sorption ($R_d < 0.1$ ml/g) of iodine and bromine on mylonite was observed under the experimental conditions used.

It was observed that the sorption coefficients of ⁸⁵Sr and ²²Na (65-110 ml/g and 2.3-3.5 ml/g respectively) were not affected by varying nuclide concentrations, provided these were kept much below their natural levels in NGW. This indicates that, in this nuclide concentration range, isotopic exchange takes place. Sorption coefficients did not vary with the rock/water ratio. Experiments with a bulky displacing cation (silver thiourea) suggested that some sodium ions were on less accessible internal sites and this could account for the slow kinetics for sodium. Further experiments with samples with smaller particle size confirmed this hypothesis.

Batch sorption experiments on mylonite at initial cesium concentrations of between $3.2 \cdot 10^{-8}$ and $5.0 \cdot 10^{-4}$ M showed that sorption was reversible and non-linear; sorption coefficients were between 3800 and 21 ml/g. Increasing the potassium concentration in the solution led to reduced sorption of cesium, suggesting that Cs and K compete for the sorption sites. At the lowest Cs concentration used, sorption appears to be due to exchange with K at specific sites on mica, together with possible isotopic exchange. For these conditions and by making some assumptions, a Cs sorption coefficient for waters with different K concentrations could be estimated. Extrapolation of laboratory data for cesium to the field is rather difficult because of slight but potentially significant differences between the mylonite used in the laboratory and the protomylonite in the field.

Zusammenfassung

Laborexperimente zur Unterstützung der Durchführung und Interpretation von Tracerexperimenten im Felslabor Grimsel (FLG) sind seit einiger Zeit im Gange. Der vorliegende Bericht umfasst die Resultate von Batch-Sorptionsexperimenten mit den Radiotraceren Jod, Brom, Natrium, Strontium und Cäsium.

Protomylonit, das Füllmaterial der Migrationstestkluft AU 96 war nicht in genügender Menge abbaubar, so dass für die Untersuchungen Mylonit aus der benachbarten Scherzone AU 126 verwendet wurde. Alle Laborexperimente sind in Handschubboxen unter Stickstoff mit sehr geringen CO_2 und O_2 Partialdrücken durchgeführt worden (<10 ppm). Der Mylonit wurde mit dem lokalen Grimsel-Formationswasser (NGW) für alle Untersuchungen vorkonditioniert. Eine erste Serie von Sorptionsexperimenten wurde ohne Schütteln durchgeführt, um die Bildung neuer Oberflächen zu vermeiden. Die Sedimentation des Mylonites hatte jedoch eine langsame Kinetik zur Folge, weshalb in den weiteren Experimenten, kontinuierlich leicht geschüttelt wurde.

Keine Sorption ($R_d < 0.1$ ml/g) von Jod und Brom an Mylonit konnte unter den experimentellen Bedingungen gemessen werden.

Die gemessenen Sorptionskoeffizienten von ^{85}Sr und ^{22}Na (65-110 ml/g beziehungsweise 2.3-3.5 ml/g) waren nicht abhängig von der Nuklidkonzentration, vorausgesetzt diese war weit unter dem natürlichen Elementgehalt im NGW. Isotopenaustausch in diesem Konzentrationsbereich kann daher angenommen werden. Die Sorptionskoeffizienten variierten ebenfalls nicht mit dem Gestein/Wasser-Verhältnis. Experimente mit einem massiven Austauschcation (Silber-Thioharnstoff) ergaben den Hinweis, dass Natrium teilweise auch weniger zugängliche Austauschstellen besetzt, was eine Erklärung für die beobachtete langsame Kinetik von Natrium liefert. Experimente mit Mylonit kleinerer Korngrösse bestätigen diese Annahme.

Batch-Sorptionsexperimente mit Cäsium bei Anfangskonzentrationen zwischen $3.2 \cdot 10^{-8}$ und $5.0 \cdot 10^{-4}$ M ergaben, dass die Adsorption reversibel und nicht-linear war. Die gemessenen Sorptionskoeffizienten waren zwischen 3800 und 21 ml/g. Eine erhöhte Kaliumkonzentration in der Lösung führte zu einer kleineren Adsorption von Cäsium, was auf eine Konkurrenz zwischen Cs und K bei der Besetzung der Austauschplätze hindeutet. Bei der tiefsten Konzentration scheint das Cs durch Ionenaustausch mit K an spezifischen Stellen sorbiert zu werden, möglicherweise mit gleichzeitigem

Isotopenaustausch. Unter diesen Bedingungen und gewissen Annahmen kann ein Sorptionskoeffizient für Cäsium für Wasser mit unterschiedlichem Kaliumgehalt berechnet werden. Eine Extrapolation von Labordaten für Cäsium auf Feldbedingungen dürfte schwierig sein wegen der leichten, jedoch potentiell signifikanten Unterschiede zwischen dem im Labor verwendeten Mylonit und dem Kluffüllmaterial der Testzone.

Résumé

Un programme "laboratoire-support" précède les expériences de migration au laboratoire souterrain du Grimsel. Ce rapport présente les résultats des expériences de sorption en "batch" réalisées avec l'iode, le brome, le sodium, le strontium et le césium dans le cadre du programme.

Puisque la protomylonite constituant la faille du site de migration (AU 96) n'est pas disponible en quantité suffisante, la mylonite d'une faille adjacente (AU 126) a été utilisée durant toutes des expériences au laboratoire. Le travail dans son ensemble a été réalisé en boîte à gant sous atmosphère d'azote avec faible concentration en O_2 et CO_2 (< 10 ppm). La mylonite était équilibrée avec l'eau souterraine naturelle du Grimsel (NGW) préalablement à tout test de sorption. La première série de test a eu lieu sans agitation (pour éviter la formation de nouvelles surfaces). Ceci engendra la sédimentation de la mylonite et conduisit à une cinétique lente. C'est pourquoi, par la suite, une agitation modérée fut utilisée.

Pour l'iode et le brome aucune sorption ($R_d < 0.1$ ml/g) n'est observée pour les conditions expérimentales en vigueur.

Il fut constaté que les coefficients de sorption de ^{85}Sr et ^{22}Na (respectivement 65-110 et 2.3-3.5 ml/g) n'étaient pas affectés par la concentration du nuclide respectif pour autant que celle-ci soit située sous le niveau de concentration naturelle dans la NGW, suggérant que dans cette gamme de concentration en nuclide un échange isotopique a lieu. De plus les coefficients de sorption ne varient pas avec le rapport roche/eau. Les expériences avec des cations à fort pouvoir de déplacement (argent thiouré) suggèrent que certains cations du sodium étaient présents sur des sites non directement accessibles et ceci peut être avancé pour expliquer la cinétique lente du sodium. Des expériences complémentaires avec des particules plus petites en taille confirment cette hypothèse.

Les expériences de sorption en "batch" avec la mylonite et une concentration initiale en césium allant de $3.2 \cdot 10^{-8}$ à $5.0 \cdot 10^{-4}$ M montrent que la sorption est réversible et non-linéaire; le coefficient de sorption varie entre 3800 et 21 ml/g. En augmentant la concentration en potassium dans la solution, la sorption du césium est réduite suggérant une compétition entre le césium et le potassium pour les sites de sorption. A la plus faible concentration de Cs étudiée, la sorption semble être due à des échanges avec K sur les sites spécifiques du mica, superposés à des échanges isotopiques. En posant quelques hypothèses de départ on peut alors calculer le coefficient de sorption du

césium en fonction de la concentration en K. L'extrapolation des données de laboratoire à celles sur le terrain présente des difficultés en raison des différences entre la mylonite utilisée au laboratoire et la protomylonite du site.

1 Introduction

Currently PSI and Nagra are carrying out a series of single fracture migration experiments in the underground laboratory at the Grimsel Test Site (GTS). A water bearing fracture (AU 96), which intersects one of the test drifts, has been selected for these experiments and several bore holes have been drilled from the drift to intersect the plane of this fracture (McKinley et al., 1988). The fracture zone has been characterized in terms of its mineralogy, hydrology and water chemistry (Bajo et al., 1989a, Herzog, 1989, Meyer et al., 1989). A series of migration experiments, between pairs of boreholes varying in separation from ~2.5 to ~5 meters, using a selection of conservative tracers were completed during the first half of 1989. The next phase of the work will involve the injection of sorbing tracers.

A laboratory support programme has been running in advance of the migration experiments. The current aims of this programme are to identify suitable sorbing radionuclides for future tracer tests and to determine their sorption properties. In this report, the results of a series of sorption experiments carried out with ^{131}I , ^{82}Br , ^{85}Sr , ^{22}Na and ^{137}Cs on fracture infill material are reported. These static batch sorption experiments are complemented by dynamic core infiltration experiments (Smith et al., 1990).

Although the provision of sorption isotherm data as input to the transport codes and as an aid to assessing the feasibility of migration experiments with sorbing tracers was one of the main aims of this work, an equally important task was to obtain a quantitative understanding of the mechanism of sorption on mylonite for the chosen radionuclides. A previous study in which the geochemistry of the migration fracture, the chemistry of the groundwater and physico-chemical interaction of the infill material with groundwater were investigated (Bradbury ed., 1989), is summarized below and forms the background and basis for these sorption studies.

As there was not enough infill material (protomylonite) available at AU-96 where the PSI/NAGRA experiments are being carried out, material sampled from a nearby fault zone (AU-126), was used for the laboratory sorption experiments. The mylonite is composed mainly of quartz, feldspar and mica. Examination of the samples from both sites (AU-96 and AU-126) revealed that while their bulk geochemistry and mineralogy are almost identical, some minor, but potentially significant, differences do exist (Meyer

et al., 1989). The protomylonite contains less of those minerals (chlorite, muscovite etc.) which could participate in sorption/exchange processes. This difference may make it difficult to predict sorption behavior in the migration zone on the basis of laboratory measurements alone.

Previous work showed that the fracture infill material ("mylonite") behaved as a weak cation exchange medium which was characterized in terms of its cation exchange capacity, fractional ion occupancies and selectivity coefficients with respect to the major ion concentrations in the groundwater (Ca, Na, Mg, Sr and K). From such data it was possible to predict the sorption behavior of these ions. On the basis of these results, ^{85}Sr and ^{22}Na were put forward as two tracers likely to exhibit "ideal" sorption characteristics i.e. linear, reversible sorption with rapid kinetics. The major assumption underlying these predictions was that ion exchange was the only mechanism determining sorption. Clearly, before such tracers could be used in migration experiments it was essential to test the validity of the assumptions and predictions by performing laboratory sorption experiments with ^{22}Na and ^{85}Sr in the groundwater-mylonite system.

In the previous report it was also suggested that tracer migration tests be carried out with a radioisotope of Cs as an example of a radionuclide exhibiting a non-linear sorption isotherm. As such, the use of cesium would represent a further step in increasing the complexity of the transport process and thereby provide a test of the capabilities of the transport codes to model the break-through curves. Sorption isotherm data for Cs were thus required as input data for the codes and also for estimating whether breakthrough in the migration tests was likely to occur within a practical time scale. Other studies with homoionic clay systems showed that the ion exchange characteristics of Cs and K are similar and competitive (Kawabata, 1967, Sawhney, 1964, Nishita et al., 1962, Titlyanova, 1964). Furthermore, earlier mylonite-groundwater interaction tests and physico-chemical characterization had shown that K exhibited non-linear selectivity, indicating a non-linear sorption. The present sorption experiments were designed with these factors in mind and with the intention of testing whether the concepts and models developed for homoionic clays might also be applied to the infill material being studied here.

2 Experimental

2.1 Glove-boxes

The in-situ Eh and pH have an important influence on sorption phenomena. Alteration of these parameters may cause irreversible changes in the rock-water system. Consequently, it is essential to carry out laboratory experiments under conditions as similar as possible to those existing within the fracture at the GTS. The concentration of CO₂ in the natural groundwater, under anoxic conditions, is $< 7 \cdot 10^{-7}$ M and any increase in PCO₂ due to contamination with air has a significant effect on the pH and the saturation indices for some major minerals present in the rock (Bajo et al., 1989a). It is necessary therefore, for sorption experiments to be carried out in an atmosphere in which the O₂ and CO₂ contents are as low as possible, i.e. using glove boxes. A one cubic meter IGA box (PSI box) and a Mecaplex box were used for all the experiments in this work. In the IGA-box system, the gas is passed through each box once, then collected, returned to a central point, scrubbed of O₂ and CO₂ and finally returned to the boxes again. The O₂ and CO₂ concentrations in the IGA-box were between 2-10 ppm.

The Mecaplex-box has its own nitrogen gas supply and the gas is continually recycled through a scrubbing system. The O₂ and CO₂ concentrations in the box are both less than 1 ppm.

2.2 Mylonite

Mylonite was freshly sampled at the Grimsel site AU-126 where the whole shear zone is about 2 m wide. The first 10-20 cm of core nearest to the tunnel wall were discarded in order to avoid including in the samples any air contaminated material. The rock sample was flushed with N₂ and immediately placed in a container which was again flushed and filled with N₂. This container was transferred into a glove-box (Mecaplex) at PSI at once. All handling, preparation and experiments were carried out in glove-boxes unless otherwise stated.

One recurrent problem in any study of this type is the possibility of sample to sample variation in the batch tests. To avoid this the whole of the selected core was ground in a

granite mortar and passed through a 250 μm sieve. In this way, mineral separation through sieving was avoided. For some experiments, mylonite was ground to < 63 μm particle size (see section 5).

Before use, the crushed mylonite was thoroughly homogenized in order to eliminate as far as possible, differences in composition of the subsamples which could lead to variations in sorption results. All the samples were stored in the glove-box, under N_2 .

Before starting any sorption experiment, it is necessary to determine the smallest subsample that displays the same homogeneity as bulk ground material. Subsamples as small as possible are required both because of limited space in the glove box and because the level of the radioactivity to be used in the sorption experiments is thus reduced.

The homogeneity of a series of subsamples was checked by measuring the concentrations of extractable cations. These experiments were carried out in the laboratory atmosphere using the AgTU method (section 3.1). Two series of experiments with either 5 g or 10 g of freshly ground (< 250 μm size fraction) mylonite were carried out. Each series consisted of 5 samples. Detailed information is given elsewhere (Aksoyoglu and Mantovani, 1989b). The extracted cations (i.e. exchangeable and soluble cations) are shown in Table 1. Within each series there was no significant sample to sample variation with respect to extracted cations. The differences between the two series are also within the experimental error range. It was decided therefore, to use 5 g as the smallest subsample for the experiments. The likely error to be expected from sample to sample variation is less than 10%.

TABLE 1 Homogeneity of the mylonite samples < 250 μm

Cations	Extracted cations ($\mu\text{eq}/100\text{g}$)	
	5 gram	10 gram
Na	103 \pm 7	97 \pm 11
Ca	250 \pm 19	242 \pm 17
Mg	76 \pm 2	66 \pm 1
K	317 \pm 7	287 \pm 16
Sr	3.7 \pm 0.4	3.6 \pm 0.2
Σ cations	750 \pm 21	696 \pm 35

2.3 Groundwater

Natural groundwater (NGW) flowing out of the AU 96 fracture zone is a groundwater with low ionic strength ($\sim 10^{-3}$ M) and high pH, with Na^+ and Ca^{2+} as major cations and Cl^- , SO_4^{2-} , F^- and $\text{CO}_3^{2-}/\text{HCO}_3^-$ as major anions. Long term (one year) characterization studies of the natural groundwater showed no significant temporal or spatial variations in its chemistry (Bajo et al., 1989a). The main species contributing to alkalinity are CO_3^{2-} , HCO_3^- , OH^- and $\text{SiO}(\text{OH})_3^-$. The composition of NGW, which is saturated with respect to calcite and slightly undersaturated with respect to fluorite, is given in Table 2.

TABLE 2 Chemical composition of groundwater (NGW) calculated as the mean of 70 analyses taken at AU 96 over a period of 12 months (after Bajo et al., 1989a). (mean of 3 measurements for Cs, one measurement for I and Br)

pH = 9.6 ± 0.2			
Specific electrical conductance = $103 \pm 1 \mu\text{S/cm}$			
$\text{Si}_T = 5.9 \pm 0.1 \text{ ppm}$			
$\text{CO}_2 < 7 \cdot 10^{-7} \text{ M}$ (2 measurements)			
Temperature = $12 \pm 1 \text{ }^\circ\text{C}$			
<hr/>			
Cations	ppm $\pm 1 \sigma$	M	meq/L
Na ⁺	15.9 ± 0.2	$6.92 \cdot 10^{-4}$	$6.92 \cdot 10^{-1}$
K ⁺	0.150 ± 0.02	$3.84 \cdot 10^{-6}$	$3.84 \cdot 10^{-3}$
Mg ²⁺	0.013 ± 0.003	$5.40 \cdot 10^{-7}$	$1.08 \cdot 10^{-3}$
Ca ²⁺	5.08 ± 0.05	$1.27 \cdot 10^{-4}$	$2.54 \cdot 10^{-1}$
Sr ²⁺	0.161 ± 0.002	$1.84 \cdot 10^{-6}$	$3.67 \cdot 10^{-3}$
Cs ⁺	0.0007 ± 0.00013	$5.3 \cdot 10^{-9}$	$5.3 \cdot 10^{-6}$
Total cations (C)			$9.55 \cdot 10^{-1}$
Anions			
F ⁻	6.26 ± 0.09	$3.30 \cdot 10^{-4}$	$3.30 \cdot 10^{-1}$
Cl ⁻	5.5 ± 0.3	$1.55 \cdot 10^{-4}$	$1.55 \cdot 10^{-1}$
SO ₄ ²⁻	5.5 ± 0.5	$5.70 \cdot 10^{-5}$	$1.15 \cdot 10^{-1}$
Alk	-	-	$4.2 \cdot 10^{-1}$
I ⁻	0.00013	$1.0 \cdot 10^{-9}$	$1.0 \cdot 10^{-6}$
Br ⁻	0.03	$3.8 \cdot 10^{-7}$	$3.8 \cdot 10^{-4}$
Total anions (A)			$10.20 \cdot 10^{-1}$
Charge balance (C-A) = $-6.5 \cdot 10^{-2} \text{ meq/L}$			

3 Methods for experiments with ^{131}I , ^{82}Br , ^{85}Sr and ^{22}Na

3.1 Determination of exchangeable cations

The exchangeable cations in the Grimsel mylonite used in these experiments (particle size $< 250\ \mu\text{m}$ or $< 63\ \mu\text{m}$) were measured after completion of the sorption experiments. This data was used to assist in interpretation of the sorption results.

The exchangeable cations were determined by displacement using a silver-thiourea complex (Chhabra et al., 1975). The experiments were carried out in the laboratory atmosphere. The silver thiourea (AgTU) solution (0.01 N Ag and 0.1 N thiourea) was buffered at pH 7 with 0.1 N ammonium acetate solution. The concentration of AgTU was chosen (on the basis of preliminary cation exchange capacity measurements) so that there was a 2-4 fold excess of AgTU in the system (Aksoyoglu and Mantovani, 1989b).

3.2 Measurement of pH, cations and anions in the solutions

All pH measurements were carried out in the glove box in a low O_2 , low CO_2 atmosphere. As the ionic strength of natural Grimsel groundwater is very low ($\sim 10^{-3}$ M), pH measurements were carried out using buffers and adjusters appropriate for low ionic strength systems (supplier: Orion Research Incorporated).

The concentrations of Na, Ca, Mg, K, and Sr were found using atomic absorption spectrometry (AAS); the measurement error was $\pm 2\%$ except for Mg and Sr where the error was $\pm 10\%$. The alkalinity was determined by acid titration. F, Cl and SO_4 were found by ion chromatography (IC) and the concentrations of Br, I and Cs in natural Grimsel groundwater were measured by inductively coupled plasma mass spectrometry (ICP-MS).

3.3 Conditioning of mylonite

It is essential that the major solution components and the rock composition remain constant during the sorption-desorption experiments because variations in these parameters can perturb the sorption data. Previous studies showed that the ionic composition of natural groundwater changes upon the interaction with mylonite (Bajo et

al., 1989b). Before any sorption measurements, therefore, mylonite was conditioned with NGW to ensure that the system was in steady-state. The conditioning method used here involved successive equilibrations of mylonite with natural groundwater until the ionic composition of water after treatment was close to that of NGW. The mylonite conditioned in this way, could then be used with fresh NGW for the sorption experiments, without further change in the composition of either the mylonite or NGW.

The method used for rock-water separation is important. One of the commonest methods, centrifugation, has the disadvantage of having no clearly defined particle size cut off. Sampling from different depths of supernatant after centrifuging can lead to errors. Filtration solves this problem by having a definite particle size cut off, but, has however, the disadvantage of sorption on the filter which leads to loss of sample. To avoid such problems, dialysis bags were used. Ions can pass freely through the interface of these bags which have a pore size of 2.4 nm, whereas the particles above this size remain inside.

The bags (Medicell International Ltd.) were prepared by cutting 15 cm lengths of dialysis tubing (14.3 mm diameter). They were washed with deionized water and a knot tied in one end. All the bags were flushed with N₂ and then transferred into the Mecaplex box. In the box, the bags were weighed and some of them were filled with about 15 ml of NGW for use as blanks. Other bags were filled with 5 g of mylonite and 10 ml of NGW to be used after conditioning for analysis of the water composition in the bags.

The effect of rock/water ratio (1/2.5, 1/10, 1/20) on sorption was investigated in a further series of experiments. In one set of experiments the bags contained 5 g of mylonite and 5 ml of NGW (for rock/water ratios of 1/10 and 1/20 in the batches during the sorption experiments) whereas in the second set, the bags were filled with 10 g of mylonite and 5 ml of NGW (for a rock/water ratio of 1/2.5 in the batch). The bags were closed with a knot and a small volume of gas left inside. Even though the high rock/water ratio inside the bag appears inconvenient, this was, in practice, the only arrangement that permitted a good bag geometry inside the container, complete coverage by solution and a total rock/water ratio of 1/2.5.

All the bags were placed in a sealed container full of NGW and the container was transferred to Grimsel test site where it was connected to the water flowing from a discharging channel (Kalotte). This procedure was adopted because preliminary investigations had suggested that large volumes of water would be needed to condition

the mylonite and sufficient water was available only at the Grimsel site. The water flowed through the inlet of the container, contacted the bags and flowed through the outlet of the container, for 10 days. The container was then brought back to the Mecaplex box. Cation analyses of the water in the container and the water in some dialysis bags showed that equilibrium had not yet been reached (see Aksoyoglu and Mantovani, 1989a for the detailed data). The concentrations of the cations in the bags, in the container and in the NGW were not the same, especially for potassium whose concentration in the bags and in the container was much higher than in NGW. It was decided therefore to continue conditioning the mylonite in the bags with NGW in the laboratory. The bags were shaken manually one by one and the NGW in the container was renewed in the glove-box. After this treatment, the bags were shaken once a day manually, and the water was again changed after 4 days, and analyzed; the K concentration continued to increase. The same procedure was repeated twice more and then, water from the container and water from bags were analyzed again. After this 3rd step, the increase in K concentration was very much lower than before and it was assumed that further significant increases would not occur. Subsequently this assumption was justified (see 4.3.3).

These results showed that without agitation it was very difficult to bring the water composition close to the original NGW composition simply by treating the mylonite with successive replacements of NGW. The potassium concentration was higher than that in NGW, but at least it remained nearly constant once a certain level was reached. It was decided therefore, to add some potassium to fresh NGW to be used for sorption experiments to keep the solution composition constant during the experiments. The total potassium concentration in the water was adjusted to 3 mg/l. This water is referred to as **NGWK**. The potassium concentration was measured in the solutions after sorption and desorption experiments and was found to have remained constant at 3 mg/l throughout the entire experiments (see 4.3.3).

Another point shown by these experiments is that with only intermittent agitation long times were required for equilibration. Continuous agitation might have overcome this difficulty. This factor was taken into account in subsequent experiments (see section 5).

The conditioned mylonite samples were used for iodine, bromine, strontium and sodium sorption experiments.

3.4 Solutions

All the solution preparations were carried out in glove box. The ^{131}I solution (74 MBq, iodide in NaOH, 740 MBq/ μg I) was obtained from Amersham Laboratories. Two solutions with total I concentrations (tracer + carrier) of $7.8 \cdot 10^{-10}$ M and $7.2 \cdot 10^{-8}$ M, respectively, were prepared by diluting the standard solution with NGWK.

76.22 MBq ^{82}Br was obtained as 25 mg NH_4Br which was irradiated by neutrons in the PSI reactor Saphir. Two solutions with total Br concentrations (tracer + carrier) of $2.6 \cdot 10^{-6}$ M and $2.6 \cdot 10^{-5}$ M, respectively, were prepared by diluting the standard with NGWK.

The ^{85}Sr solutions were prepared from a standard solution (74 MBq, strontium chloride in aqueous solution, 0.2 μg Sr/ml, carrier free) obtained from Amersham Laboratories. The spike was diluted to 50 ml with O_2/CO_2 free deionized water. This stock solution was diluted with NGWK to give four solutions with ^{85}Sr concentrations of $3.8 \cdot 10^{-11}$ M, $1.2 \cdot 10^{-10}$ M, $1.2 \cdot 10^{-9}$ M and $1.2 \cdot 10^{-8}$ M.

^{22}Na stock solution was prepared by diluting a standard ^{22}Na solution (7.4 MBq, sodium chloride, in aqueous solution, 0.7 μg Na/ml, 1ml, carrier free) obtained from Amersham Laboratories, to 50 ml with deionized water. The solutions with ^{22}Na concentrations of $2.4 \cdot 10^{-8}$ M, $2.4 \cdot 10^{-9}$ M and $2.4 \cdot 10^{-10}$ M were prepared by diluting the stock solution with NGWK.

3.5 Sorption measurements

3.5.1 General method

The batch sorption method involves "equilibration" of the crushed rock samples with the appropriate spike solution, followed by measurement of the activity remaining in the solution at the conclusion of the equilibration period. The extent of sorption is calculated from the difference between the final and the initial solution activities. All sorption experiments were carried out in a controlled atmosphere, in the glove box.

Before starting the sorption experiments, the crushed rock was conditioned with NGW in dialysis bags (see 3.3). After conditioning, the bags containing the suspensions of crushed rock and NGW were placed in polyethylene bottles which were filled with the appropriate amount of spiked NGWK. The rock-water ratios were adjusted to 1/2.5,

1/10 or 1/20. A range of rock-water ratio was chosen to check the effect of rock-water ratio on the sorption coefficients. For the tracers expected to be non-sorbing or weakly sorbing, only the highest rock water ratio (1/2.5) was used because, with a high rock water ratio, it is easier to determine the differences (if any) in the activity of the solutions.

The bottles holding the dialysis bags were shaken manually once per day. This method of agitation was chosen to avoid disturbing the system by creating fresh rock surfaces. However, during the course of these experiments, it became apparent that continuous agitation was needed for equilibrium to be attained in a reasonable time. This method was adopted for later experiments (see section 5).

For each series of sorption experiments, one set of samples was used for kinetic experiments to define the time required to reach steady-state sorption. For kinetic experiments sufficient samples were prepared to allow at least four samplings during the experiment. Sampling involved removing an aliquot from the solution surrounding the dialysis bags. When the kinetic experiments showed the steady-state to have been reached, all other bottles in the series were sampled and activities measured and sorption coefficients calculated (see Appendix A for the calculation of sorption (R_d) and desorption ($R_{d,de}$) coefficients).

On completion of sorption, desorption experiments were carried out by replacing the solutions in the bottles by NGWK. A certain amount of the solution used in the sorption experiments still remained (in the dialysis bag and as a trace on the walls of the vessels): the volume of this solution was determined by weighing the samples at each step, in order to correct for its contribution to the activity of the system.

During desorption experiments, the bottles were shaken manually once a day and at intervals aliquots of solution were withdrawn for activity measurement.

3.5.2 Use of dialysis bags

The conditioning experiments and some of the sorption experiments were carried out with the rock water suspensions being held in dialysis bags. These bags were used to ensure efficient phase separation of solid and solutions. However, the first series of experiments showed that in the absence of continuous agitation, the samples sedimented in the bags and became compacted. Another point to consider was the possibility of

nuclide adsorption on the walls of the bags: Some sorption of Sr occurred and it was thought it might have to be taken into account for other nuclides. Such an effect could be quite important for the nuclides which sorb very weakly on mylonite. For some sorption experiments therefore, dialysis bags were not used. Instead, mylonite which had been conditioned in the bags was transferred to the bottles and spiked solutions added to the mylonite suspensions with the appropriate rock water ratio. These suspensions were sampled by withdrawing an aliquot and filtering it through a 0.45 μm one-way filter.

3.5.3 Sorption experiments with ^{131}I and ^{82}Br

Dialysis bags were not used for sorption experiments involving ^{131}I and ^{82}Br . This was because these nuclides are considered to be non-sorbing or very weakly sorbing, so any sorption on the bags would be expected to perturb the sorption data for mylonite.

In these experiments, the bags in which the mylonite had been conditioned were opened and the contents transferred to the containers and weighed. NGWK was added to 50 % of the total volume required and the volume made up to 100 % with the spiked solution.

These experiments were performed with a rock water ratio of 1/2.5. Two initial Br concentrations of $1.3 \cdot 10^{-6}$ M and $1.3 \cdot 10^{-5}$ M were used. Both these concentrations are above the measured concentration of about $\sim 10^{-7}$ M of stable Br in NGW (Degueldre 1989). These high concentrations were chosen because of the low specific activity and the short half-life of the tracer.

Two concentrations of I, $3.9 \cdot 10^{-10}$ M and $3.6 \cdot 10^{-8}$ M, which are an order of magnitude lower and higher respectively than the stable iodine concentration in NGW ; $\sim 10^{-9}$ M (Degueldre, 1989), were used in sorption experiments. Blanks were run in parallel with bromine and iodine sorption experiments.

3.5.4 Sorption experiments with ^{85}Sr and ^{22}Na

These experiments were carried out on conditioned mylonite with a particle size fraction of $<250\ \mu\text{m}$. Sorption experiments -all carried out in the glove box- were performed both with and without dialysis bags for strontium, whereas sodium sorption experiments were carried out without dialysis bags.

Where dialysis bags were used, these bags, each containing a suspension of mylonite/NGW, were placed in containers, NGWK was added to 50 % of the total volume required and the volume was made up to 100 % with the spiked solution. Manipulation of the bags in the box is difficult and during bag preparation, some NGW water was occasionally lost from the bags during closure. Possible water loss was checked by weighing the bags and where it had occurred corresponding volumes of NGWK water were added to the containers so that the rock water ratio were the same for all samples.

Rock water ratios used for these experiments were 1/2.5 (10g solid, 25 ml solution), 1/10 (5 g solid, 50 ml solution) and 1/20 (5 g solid, 100 ml solution). The rock water ratio was the ratio of mylonite in the bag to the total volume of water in the bag plus that in the container.

The bags were placed vertically in the containers whose size was chosen so that the bag could be completely covered with solution. The size of the container therefore depended on the rock water ratio used and ranged from 30 ml polyallomer centrifuge tubes to 100 ml polyethylene flasks. Containers of blanks which were run in parallel, were of same type of material and size as the corresponding sample. All containers were weighed before addition of the bags and also during each stage of the experiment to check for possible losses due to evaporation. In these first series of experiments (with $< 250\ \mu\text{m}$ particle size mylonite) the containers were shaken manually once a day. In later experiments continuous agitation with an end over end shaker was used (see section 5). Blanks were of two kinds- solution filled bags in solution filled containers and also just solution filled containers.

After completion of sorption, each container was weighed and an aliquot of solution was withdrawn for measurement of pH and activity. For the blanks, aliquots were taken both from the solution in the container and from within the bags. The aliquots for activity measurements were adjusted according to the concentration of the spiked

solutions (maximum 5 ml), and they were made up to 5 ml with NGWK (to maintain a constant geometry during measurement).

Once the adsorption experiments were completed, the solution in each container was decanted and the bag and empty container weighed together to determine the volume of solution remaining. NGWK was added to the container to give the required rock/water ratio for the desorption experiments. The containers were again shaken manually once a day and at the end of the desorption period, an aliquot was taken to measure the pH and the activity of the solution.

Sorption experiments with Na and also some experiments with Sr, were carried out without dialysis bags. In this case, bags containing conditioned mylonite were opened, the contents were transferred to tared containers and NGWK and spiked solutions were added in a similar manner to that described previously. Aliquots for counting were withdrawn and filtered through 0.45 μm Acrodisc one-way filters. The pH and the activity of this aliquot were measured. After the completion of sorption, the solutions in the containers were decanted off and the containers containing wet mylonite were weighed to determine the volume of the solution remaining. NGWK was added to achieve the required rock-water ratio. The sampling procedure in desorption experiments was the same as that described above.

3.6 Counting

The γ - activities of ^{131}I (364 keV), ^{82}Br (777 keV), ^{85}Sr (514 keV) and ^{22}Na (1275 keV) were measured using a NaI well detector connected to a single-channel analyzer (a multichannel analyser was not available at that time, however, the spectra of the solutions were checked for any contamination). The same volume- 5ml- was used for each aliquot to maintain the same geometry for all the samples and the standards. For each sample measured, the corresponding standard solutions (3 parallel) were measured too in order to avoid decay corrections. The counting time was adjusted so that for each aliquot the counting statistics were good enough ($\sigma < 2\%$). The background, counted long enough to achieve reliable results, was subtracted from the counts of the samples. In further experiments with mixed radionuclides (section 5), the gamma peaks of ^{85}Sr (514 keV), ^{22}Na (1275 keV) and ^{137}Cs (661 keV) were analyzed by means of an intrinsic germanium detector connected to a multichannel analyzer. The data were evaluated by Geligam and Lotus-123 software.

4 Results and discussion of sorption experiments with ^{131}I , ^{82}Br , ^{85}Sr and ^{22}Na

4.1 General

The first phase of the work involved the conservative tracers ^{82}Br and ^{131}I . Although both these tracers are generally considered to be non-sorbing, there are some instances where iodine sorption on geological material has been observed (Allard et al., 1984, Hoeglund et al., 1985, Salter et al., 1981). Such sorption may be due to non-specific electrostatic interaction, physical adsorption or chemisorption by specific compounds (Liu and von Gunten, 1988). It was of interest to check whether any sorption of I on mylonite occurred.

For the second series of migration experiments at GTS, a sorbing tracer which exhibits rapid, linear, reversible sorption was required. Two sorbing tracers, ^{85}Sr and ^{22}Na , which fulfil these requirements were proposed on the basis of physico-chemical characterization studies of mylonite (Bradbury and Baeyens, 1989).

If Na or Sr is added at low enough levels (at concentrations ~ 100 times less than their respective equilibrium aqueous concentrations) then neither the overall equilibrium, the individual concentrations in the liquid phase, nor the ion occupancies on the mylonite should be significantly influenced. This means that tracer additions of such cations will not change the naturally existing distributions. If the cations are added as radioactive isotopes, isotopic exchange will take place (Bradbury and Baeyens, 1989). From the point of view of the activities measured in the liquid phase, the radioactive isotopes will behave as though they were sorbing linearly (i.e. concentration independent sorption).

The main aim of the present work was to test the above assumption and to estimate the R_d values that might be expected for these tracers at GTS. In these experiments, therefore, the concentrations of ^{85}Sr and ^{22}Na in the groundwater were at least 100 times lower than their corresponding concentrations in NGW. A series of rock water ratios (1/2.5, 1/10, 1/20) and radionuclide concentrations, were used to check the prediction that at these nuclide concentrations and under equilibrium conditions, the R_d values are independent of rock water ratio and radionuclide concentration.

As a further aid to interpretation of data, the exchangeable cations of mylonite samples were measured after completion of the sorption experiments.

4.2 Results of experiments with ^{82}Br and ^{131}I

Only a limited number of tests with ^{82}Br and ^{131}I were carried out to see whether in fact sorption was taking place. Tables 3 and 4 show the results obtained from the experiments carried out with ^{82}Br and ^{131}I respectively (see Appendix A for the calculation of R_d). If the estimated total error (± 0.30 ml/g) in R_d was taken into account there was no detectable sorption of bromine on mylonite (cf Skoog and West, 1986, Friedlander et al., 1981 for the propagation of errors). The loss in the activities of the blanks was less than 5 %.

Under anoxic conditions and at a pH > 9, the expected predominant iodine species is I^- (Liu and von Gunten, 1988). At such a high pH, sorption due to electrostatic attraction is unlikely because the surfaces in contact with aqueous media are negatively charged (Shaw, 1980). An alternative mechanism of uptake - anion exchange - is unlikely for steric reasons (the ionic radius of I^- is 2.20 Å) (Liu and von Gunten, 1988). Furthermore, the anion exchange capacity of rocks is usually very small compared to the cation exchange capacity. In view of these considerations, sorption of iodine was not expected. The present work also suggests that under the conditions used, iodine does not adsorb on mylonite. The estimated total error in R_d is ± 0.19 ml/g. The loss in the activities of blanks was less than 8 %. There is no detectable difference in R_d value for two tracer concentrations an order of magnitude above and an order of magnitude below the NGW level of 10^{-9} M.

TABLE 3 Results of sorption experiments with ^{82}Br

initial [Br] (M)	sorption time (d)	R_d^* (ml/g)
$1.3 \cdot 10^{-6}$	1	0.03 ± 0.01
$1.3 \cdot 10^{-6}$	3	0.04 ± 0.00
$1.3 \cdot 10^{-6}$	7	-0.01 ± 0.01
$1.3 \cdot 10^{-6}$	10	0.05 ± 0.04
$1.3 \cdot 10^{-5}$	10	0.03 ± 0.04

* The values are the means and ranges of duplicates. The estimated total error in R_d is ± 0.30 ml/g

TABLE 4 Results of sorption experiments with ^{131}I

initial [I] (M)	sorption time (d)	R_d^* (ml/g)
$3.9 \cdot 10^{-10}$	3	0.03 ± 0.02
$3.9 \cdot 10^{-10}$	5	0.04 ± 0.01
$3.9 \cdot 10^{-10}$	7	0.03 ± 0.00
$3.9 \cdot 10^{-10}$	12	0.05 ± 0.01
$3.6 \cdot 10^{-8}$	12	0.08 ± 0.01

* The values are the means and ranges of duplicates. The estimated total error in R_d is ± 0.19 ml/g

4.3 Results of experiments with ^{85}Sr

4.3.1 Sorption on dialysis bags

Blank experiments using solutions with and without dialysis bags indicated that some sorption of Sr on dialysis bags occurs. After 34 days equilibration, the activities of a series of 12 blank solutions of varying ^{85}Sr concentrations containing dialysis bags were compared with the activities of the same series of solutions without dialysis bags (see Aksoyoglu and Mantovani, 1989a for the detailed data). The differences between the ^{85}Sr activities inside and outside the bags for the blanks were negligible. These results showed that equilibrium between the inner and outer solutions had been achieved. In the absence of dialysis bags, the solution activities decreased over this time by less than 3% (probably there was slight uptake on the walls of the container). Greater decreases in solution activities were observed for the blanks with dialysis bags. For example, in one experiment, the concentration of ^{85}Sr fell from $5.8 \cdot 10^{-9}$ M to $\sim 4 \cdot 10^{-9}$ M (~32 % decrease). This example refers to 25 ml solution containing 0.2 g of dialysis bag.

In all the blank experiments, a constant weight of bag (0.2 g) with varying volume of solution was used. Activity loss was inversely proportional to the volumes of the solutions. From these results, a constant sorption coefficient of strontium on the dialysis bags was found (~50 ml/g) and a correction for ^{85}Sr sorption on the bags was included in the calculations (see Appendix B for correction).

4.3.2 Kinetic studies

The change of sorption/desorption coefficients with time was investigated for samples with rock/water ratio of 1/10 and two different ^{85}Sr concentrations of $5.8 \cdot 10^{-10}$ M and $5.8 \cdot 10^{-11}$ M. Figure 1 shows results for the system with $[^{85}\text{Sr}] = 5.8 \cdot 10^{-10}$ M. Similar results were observed for the lower ^{85}Sr concentration.

A reversible sorption reaction requires that at the steady-state and after allowing for experimental error, sorption and desorption coefficients are equal. This appeared to be the case in this system (see Table 5). However, for sorption, equilibrium appeared to be achieved after only 5 weeks (Figure 1). This time scale suggests that diffusion rather than ion-exchange (which is usually rapid) is rate limiting. This diffusion control can be

attributed to the minimal agitation of the system during the sorption experiments. As the experiments progressed, it was observed that, manual shaking once a day was not sufficient to resuspend the mylonite completely in the dialysis bags. Presumably, this sedimentation retarded penetration of the tracer. In view of this problem a further series of sorption/desorption experiments was repeated without using the dialysis bags. In Figure 1, the results for sorption experiments with rock/water ratio of 1/2.5 and $[^{85}\text{Sr}] = 5.8 \cdot 10^{-10}$ M, are shown. Even though sorption in this case was faster - the same R_d value as for the system with the bags appeared to be attained in two weeks instead of five weeks - it seems that a complete steady state was not yet attained after 45 days presumably due to insufficient agitation. This will be further discussed in section 5. The fact that the $R_{d,de}$ value is slightly lower than the sorption coefficients can be attributed to the errors on R_d and $R_{d,de}$.

These experiments indicated that sedimentation of the suspensions retarded sorption/desorption processes and showed that whether dialysis bags were used or not, a system of continuous agitation should be adopted in future experiments. Limited agitation was chosen initially to avoid creation of fresh particle surfaces due to disaggregation of the particles. However, this problem appears to be outweighed by the disadvantage attached to a low level of agitation.

4.3.3 Sorption/desorption results

Despite the slow sorption and desorption, reasonable agreement between the sorption and desorption experiments was obtained for experiments both with and without the bags indicating that sorption was reversible (Table 5 and Figure 1). Slight discrepancies between the sorption and desorption coefficients can be attributed to the various experimental errors involved. The pH of the solutions was above 8.8 during all the experiments suggesting good atmospheric control in the glove-box.

The sorption coefficients for different rock/water ratios and for different radionuclide concentrations are nearly the same (between 60-73 ml/g). Although it seems that the R_d values decreased very slightly with decreasing rock/water ratio, it is difficult to decide whether the differences are significant or not. If it is assumed that they are not significant, then it is possible to derive a best estimate for R_d and $R_{d,de}$, expressed as mean \pm standard deviation, of :

$$R_d = 66.9 \pm 3.8 \text{ ml/g} \quad \text{and} \quad R_{d,de} = 72.9 \pm 6.7 \text{ ml/g}$$

Figure 2 shows that the sorption coefficient is independent of radionuclide concentration. These results support the prediction that under equilibrium conditions, at radionuclide concentrations at least 100 fold lower than the natural stable isotope levels, R_d is independent of the isotopic concentration and rock/water ratio, i.e. that sorption involves an isotopic exchange.

The analyses of solutions after completion of sorption and desorption experiments showed that K concentration remained approximately the same (Table 6). The solution composition was approximately the same as at the beginning, except Mg (as observed in previous studies; Bajo et al., 1989b).

TABLE 5 Strontium sorption-desorption results (with dialysis bags)

rock/water (g/ml)	initial [⁸⁵ Sr] (M)	sorption time (d)	R_d^* (ml/g)	desorption time (d)	$R_{d,de}^*$ (ml/g)	pH
1/2.5	$1.9 \cdot 10^{-11}$	34	69.8 ± 1.2	62	82.5 ± 5.7	8.8
1/2.5	$5.8 \cdot 10^{-11}$	34	71.6 ± 0.7	62	82.0 ± 0.3	8.9
1/2.5	$5.8 \cdot 10^{-10}$	34	72.8	84	77.9	8.8
1/2.5	$5.8 \cdot 10^{-9}$	34	71.9	84	82.5	8.8
1/10	$1.9 \cdot 10^{-11}$	34	62.7 ± 2.3	62	68.5 ± 4.2	9.0
1/10	$5.8 \cdot 10^{-11}$	34	67.9 ± 0.6	62	71.4 ± 2.5	9.0
1/10	$5.8 \cdot 10^{-10}$	34	64.8 ± 0.3	84	69.9 ± 3.9	9.0
1/10	$5.8 \cdot 10^{-9}$	34	65.4 ± 1.9	84	72.1 ± 0.3	9.0
1/20	$1.9 \cdot 10^{-11}$	34	63.4 ± 1.8	62	63.0 ± 1.9	9.0
1/20	$5.8 \cdot 10^{-11}$	34	66.8 ± 0.7	62	69.2 ± 0.1	9.0
1/20	$5.8 \cdot 10^{-10}$	34	62.1 ± 1.4	84	66.5 ± 0.6	9.1
1/20	$5.8 \cdot 10^{-9}$	34	63.6 ± 0.6	84	69.3 ± 3.3	9.0

* The values are the means and ranges of duplicates. The highest estimated total error in R_d and $R_{d,de} = \pm 10\%$

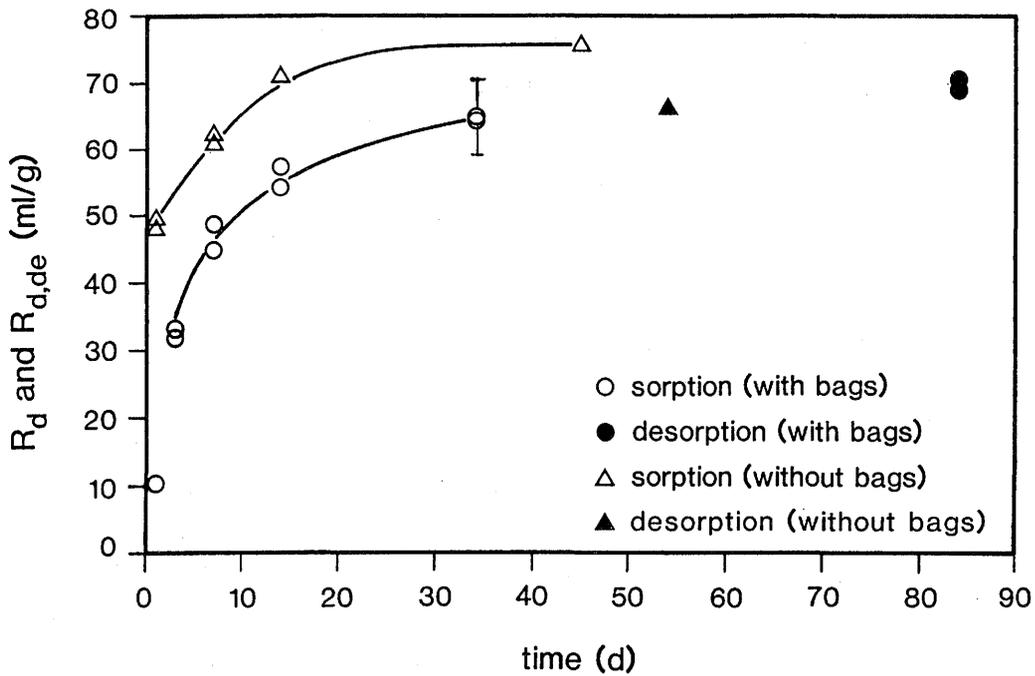


Figure 1 Sorption/desorption coefficients of Sr on mylonite < 250 μm as a function of time. The error bar shows the estimated uncertainty.

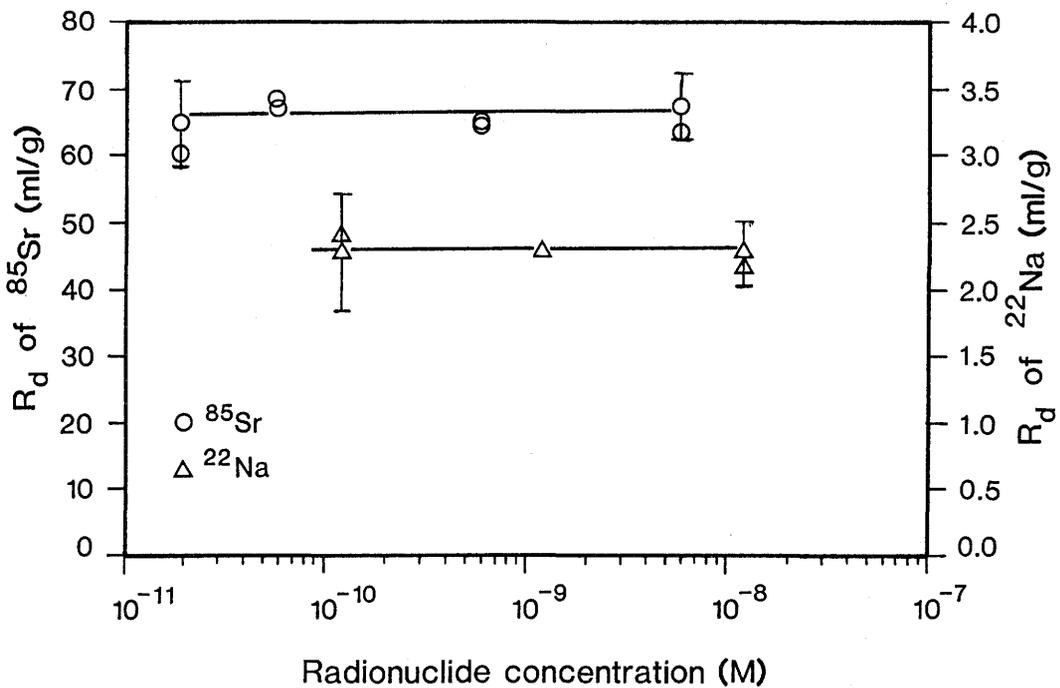


Figure 2 Change of sorption coefficients with radionuclide concentration. Error bars show the estimated uncertainties.

TABLE 6 Cation concentrations and alkalinities of NGWK and of solutions after completion of sorption/desorption experiments (means of 3 measurements)

ions	concentrations (M)		
	NGWK	after Sr experiments	after Na experiments
Na	$(7.00 \pm 0.14) \cdot 10^{-4}$	$(6.96 \pm 0.12) \cdot 10^{-4}$	$(7.13 \pm 0.14) \cdot 10^{-4}$
K	$(7.70 \pm 0.38) \cdot 10^{-5}$	$(7.70 \pm 0.34) \cdot 10^{-5}$	$(7.00 \pm 0.35) \cdot 10^{-5}$
Mg	$(2.00 \pm 0.50) \cdot 10^{-6}$	$(2.50 \pm 0.70) \cdot 10^{-6}$	$(5.70 \pm 1.60) \cdot 10^{-6}$
Ca	$(1.40 \pm 0.02) \cdot 10^{-4}$	$(1.38 \pm 0.07) \cdot 10^{-4}$	$(1.16 \pm 0.01) \cdot 10^{-4}$
Sr	$(1.94 \pm 0.30) \cdot 10^{-6}$	$(1.55 \pm 0.25) \cdot 10^{-6}$	$(1.42 \pm 0.23) \cdot 10^{-6}$
alkalinity (N)	$(4.2 \pm 0.1) \cdot 10^{-4}$	$(4.1 \pm 0.1) \cdot 10^{-4}$	$(4.2 \pm 0.1) \cdot 10^{-4}$

The measured sorption coefficients are about three times higher than those predicted for the unconditioned, bulk mylonite samples, taken from the first sampling (Baeyens et al., 1989). This is because the mylonite used in the present work had a higher CEC (Aksoyoglu and Mantovani 1989b), a smaller particle size ($< 250 \mu\text{m}$) and in addition, was conditioned with NGW.

The sorption coefficients ($[\text{Sr}]_{\text{on solid}} / [\text{Sr}]_{\text{in solution}}$) were calculated using solution activities (see Appendix A), i.e. the amount of ^{85}Sr adsorbed on the mylonite was taken as the difference between initial and final ^{85}Sr solution activities. Sorption coefficients can also be determined by directly measuring the total strontium on mylonite together with equilibrium strontium concentration in the solution after the sorption experiments. The amount of strontium on mylonite was measured by displacing it with a high indexing cation, after the completion of the sorption experiments. The sorption coefficient was then given by the ratio of exchangeable strontium to equilibrium solution strontium concentration. Table 7 compares R_d calculated for the same sample

using the two methods. The values are the means and standard deviations of triplicates. R_d values agree with each other which suggests that most of the strontium ions in mylonite are at sites accessible to exchange with AgTU.

Further experiments were carried out on smaller particle size mylonite, with continuous agitation to check for the effects of particle size and agitation on kinetics and to assist the interpretation of the results (see section 5).

TABLE 7 Comparison of R_d 's of Sr obtained from strontium exchanged by AgTU and from solution activities ($< 250 \mu\text{m}$ particles). The values are the means of 3 measurements.

Exchangeable Sr on mylonite ($\mu\text{eq}/100\text{g}$)	equilibrium [Sr] in solution ($\mu\text{eq}/\text{l}$)	R_d using exchangeable Sr (ml/g)	R_d using solution activities (ml/g)
19.0 ± 0.4	3.10 ± 0.50	61 ± 10	64 ± 4

4.4 Results of experiments with ^{22}Na

The first series of experiments with sodium were carried out with conditioned mylonite $< 250 \mu\text{m}$ and NGWK with rock water ratio of 1/2.5. This high rock water ratio was chosen because sodium sorption was expected to be low and differences in activities of solutions are more readily detected at high rock water ratios.

Dialysis bags were dispensed with because the experiments with strontium suggested that use of the bags without continuous agitation increased the time needed to attain equilibrium.

Throughout the sorption/desorption experiments the pH remained above 8.8 (Table 8). For the blanks, the loss of activity of the solution was negligible, indicating that sorption on the walls of the container could be neglected.

The sorption of sodium was very slow. The changes in R_d with the time, for the sample containing a ^{22}Na concentration of $1.2 \cdot 10^{-9}$ M, are shown in Figure 3. The steady-state was not reached even after 49 days. However, there was no difference in R_d for samples with different ^{22}Na concentrations after 49 days ($R_d = 2.3 \pm 0.1$ ml/g). This result supports the concept of an isotopic exchange mechanism operating in these systems (Figure 2). Sorption experiments were stopped after 49 days.

The desorption coefficient was found to be 3.4 ml/g after 99 days. This suggests that the sorption coefficient for sodium on mylonite at steady-state, is about 3-3.5 ml/g, assuming a reversible mechanism.

As in the case of strontium, the sorption coefficients were determined not only from the solution ^{22}Na activities, but also from the exchangeable sodium on the mylonite after the sorption tests. Table 9 shows that R_d obtained from exchangeable sodium is much lower than the value found using solution activities on the same samples. This unexpected result together with the slow kinetics, may be explained as follows: if a proportion of sodium ions was located on less accessible - presumably internal - sites which for steric reasons could not be exchanged by the large AgTU ions, the measured exchangeable Na leads to an underestimated R_d value. On the other hand, the smaller ^{22}Na ion used in sorption experiments, could slowly penetrate the particles and exchange with stable sodium on the internal sites. This process could account for the slow kinetics of sorption on the < 250 μm particle size.

In order to investigate this point, this work was followed by a further series of experiments in which continuous agitation was used to prevent sedimentation of the particles and to accelerate the kinetics of uptake. In these experiments, sorption of ^{85}Sr and ^{22}Na on mylonite with particle size < 63 μm was investigated. A rock water ratio of 1/10 was used. The suspensions were held in dialysis bags and were agitated continuously on an end over end shaker. Details of these experiments and results are given in the following section. The main result was that the sorption was much faster in this system; a steady-state was achieved within 24 hours. The R_d for Na was 3.5 ml/g which agrees well with the values obtained from particles < 250 μm with a very slow kinetics. Despite the differences in particle size, rate of agitation and the use or not of dialysis bags, the same R_d for sodium was obtained in both series of experiments. This

result suggests that the most significant factor influencing sorption under conditions where simple isotopic exchange operates, is the kinetic one.

TABLE 8 The results of sodium sorption experiments.

initial [²² Na] (M)	sorption time (d)	R _d [*] (ml/g)	pH
1.2·10 ⁻⁹	1	1.2 ± 0.0	9.1
1.2·10 ⁻⁹	7	1.5 ± 0.1	9.0
1.2·10 ⁻⁹	39	1.9	8.9
1.2·10 ⁻⁹	49	2.3	8.9
1.2·10 ⁻⁹	1	1.2 ± 0.0	9.1
1.2·10 ⁻⁸	49	2.3 ± 0.1	8.8
1.2·10 ⁻¹⁰	49	2.4 ± 0.1	8.9

* The values are the means and ranges of duplicates. The highest estimated total error in R_d is ± 20 %.

TABLE 9 Comparison of R_d's of Na obtained from sodium exchanged by AgTU and from solution activities. The values are the means of 3 measurements.

Exchangeable Na on mylonite (μeq/100g)	equilibrium [Na] in solution (μeq/l)	R _d using exchangeable Na (ml/g)	R _d using solution activities (ml/g)
46 ± 3	713 ± 14	0.7 ± 0.1	2.3 ± 0.1

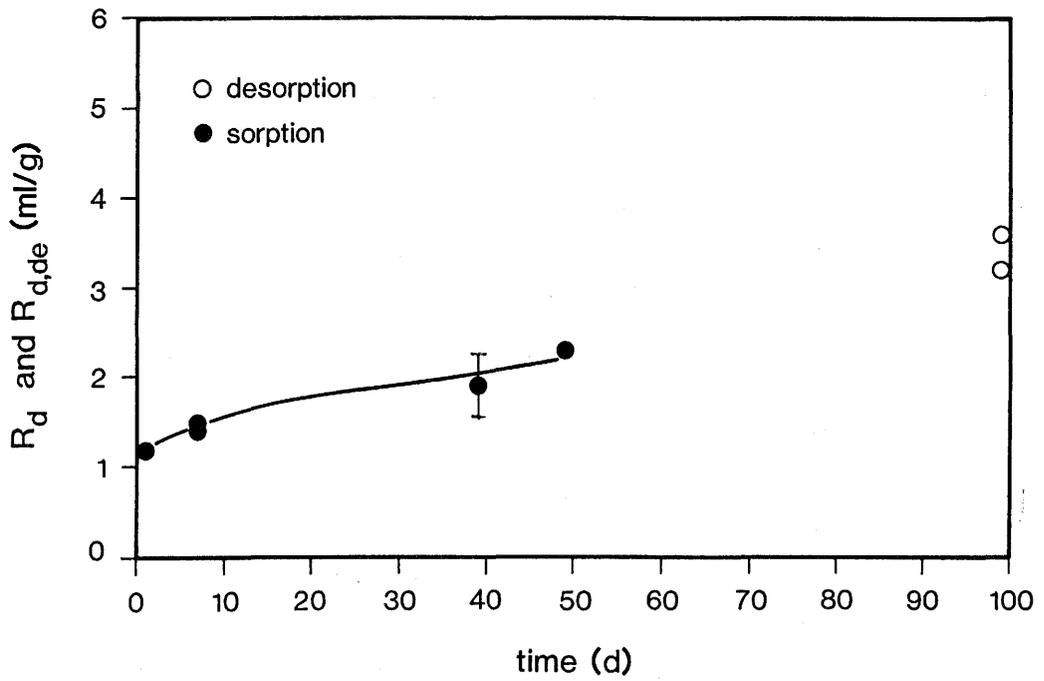


Figure 3 Sorption/desorption coefficients of Na on mylonite < 250 μm as a function of time. The error bar shows the estimated uncertainty.

5 Sorption of cesium and additional experiments with ^{85}Sr and ^{22}Na

5.1 Introduction

The third section of the adsorption studies is concerned with a strongly sorbing nuclide - cesium. Cesium has a simple chemistry; Cs^+ ions do not form stable complexes with anions usually found in groundwater and changes in pH and Eh do not influence its speciation. Hence Cs is particularly suitable for an initial investigation of sorption of a strongly sorbing tracer.

The sorption behavior of Cs on various rocks has been studied intensively (e.g. Sawhney, 1964, Titlyanova, 1964, Kawabata, 1967, McKinley and West, 1984, Ohe, 1984, Grütter et al., 1986, Eriksen and Lochlund, 1987, Cremers et al., 1988). The extent of uptake on micas depends on the presence of competing cations (Kawabata, 1967, Ohe, 1985, Cremers et al., 1988, Lieser and Steinkopff, 1989), particularly potassium. It is the size and extent of hydration of such cations, rather than their valence, which determines competitiveness with cesium.

Adsorption of cesium on the other major phases of the mylonite -quartz, feldspar and plagioclase- is very small in comparison with that on mica (Pinnioja et al., 1984). Hence, the remainder of this section will concentrate on sorption of cesium on mica.

Two types of cesium ion exchange may be distinguished - 1) normal ion exchange on the planar sites in mica and 2) high affinity exchange in which a very low level of cesium is strongly bound to a limited number of sites (sometimes termed frayed edges) (Cremers et al., 1988). High affinity exchange has also been described by some authors as fixation although evidence as to whether this type of adsorption is really irreversible, is not conclusive. High affinity exchange often involves replacement of K at sites at the edges of the mica particles by cesium (Sawhney, 1964). The previous experiments showed that, when water was contacted with mylonite, the potassium concentration increased significantly in the solution (Bajo et al., 1989b), so the potassium concentration of the equilibrated water is much higher than that of the in-situ Grimsel water. Partly for this reason, the K_d of Cs on mylonite measured in the laboratory can differ from that in the field, and extrapolation of the laboratory value to in-situ conditions required an investigation of the competition between cesium and potassium for sorption sites.

Cesium sorption/desorption experiments were carried out under rather different conditions from those used for earlier nuclides in an effort to overcome the slow kinetics observed earlier. All cesium sorption studies were carried out using mylonite with particle size fraction $< 63 \mu\text{m}$ and using continuous agitation.

In order to obtain further information about strontium and sodium sorption on smaller particles than those used earlier, some sorption experiments with ^{22}Na and ^{85}Sr were run together with cesium experiments.

5.2 Materials and methods

5.2.1 Conditioning of mylonite

In the present conditioning work, samples of mylonite ($< 63 \mu\text{m}$) held in dialysis bags were shaken slowly (end over end) in containers in contact with sufficient NGW to have a rock water ratio of 1/10. The water (NGW) was renewed every few days and on each occasion analysed for cations present. The steady-state water composition was reached after the third renewal, so water from the fourth renewal (CW-1) was used directly (instead of adding K to NGW) for sorption experiments with cesium (and also for a final series of experiments with sodium and strontium). The main difference of this conditioning procedure from the previous one is that continuous shaking was used. The water composition is nearly the same as NGWK which was used in the previous experiments except Mg and Sr which were higher and lower respectively in CW-1.

In parallel, another series of samples was prepared in NGW with a higher potassium concentration in order to study the competitive behavior of K for cesium sorption. Some bags were equilibrated with NGW to which sufficient KCl was added to achieve a potassium concentration of $6.4 \cdot 10^{-4} \text{ M}$. After four renewals, the water from the last step, referred to as CW-2, was used for Cs sorption-desorption experiments. The analyses of the equilibrated groundwaters are given in Table 10. Cesium concentration in CW-2 could not be measured because the ICP-MS facility was no longer available.

5.2.2 Solutions

^{137}Cs tracer solution (187.9 MBq/ml, 0.17 mg Cs/ml, in 1 M HCl) was obtained from Amersham Laboratories. In the glove-box, five solutions with total cesium concentrations of $9.90 \cdot 10^{-4}$ M, $9.91 \cdot 10^{-5}$ M, $9.96 \cdot 10^{-6}$ M, $1.05 \cdot 10^{-6}$ M and $6.4 \cdot 10^{-8}$ M were prepared by diluting with equilibrated water (CW-1) and by adding inactive CsCl. The contributions to the total cesium concentration from the equilibrated groundwater which contains $2 \cdot 10^{-10}$ M stable cesium, was also taken into account in the calculations of initial concentrations. Four other cesium solutions ($9.91 \cdot 10^{-5}$, $9.96 \cdot 10^{-6}$, $1.05 \cdot 10^{-6}$, $6.4 \cdot 10^{-8}$ M) were prepared in the same way, using CW-2 as equilibrated water. ^{22}Na stock solution ($6.09 \cdot 10^{-7}$ M ^{22}Na , $1.48 \cdot 10^5$ Bq/ml) which was described in 3.4. was used for the additional sodium sorption experiments. ^{85}Sr tracer solution (37 MBq, SrCl_2 in aqueous solution, 1.2 μg Sr/ml, carrier free) was obtained from Amersham Laboratories and a solution with a ^{85}Sr concentration of $2.93 \cdot 10^{-7}$ M was prepared by dilution.

TABLE 10 Composition of equilibrated waters

Ions	Concentration (M)	
	CW-1	CW-2
Na^+	$(6.70 \pm 0.18) \cdot 10^{-4}$	$(6.40 \pm 0.10) \cdot 10^{-4}$
K^+	$(7.70 \pm 0.90) \cdot 10^{-5}$	$(6.40 \pm 0.14) \cdot 10^{-4}$
Mg^{2+}	$(9.20 \pm 1.60) \cdot 10^{-6}$	$(7.80 \pm 2.00) \cdot 10^{-6}$
Ca^{2+}	$(1.10 \pm 0.01) \cdot 10^{-4}$	$(1.40 \pm 0.02) \cdot 10^{-4}$
Sr^{2+}	$(8.20 \pm 0.50) \cdot 10^{-7}$	$(2.10 \pm 0.20) \cdot 10^{-6}$
Cs^+	$(2.0 \pm 1.5) \cdot 10^{-10}$	not measured
F^-	$(3.40 \pm 0.13) \cdot 10^{-4}$	$(3.10 \pm 0.03) \cdot 10^{-4}$
Cl^-	$(1.60 \pm 0.04) \cdot 10^{-4}$	$(4.40 \pm 0.05) \cdot 10^{-4}$
SO_4^{2-}	$(7.40 \pm 0.24) \cdot 10^{-5}$	$(7.10 \pm 0.18) \cdot 10^{-5}$
alkalinity	$(4.1 \pm 0.1) \cdot 10^{-4}$	$(4.1 \pm 0.1) \cdot 10^{-4}$

5.2.3 Procedures

Two series of samples with different potassium contents were used for sorption-desorption experiments. For the first series, the equilibrated bags containing 5 g mylonite, were placed in tared 50 ml polyethylene bottles. For each Cs concentration, duplicates were used. 25 ml of the Cs solution of a particular concentration was added and the volume made up to 50 ml by adding CW-1. The cesium concentrations in the batch were $5.0 \cdot 10^{-4}$, $5.0 \cdot 10^{-5}$, $5.0 \cdot 10^{-6}$, $5.3 \cdot 10^{-7}$ and $3.2 \cdot 10^{-8}$ M.

Further samples were prepared with a Cs concentration of $5.0 \cdot 10^{-6}$ M, to determine the contact time required to reach the steady-state for sorption coefficients. These experiments were run in triplicate. Nothing was added to one of them, i.e. it contained only Cs in CW-1. To the second one, 1 ml of ^{85}Sr tracer (^{85}Sr in the batch : $5.9 \cdot 10^{-9}$ M) and to the third one, 1 ml of ^{22}Na tracer (^{22}Na in the batch: $1.2 \cdot 10^{-8}$ M) was added i.e. one of the triplicates contained only Cs whereas the second one had both Cs and ^{85}Sr , and the third one Cs and ^{22}Na . The activity measurements were carried out with a high energy resolution intrinsic germanium detector which permitted simultaneous measurement of two radionuclides in the same sample.

The second series of samples (with higher potassium content) with the CW-2 cesium solutions were prepared in the same way, in duplicate, but without addition of other tracers.

Blanks with and without bags, were prepared for each series. All the samples were shaken gently, in an end-over-end shaker. For sampling, aliquots were taken by pipette, the pH measured and the activity counted.

For desorption experiments, 25 ml of the solution left after sorption was replaced by the corresponding equilibrated water (CW-1 or CW-2). The samples were shaken as before and sampled after 20 and 40 days.

5.3 Results and discussion

5.3.1 Additional sorption experiments with ^{85}Sr and ^{22}Na

The results of kinetic tests with a rock/water ratio of 1/10 and one isotope concentration (^{85}Sr : $5.9 \cdot 10^{-9}$ M, ^{22}Na : $1.2 \cdot 10^{-8}$ M) are shown in Figure 4. Sorption was much faster in this system; a steady state was achieved within 24 hours. These results suggest that continuous agitation helped to reach equilibrium quickly and that most of the accessible sites were already available from the beginning of the sorption experiments because the samples were ground finely (presumably the aggregates were broken up). ^{22}Na and ^{85}Sr tracers could, therefore, exchange readily with their corresponding stable isotopes, i.e. they did not need to diffuse through the particles to the exchange sites. The R_d value obtained for Na was 3.5 ml/g which agrees well with the value estimated from desorption after 99 days, in the system with $< 250 \mu\text{m}$ particle size mylonite.

After the conclusion of sorption/desorption experiments, Sr and Na on mylonite were exchanged by AgTU and the exchangeable Sr and Na were used to calculate R_d 's. These values were compared with those calculated using the difference in solution activities (Table 11). Since the exchangeable strontium from both particle sizes ($< 63 \mu\text{m}$ and $< 250 \mu\text{m}$) is the same (see Tables 7 and 11), it seems that there are no additional accessible strontium sites on the smaller particles. The R_d calculated using Sr exchanged, agrees very well with the one measured using the solution ^{85}Sr activities.

Much more exchangeable sodium was obtained from the smaller particles than larger ones (see Tables 9 and 11). Thus, for the small particle size, the R_d obtained using exchangeable Na as the amount of sodium on mylonite, agrees much better with the R_d value determined using the solution ^{22}Na activities than it did for the larger particles. Hence, the assumption that there is additional exchangeable sodium located on the less accessible internal sites seems to be supported.

It should be noted that R_d for both Na and Sr increased as particle size decreased, reflecting the influence of surface area on sorption.

TABLE 11 Comparison of R_d 's calculated using cations exchanged by AgTU and using solution activities (mylonite < 63 μm) (means of 3 measurements).

	cations exchanged ($\mu\text{eq}/100\text{g}$)	equilibrium [Na] or [Sr] in solution ($\mu\text{eq}/\text{l}$)	R_d using exchanged cations (ml/g)	R_d using solution activities (ml/g)
Sr	18.2 ± 0.3	1.64 ± 0.10	111 ± 7	110 ± 10
Na	164 ± 10	670 ± 18	2.5 ± 0.2	3.5 ± 1.0

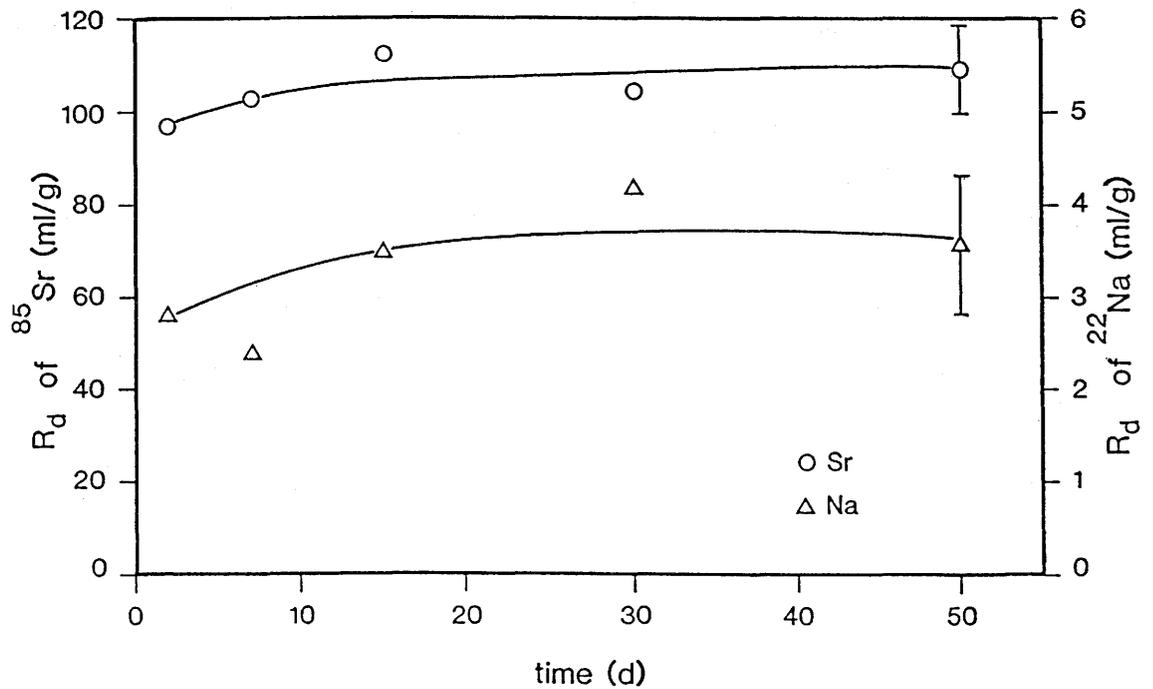


Figure 4 Sorption coefficients of Sr and Na on mylonite < 63 μm as a function of time. Error bars show estimated uncertainties.

5.3.2 Cesium

The change of cesium sorption coefficients with time was studied with a cesium concentration of $5.0 \cdot 10^{-6}$ M to determine the time required to reach a steady-state. The results of the duplicates are shown in Figure 5. The discrepancies between the samples are mostly within the range of experimental error except for the sample taken after 7 days which could be an experimental artifact.

The R_d values seem to reach a steady-state after 15 days of sorption. Since the steady state for Na and Sr with the same samples, was reached within 24 hours, some factor must affect the kinetics of cesium sorption. This result suggests that there is more than one type of site available for sorption i.e. sorption occurs on the more accessible sites first, followed by slower uptake on less accessible sites. The other samples with different cesium concentrations, therefore, were sampled for sorption after 30 days.

Desorption samplings were carried out twice, 20 and again 40 days after sorption, to be sure that equilibrium had been reached.

Data obtained from blanks showed that the loss of cesium activity on the containers was negligible (<1%) whereas use of dialysis bags caused an activity loss between 0 and 5% depending on the cesium concentration in the solution. However, if the high sorption of Cs on mylonite is taken into account, this loss is not significant.

Figure 6 shows plots of R_d and $R_{d,de}$ values against Cs loading on mylonite for the two series with different K content. The sorption-desorption coefficients of cesium for samples with higher K concentrations are lower than those with lower K concentrations due to the competition of K for the exchangeable sites. Generally, the values of duplicates for sorption are close to each other and there is no significant difference between 1st and 2nd desorption data. Sorption coefficients vary between 21 and 3800 ml/g, depending on the cesium concentration. The changes in the coefficients with the cesium loading in both cases (high and low K levels) are similar. Both sorption and desorption coefficients increase as the cesium loading decreases. At the lowest Cs loading, the solution concentrations are at nearly the same level as stable Cs in water ($\sim 10^{-10}$ M) i.e. an isotopic exchange might happen. Between $3 \cdot 10^{-7}$ meq/g and $5 \cdot 10^{-6}$ meq/g Cs loading, R_d changes only slightly, whereas, at loadings of between $5 \cdot 10^{-6}$ meq/g and $3 \cdot 10^{-3}$ meq/g, it decreases significantly; this again suggests that different sites became involved upon changing the Cs concentration.

If the sorption at low cesium concentrations were due to the fixation of cesium on micas via incorporation in the structure of the minerals, sorption at those concentrations would have been irreversible. This is not the case here, at least within the experimental timescales used.

However, trace amounts of cesium are known to be preferentially adsorbed at certain specific sites located at the crystal edges (Sawhney 1964, Bolt et al., 1963). These sites are known as "frayed edge sites" (FES) or edge interlattice sites; they have a high selectivity for Cs and K and exchange at these sites is very rapid. The high sorption of cesium in the low concentration range can be interpreted in terms of such sites as discussed in the following section.

Selectivity coefficient

The stoichiometric selectivity coefficient, K_C , for exchange between two monovalent ions A and B can be written as (Rieman and Walton, 1970):

$$K_C(A-B) = \frac{N_A \cdot [B^+]}{N_B \cdot [A^+]}$$

where N denotes the fractional occupancies of the cations, and $[A^+]$ and $[B^+]$ are the molar concentrations.

If we assume an exchange between Cs and K at frayed edge sites only, (at very low Cs concentrations), the selectivity coefficient K_C for this process at these sites can be defined as :

$$K_C(Cs-K) = \frac{z_{Cs} \cdot [K^+]}{z_K \cdot [Cs^+]}$$

where z denotes the the fraction of FES occupied by Cs or K. Since these sites are usually occupied by potassium, i.e. ($z_K \sim 1$), (Cremers et al., 1988) the equation for the case of very low Cs loadings becomes

$$K_c(z_{Cs} \rightarrow 0) = \frac{z_{Cs} \cdot [K^+]}{1 \cdot [Cs^+]}$$

When we replace z_{Cs} with $m_{Cs} / [FES]$ where m_{Cs} is the amount of cesium on the frayed edge sites (meq/g) and $[FES]$ is the number of these sites (meq/g), the equation becomes:

$$K_c(z_{Cs} \rightarrow 0) = \frac{\frac{m_{Cs}}{[FES]} \cdot [K^+]}{1 \cdot [Cs^+]}$$

In this equation, $m_{Cs} / [Cs^+]$ corresponds to the R_d of cesium at the lowest Cs loading, assuming that Cs is sorbed predominantly on such sites. Therefore, the equation rearranges to:

$$K_c(z_{Cs} \rightarrow 0) = \frac{R_d(Cs) \cdot [K^+]}{[FES]}$$

Since at the lowest Cs loading (obtained using ^{137}Cs tracer alone), K_c and $[FES]$ are constant, the product of $R_d(Cs)$ and $[K^+]$ should remain constant as potassium concentration varies. In fact, this product was almost invariant, 0.30 and 0.34 meq/g for low and high potassium concentrations respectively. Using these values for $R_d(Cs) \cdot [K^+]$, an estimation of the R_d for cesium (at Cs loadings $< 10^{-6}$ meq/g), for other potassium levels in the water can be made, assuming that the exchange takes place mainly at these sites.

Competition of other ions (eg. Na, Ca and Sr) in the equilibrated water with Cs for these specific sites at the low Cs concentration, was not considered here because hydrated ions with a comparatively small size (such as Cs^+ and K^+) are taken up by such sites more readily than larger hydrated ions (Bolt et al., 1963, Nishita et al., 1962, Fergusson, 1982). At other exchange sites, however, the competition of other ions will be significant. The Na/K ratio in water at GTS is higher (~ 180) than that in the equilibrated water (~ 9) used in the laboratory. The possibility of competition of Na (besides K) therefore, under those conditions has to be kept in mind. Another potential competitor Rb was not considered, because its concentration ($< 2 \cdot 10^{-8}$ M) is too low.

There are two points which makes the extrapolation of laboratory results to field conditions difficult. One is the difference in water composition, mainly in potassium concentration. A higher K concentration in water equilibrated with mylonite was unavoidable. However, bearing in mind the competition of K with Cs for the sorption sites, higher cesium sorption in the field where K concentration is 20 times lower, might be expected (an R_d value of ~ 80000 ml/g can be estimated, assuming that the sorption properties of the rock is the same in the field as in the laboratory and cesium sorption at low concentrations occurs only due to exchange with K on the frayed edge sites; this value is unrealistically high however, probably because of the second point discussed below).

A second point is the slight but potentially significant differences between the mineralogy of mylonite used in the laboratory taken from AU-126 site and that of protomylonite at AU-96 site where the field experiments are carried out. The protomylonite contains fewer mica type minerals and since mainly micas are responsible for the bulk of the Cs uptake, (compared to the other components of mylonite), the cesium sorption coefficient in the field might be expected to be lower than that found in the laboratory experiments. The changes on the surfaces created by crushing the rock for batch experiments, may cause additional differences between the rocks used in the laboratory and in the field.

It cannot be predicted as yet which of these two factors would be more important. All that can be said with certainty at the moment, is that a long breakthrough time (i.e. longer than for Na and Sr) for Cs can be expected. For comparison, the ratio of laboratory sorption coefficients can be given as ; $R_d(\text{Cs}) / R_d(\text{Sr}) = 35$, $R_d(\text{Cs})/R_d(\text{Na}) = 1090$.

Isotherms

Data obtained from cesium sorption experiments over the equilibrium concentration range of $2 \cdot 10^{-9}$ - $1.3 \cdot 10^{-4}$ M were fitted to the Freundlich isotherm (Freundlich, 1926). The data with the lowest Cs concentration of $8.3 \cdot 10^{-11}$ M (with low K) and $6.7 \cdot 10^{-10}$ M (with high K), were close to the natural Cs concentration level in groundwater, and at this concentration level, linear isotopic exchange can be expected. This linear part of the isotherm, therefore, was not used for fitting, in order that the modellers could use the data for non-linear sorption model.

Although the Freundlich isotherm does not take the solid's finite capacity for adsorption at high concentrations into account, it often describes adsorption of low amounts of adsorbing species satisfactorily (Sposito, 1980, Sposito, 1981). The linearized Freundlich equation is:

$$\log X = \log A + N \log C$$

where;

X : amount of solute adsorbed per unit weight of solid (meq/g)

C : equilibrium solute solution concentration (meq/ml)

A, N : constants

The Freundlich isotherm for Cs sorption is shown in Figure 7. Linear regression gave a slope of less than 1, indicating a concentration dependent sorption of cesium in the concentration range used. The Freundlich parameters obtained for systems with different potassium concentrations are given in Table 12.

The Freundlich exponents (N) and high correlation coefficients are comparable with those found in other studies (0.52-0.75) on granitic rocks with the same cesium concentration range (e.g. McKinley and West, 1981, Skagius et al., 1982, Erdal, 1980, Barney and Anderson, 1978, Barney, 1984).

TABLE 12 Freundlich parameters for cesium sorption on mylonite

	K ⁺ (M)	A	N	r [*]
sorption	7.7·10 ⁻⁵	1.02	0.603	0.994
desorption	7.7·10 ⁻⁵	1.78	0.624	0.988
sorption	6.4·10 ⁻⁴	0.71	0.588	0.997

* : correlation coefficient

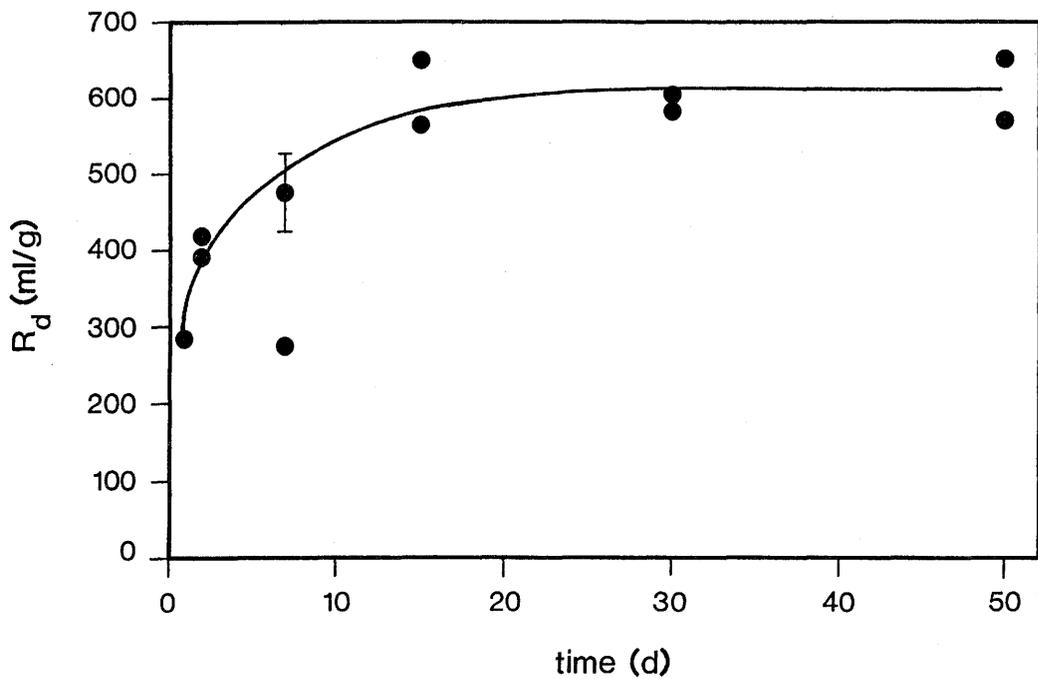


Figure 5 Sorption coefficients of Cs on mylonite < 63 μm as a function of time. The error bar shows the estimated uncertainty.

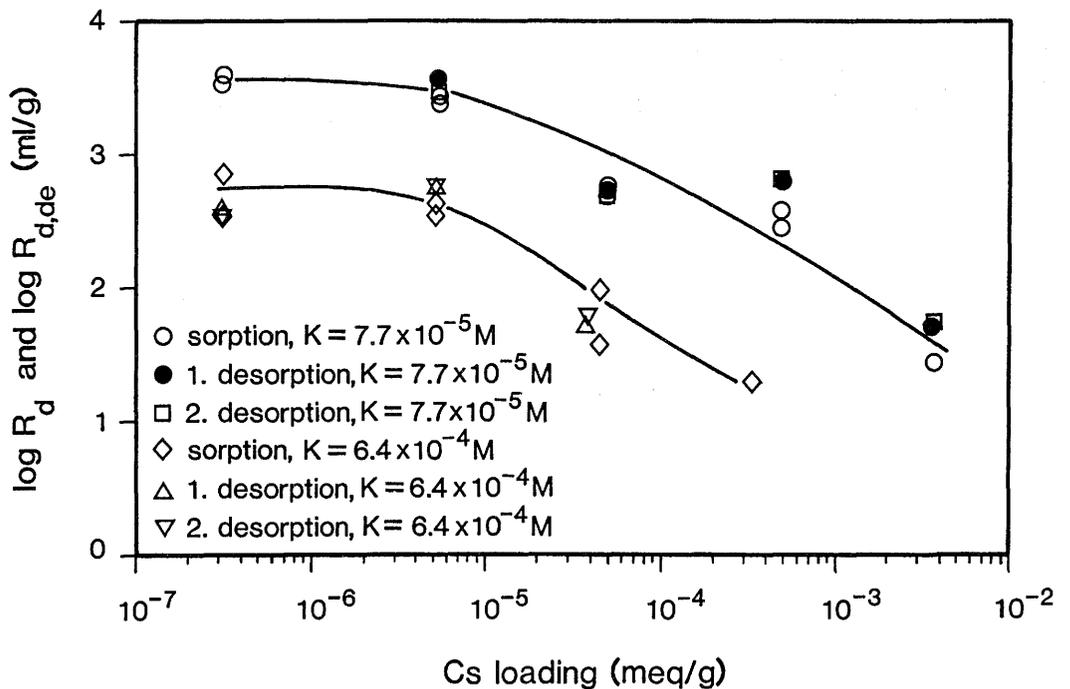


Figure 6 Change of R_d and $R_{d,de}$ with Cs loading

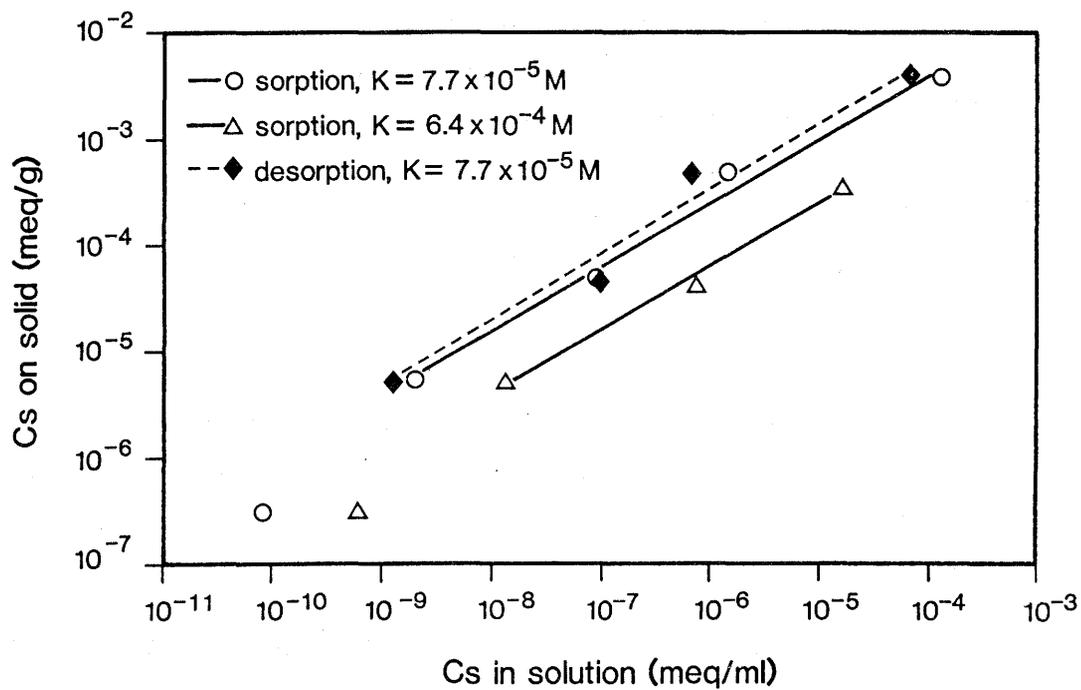


Figure 7 Freundlich isotherm of cesium sorption on mylonite

6 Conclusions

- Equilibration of groundwater with mylonite is essential in order that the major solution components and the rock composition remain constant during the sorption/desorption experiments.
- Dialysis bags with a small pore size (2.4 nm) permit good phase separation. However, they need to be checked for the possible adsorption of each individual nuclide.
- Manual shaking once a day during batch sorption experiments was found to be insufficient to resuspend the mylonite whether dialysis bags were used or not. Sedimentation of mylonite presumably retarded the penetration of tracer and caused slow kinetics. In later experiments with continuous agitation sorption was rapid (<24 hours).
- No sorption of iodine and bromine on mylonite ($R_d < 0.1$ ml/g) was observed under the experimental conditions used.
- The sorption experiments using mylonite < 250 μm , with varying rock water ratios (1/2.5, 1/10, 1/20) showed that in equilibrated system the sorption coefficients of ^{85}Sr and ^{22}Na were approximately independent of rock/water ratio ($R_d(\text{Sr}) = 66.9 \pm 3.8$, $R_d(\text{Na}) = 2.3 \pm 0.1$).
- It was observed that the sorption coefficients of ^{85}Sr and ^{22}Na were not affected by different nuclide concentrations provided these were all kept much below their natural levels in NGW. This supports the previous hypothesis that in this concentration range isotopic exchange takes place.
- Exchangeable Sr and Na measurements performed on the same samples (< 250 μm) as those used in sorption experiments, suggested that some exchangeable Na on the internal sites was not accessible to the bulky exchanging complex (AgTU). The presence of Na on less accessible internal sites could account for the slow kinetics.
- Additional tests on smaller particles (< 63 μm) supported the above hypothesis. For this system, sorption coefficients obtained from batch sorption experiments ($R_d(\text{Sr}) = 110 \pm 10$ ml/g, $R_d(\text{Na}) = 3.5 \pm 1$ ml/g) and from exchangeable Sr and Na measurements were in good agreement.

- Batch sorption experiments on mylonite ($< 63 \mu\text{m}$) with ^{137}Cs tracer, at initial Cs concentrations of between $3.2 \cdot 10^{-8}$ and $5.0 \cdot 10^{-4}$ M showed that sorption was reversible and non-linear. Sorption coefficients varied between 21 and 3800 ml/g.
- At least two different types of sorption sites may be involved in Cs sorption depending on whether the cesium uptake on the solid is low ($3 \cdot 10^{-7}$ - $5 \cdot 10^{-6}$ meq/g) or high ($5 \cdot 10^{-6}$ - $3 \cdot 10^{-3}$ meq/g).
- Sorption data fitted to Freundlich isotherm for Cs concentrations of between $2 \cdot 10^{-9}$ and $1.3 \cdot 10^{-4}$ M yielded Freundlich exponents of between 0.588 and 0.603 which are in agreement with literature values.
- Additional experiments in which the potassium concentration in solution was increased, led to reduced sorption of cesium suggesting that there was competition between Cs and K for the available sorption sites.
- It seems likely that at very low cesium concentrations, besides a possible isotopic exchange, sorption is due to exchange with K at the crystal edges of micas. If it is assumed that at low Cs concentrations sorption is only due to Cs-K exchange on the edge sites of mica, a cesium sorption coefficient for waters with different K concentrations can be estimated, using data obtained from batch sorption tests with two different K concentration levels in equilibrated water.
- There are two considerations which makes the extrapolation of laboratory data to field difficult. Since the K concentration in the NGW in the field is lower than that used in the laboratory experiments, K competition will be reduced hence Cs uptake in the field may be greater than in the laboratory experiments. On the other hand, protomylonite in the field contains less mica than the mylonite used for laboratory experiments, hence lower sorption of cesium would be expected. Another consideration is the creation of new surfaces in the crushing procedure for batch experiments which may lead to large discrepancies between laboratory and field data. It is not known to what extent these differences will influence sorption of cesium in the field. However, a long breakthrough time is quite likely (i.e. longer than for Na and Sr).

7 Acknowledgements

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9 Appendices

A- Calculations

A-1. Calculation of sorption coefficient, R_d

The sorption coefficient, R_d , is defined as the ratio of the concentration of an element which is sorbed on the solid phase to the concentration remaining in the solution at equilibrium, as given in the following equation:

$$R_d = \frac{C_S}{C_L} \quad (1)$$

where;

R_d : sorption coefficient (ml/g)

C_S : concentration of sorbant on the solid phase at equilibrium (meq/g)

C_L : concentration of sorbant in the solution at equilibrium (meq/ml)

The mass balance for the sorbant can be written as:

$$M \cdot C_S = V \cdot C_L^0 - V \cdot C_L \quad (2)$$

where;

M : weight of the solid phase (g)

V : volume of the solution (ml)

C_L^0 : initial concentration of sorbant in the solution (meq/ml)

If we take C_S from this equation and place in the equation 1;

$$R_d = \left(\frac{C_L^0 - C_L}{C_L} \right) \cdot \frac{V}{M} \quad (3)$$

Since,

$$C_L = \frac{A_L \cdot C_L^0}{A_L^0} \quad (4)$$

where;

A_L : count rate per unit volume of solution at time t (cps/ml)

A_L^0 : initial count rate per unit volume of solution (cps/ml)

By placing equation 4 into equation 3 and reorganizing, we get the following equation;

$$R_d = \left(\frac{A_L^0 - A_L}{A_L} \right) \cdot \frac{V}{M} \quad (5)$$

A-2. Calculation of desorption coefficient, $R_{d,de}$

Desorption coefficient is given as the following equation;

$$R_{d,de} = \frac{C_{S,de}}{C_{L,de}} \quad (6)$$

where;

$R_{d,de}$: desorption coefficient (ml/g)

$C_{S,de}$: concentration of sorbant on the solid phase after desorption (meq/g)

$C_{L,de}$: concentration of sorbant in the solution after desorption (meq/ml)

Then the mass balance can be written as;

$$M \cdot C_S + V_T \cdot C_L = V_{de} \cdot C_{L,de} + M \cdot C_{S,de} \quad (7)$$

where;

V_T : volume of solution left with the solid phase at the end of sorption (ml)

V_{de} : volume of solution for desorption (ml)

Replacing $C_{S,de}$ from equation 7 into the equation 6 and by rearranging;

$$R_{d,de} = \frac{M \cdot C_S + V_r \cdot C_L - V_{de} \cdot C_{L,de}}{M \cdot C_{L,de}} \quad (8)$$

or;

$$R_{d,de} = \frac{A_L^0 \cdot V - A_L \cdot V + A_L \cdot V_r - A_{L,de} \cdot V_{de}}{A_{L,de} \cdot M} \quad (9)$$

B- Corrections due to sorption on the dialysis bags

B-1. Correction of sorption coefficient, R_d

In the case of the presence of the dialysis bags in the system, (as in the case of strontium sorption experiments) corrections in the R_d and $R_{d,de}$ calculations are necessary. The mass balance in the system, where the mylonite is in the bag, can be given as follows ;

$$C^0 \cdot V = C_L \cdot V + M \cdot R_d \cdot C_L + m \cdot R_{db} \cdot C_L \quad (10)$$

or

$$R_{db} = \frac{C^0 \cdot V - C_L \cdot V - M \cdot R_d \cdot C_L}{m \cdot C_L} \quad (11)$$

where;

m : mass of the dialysis bag (g)

R_{db} : sorption coefficient on bags (ml/g)

On the other hand, the mass balance in the blanks, where there is only the dialysis bag in the solution (i.e. no mylonite) can be written as follows:

$$C^0 \cdot V = C_{Lb} \cdot V + m \cdot R_{db} \cdot C_{Lb} \quad (12)$$

or

$$R_{db} = \frac{C^0 \cdot V - C_{Lb} \cdot V}{m \cdot C_{Lb}} \quad (13)$$

where;

C_{Lb} : the concentration of sorbant remaining in the solution after the sorption, in the blanks with the bags (meq/ml)

Using the fact that the R_{db} is constant for all the rock/water ratios (including 0) and for all the initial concentrations (see 4.3.1) and rearranging the equations 11 and 13, we can get the following equation :

$$R_d = C^0 \cdot \left(\frac{1}{C_L} - \frac{1}{C_{Lb}} \right) \cdot \frac{V}{M} \quad (14)$$

or

$$R_d = A^0 \cdot \left(\frac{1}{A_L} - \frac{1}{A_{Lb}} \right) \cdot \frac{V}{M} \quad (15)$$

B-2. Correction of desorption coefficient, $R_{d,de}$

The mass balance in the samples containing mylonite in the bags, after desorption can be written as follows:

$$M \cdot C_S + C_L \cdot V_R + m \cdot C_b - C_{L,de} \cdot V = M \cdot C_{S,de} + m \cdot C_{deb} \quad (16)$$

where;

C_b : concentration of sorbant on the bag after sorption (meq/g)

C_{deb} : concentration of sorbant on the bag after desorption (meq/g)

By rearranging, equation 16 can be written as;

$$M \cdot (C^0 - C_L) \frac{V}{M} + C_L \cdot V_r + m \cdot R_{db} \cdot C_L - C_{L,de} \cdot V = M \cdot R_{d,de} \cdot C_{L,de} + m \cdot R_{deb} \cdot C_{L,de} \quad (17)$$

where ;

R_{deb} : desorption coefficient on bags (ml/g)

Assuming $R_{db} = R_{deb}$,

$$R_{d,de} = \frac{(C^0 - C_L) \cdot V + C_L \cdot V_r - C_{L,de} \cdot V + m \cdot R_{db} \cdot (C_L - C_{L,de})}{M \cdot C_{L,de}} \quad (18)$$

or

$$R_{d,de} = \frac{(A^0 - A_L) \cdot V + A_L \cdot V_r - A_{L,de} \cdot V + m \cdot R_{db} \cdot (A_L - A_{L,de})}{M \cdot A_{L,de}} \quad (19)$$