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Experimental study of strontium sorption on fissure filling material

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ABSTRACT

We have carried out a comparative study of sorption and desorption of strontium in groundwater on separated magnetic and size fractions of fissure filling material taken from natural fissures in granitic rock.

Complete reversibility of the sorption process was demonstrated by identical Freundlich isotherms, isotopic exchangeability and pH dependence of the distribution coefficients Rd.

The sorption was found to be strongly pH dependent in the range 3-11. The pH effect can be accommodated in the sorption model by considering the surface areas and surface charges of the minerals in the fissure filling material.

ABSTRACT (Swedish)

Sorption av Sr^{2+} på granitiskt sprickfyllnadsmaterial har studerats i laboratorieförsök.
Identiska Freundlich isotermer och kvantitativt isotoputbyte mellan fast fas och lösning visar att sorptionsprocessen är reversibel.
Sorptionens pH-beroende i området 3 - 11 kan förklaras med en sorptionsmodell som innefattar sprickfyllnadsmineralens ytor och laddning.

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1. INTRODUCTION

Granitic rock has been chosen by several countries [1] as a major candidate for deep geological disposal of high level radioactive wastes. The design of a repository is based on several engineering barriers, such as metallic containers and backfill material, intended to inhibit and retard the release and transport of radionuclides into the biosphere. The most probable pathway of radionuclide transport in the bedrock surrounding a repository is the water carrying fracture systems in the surrounding rock. This transport is retarded by solubility constraints and by sorption of radionuclides on the fissure filling material in water carrying fractures.

Models, used to describe the radionuclide transport, normally incorporate advection, dispersion, decay and reaction processes. In most cases it is assumed that sorption is reversible and that the rate of sorption processes are high compared to the rate of water transport i.e local equilibria are assumed to prevail along the flow path.
Models for characterizing the equilibrium distribution of radionuclides between phases and interfaces in geologic systems typically relate q_r the amount of radionuclide sorbed per unit mass of the sorbing phase to the radionuclide concentration in the aqueous phase $C_r(aq)$.

Geologic material inherently exhibit heterogeneity with respect to surface properties and the empirical Freundlich isotherm is widely used to quantify the sorption on solids with heterogeneous surface properties [2-8]. This model has the general form $q_r = K\,C_r(aq)^N$, where the parameter K relates to the sorption capacity and N to the sorption intensity and heterogeneity of the sorbent. The reversibility of the sorption process is of fundamental importance for the understanding of the fate of the radionuclides in geologic systems. If reversible, the same isotherm should be valid for sorption and desorption under the same experimental conditions. Hence, the N_d/N_s and K_d/K_s ratios [5,6], where the subscripts d and s denote desorption and sorption respectively, as well as isotopic exchangeability [7,8] have been used to assess the reversibility of solute sorption on mineral surfaces.

Sorption of Sr^{2+} on granite and other rocks has been studied rather intensively [9-13] and the sorption isotherm has generally been observed to be linear or near linear. Reversibility has often been invoked in spite of the fact that the

desorption process has been given relatively little attention. Moreover, the sorption/desorption has more seldom been studied under identical experimental conditions. In the present work we have studied the sorption and desorption of Sr^{2+} on magnetic and size separated fractions of fissure filling material from natural fissures in granitic rock and demonstrated complete reversibily of the sorption process.

2. EXPERIMENTAL

2.1 Materials

The experiments were carried out at ambient temperature (22 ±2°C) in a conditioned laboratory. All chemicals were of analytical grade and used as received. ^{85}Sr was purchased from Amersham as strontium chloride in aqueous solution. Synthetic groundwater with the composition given in Table I was prepared from Millipore deionized, triple distilled water.

Table I.　　　　Composition of Synthetic Groundwater

Species	HCO_3^-	SO_4^{2-}	Cl^-	SiO_2	Ca^{2+}	Mg^{2+}	K^+	Na^+
Concentration mg·dm^{-3}	123	9.6	70	12	18	4.3	3.9	65

The pH measurements were made with a Metrohm 632 pH meter and a GK 2331 combined glass/reference electrode. The electrode was calibrated using standard buffer solutions. Solution samples were analyzed for ^{85}Sr in a 2"·2" well type NaI detector connected to a 256 channel analyzer. The amount of solid, aqueous solution and samples of the aqueous phase was measured gravimetrically using an electric balance with 10^{-4}g accuracy. The sorbent used in the experiments was fissure filling material taken from natural fissures in the granite 360m below ground level in the Stripa mine. The fissure filling material was crushed, using a Agat mortar and pestle, and sieved to 60-90, 90-125, 125-250 and 250-500 μm size fractions and washed with acetone in an ultrasonic bath. The 125-250 μm fraction was separated with respect to iron content using a Frantz Model L-1 isodynamic separator. The mineral composition was determined by semiquantitative X-ray diffraction, the BET surface area was measured using a Micromeritics Flow Sorb II 2300 apparatus with N$_2$ as sorbing gas and the cationic exchange capacity (CEC) was measured by isotope dilution [13] using a 0.5 mol·dm^{-3} NaCl solution with ^{22}Na as tracer. The sorbent properties are given in Table II. The muscovite and chlorite used in the

surface experiments were supplied by the Department of Mineralogy, Swedish Museum of Natural History.

Table II.   Sorbent Analysis

Fraction No.	original	fraction A	fraction B	fraction C	fraction D	fraction E
Weight%	100	31.18	18.45	7.92	18.9	6.68
BET surface m^2/g	0.83	0.3	0.46	0.97	2.44	4.29
CEC mquiv./g	22.7	3.6	9.1	21.4	30	53.2
Fe%	1.256	0.136	0.383	1.143	1.938	3.622
Quartz%	22	26	22	19	18	19
Microcline%	23	23	25	21	21	22
Albite%	37	35	38	41	38	31
Intermediate plagioclase%	15	16	13	16	17	18
Fe-chlorite%	0.8	--	--	0.5	0.7	2
Muscovite mica%	1.7	--	0.1	2	4	7

2.2 Sorption

Sorption on different fractions of fissure filling material, separated with respect to magnetic properties and particle size, was studied in batch experiments. 2.2 g of each fraction was equilibrated with 6.7 cm ^{3} groundwater in 20 cm^3 bottles. Aliquots (0.37 cm^3) of ^{85}Sr spiked Sr^{2+} groundwater solution was thereafter added to each bottle giving an initial Sr^{2+} concentration of $9 \cdot 10^{-7}$ mol·dm^{-3}. The bottles were placed on a 40 rpm time controlled rotator. The rotator was run continuously for the first three hours of the experiment thereafter 1 minute every half hour for the the first day and 1 minute every 2 hours for the remaining experimental time. Samples, 0.05-0.1 cm^3, of the aqueous phase were taken at intervals and analyzed for ^{85}Sr. The bottles were, except for the first samples, centifugated for 15 minutes at 2000 rpm before drawing the samples.

2.3 Desorption

At the end of the sorption experiment, the aqueous phase was removed and the solid phase washed thoroughly to remove free Sr^{2+} in solution. Desorption from the solid phase was thereafter carried out in batch experiments using the same solid to solution ratio and sampling routine as in the sorption experiments.

2.4 Sorption-Desorption Isotherms

Sorption experiments were carried out using the 90-125 μm size fraction of the natural fissure filling material as sorbent. The experiments were carried out for 35 days in 6 cm^3 propylene bottles containing 250 mg solid and 2 cm^3 ^{85}Sr spiked 10^{-8}-10^{-3} mol·dm^{-3} groundwater solutions of Sr^{2+}. At the end of the sorption experiment the aqueous phase was removed and the solid thoroughly washed. Desorption experiments were thereafter carried out using the same solid to groundwater ratio as in the sorption experiments.

2.5 pH dependence

Sorption experiments at different pH were carried out in 6 cm^3 bottles with 0.5 g of the 90-125 μm size fraction of natural fissure filling material and 4cm^3 ^{85}Sr spiked $2.7 \cdot 10^{-6}$ mol·dm^{-3} groundwater solution of Sr^{2+}. The initial pH was adjusted by titration with HCl and CO_2-free NaOH. After 47 days of sorption the pH was measured and 0.1 cm^3 samples of the aqueous phase, drawn after centrifugation, counted for ^{85}Sr.

In a second series of experiments, using the same solid to solution ratio and 10^{-6} mol·dm^{-3} Sr^{2+} solution, pH of the aqueous phase was changed after 35 and 68 days sorption respectively. The pH was measured and samples of the aqueous phase drawn for ^{85}Sr analysis immediately before changing the pH and at the end of the experiment (101 days).

2.6 Isotopic exchangeability

The experiment was carried out using 250 mg of the 90-125 μm fraction of natural fissure filling material and 2 cm^3 ^{85}Sr spiked 10^{-3} mol·dm^{-3} groundwater solution of Sr^{2+}. The system was equilibrated for 40 days whereby the initial Sr^{2+} concentration in the aqueous phase decreased to $7.3 \cdot 10^{-4}$ mol·dm^{-3}. The concentration of the tracer ^{85}Sr was changed without significantly changing the overall Sr^{2+} concentration. Aqueous samples were drawn at intervals for ^{85}Sr analysis.

A second parallell sorption experiment with the same initial Sr^{2+} concentration and solid to solution ratio was carried out to compare the kinetics.

2.7 Surface titrations

Alkalimetric and acidimetric titrations of suspensions of crushed fissure filling material, chlorite and muscovite in 0.2 M $NaClO_4$ solution were carried out with CO_2 free NaOH and $HClO_4$ solutions respectively.

3. EXPERIMENTAL RESULTS

All experimental data have been corrected for ^{85}Sr decay and volumes of samples and washing solution.

3.1 Sorption- Desorption

The experimental sorption and desorption data for electromagnetic and size separated fractions of fissure filling material are depicted in distribution coefficient (R_d) versus time plots in Figure 1. The distribution coefficients were calculated using equation 3.1.

$$R_d = [V/m] \cdot [C_0 - C_t]/C_t \qquad (3.1)$$

C_0 = initial Sr^{2+} concentration in aqueous phase
C_t = Sr^{2+} concentration in aqueous phase at time t
m = weight of solid phase (g)
V = volume of aqueous phase (cm^3)

The BET surface area is used, for convenience only, as a third parameter in the 3D plot.
The kinetics of equilibrium attainment to the sorption process is given by the equation:

$$U_s(t) = q_t/q_e = [C_0 - C_t]/[C_0 - C_e] \qquad (3.2)$$

where

q_t, q_e = amount of Sr^{2+} sorbed per unit mass of sorbent at time t and at equilibrium respectively

C_0 = initial Sr^{2+} concentration in aqueous phase

C_t, C_e = Sr^{2+} concentration in aqueous phase at time t and at equilibrium respectively
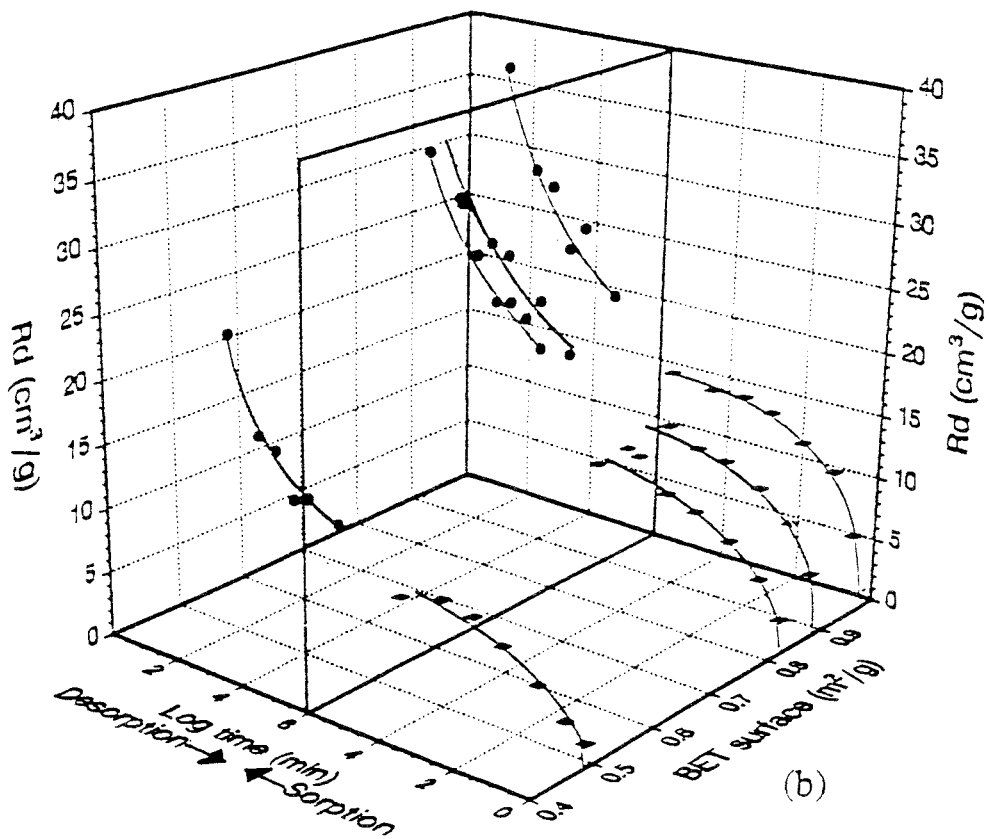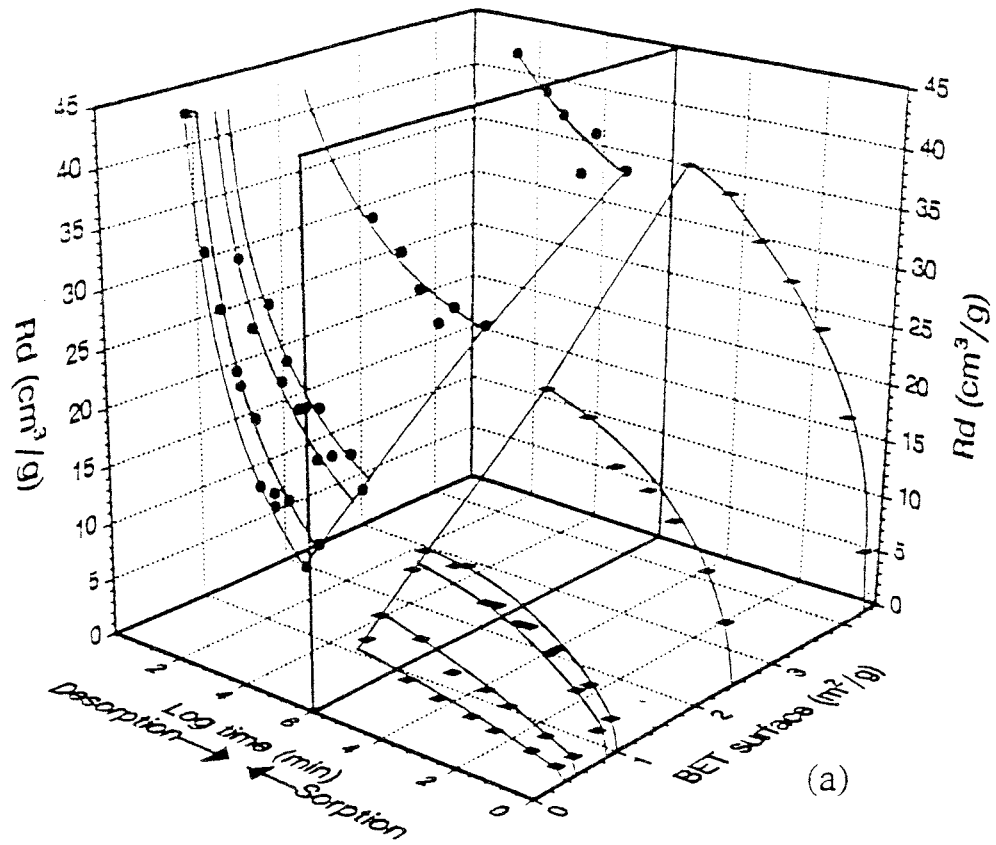
Figure 1. 3 dimensional plot of the distribution coefficient R_d vs BET surface area and Log time. (a) magnetic fractions (b) size fractions of natural fracture fillings.
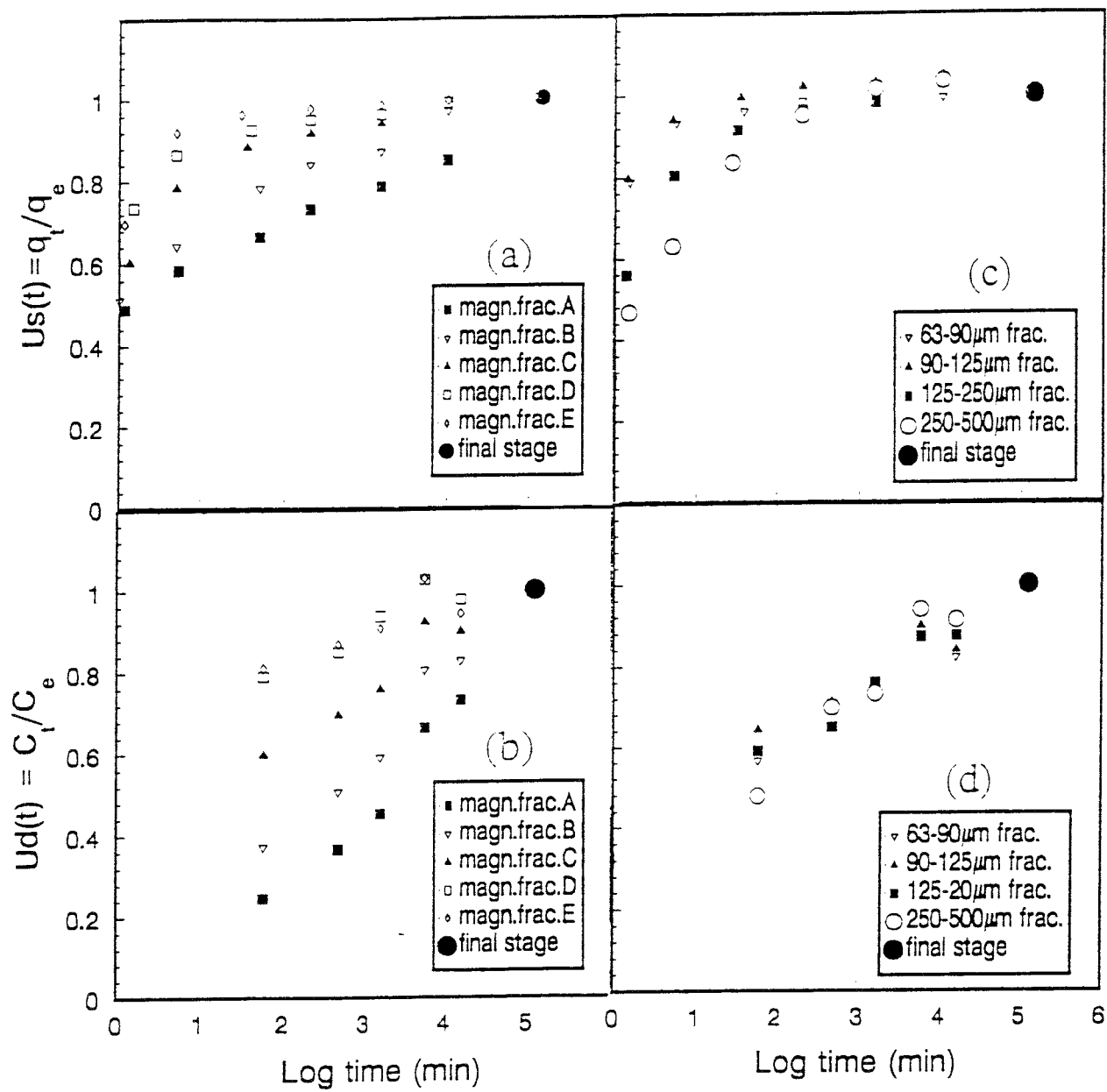
Figure 2. Equilibrium attainment Us(t) and Udd(t) plotted vs Log time. The clay content is increasing in the order A to E for magnetic fractions.

The corresponding equation for the desorption process is given by equation 3.3.

$$U_d(t) = C_t/C_e \qquad (3.3)$$

Assuming equilibrium to prevail at the end of the sorption and desorption experiments, the experimental data are depicted in $U_s(t)$, $U_d(t)$ versus time plots in Figures 2(a-d).
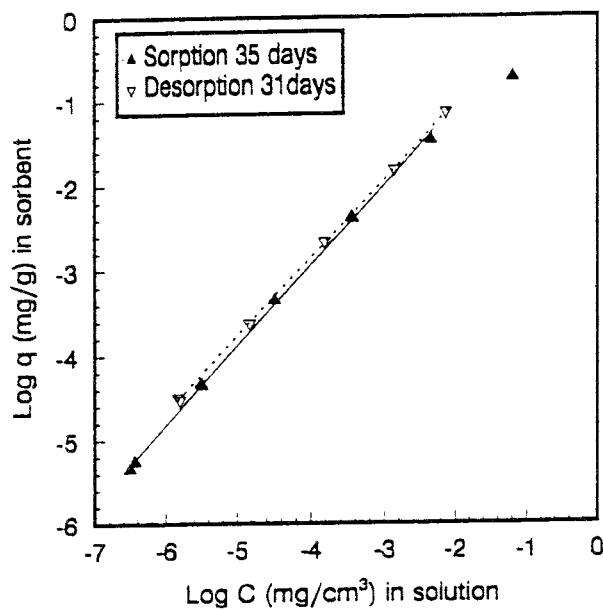

Figure 3. Sorption and desorption isotherms, 90 - 125 μm natural fracture fillings.

3.2 Sorption-Desorption Isotherms

The data from the isotherm experiments are shown as log q versus log C plots in Figure 3.

The Freundlich isotherms obtained by fitting the sorption and desorption data separately are given in equations 3.4 and 3.5 respectively, where the errors are given as 1 d.

$$q(s) = K_s \cdot C^{N_s} \text{ with } K_s = 6.58 \pm 0.02 \text{ and } N_s = 0.940 \pm 0.010 \qquad (3.4)$$
$$q(d) = K_d \cdot C^{N_d} \text{ with } K_d = 6.45 \pm 0.03 \text{ and } N_s = 0.914 \pm 0.006 \qquad (3.5)$$

3.3 Isotopic Exchangeability

The isotopic exchangeability of the total amount of adsorbed Sr^{2+} (E) can, according to the principle of itotope dilution, be calculated from the mass

balance and the fraction of added radiotracer (^{85}Sr) remaining in solution after equilibration

$$f = a_e/a_0 = C_e/(C_e + E \cdot q_e \cdot V/m) \qquad (3.6)$$

where a_0, a_e = initial and equilibrium activity of added ^{85}Sr in the aqueous phase.

The sorption and isotope exchange data are shown in C_t/C_0 and a_t/a_0 versus time plots in Figure 4.
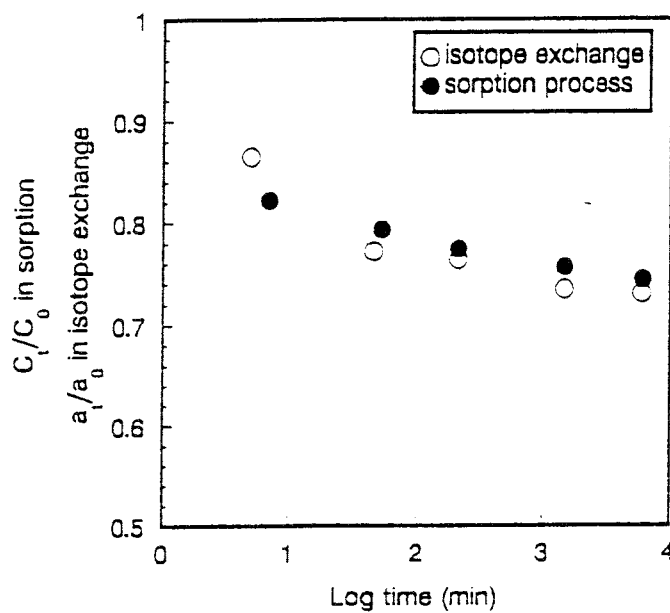

Figure 4. Comparison of reaction kinetics between isotopic exchange and sorption

Rearranging equation 3.6 we obtain

$$E = (1-f) \cdot C_e/(f \cdot q_e \cdot V/m) \qquad (3.7)$$

From the plots in Figure 4 the isotopic exchangeability E calculated to be 1.04±0.1.

3.4 pH dependence

The pH dependence of Sr^{2+} sorption on the 90-125 μm fraction of natural fissure filling material is shown in a Rd versus pH plot in Figure 5.
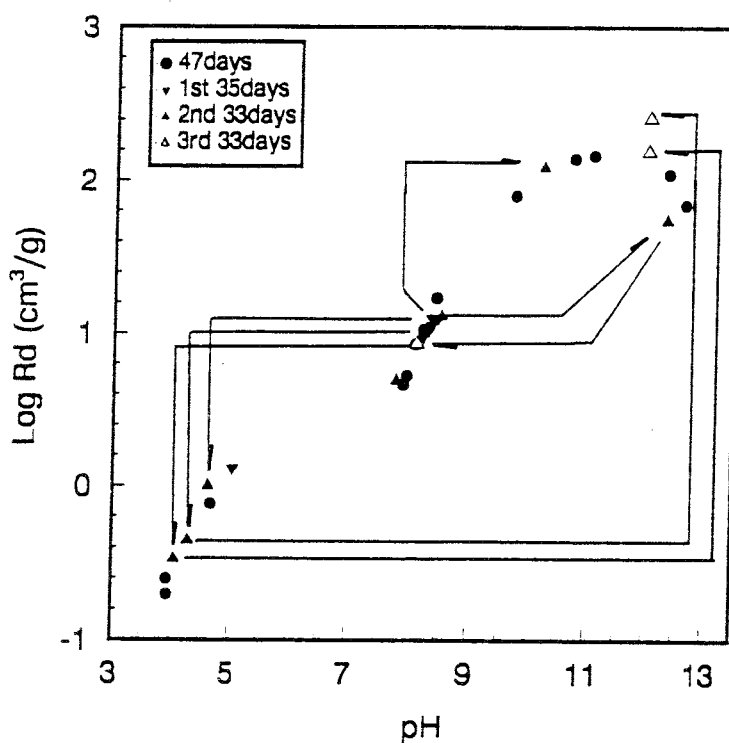

Figure 5. Rd plotted vs pH of aqueous phase.

3.5 Surface Charge

The surface charge, due to protonation or deprotonation of functional groups, on a solid suspended in an inert electrolyte can be calculated from the experimental alkalimetric and acidimetric titration data [14].

For any point on the titration curve the mass balance is given by the equations

$$C_a\text{-}C_b + [OH^-] - [H^+] = [>SOH_2^+] - [>SO^-] \qquad (3.8)$$

$$[>SOH_{tot}] = [>SOH_2^+] + [>SOH] + [>SO^-] \qquad (3.9)$$

C_a, C_b = concentration added to the suspension of acid and base respectively and [ ] denotes the concentration of solutes and surface species per unit volume of solution.

The surface charge per unit area $Q(mol \cdot m^{-2})$ is thus given by equation 3.10

$$Q = (C_a - C_b + [OH^-] - [H^+])/(m/V) \cdot S \qquad (3.10)$$

m/V = solid to solution ratio
S = specific surface area $(m^2 \cdot g^{-1})$

The surface charge, calculated from the titration curve for the natural fissure filling material, is plotted versus pH in Figure 6. The pH at zero point of charge (pH_{zpc}) obtained from this plot is approximately 9.2.

For a pure mineral the uptake and release of protons can be descibed by the surface acidity constants

$$Ka_1^S = \{>SOH\}[H^+] / \{>SOH_2^+\} \qquad (3.11)$$

$$Ka_2^S = \{>SO^-\}[H^+] / \{>SOH\} \qquad (3.12)$$

where { } denotes the surface concentration $(mol \cdot m^{-2})$

Combining equations 3.8-3.11 we obtain

$$Ka_1^S = (\{>SOH_{tot}\} -Q)[H^+] / Q \quad \text{for pH} <pH_{zpc} \qquad (3.13)$$

$$Ka_2^S = Q[H^+] / (\{>SOH_{tot}\} -Q) \quad \text{for pH} >pH_{zpc} \qquad (3.14)$$

The titration, surface charge and surface acidity plots for the clay minerals muscovite and chlorite are shown in Figures 7 and 8 respectively.
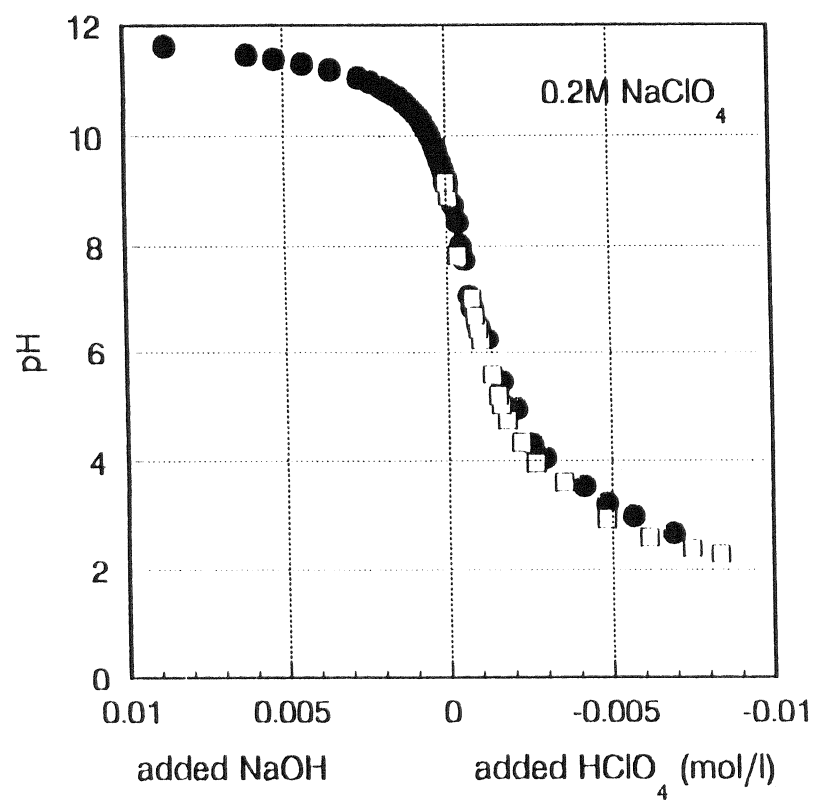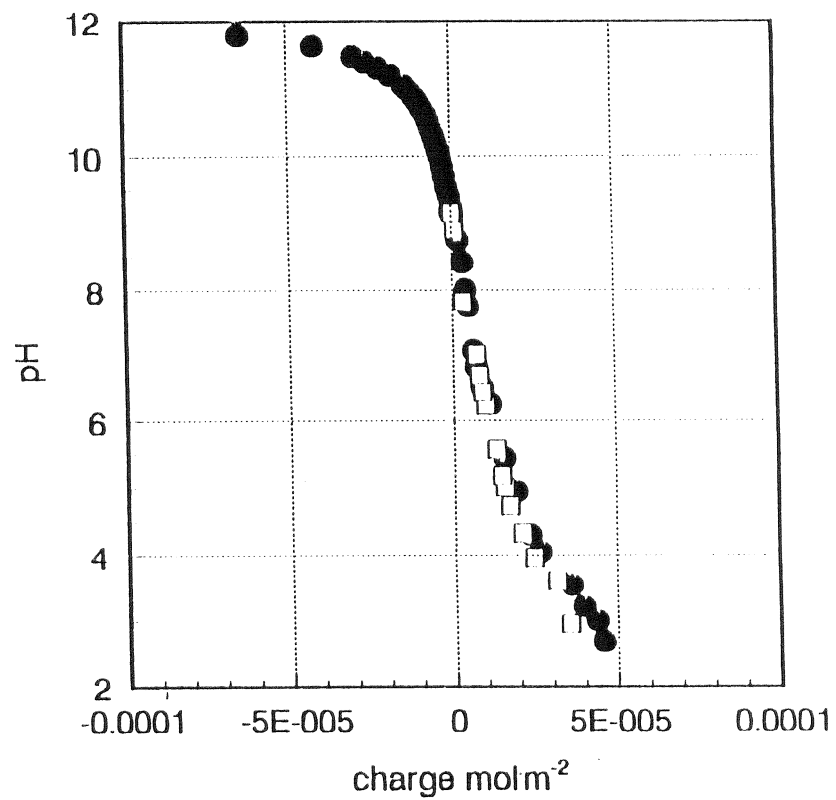
Figure 6.

Titration of fissure fillings suspension. 15.0 g fracture fillings with specific surface area 3.25 (m^2/g) in 450 cm^3 0.2 M perchlorate solution. (a) Acidimetric titration (b)Surface charge calculated from titration curve
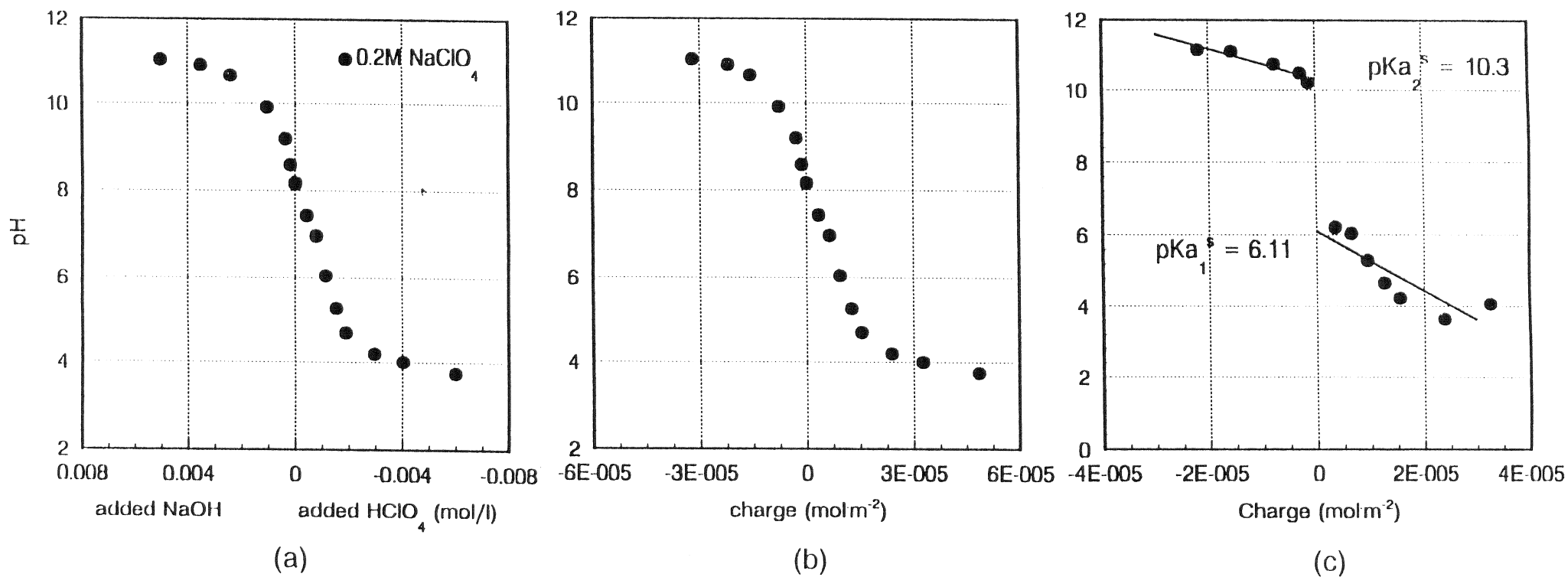
Figure 7.

Titration of muscovite suspension. 0.661 g muscovite with specific surface area 15.04 m2/g in 80 cm3 0.2 M perchlorate solution. (a) Acidimetric-Alkalimetric titration
(b) Surface charge calculated from the titration curve. (c) Calculated acidity constants.

Figure 8.

Titration of chlorite suspension. 1.070 g chlorite with specific surface area 8.73 cm^2/g in 80 cm^3 0.2 M perchlorate solution. (a) Acidimetric-Alkalimetric titration (b) Surface charge calculated from the titration curve. (c) Calculated acidity constants.
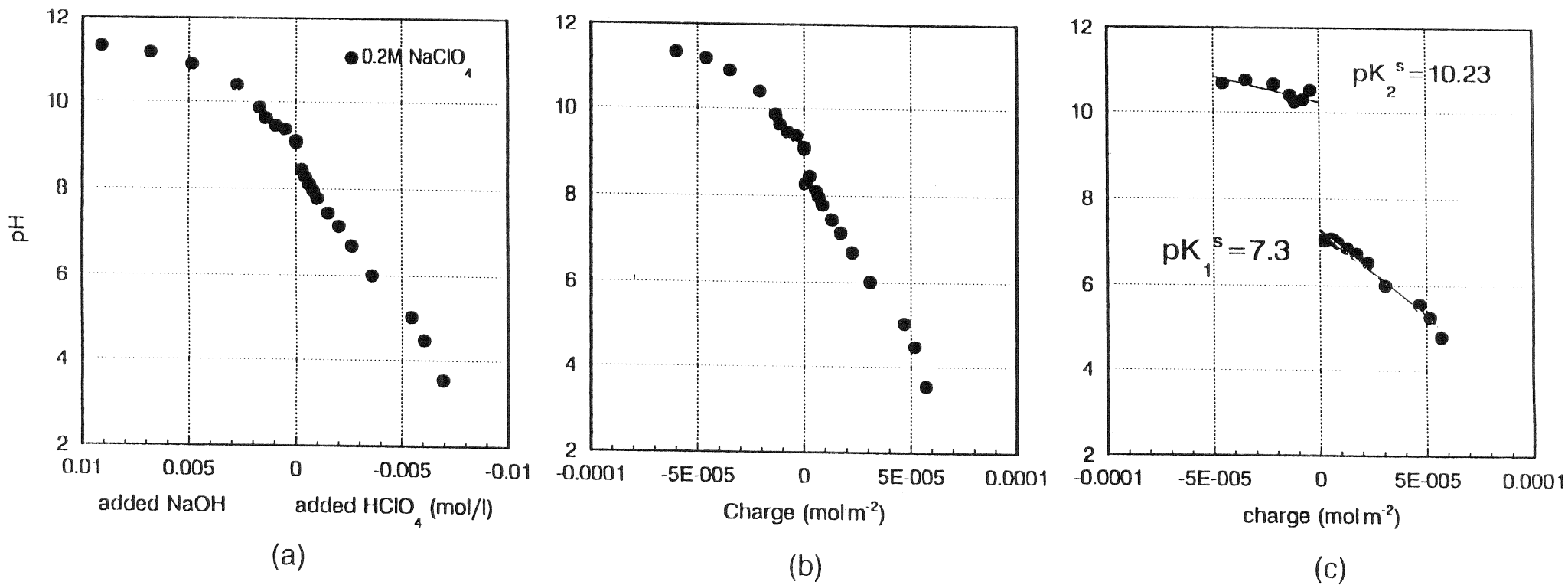
4. DISCUSSION

The sorption/desorption processes display the following pronounced kinetic effects:

(1) A fast initial sorption step is followed by a slow sorption process (see Figure 2).

(2) The time required to reach equilibrium is shorter for smaller than for larger particles (see Figure 2c).
Observations (1) and (2) are in agreement with earlier reported observations [9, 10 and 13].

(3) Comparing different magnetic fractions of the fissure fillings, the equilibrium attainment for the clay richer fractions (with relatively higher iron content and higher magnetic response) is faster for both sorption and desorption processes, as shown in Figure 2a and 2b.

(4) The equilibrium attainment for the sorption process is seemingly faster than for the desorption process for all fractions of fissure filling material, as shown in Figure 2. It should, however, be pointed out that the part of sorbed Sr $^{2+}$ that can be quickly desorbed had been washed away, and only the slow step was followed in the desorption experiments.

(5) The isotopic exchange between sorbed Sr^{2+} and Sr^{2+} in solution shows a similar equilibration pattern as an initially started sorption process, (see Figure 4).
Observations (4) and (5) correspond to those reported by Comans (1987) [8] for Cd^{2+} sorption on illite.

As shown in Figure 1, R_d values in the sorption processes and that in the desorption processes are approaching each other, indicating the reversibility of strontium-sorption processes. As seen, there is a small difference between the final R_d values observed in the sorption and in desorption processes. This difference is clearly correlated to the difference in final aqueous concentrations. It can be explained by the slight unlinearity of the sorption/desorption isotherms of each sorbent fraction. In the present work, the sorption/desorption isotherms for the 90-125 μm size fraction of fissure filling material were found to be slightly unlinear, as shown in Equations (3.4) and (3.5), respectively.

According to Van Genuchten and Barney [5, 6], if the sorption is completely reversible, $N_d = N_s$ and $K_d = K_s$, otherwise, $N_d/N_s < 1$ and $K_s = K_s > 1$. In the present study, it was observed that for trace level ($10^{-8} - 10^{-4}$ M) Sr^{2+} sorption/desorption on fissure filling material in groundwater, $N_d/N_s = 0.97 \pm 0.02$ $K_d/K_s = 0.980 \pm 0.02$. This demonstrate that the sorption process is completely reversible.

Isotopic exchangeability E, was found to be complete (1.04 ± 0.1), which means that all sorbed Sr^{2+} is in a dynamic equilibrium with Sr^{2+} in groundwater; in other words, their reversibility is at hand.

The reversibility was also proved by the dependence of R_d on the pH of aqueous phase, as shown in Figure 5. In the second series of experiments, equilibrated R_d values can be increased or decreased by adding NaOH or HCl according the R_d-pH relationship that was established during the first 47 days' experiment. This provides useful information for judging sorption mechanisms. It is indicated that the reversible cation (proton/Sr^{2+}) exchange is the dominant sorption mechanism. This conclusion is also supported by the following two evidences:

(a) The major part of Sr^{2+} sorption is caused by the fast sorption mechanism (see Figure 2).

(b) For magnetic fractions of fissure filling, their R_d values in final stage of sorption or desorption processes are positively related to their CEC values (see Figure 1 and Table II).

Diffusion into the sorbent [15], surface precipitation [16] and dissolution [17] reactions have been offered as explanations for slow sorption/desorption kinetics. In this study we have no evidence for the latter processes. The dependence of equilibration time on particle size and mineral composition favours diffusion into the sorbent as the most plausible cause for the slow kinetics.

The sorption process display strong pH dependence and a closer look at the Rd versus pH plot in Figure 5 reveals three regions with marked pH influence. In the pH range 3-7 Rd increases by one order of magnitude although the sorption is rather low. In the pH range 7-11 the Rd increases by nearly two orders of magnitude. At pH>11.5 the Rd decreases with increasing pH.

The aqueous strontium speciation is, in the pH range studied, given by the hydrolysis equilibrium

$$Sr^{2+} + OH^- = SrOH^+ \tag{4.1}$$
$$\log K = 0.86$$

The fissure filling material consists of several minerals with different pH dependent surface properties. Based on the surface titration curve and the BET-surface for the natural fissure filling material we have calculated the surface charge per unit area (Fig 6b). It should be pointed out that this gives no detailed information about the surface charge on the different minerals, but merely characterizes the surface charge as a gross property for the total sample. The pH_{zpc} was found to be approximately 9.2.

The pH_{zpc} for the mass dominating minerals are in the range 2-2.3 (Table III) whereas we found pH_{zpc} to be 8-8.5 for chlorite and muscovite.

Table III

Surface properties of some minerals

Mineral	pH_{zpc}	pK_{a1}^s	pK_{a2}^s	Ref
SiO2	2.0			14
	2.0		6.9	18
	2.5	-2	7	19
Albite	2.0			14
"	2.0			20
Microline	2.4			20

A plausible explanation for the pH dependence of the sorption process is sorption on increasingly negatively charged surfaces of the mass dominating minerals in the pH range 3-7 followed by increasing sorption on the negatively charged surfaces of the clay minerals muscovite and chlorite in the pH range 8-11. The decrease in sorption at pH >11.5 is most probably due to hydrolysis of Sr^{2+}.

Based on these simple assumptions the effective Rd values is given by the equation.

$$Rd(eff)=Rd(1)/(1+Ka_2^S(1)/[H^+])+Rd(2)/(1+Ka_2^S(2)/[H^+]) \quad (4.2)$$

where $Rd(1)$, $Ka_2^S(1)$ and $Rd(2)$, $Ka_2^S(2)$ denote the distribution coefficients for the negatively charged surfaces and the second protonation constants for the major and clay minerals respectively.

The sorption data are plotted in a C_{sorbed}/C_0 versus pH plot in Figure 9. The full line, fitted to the experimental data, was obtained using $Rd(1)=4(cm^3 \cdot g^{-1})$, $pKa_2^S(1)=5.3$ and $Rd(2)=140(cm^3 \cdot g^{-1})$ $pKa_2^S(2) = 10.2$ in excellent agreement with the surface charge data obtained in the titration experiments.

5. CONCLUSIONS

(1) Reversible cation exchange is a dominant Sr^{2+} sorption mechanism.

(2) Complete of attainment equilibrium requires at least 1 month. Shorter equilibratiom time was required for separated sorbent fractions with smaller particle size or higher clay content.

(3) The sorption is strongly pH dependent and the presence of clay minerals i.e. chlorate, muscovite, even in low concentrations, will dominate the sorption process for pH>8.
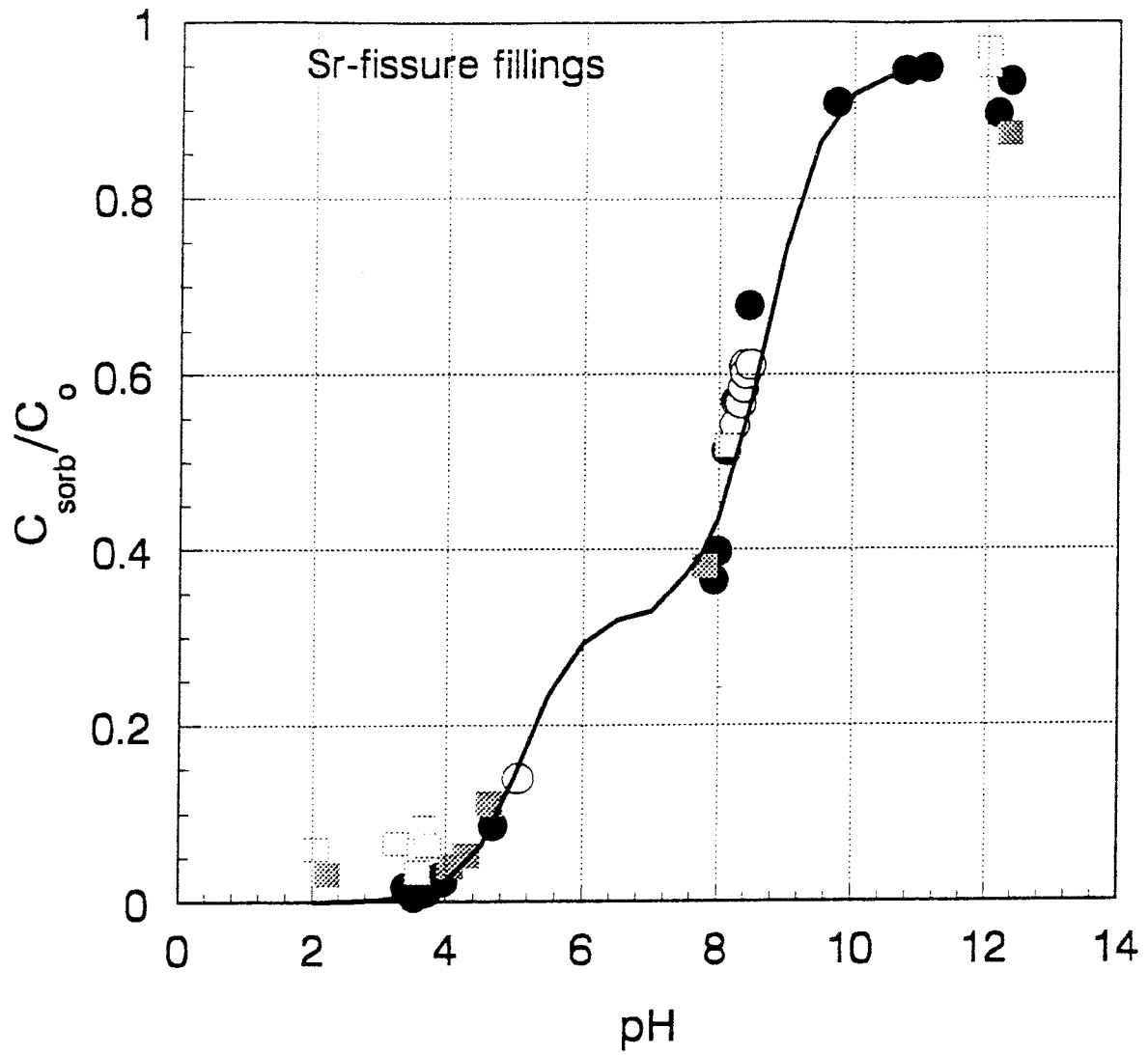
Figure 9.

Sr^{2+} sorption in fissure fillings plotted in the form C $_{sorbed}$ / C$_o$ in solution vs pH.
Full line is calculated using surface titration data from the different minerals
constituting the fissure fillings

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[2] Section for Solid Earth Physics, Department of Geophysics, Uppsala University, Sweden
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2 SKB
3 CTH
4 VBB/VIAK
5 RS Consulting
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