

# **Diffusion measurements of cesium and strontium in biotite gneiss**

Kristina Skagius and Ivars Neretnieks

Dep of Chemical Engineering,  
Royal Inst of Technology Stockholm

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BIOTITE GNEISS

Kristina Skagius, Ivars Neretnieks

Department of Chemical Engineering, Royal Institute of  
Technology, S-100 44 Stockholm, Sweden, 1985-12-30

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## SUMMARY

A significant retardation of radionuclides transported by flowing water from an underground repository can be expected if the nuclides are able to diffuse into the water filled micropores in the rock. This diffusion into the pores will also increase the surface available to interactions between the nuclides in the groundwater and the rock material, such as sorption. To calculate the retardation it is necessary to know the sorption properties and the diffusivities in the rock matrix for the radionuclides.

Diffusion experiments with cesium and strontium in biotite gneiss samples have been performed. Both the transport of strontium and cesium through rock samples and the concentration profiles of cesium and strontium inside rock samples have been determined. The result shows that diffusion of cesium and strontium occurs in the rock material.

A diffusion model has been used to evaluate the diffusivity. Both pore diffusion and surface diffusion had to be included in the model to give good agreement with the experimental data. If surface diffusion is not included in the model, the effective pore diffusivity that gives the best fit to the experimental data is found to be higher than expected from earlier measurements of iodide diffusion in the same type of rock material. This indicates that the diffusion of cesium and strontium (sorbing components) in rock material is caused by both pore diffusion and surface diffusion acting in parallel.

## INTRODUCTION

In Sweden and many other countries the most interesting alternative to dispose of the waste from nuclear power plants is to place the waste in deep underground repositories in crystalline rock. An eventual release of radionuclides from the repository into the geosphere must then be considered. To decrease the risk of rapid release, a number of barriers will be introduced in the repository, e.g. a waste form of

low solubility, corrosion-resistant encapsulation material and back-fill materials of low permeability and capable of radionuclide sorption. The major barrier would, however, be the host rock itself.

If radionuclides are released from an underground repository they would be transported with the moving groundwater in fissures in the rock. Besides fissures the rock matrix contains micropores filled with stagnant groundwater. Diffusion of nuclides into the micropores can act as a retarding and diluting mechanism by removing the nuclides from the flowing groundwater in the fissures, Neretnieks [1980]. If the nuclides are also being sorbed on the rock material, the sorption may occur not only on the fissure surfaces but on the micropore surfaces in the rock body as well.

The diffusivity of nonsorbing species in micropores in different rock materials has been studied by several investigators, Bradbury et al [1982], Wadden et al [1982], Melnyk [1983], Skagius et al [1985]. The effective diffusivity (pore diffusivity times porosity) was found to be of the order of  $10^{-14}$  m<sup>2</sup>/s to  $10^{-12}$  m<sup>2</sup>/s.

The diffusivity of sorbing species in micropores in rock materials has also been studied previously. Skagius et al [1982a] studied the diffusion of cesium and strontium in crushed granite. The effective diffusivity of both cesium and strontium was found to be on the order of  $10^{-12}$  to  $10^{-11}$  m<sup>2</sup>/s. Effective diffusivities of the same order of magnitude were found when studying the diffusion of cesium and strontium in granite plates, Skagius et al [1982b]. Bradbury et al [1985] studied the diffusion of cesium and strontium in sandstone and found the effective diffusivities to be of the order of  $10^{-11}$  m<sup>2</sup>/s to  $10^{-10}$  m<sup>2</sup>/s.

In some of the above mentioned investigations, Skagius et al [1982b] and Bradbury et al [1985], the diffusivity of iodide, cesium and strontium has been determined in the same type of rock material. The bulk phase diffusivity of cesium and strontium in water is approximately the same as that of iodide. The measured effective diffusivity of strontium and cesium in the rock materials was, how-

ever, found to be about 10 times higher than the effective diffusivity of iodide in the same type of rock materials. This could be due to a diffusional transport of the adsorbed component at the pore surfaces, surface diffusion, acting in parallel with the pore diffusion.

This paper describes two types of diffusion experiments with cesium and strontium in a biotite gneiss. The results are compared with iodide diffusion data from experiments with the same type of biotite gneiss, Skagius et al [1985].

#### EXPERIMENTAL

The rock material used in the experiments was from Fjällveden, located in central Sweden. The samples were taken from part of a drillcore which was from 508-509 meters depth. The rock material was a biotite gneiss containing dark stripes of quartz and biotite and light stripes of quartz and feldspar.

Two types of diffusion experiment were performed. In the first experiment, further referred to as the "in-diffusion" experiment, a piece of the rock core (diameter = 42 mm, length = 32 mm) was placed in 0.44 l of a 100 mg/l cesium solution. Another piece of the core (diameter = 42 mm, length = 40 mm) was placed in 0.56 l of a 100 mg/l strontium solution. The core in the strontium solution and the core in the cesium solution were removed after 385 and 470 days respectively.

From the center of each core a smaller core was drilled out (Figure 1). The diameter of the new core was 22 mm, and the length the same as the original core. The new core was divided into halves and ~ 0.2 mm thick sections of one half of the core was ground off, starting at the surface that had been in contact with the solution. The amount of cesium or strontium in the ground material from each section was determined by atomic absorption spectrometry on the dissolved material, Analytica [1985].

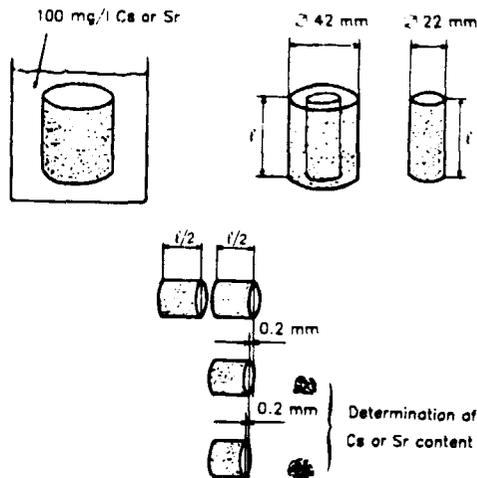


Figure 1: A description of the procedure to determine the concentration profile in the rock sample

By drilling out the smaller core from the center of the original core, the contribution of cesium and strontium in the smaller core caused by diffusion through the cylindrical surface was reduced or even eliminated.

The second experiment, further referred to as the "through-diffusion" experiment, was performed in the same way as earlier diffusion experiments with iodide, Skagius et al [1985]. A hole with the same diameter as the rock core was made in a 10 mm thick PVC-plate. The piece of rock ( $d \sim 10$  mm) was fixed in the hole with silicon glue. The plate with the

rock sample was then placed above a pan of distilled water in a vacuum chamber. A pressure close to the boiling point of water at ambient temperature ( $\sim 25$  mm Hg) was maintained for several hours, and then the PVC-plate with the rock sample was dropped into the water. After a week the PVC-plate with the rock sample was removed from the water. The micropores of the rock sample were now filled with water. Two chambers made of transparent PVC were fastened on the PVC-plate, one on each side. One of the chambers was filled with distilled water and the other was filled with a solution containing cesium ( $0.1$  mol/l =  $13.29$  g/l) or strontium ( $0.1$  mol/l =  $8.76$  g/l).

The concentration increase of cesium or strontium in the chamber that at the outset was free from the diffusing component was determined by atomic absorption spectrometry on small samples (1 ml). Each time a sample had been taken out, the same amount of distilled water was added to the chamber to keep the volume in the chamber constant.

After 315 days for cesium, and after 412 days for strontium, the diffusion experiments were stopped. The rock samples were removed from the PVC-plates. Small sections,  $\sim 0.2$  mm thick, was then ground off, starting at the surface that had been in contact with the high concentrated solution. The concentration of cesium and strontium in the ground off material was determined by atomic absorption spectrometry, Analytica [1985], to give the concentration profile in the samples. Both the cesium and strontium concentrations were measured in all ground samples. This was to get values of the background content of cesium and strontium in the rock material.

## RESULTS

The result from the in-diffusion experiments are presented in Figures 2 and 3 as the solid phase concentration versus distance from the end surface that had been in contact with the solution.

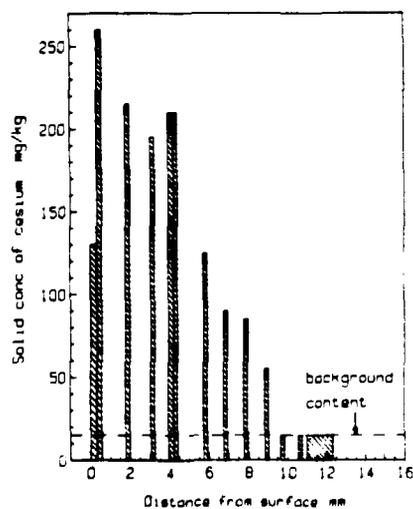


Figure 2: The concentration profile of cesium in the rock sample from the in-diffusion experiment

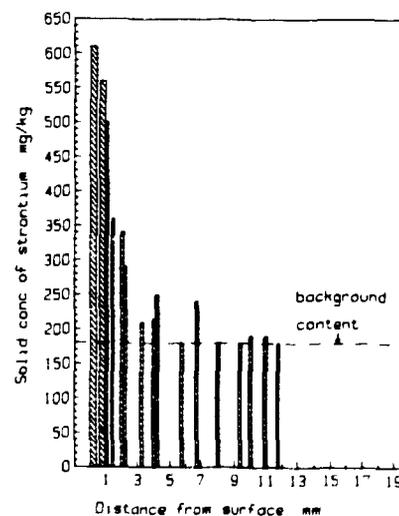


Figure 3: The concentration profile of strontium in the rock sample from the in-diffusion experiment

The background content of cesium was about 15 mg/kg, determined in the ground samples from the strontium diffusion experiments. From the measurement of strontium, in the ground samples from the cesium diffusion experiments, the background content of strontium in the rock material was found to be about 180 mg/kg. Since the concentration of cesium and strontium, some mm away from the surface, is equal to the background contents, the concentration profile caused by the in-diffusion through the outer cylindrical surface of the original core had not reached the outer cylindrical surface of the smaller core when it was drilled out. The concentration profiles showed in Figures 2 and 3 can then be looked upon as the result of one dimensional diffusion in the axial direction of the core.

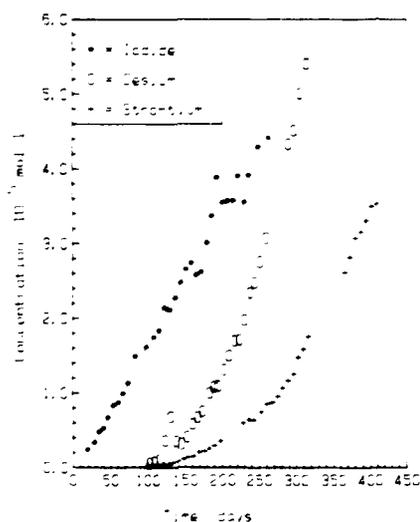


Figure 4: Concentrations of cesium, strontium and iodide on the low concentration side of the rock samples in through-diffusion experiments, versus time

The concentration increase of cesium and strontium in the chambers that at the outset were free from diffusing component in the through diffusion experiments is shown in Figure 4. As a comparison results from an iodide diffusion experiment performed in the same way, Skagius et al [1985], is presented. The iodide diffusion was measured in a rock piece of equal dimension and of the same type of rock material as the strontium and cesium diffusion. The concentration of iodide in the concentrated solution was the same as the concentration of cesium and strontium, 0.1 mol/l. Because strontium and cesium sorb on the rock material the breakthrough time for these components is longer than for iodide.

The concentration profiles of cesium and strontium in the samples, when the through-diffusion experiments were stopped, are given in Figures 5 and 6. The distance in the Figures is the distance from the surface that was in contact with the concentrated solution. The dashed line is the background level. Some parts of the sample in the through diffusion experiment with cesium, seems to have a higher sorption capacity than the rest of the sample (Figure 5). This could be due to local differences in the mineral content of the sample. Vandergraaf et al [1982], have shown that there is an enhanced sorption on mafic minerals, such as biotite, hornblende and the pyroxenes.

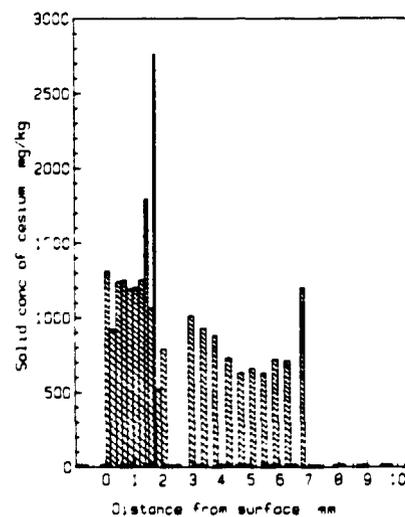


Figure 5: The concentration profile of cesium in the rock sample from the through-diffusion experiment

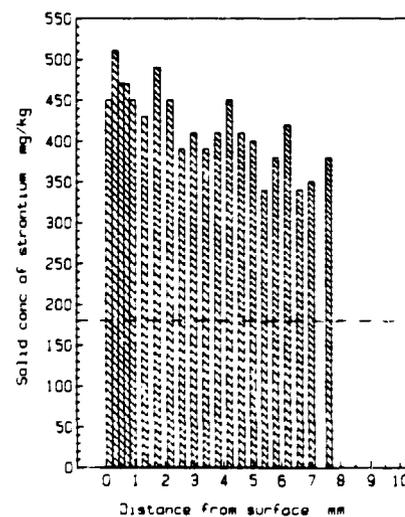


Figure 6: The concentration profile of strontium in the rock sample from the through-diffusion experiment

## DETERMINATION OF DIFFUSIVITY

The diffusion equations

The adsorption and diffusion of a component in the rock material can be described by a two step process, transport through the "film" to the outer surface of the rock sample and diffusion into the pores in the rock sample. The latter transport may be diffusion in the pore liquid, pore diffusion, or diffusion in the adsorbed phase, surface diffusion, or a combination of the two. The equation that describes this transport is

$$\epsilon_p \frac{\partial c_p}{\partial t} + \rho \frac{\partial q}{\partial t} = D_p \epsilon_p \frac{\partial^2 c_p}{\partial x^2} + D_s \rho \frac{\partial^2 q}{\partial x^2} \quad (1)$$

where  $\rho$  = density of the rock material

$\epsilon_p$  = porosity of the rock sample

$c_p(x,t)$  and  $q(x,t)$  = concentrations in the pore fluid and in the solid phase, respectively

$D_p$  = pore diffusivity

$D_s$  = surface diffusivity

$x$  = length coordinate in the diffusion direction

Local chemical equilibrium is assumed at every point inside the sample, and the connection between the concentrations  $c_p$  and  $q$  is given by an equilibrium relation. Two simple and well-known equations are the Freundlich equation and the Langmuir equation.

$$q = k_f c_p^B \quad \text{Freundlich isotherm} \quad (2)$$

$$q = \frac{k_1 c_p}{1+k_2 c_p} \quad \text{Langmuir isotherm} \quad (3)$$

The initial and boundary conditions in the in-diffusion experiments are

$$q(x,0) = q_b, \quad -\ell/2 < x < +\ell/2 \quad (4)$$

$$c_p(x,0) = \begin{cases} f(q_b) \\ 0 \end{cases} \quad -\ell/2 < x < +\ell/2 \quad (5)$$

$$c(0) = c_0 \quad (6)$$

$$c_p(\pm\ell/2, t) = c \quad t > 0 \quad (7)$$

$$\frac{\partial c_p}{\partial x}(0, t) = \frac{\partial q}{\partial x}(0, t) = 0, \quad t > 0 \quad (8)$$

$\ell$  is the axial length of the sample,  $c$  is the bulk solution concentration and  $q_b$  is the background concentration in the sample.  $c_p$  at  $t = 0$  is either a function of the background concentration or equal to zero depending on whether the background concentration participates in the equilibrium or not.

In the in-diffusion experiments, the components have been diffusing from a limited solution volume  $V$  to a rock sample with a length of  $\ell$ . The area of the rock sample normal to the diffusing direction is  $A$ . Because of symmetry in  $x = 0$  the mass balance for the component could be written

$$V \frac{dc}{dt} = -2 A (D_p \epsilon_p \left. \frac{\partial c_p}{\partial x} \right|_{x=+\ell} + D_s \rho \left. \frac{\partial q}{\partial x} \right|_{x=+\ell}) \quad (9)$$

In the through-diffusion experiments the initial conditions inside the sample are the same as in the in-diffusion experiments, eq. 4 and 5. The other initial and boundary conditions are

$$c_1(0) = c_0 \quad (10)$$

$$c_2(0) = 0 \quad (11)$$

$$c_p(-l/2, t) = c_1 \quad (12)$$

$$c_p(+l/2, t) = c_2 \quad (13)$$

$c_1$  is the concentration in the concentrated solution and  $c_2$  is the concentration in the solution on the other side of the rock sample.

In the through-diffusion experiments the mass balance between the concentrated solution and the rock sample is

$$V_1 \frac{dc_1}{dt} = A \left( D_p \epsilon_p \frac{\partial c_p}{\partial x} \Big|_{x=-l/2} + D_s \rho \frac{\partial q}{\partial x} \Big|_{x=-l/2} \right) \quad (14)$$

and between the rock sample and the solution on the other side of the sample

$$V_2 \frac{dc_2}{dt} = -A \left( D_p \epsilon_p \frac{\partial c_p}{\partial x} \Big|_{x=+l/2} + D_s \rho \frac{\partial q}{\partial x} \Big|_{x=+l/2} \right) \quad (15)$$

$V_1$  and  $V_2$  are the bulk solution volumes. The film resistance has been assumed to be negligible.

#### The equilibrium relation

In these experiments no separate determination of the equilibrium relation has been made. The in-diffusion and through-diffusion experiments give, however, two values on the isotherm from the corresponding bulk solution concentrations and the surface solid concentrations of the samples. In Figures 7 and 8 the experimental points of the isotherms have been plotted. In the case with strontium diffusion two points from the in-diffusion experiment and two points from the through-diffusion experiment are given (Figure 8). One point is without the background concentration and the other is with the back-

ground concentration included. To get some more information about the isotherms, experimental data obtained by L. Moreno [1985] on gneiss-granite slabs and by Skagius et al [1982b] on granite slabs, have been used. Also results obtained on crushed granite particles, Skagius et al [1982a] have been considered. There it was found that the isotherm for strontium was linear for concentrations below 10 mg/l and that the Freundlich exponent  $\beta$  in the isotherm for cesium was about 0.5 for concentrations below 15 mg/l. Based on the above mentioned experimental data one Langmuir isotherm and one Freundlich isotherm were chosen for the determination of the diffusivity of cesium. In the Freundlich isotherm the exponent  $\beta$  was changed from 0.5 at concentrations below 15 mg/l to 0.27 at concentrations above 15 mg/l. In the strontium case one Langmuir and two Freundlich isotherms were chosen. One Freundlich isotherm was assumed to be linear up to the experimental point from the in-diffusion experiment ( $c = 60$  mg/l) with a constant sorption capacity at higher concentrations. The other Freundlich isotherm chosen was assumed to be linear at concentrations below 10 mg/l and with an exponent  $\beta = 0.21$  at concentrations above 10 mg/l.

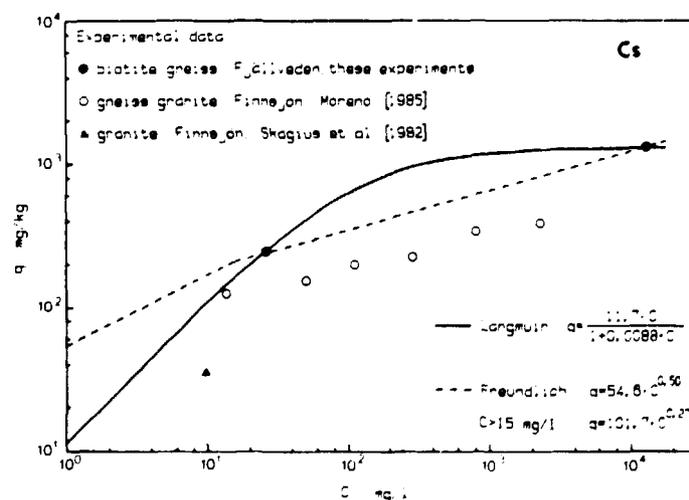


Figure 7: Experimental equilibrium results and isotherm fits for cesium

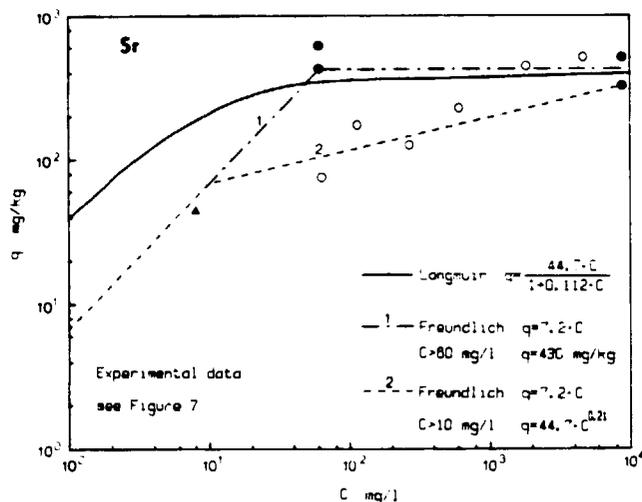


Figure 8: Experimental equilibrium results and isotherm fits for strontium

#### RESULTS AND DISCUSSION

The diffusion equation (eq 1) has been solved numerically by the implicit Crank-Nicolsson method, with Newton-Raphson iterations at each time step. Since the derivatives at  $c = 0$  becomes infinite for the case using the Freundlich isotherm, a second degree equation was used at concentrations below 0.001 mg/l. (The solution is very insensitive to the choice of the concentration where the Freundlich isotherm is not used.)

Based on values of the formation factor for the biotite gneiss, determined from iodide diffusion experiments, Skagius et al [1985], the effective diffusivity  $D_e = D_p \epsilon_p$  of cesium and strontium can be calculated by the equation

$$\frac{D_e}{D_v} = \frac{\epsilon_p \delta_D}{\tau^2} = \text{formation factor} \quad (16)$$

$D_v$  is the bulk solution diffusivity of cesium or strontium,  $\epsilon_p$  the porosity of the rock material,  $\delta_p$  the constrictivity and  $\tau$  the tortuosity of the pores.

The bulk solution diffusivity of cesium and strontium was estimated by an equation from Sherwood et al [1975].

$$D_v = \frac{RT}{F^2} \frac{(1/n_+ + 1/n_-)}{(1/\lambda_+^0 + 1/\lambda_-^0)} \quad (17)$$

Here  $R$  is the gas constant,  $F$  the Faraday's constant,  $T$  the absolute temperature,  $\lambda_+^0$  and  $\lambda_-^0$  the cationic and the anionic conductances at infinite dilution,  $n_+$  and  $n_-$  the valence of cation and anion respectively. The anion was chloride. The bulk solution diffusivity of cesium was determined to be  $2 \cdot 10^{-9} \text{ m}^2/\text{s}$  and of strontium  $1.3 \cdot 10^{-9} \text{ m}^2/\text{s}$ .

With the value of the formation factor =  $4.6 \cdot 10^{-5}$  and the estimated bulk solution diffusivities of cesium and strontium, the effective diffusivity of cesium is about  $1 \cdot 10^{-13} \text{ m}^2/\text{s}$  and of strontium  $6 \cdot 10^{-14} \text{ m}^2/\text{s}$  (from eq. 16).

Figure 9 shows results from the in-diffusion experiment with cesium for the case with no surface diffusion and the Freundlich isotherm. The effective diffusivity calculated from the formation factor of the rock material gives a penetration depth of about 2 mm while the experimental penetration depth is about 10 mm. The effective diffusivity has to be about 100 times higher to fit the experimental data. This suggests that the pore diffusion is not the only transporting mechanism. Another fact that confirms the existence of an additional transport mechanism is that an effective diffusivity of  $1 \cdot 10^{-11} \text{ m}^2/\text{s}$  and a porosity of the material of 0.2 %, Skagius et al [1985], would give a pore diffusivity  $D_p$  equal to  $5 \cdot 10^{-9} \text{ m}^2/\text{s}$  which is higher than the bulk solution diffusivity of cesium.

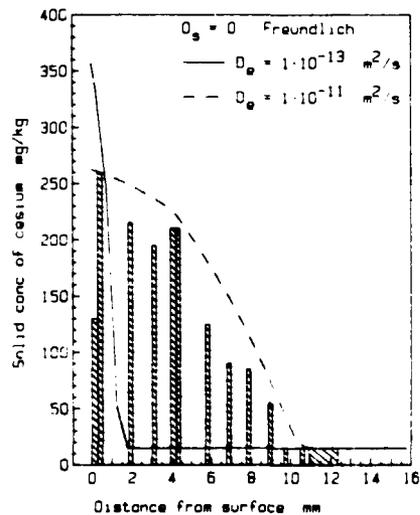


Figure 9: Experimental concentration profile of cesium in the rock sample from the in-diffusion experiment, and theoretical curves from the diffusion model. Only pore diffusion

Results from the through-diffusion experiment with cesium also show that the effective diffusivity determined from the formation factor of the rock material is too low if no surface diffusion occurs (Figure 10). A higher value of the effective diffusivity, for the case of no surface diffusion, still does not give a good fit to the experimental data (Figure 11). A further increase of the effective diffusivity values presented in Figure 11 will make the breakthrough time of the curves shorter, but will also increase the slope of the curves. A decrease of the effective diffusivity values will decrease the slope of the curves but will also lead to an increase in the breakthrough time.

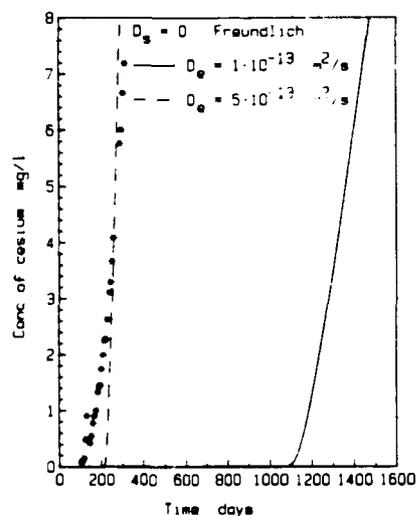


Figure 10: The concentration increase of cesium on the low concentration side of the rock sample in the through-diffusion experiment, and theoretical curves from the diffusion model. Only pore diffusion

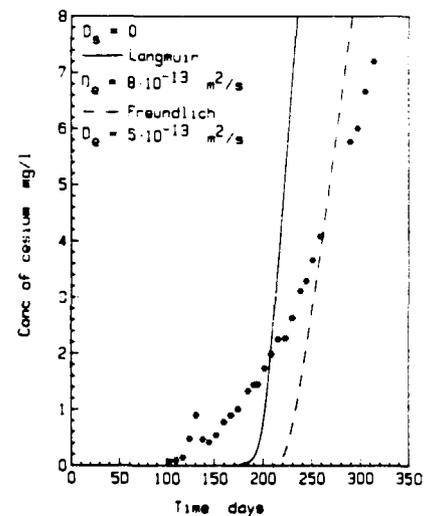


Figure 11: The concentration increase of cesium on the low concentration side of the rock sample in the through-diffusion experiment, and theoretical curves from the diffusion model. Only pore diffusion.

For the case with both pore diffusion (effective diffusivity from the formation factor of the rock material) and surface diffusion, the fit to the experimental data from both the in-diffusion and the through diffusion experiment with cesium is rather good (Figures 12-14). In the in-diffusion experiment, however, the theoretical curves gives higher concentrations than measured in the solid material at larger penetration depths (Figure 12). The surface diffusivity is, in all probability, concentration dependent. The theoretical curve, where a constant surface diffusivity has been used, that fits the higher concentrations will then overestimate the concentrations in the low

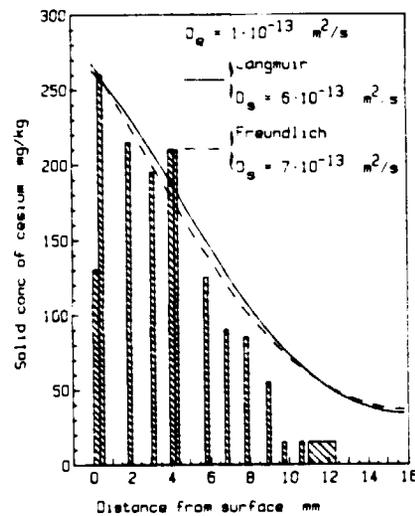


Figure 12: The best fit of the diffusion model to the experimental concentration profile of cesium in the rock sample from the in-diffusion experiment.

concentration range. Comparing the in-diffusion experiment with the through-diffusion experiment a somewhat higher surface diffusivity has to be used in the through diffusion experiment to fit the experimental data. Since the concentration range in the through-diffusion experiment was higher than in the in-diffusion experiment the difference in surface diffusivity could be the result of concentration dependence. The model gives a better fit to the experimental data when using the Freundlich isotherm.

When solving the diffusion equation for the experiments with cesium the assumption that the background concentration (15 mg/kg) in the rock material does not participate in the equilibrium has been made.

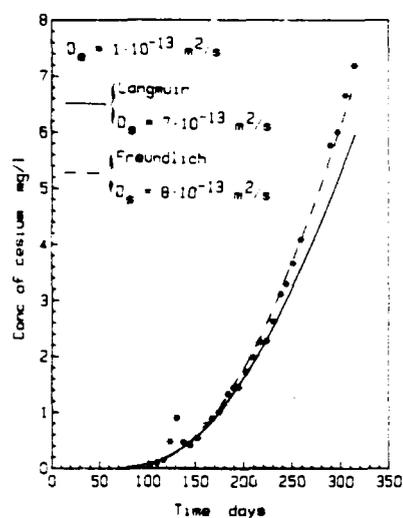


Figure 13: The best fit of the diffusion model to the experimental concentration increase of cesium on the low concentration side of the rock sample in the through-diffusion experiment.

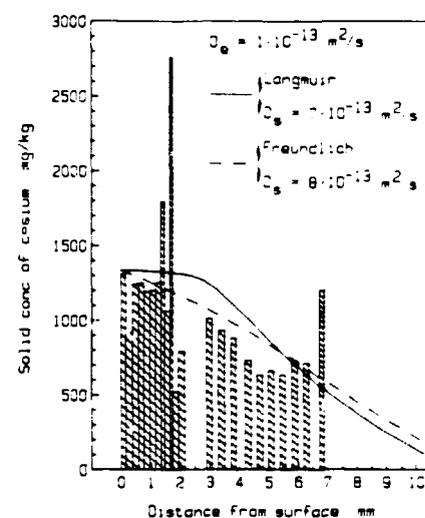


Figure 14: Experimental and theoretical concentration profiles of cesium in the rock sample from the through-diffusion experiment.

Figure 15 shows the result from the in-diffusion experiment with strontium for the case with no surface diffusion. As in the in-diffusion experiment with cesium an effective diffusivity based on the formation factor of the material ( $D_e = 6 \cdot 10^{-14} \text{ m}^2/\text{s}$ ) is too low to be in accordance with the experimental data. The Freundlich isotherm No. 1 has been used since it is the only isotherm of the three that includes the experimental point from the in-diffusion experiment.

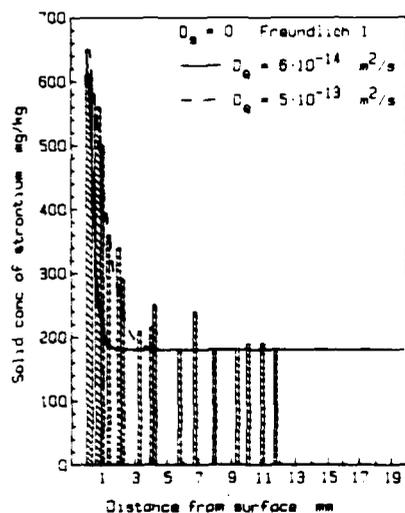


Figure 15: Experimental concentration profile of strontium in the rock sample from the in-diffusion experiment, and theoretical curves from the diffusion model. Only pore diffusion.

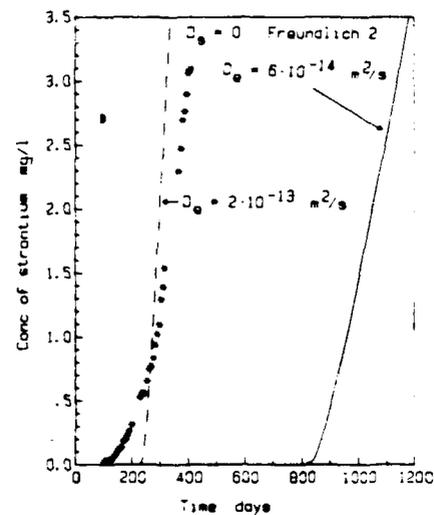


Figure 16: The concentration increase of strontium on the low concentration side of the rock sample in the through-diffusion experiment, and theoretical curves from the diffusion model. Only pore diffusion.

The through-diffusion experiment gives similar results (Figure 16). The effective diffusivity, from the formation factor of the rock material, is too low. Here the Freundlich isotherm No. 2 has been used. Using the Freundlich isotherm No. 1 or the Langmuir isotherm will increase the breakthrough time still more. Increasing the effective diffusivity, using the Freundlich isotherm No. 2, still does not give a good fit to the experimental data.

In Figure 17 the theoretical curves using an effective diffusivity equal to  $6 \cdot 10^{-14} \text{ m}^2/\text{s}$ , from the formation factor of the material, and a surface diffusivity equal to  $8 \cdot 10^{-14} \text{ m}^2/\text{s}$  are shown. The Langmuir isotherm gives too low solid concentrations near the surface of the sample.

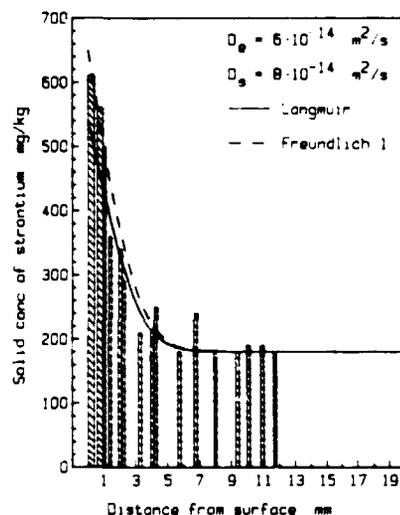


Figure 17. The best fit of the diffusion model to the experimental concentration profile of strontium in the rock sample from the in-diffusion experiment.

In the through-diffusion experiment with strontium, using an effective diffusivity based on the formation factor of the material, the two Freundlich isotherms give the best fit to the experimental data (Figure 18). A much higher value of the surface diffusivity has to be used compared to the in-diffusion experiment. The concentration profile in the sample from the through-diffusion experiment shows that it is only the Freundlich isotherm No. 2 that gives results that fairly agree with the experimental data (Figure 19).

In all the curves presented, describing the strontium diffusion, the assumption that the background concentration (180 mg/kg) does not participate in the equilibrium has been made. Since the background concentration of strontium in the rock material is rather high, the model was tested on the through-diffusion experiment with the assumptions that 10 % and 50 % of the background concentration participates in the equilibrium. The test was made for the cases with only pore diffusion (Figure 20) and with both pore and surface diffusion (Figure 21). The results indicate that the background concentration does not take part in the equilibrium.

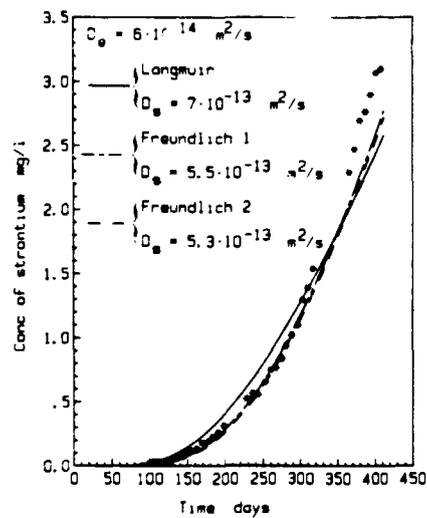


Figure 18: The best fit of the diffusion model to the concentration increase of strontium on the low concentration side of the rock sample in the through-diffusion experiment.

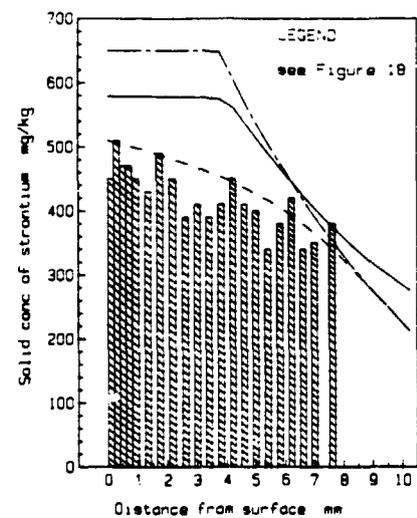


Figure 19: Experimental and theoretical concentration profiles of strontium in the rock sample from the through-diffusion experiment.

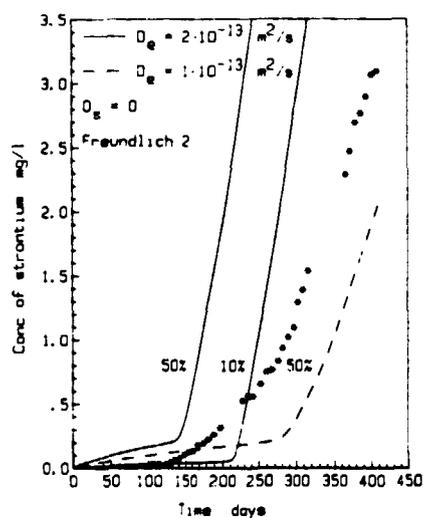


Figure 20: Experimental concentration increase of strontium on the low concentration side of the sample, and theoretical curves from the diffusion model when the background content participates in the equilibrium. Only pore diffusion.

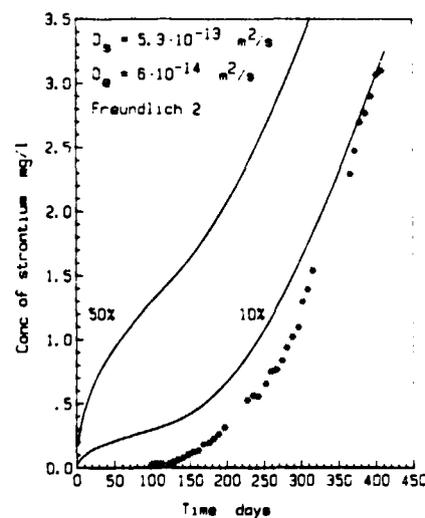


Figure 21: Experimental concentration increase of strontium on the low concentration side of the sample, and theoretical curves from the diffusion model when the background content participates in the equilibrium. Both pore and surface diffusion.

In the diffusion model used here the film resistance has been neglected, which means that the dominating resistance to diffusion lies in the rock material. The resistance to diffusion in the bulk phase near the rock surface, the film, is  $L_1/D_v$ . The corresponding resistance in the rock sample consists of the resistance to pore diffusion acting in parallel with the resistance to surface diffusion. The total resistance in the rock sample could then be written  $L_2 \cdot K / (K \cdot D_e + D_s)$ .  $L_1$  and  $L_2$  are characteristic length and  $K$  is the equilibrium constant. Assuming that  $L_1 = L_2 = \lambda$ , the length of the

rock sample, and that the equilibrium constant  $K$  is equal to the experimental value from the through-diffusion experiment, the resistance to diffusion in the film is  $5 \cdot 10^8 \cdot \lambda$  and in the rock sample in the through-diffusion experiment about  $3 \cdot 10^{11} \cdot \lambda$  and in the in-diffusion experiment about  $4 \cdot 10^{11} \cdot \lambda$ . This is for the cesium case. For the strontium case the resistance to diffusion in the film is  $8 \cdot 10^8 \cdot \lambda$  and in the rock sample in the through-diffusion experiment about  $2 \cdot 10^{11} \cdot \lambda$  and in the in-diffusion experiment about  $1 \cdot 10^{12} \cdot \lambda$ . These values show that the film resistance is at least two orders of magnitude lesser than the resistance to diffusion in the rock material, and could therefore be neglected.

#### CONCLUSIONS

Both the in-diffusion experiments and the through-diffusion experiments show that cesium and strontium are transported in the rock material by diffusion. In the cesium case it is rather obvious that the transport cannot be due to only pore diffusion. Adding a surface diffusion mechanism greatly improves the fit to the experimental data. In the strontium case the existence of surface diffusion is not as obvious as in the cesium case. The through-diffusion experiment, however, indicates that surface diffusion is active even for strontium.

One big uncertainty is the equilibrium relations. Too little experimental data was available to get a good description of the isotherms. The diffusivities given in the Figures must then be looked upon as approximative but probably of the right order of magnitude. The problem with the isotherms concerns in the first place the strontium equilibrium. Different isotherms had to be used in the evaluation of the through-diffusion experiment and the in-diffusion experiment to get agreement with the experimental data.

## NOTATION

A	cross-sectional area of rock sample	$m^2$
$c_0$	initial bulk solution concentration	$mg/m^3$
$c, c_1, c_2$	bulk solution concentrations	$mg/m^3$
$c_p$	pore solution concentration	$mg/m^3$
$D_e = D_p \epsilon_p$	effective diffusivity	$m^2/s$
$D_p$	pore diffusivity	$m^2/s$
$D_s$	surface diffusivity	$m^2/s$
$D_v$	bulk solution diffusivity	$m^2/s$
F	Faraday's constant = $9.6487 \cdot 10^4$	As/mol
$k_f$	constant in Freundlich isotherm	
$k_1, k_2$	constants in Langmuir isotherm	
K	equilibrium constant	$m^3/m^3$
$l$	length or thickness of rock sample	m
$L_1, L_2$	characteristic lengths	m
$n_+, n_-$	valence of cation and anion	
q	solid concentration	mg/kg
$q_b$	background concentration in the solid material	mg/kg
R	gas constant = 8.3143	J/mol, $^{\circ}K$
t	time	seconds
T	temperature	$^{\circ}K$
$V, V_1, V_2$	bulk solution volumes	$m^3$
x	length coordinate	
$\beta$	exponent in Freundlich isotherm	
$\delta_D$	constrictivity for diffusion	
$\epsilon_p$	porosity of the rock material	
$\lambda_+, \lambda_-^0$	cationic and anionic conductance at infinite dilution	$cm^2/\Omega, equiv$
$\rho$	density of the rock material	$kg/m^3$
$\tau$	tortuosity	
$\frac{\epsilon_p \delta_D}{\tau^2}$	formation factor	

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