

**Retardation of escaping nuclides
from a final depository**

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Final report on the KBS-object 21.05

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Summary

A study has been made on retardation of radionuclides in various materials, which could be suited for use in the final repository. A literature survey has shown that except for Cs and Sr very little is known on ion exchange equilibria in ground water surroundings. Measurements were made to determine equilibrium data for Cs, Sr, Eu and U in five natural zeolites, which could be used as filling material. Diffusivities in zeolite particles and beds as well as clay beds were also determined.

The measured equilibrium data could not be predicted by using published data on binary equilibria. Bed diffusivities were of a magnitude that was expected.

With the aid of these data the function of the ion exchange barrier was investigated. The barrier is so short that the nuclide transport is by diffusion. An 0.2 m barrier of a zeolite will delay Cs and Sr so long that they will decay totally. Am²⁴¹ will also be considerably delayed. An 0.2 m clay-quartz barrier will have very little effect on these nuclides. A 1 m clay-quartz barrier will have about the same effect as an 0.2 m zeolite barrier. Most other nuclides have so long lives that they will only be delayed, but not sufficiently long to decay.

The rock itself interacts with many of the radionuclides. A simple model has been made to describe the nuclide retardation and dispersion in fissured rock. With the aid of this, tracer experiments in actual underground rock have been analysed. For Sr at least, laboratory measured equilibrium data on rock, predicted the in-situ runs fairly well. A retardation factor 3-6 was predicted and a value of 6 was measured.

This is expressed as a mean retardation. Due to the fact that some water flows faster than other, the first nuclides arrive at about one fifth of the mean time. This dispersion effect is much larger than what has been observed in sand and similar materials. Using laboratory data, the model and expected water velocities and dispersion, a one km path in the rock would give time enough for Cs and Am²⁴¹ to decay totally. Sr and Am²⁴³ are considerably delayed. The above must be confirmed by further experiments.

Background

When depositing radioactive wastes in the ground, a leak may occur in the capsules. The leaking nuclides must be hindered from reaching the ground water. One possible way of hindering the nuclides from reaching the ground water is to fill the space around the capsules by a buffer material. The buffer material should guard the capsules mechanically and act as an ion exchange barrier and so retard the wandering ions. The ion exchange material must be stable for long times. Ion exchange materials which can be considered are natural zeolites, clays and synthetic zeolites. The ions which will be primarily retarded are the metal ions with positive charges. The negative ions will probably not be retarded. Even if the ions have passed the ion exchange barrier they will be further retarded in the rock by ion exchange, adsorption and precipitation mechanisms. Ideally the ions will be retarded by a factor depending only on the equilibrium constants. When, however, water flows in porous media we will have to consider the mechanisms of diffusion in the bed, as well as diffusion effects into the particles themselves. In addition to this there will be dispersion effects. The dispersion effects arise from the fact that water flows with different velocities in different channels. This will lead to a spreading of the break-through front. The same mechanisms will apply to the flow in a rock. The fissures in the rock are probably of different sizes, directions and spacings. Very little is known of the exchange mechanisms in the rock.

The object of this investigations has been a) to make a literature survey of what is known on ion exchange equilibria in soils, clays and zeolites with regard to the nuclides of interest, b) by experiments to determine the influence of

diffusion in the particles, diffusion in the bed and equilibria for various nuclides and zeolites. In addition to this it has been the object of this work to assess how effective ion exchange barriers are and what can be expected by using them. The same applies to rock. In addition to this we have made a number of supporting investigations.

3 Literature survey

3.1 Most important radionuclides

According to Cohen (1976) the most important nuclides to contain are those which may give rise to most cancer deaths. These nuclides will not always be the same as those which are most radioactive or are most abundant. Cohen makes an assessment of how a radionuclide will enter the body, how long it will stay and how many cancer doses it may give rise to. The most dangerous of the nuclides are Sr^{90} and Cs^{137} followed by Am^{241} and Am^{243} . Pu^{239} , Pu^{240} , I^{129} , Tc^{99} , Ra^{226} and Np^{237} must also be considered as very dangerous. The relative danger of different nuclides at various times after burial are shown in figure 3.1. The data are taken from Cohen (1976). They apply to reprocessed fuel.

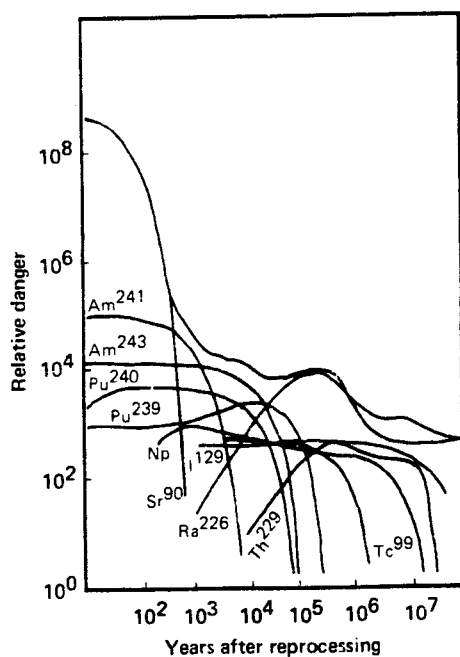


Fig. 3.1 Relative danger of various nuclides as a function of the time after reprocessing. From Cohen (1976)

3.2 Migration of radionuclides in the ground

Much work has been done regarding the migration of radionuclides in the ground. At the Vienna conference IAEA 1967 a number of papers were presented on this and related subjects. Practically all investigations were concerned with soils, sand and clayey materials. Practically no investigations were done on consolidated rock.

Levi (1967) found that Cesium was very strongly bound to Vermiculite. It was found that this ion was practically fixed and only about 10 % of one Cesium isotope could be exchanged by other Cesium isotopes. Strontium was not fixed all and could be readily displaced by other ions. Spitsyn (1967) investigated the sorption capability of a large number of different materials including clays, sand, limestone and sandstone. Sorption capacities were determined for various compositions of the water. Inoue (1967) measured mass equilibrium constants for Strontium and Cesium in sand. He found values corresponding to retardation factors of 36 for Strontium and about 1000 for Cesium. Brown (1967) similarly found retardation factors 50 and 300 for Strontium and Cesium respectively in the sedimentary ground beneath the Hanford reservation. Rancon (1967) gives data on carbonate rock for Strontium and Cesium. His results indicate a surface reaction mechanism. Allard (1977a) and Vandergraaf 1976 a,b,c,d and 1977 have measured equilibria for various nuclides in granitic rock and other materials.

Landström (1977) has made in situ measurements of Strontium and Cesium retardation in granitic rock in Studsvik. The water is transported in fissures and it is thought that the nuclides are adsorbed on the surface of the rock by some mechanism. Strontium was retarded by a factor 6 and Cesium did not appear

at all in the measuring well. Iodine and Technetium travel with the velocity of water as was expected. There was a considerable dispersion when the water travelled between the boreholes spaced at 22 and 51 m. The first breakthrough occurs at about one tenth to one fifth of the time it takes for the peak to arrive. Papadopulos and Winograd (1974) make a review of mathematical models used for predicting water movement in the ground as well as the data needed for such computations. They conclude that it may be possible to predict radionuclide movement in homogenous porous ground with the present methods, but that they are not suited for prediction of water and nuclide movement in fractured rock. This is mainly due to the difficulty in describing the size and structure of the fissures.

Burkholder et al (1976) have made computations of nuclide movement in Western U.S. desert subsoil using a sophisticated mathematical treatment which takes in account the decay of the nuclides and the appearance of other nuclides in the decay chain. The model is named the Geosphere model. They also give retardation factors for most of the nuclides present in the spent fuel. Burkholders equilibrium data for Western U.S. desert subsoil are given in table 3.1.

According to Burkholder the Geosphere model can be applied to "faulted monolithic media" also.

Hägglom (1977) used a similar technique to study the migration of radionuclides. In his study the only transport mechanism is assumed to be diffusion, whereas the Burkholder treatment includes convection and diffusion. From both treatments it may be concluded that diffusion is of no importance for distances as large as hundreds of meters.

Table 3.1

Half lives $T_{1/2}$ and retardation factors k_i in "Western U.S. desert subsoil".

Nuclide	$T_{1/2}$ years	k_i
H-3	12.26	1
C-14	5730	10
Ni-59	$8 \cdot 10^4$	330
Ni-63	92	330
Se-79	$6.5 \cdot 10^4$	100
Rb-87	$5 \cdot 10^{11}$	500
Sr-90	28.1	100
Zr-93	$1.5 \cdot 10^6$	10^4
Mo-93	> 100	25
Tc-99	$2.1 \cdot 10^5$	1
Pd-107	$7 \cdot 10^6$	1100
Cd-113	14	10^4
Sn-126	10^5	1100
I-129	$2 \cdot 10^7$	1
Cs-135	$3 \cdot 10^6$	1000
Cs-137	30	1000
Sm-151	93	2500
Eu-152,154	13,16	2500
Ho-166	$1.2 \cdot 10^3$	2500
Ra-226	1600	500
Th-229	7340	$5 \cdot 10^4$
Th-230	$8 \cdot 10^4$	$5 \cdot 10^4$
Pa-231	$3.3 \cdot 10^4$	$1.8 \cdot 10^4$
U -236	$2.4 \cdot 10^7$	$1.3 \cdot 10^4$
U -233	$1.6 \cdot 10^6$	"-
U -238	$4.5 \cdot 10^9$	"-
U -234	$2.5 \cdot 10^5$	"-
U -235	$7.1 \cdot 10^8$	"-
Np-237	$2.1 \cdot 10^6$	100
Pu-240	6530	10^4
Pu-244	$8 \cdot 10^7$	"-
Pu-241	13.2	"-
Pu-242	$3.8 \cdot 10^5$	"-
Pu-238	86	"-
Pu-239	$2.4 \cdot 10^4$	"-
Am-241	458	10^4
Am-242	152	"-
Am-243	7370	"-
Cm-248	$4.7 \cdot 10^5$	3300
Cm-245	$9.3 \cdot 10^3$	"-
Cm-246	$6.5 \cdot 10^3$	"-
Cm-242	0.4	"-
Cm-247	$1.6 \cdot 10^7$	"-
Cm-243	32	"-

Data from Burkholder (1976)

3.3 Ion exchange materials and equilibria

Many inorganic materials found in nature have ion exchange properties. Some investigations regarding the properties of sands, clays, peat, gravel and silt were already mentioned above. Another large group of natural materials with excellent ion exchange properties are the natural zeolites. Zeolites may also be synthesized from clays. There are many different kinds of zeolites. They are often selective ion exchangers due to the size of the cavities formed by the crystal structure. A very thorough compilation of the natural zeolites can be found in Breck's book (1973). Theoretical treatment of ion exchange, as well as equilibrium and diffusivity data may be found in Helfferich (1962) and Amphlett (1964). Ames (1960) has studied one of the most common zeolites in connection with radionuclides. Ames (1960, 63, 64), Mercer and Ames (1963) and Amphlett (1956) have studied the ion exchange properties of natural and some synthetic zeolites in connection with Strontium and Cesium. Arnek (1977) has made an investigation using Strontium, Cesium and Europium and 10 different zeolites. Allard (1977a) has made a series of measurements using montmorillonite clay and granite particles as ion exchange materials and Cs, Sr, Eu, Zr, Tc, I, Ce, Nd, Ra, Th, U, Np, Pu and Am nuclides.

3.4 Water transport in rock

Water transport in consolidated rock is usually described in the same way as for porous materials. Darcy's equation simply relates the flow of water to the hydraulic gradient i . The proportionality factor is called the permeability K_p

$$u_o = K_p \cdot i$$

u_o is the bulk velocity. The velocity in the pores u_p is u_o/ϵ_B , where ϵ_B is the porosity of the medium. K_p is a lumped

parameter and depends on the pore size, temperature, porosity and even velocity if this is large.

The other frequently used way for describing flow in porous media is given by the Kozeny-Karman equation. Bird (1960).

$$u_o = \frac{d_p^2 \epsilon_B^3 g}{150 \nu (1-\epsilon_B)^2} \cdot i$$

Here only that part of the equation is given which is valid for laminar flow. This expression accounts for the influence of porosity, particle size or channel width and temperature via the viscosity. A similar expression is arrived at by the treatment of Snow (1968). The Kozeny-Karman equation was derived by considering flow in a channel formed by the pores in a bed of spherical particles, whereas Snow's treatment assumes a flat semiinfinite channel formed by the space between two parallel slabs.

Neither of these models give any information on the variation of velocities in the different channels - axial dispersion - nor on the spreading and mixing perpendicular to the flow direction.

Åberg (1975) gives some data on the frequency of fissures, measured down to a few hundred meters. He also indirectly gives information on the size of the fissures by giving the variation of the permeability at different levels in the borehole. Similar data are given in Landströms report (1977). At present few data are available at depths lower than a few hundred meters. Åberg's data indicate that the permeability decreases with the depth. As the permeability measurements are made by a method which very strongly emphasizes the conditions near

the borehole, the data may not be applicable over a larger distance. The only measurements available at present where water and nuclides were transported over a large distance in rock are those of Landström.

3.5 Dispersion and diffusion

Dispersion has been much studied in the literature on chemical reaction engineering. Levenspiel (1962) gives a comprehensive chapter on these effects in his book. Bischoff (1962 a,b) has given very thorough treatment of dispersion, experimentally as well as theoretically. For very small velocities in porous media the axial and radial dispersion coefficients may be determined from

$$\log (D_x) = \log \left[\frac{u_p d_p \epsilon_B}{(1-\epsilon_B)} \cdot 5.3 \right] \quad \text{axial}$$

$$\log \left(\frac{D_r}{v} \right) = 0.57 \log \left[\frac{u_p d_p \epsilon_B}{v(1-\epsilon_B)} \cdot \frac{2}{3} \right] \quad \text{radial}$$

Baetsle (1967) gives very similar expressions

$$\log (D_x) = \log (u_p) - 3 \quad \text{axial}$$

$$\log (D_r) = 0.47 \log (u_p) - 6.1 \quad \text{radial}$$

Burkholder in his computations used an axial dispersion coefficient $D_x = .008 \text{ cm}^2/\text{min}$. This compares very well with the values predicted by the above expressions. These expressions for the dispersion coefficient will have a lower limit of validity. When the molecular diffusion is larger than the dispersion due to flow, the former will dominate. The above expressions indicate that radial dispersion will be very small in comparison with the axial dispersion. Burkholder used this to simplify the model for nuclide transport and spreading.

In his treatment he only accounts for the axial dispersion.

This is probably a very good approximation for soils, sands, gravel and other similar unconsolidated materials. This may be seen from the very simple expression showing how a point source will spread with time into the three dimensions

$$C_{xyz} = \frac{M}{8(\pi t)^{3/2} (D_x \cdot D_y \cdot D_z)^{1/2}} e^{-\left[\frac{X^2}{4D_x t} + \frac{Y^2}{4D_y t} + \frac{Z^2}{4D_z t} + \frac{0.693}{T_{1/2}} \cdot t \right]}$$

The point may be made to travel with the liquid by the following transform.

$$X = x - u_x t ; Y = y - u_y t ; Z = z - u_z t$$

The effect of varying dispersion coefficients may be visualized in the following way. If D_y is 100 times smaller than D_x , the nuclide will spread the square root of 100 - which is a 10-times smaller distance in the y-direction as compared to the x-direction.

No dispersion data have been found on consolidated rock with fractures. The "particle sizes" in rock are of meter dimensions and porosities are in the range 10^{-4} to 10^{-5} or even smaller. It is very doubtful if the same expressions are valid for rock as for other porous beds.

Allard (1977 b) measured a bed diffusivity $D_B \epsilon_B = 0.5 \cdot 10^{-10} \text{ m}^2/\text{s}$ using Silver ions and a clay/quartz mixture.

4 Theoretical considerations

4.1 The effect of an ion exchange barrier

In the repository the capsule containing the radioactive material will be surrounded by some buffer material. The repository is to be situated far below the surface of the earth and also far below the ground water surface. The repository is in rock and the site is chosen so as to minimize water flow. The hydraulic gradient is small and the permeability of the rock is low. According to AKA-utredningen II (1976) the bulk velocity of the water may be expected to be less than $10^{-3} \text{ m}^3/\text{m}^2/\text{year}$. The water velocity in the filling material will depend on its permeability, the orientation of the repository in relation to the hydraulic gradient and on the magnitude of the gradient. If the permeability of the filling material is less than that of the rock, the water velocity will be roughly proportional to the permeability of the filling material. If it is the other way around, the water velocity will increase by a small amount only, if the gradient is perpendicular to the hole. If it is parallel to the hole, the velocity may increase considerably.

The water velocity in the filling material, has a large importance. It may determine the mechanism of nuclide transport. This will be discussed in detail later.

When the water flows through the filling material, the ions in the water will interact with the solids. The interaction mechanisms of interest here are ion exchange, adsorption, precipitation and irreversible reaction. If the mechanism is irreversible reaction, the reacting ions will be definitely caught, provided there is enough reacting material. Ion exchange and

adsorption are reversible and the ions will only be retarded by this mechanism. They will travel slower than the bulk velocity of the water by a factor k_i , which is determined by the equilibrium data of the system. If there is precipitation in addition to ion exchange and adsorption this will further decrease the ion velocity.

At present the mechanisms are not known for every ion of interest in the type of surroundings which may occur. The conservative assumption is therefore made that the mechanism is ion exchange or adsorption. The retardation factor which may be determined by experiments is a mean value. Figure 4.1 below shows how the concentration of ion "i" varies with the distance from the capsule wall in the direction of the flow.

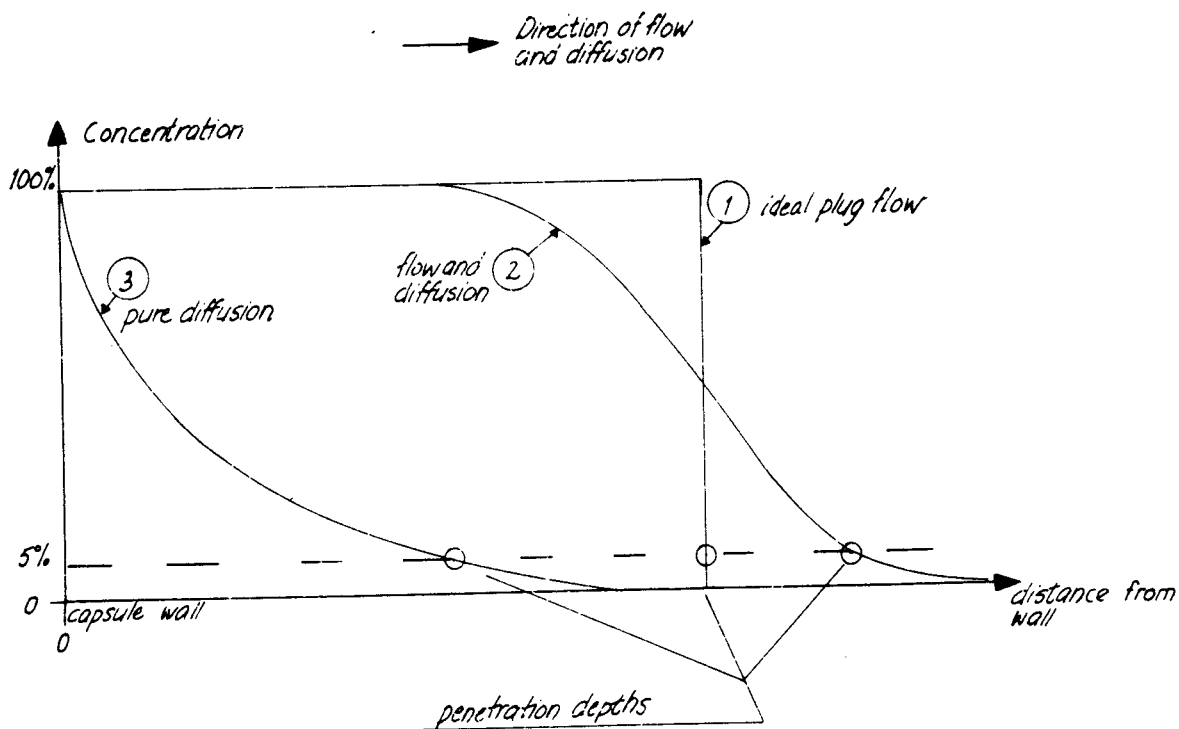


Fig. 4.1 Distance travelled for plug flow, pure diffusion and a combination of flow and diffusion

It is assumed that the leakage gives rise to a constant concentration at the capsule wall. This assumption is only made to simplify the description of the transport. Ideally the front would be very steep—Curve 1— in the figure. In practice the front will be elongated due to various effects. This is shown in Curve 2. If flow in the bed is very slow in comparison to diffusion the transport may be due to this effect entirely — Curve 3. The elongation may also result from diffusion resistance in the particles of the filling material and due to dispersion effects in the bed. Dispersion results from the variation in flow velocities in different channels.

Pure dispersion effects will be very small in this case compared to molecular diffusion in the bed. Diffusion resistance in the particles will be of importance if the time needed to saturate the particles is larger than the time it takes the front to pass the depth of the bed. For transport by diffusion only, the following simple criterion may be used to assess the importance of particle resistance.

If $\frac{D_p \epsilon_p}{r_o^2} > 100 \frac{D_B \epsilon_B}{z_o^2}$ then the particle resistance does not

have any influence on the transport. (Ruckenstein et al. 1971). The bed and particle diffusivities were determined (see experimental section) to be $D_B \epsilon_B = 10^{-10}$ and $D_p \epsilon_p = 2 \cdot 10^{-12} \text{ m}^2/\text{s}$ for Sr in Clinoptilolite. This means that if the barrier is 1 m thick the particle diameter must be less than 2.8 cm. Ions with higher valences may diffuse slower and then smaller particles will be needed. The same kind of analysis can be used if flow is much faster than assumed. The particles will have to be made smaller then, but the margins are so large that there will be no difficulty in making sufficiently small particles.

To simplify the following analysis it is assumed that the flow and the diffusion is one-dimensional. The errors introduced by this assumption are small in comparison to other inaccuracies. It is further assumed that the concentration at the capsule wall is constant after the occurrence of a leak. This simplifies the description but has little other influence as we deal with linear systems. It is further assumed that the concentration of any nuclide is small in comparison to the total concentration in the groundwater. This case has been modelled and mathematically treated by Lapidus and Amundsen (1952). The Lapidus and Amundsen model describes a case where a fluid flows through a porous bed. Some of the species originally in the fluid will be taken up by the solids. The species will thus be retarded in relation to the fluid velocity. The retardation will depend on the ratio of the concentrations in the solids and in the fluid. This may be expressed as a retardation factor k_1 . k_1 is the ratio of the fluid bulk velocity u_0 to the velocity of the species, u_1 . On top of this transport is added an effect of diffusion. The travelling front will spread out when it travels along the bed. With the aid of this model the time to travel 1 m and 3 m was computed. When there is no diffusion the time is given directly by the velocity of the species u_1 . With diffusion there is a gradual increase in concentration. In this case the time was chosen when the concentration reaches 5 % of the inlet concentration. The results are shown in figure 4.2

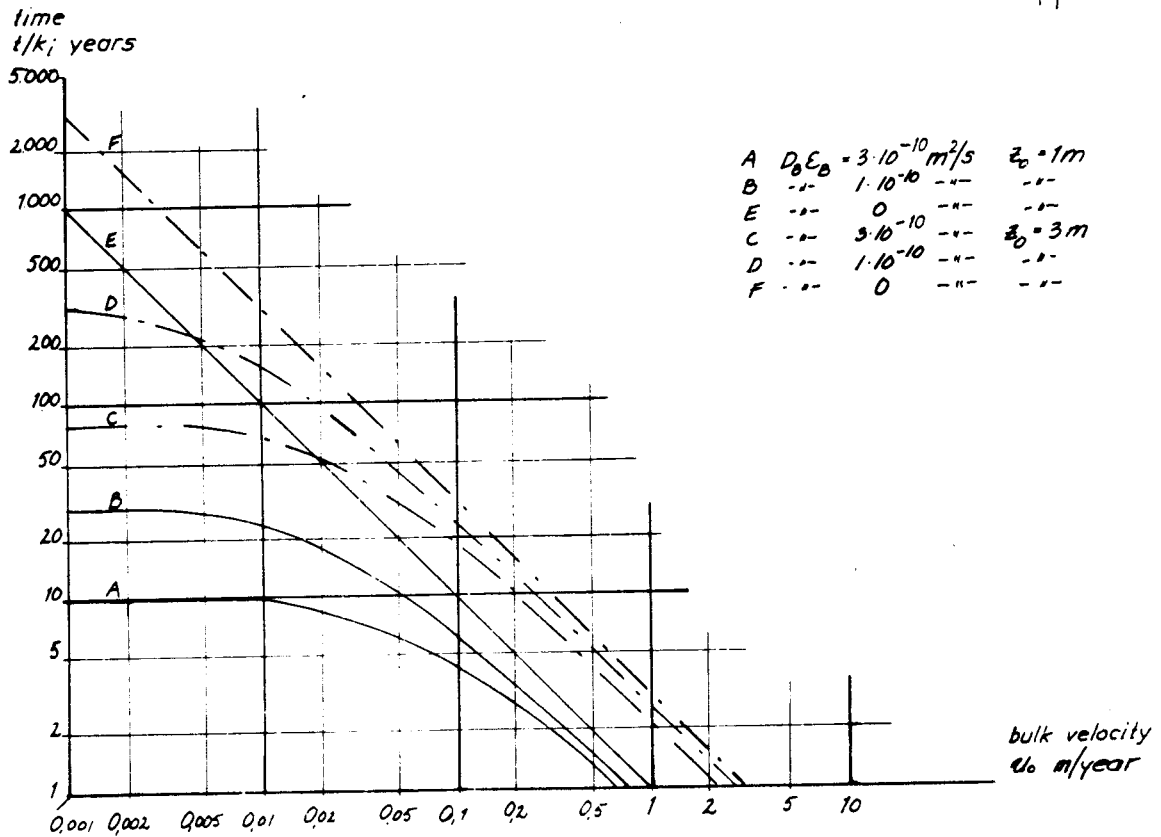


Fig. 4.2 Time for a nuclide to travel 1 and 3 m respectively in an ion exchange barrier with retardation factor k_i as a function of the bulk velocity u_0

Two different diffusivities were used. $D_B \epsilon_B = 10^{-10} \text{ m}^2/\text{s}$ and $3 \cdot 10^{-10} \text{ m}^2/\text{s}$. The results show that diffusion will be the dominating mechanism when the bulk velocity u_0 is less than about 0.01 m/year. Flow will be the dominating mechanism for transporting the ions through the barrier when the bulk velocity is larger than 0.1 m/year. With the lower diffusivity it will take $30 \cdot k_i$ years to pass a one meter barrier for an ion "i" which has a retardation factor k_i . If the barrier is increased in thickness, the retardation time will increase proportionally in the flow dominated case. In the diffusion dominated case the retardation will increase with the square of the thickness.

The diagram in figure 4.2 may be considered as consisting of three parts. In the left part the transport is only due to diffusion. In the right part it is only due to flow. In the middle part both mechanisms are of importance. For the diffusion case a very simple expression may be used to determine the time for the concentration at the outside of the barrier to reach 5 % of the leak concentration. (Carslaw and Jaeger 1959). If the barrier is assumed to be flat

$$t = \frac{0.1 \cdot z_0^2 \cdot k_1}{D_B \epsilon_B}$$

For a cylindrical barrier the constant 0.1 will be somewhat larger and will depend on the ratio of the inner and outer radius of the cylindrical barrier.

When the flow dominates, the time may be determined from

$$t = \frac{z_0 \cdot k_1}{u_0}$$

The above equations may be used to approximately determine the retention times of the nuclides.

In the table below the decay of a radioactive nuclide is given for different numbers of half lives $T_{1/2}$.

Number of				
half lifes	0	10	20	30
Activity	1	10^{-3}	10^{-6}	10^{-9}

After $30 \cdot T_{1/2}$ the activity will be gone for practical purposes. Thus if the retention time is larger than this the nuclides will decay in the filling material.

As the retention time in a one meter barrier is $30 \cdot k_1$ years in the diffusion case, we have a very simple criterion

for determining which nuclides will decay. This will happen when

$$k_1 > T_{1/2}$$

As there normally should be so low water velocities that diffusion dominates, this simple criterion may be used to sort out the clearcut cases.

A compilation of the most important nuclides is given in table 4.1. The retention times are given for a one meter barrier consisting of 10 % clay and 90 % quartz as proposed by Jakobson and Pusch (1977): column 3. In column 4 the retention in a one meter barrier of Clinoptilolite is shown. Retardation factors for clay/quartz are computed from Allards (1977) equilibrium data and for Clinoptilolite our own measurements are used.

Table 4.1

Retention times in 1 m clay/quartz and clinoptilolite barriers for various nuclides

Nuclide	Half life $T_{1/2}$ years	Retention times-years	
		clay/quartz	k_1 Clinoptilolite*
Sr ⁹⁰	28.1	<u>30</u>	<u>600 - 1400</u>
Tc ⁹⁹	$2.1 \cdot 10^5$	1	1
I ¹²⁹	$2 \cdot 10^7$	1	1
Cs ¹³⁷	30	<u>20-30</u>	<u>2200-5200</u>
Ra ²²⁶	1600	40-50	<u>600¹-1400</u>
Th ²²⁹	7340	50-300	Unknown
Np ²³⁷	$2.1 \cdot 10^6$	10	Unknown
Pu ²³⁹	$2.4 \cdot 10^4$	60-80	Unknown
Pu ²⁴⁰	6550	60-80	Unknown
Am ²⁴¹	458	<u>200-4000</u>	<u>1000²-30000</u>
Am ²⁴³	7370	200-4000	<u>1000²-30000</u>

¹From value of Sr

²From value of Eu

Underlined cases are retarded

Using the above criterion to determine which nuclides will be retarded, it is seen that a one meter clay-quartz barrier will retard Sr, Cs and probably Am^{241} . If the barrier thickness is reduced to 0.2 m no nuclides will be appreciably retarded. A one meter thick barrier of Clinoptilolite will retard Sr, Cs, Am^{241} and probably Ra and Am^{243} . In the case of Ra the matter is not as straight-forward as for the other nuclides. Radium is not originally present in the spent fuel, it is a decay product of other wandering nuclides. The above therefore only applies to those Radium atoms which start their life inside the barrier.

4.2 Flow and adsorption in fractured rock

4.2.1 Flow in rock

Rock is not impervious to water. The stone substance itself has a very low permeability, but as the rock is cracked, water will flow in the fissures. Normally the flow of water is proportional to the hydraulic gradient and may be described by the following expression.

$$u_o = K_p \cdot i \quad \text{or} \quad u_p = \frac{K_p i}{\epsilon}$$

K_p is the permeability of the rock, u_o is the bulk velocity, u_p the water velocity in the pores, ϵ is the porosity. This very simple description does not consider the size, frequency or orientation of the fissures. More detailed models are necessary to determine how the water flows in the fissures in the rock. In a large fissure the water will flow very much faster than in a small one. Due to this some water may travel much faster than the mean velocity. From the point of view of retarding radioactive nuclides, it is more interesting to know when the first nuclides reach the ground, than when the mean

arrives. One model which gives a better description of how the water flows is the Snow model (1968). It is based on the assumption that the rock consists of a number of parallel slabs. Water flows in the channels between the slabs. Given the channel spacing and width it is possible to determine the permeability. Snow assumed that the channel width was constant, or that a mean channel width can be used. This is not a good assumption for the purposes of this investigation, as the flowrate in a channel is proportional to the width raised to the third power. An example of the consequences is shown below. A frequency distribution of the channel widths is assumed. In this example it is chosen to have a standard deviation of 0.3 of the mean width. The distribution is shown below in figure 4.3. This frequency distribution gives a very good fit between computed and experimentally determined residence time distributions in actual rock in Studsvik. A detailed description is given in appendix 1.

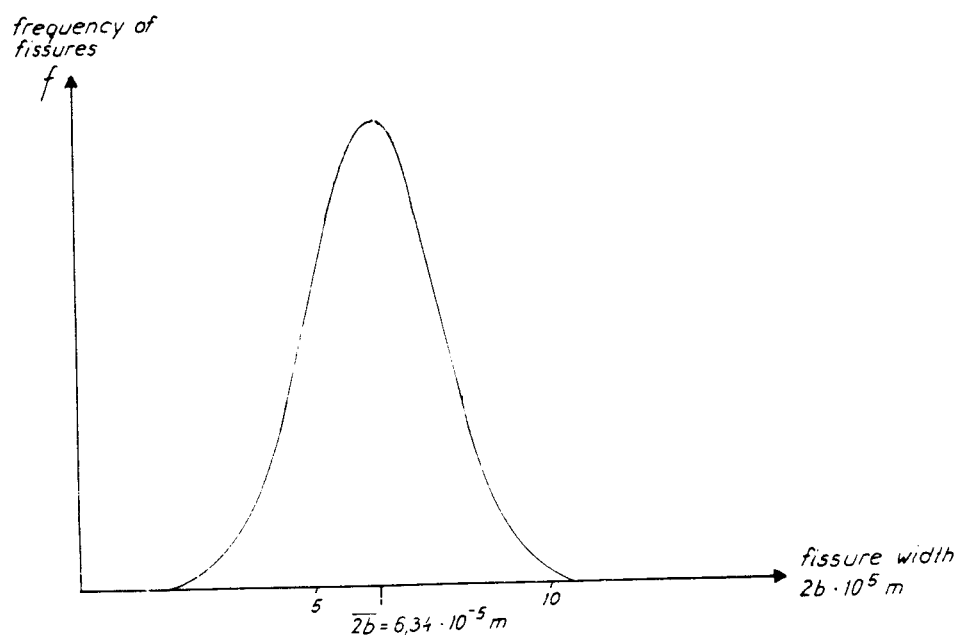


Fig. 4.3 Frequency of fissure widths in rock, determined from the Studsvik experiments

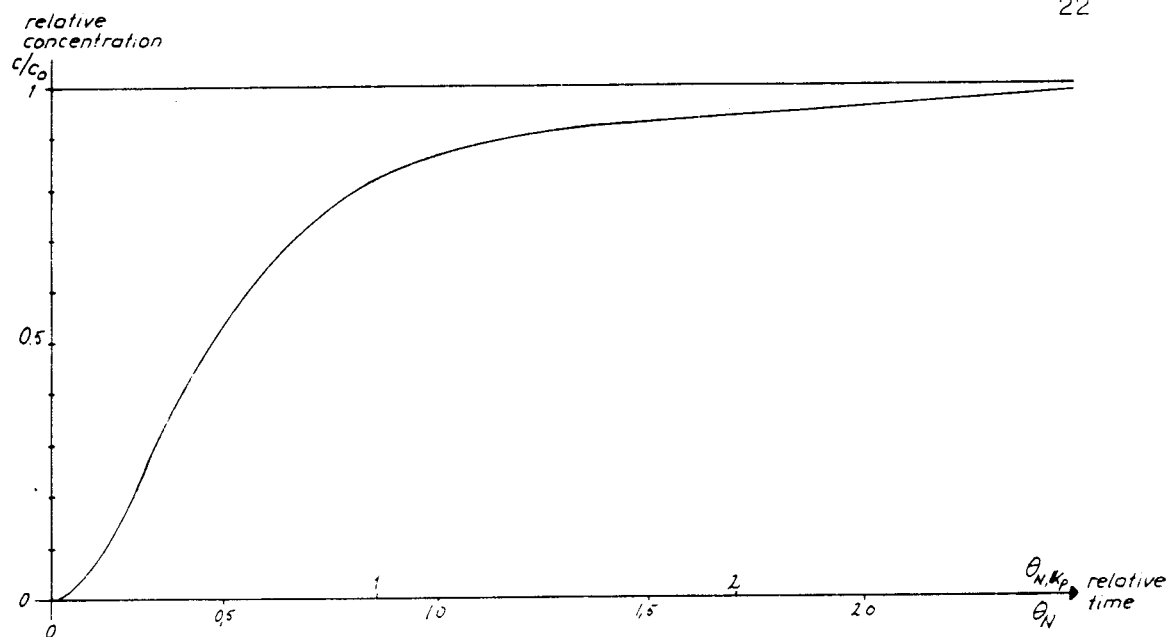


Fig. 4.4 Theoretical breakthrough curve in rock

Figure 4.4 shows how an even front spreads out when the water travels in the rock with this distribution of channel widths. Ideally the nuclide travelling at a given velocity reaches a point at a certain time. Some mean time can be computed if the channel widths are known. The relative times θ in Figure 4.4 are related to two such computed mean times. θ_N is related to a time of travel in a fissure of width $\bar{2b}$. θ_{N,K_D} is related to a mean time of travel which can be determined from the permeability of the rock. The permeability may be computed from the frequency distribution of the fissures. The figure shows clearly that the first part of the front reaches a given point very much faster than is predicted by the permeability model. This must be taken in account when the retardation of the nuclides is determined.

4.2.2 Nuclide retardation by the rock

Many of the nuclides of interest interact with the rock by ion exchange, adsorption or other mechanisms. Ion exchange

equilibria have been measured by various investigators. Allard (1977a), Vandergraaf (1976, 1977), Rancon (1967) and Fried (1975). Usually the equilibrium was assumed to be due to a surface reaction. Rancon (1967) showed that in carbonate rock the surface concentration of Strontium on the outer particle surface is independent of the particle size down to particle diameters of 0.2 mm. A decrease below 0.2 mm decreased the surface concentration. Vandergraaf used finely polished slices of rock as a standard for determining the surface of crushed rock particles. He first determined how much was adsorbed on the slice with the known surface. After determining how much a known amount of crushed rock adsorbs, the area of the particles was determined. For granite this area turned out to be smaller by about a factor 5, than the area which may be calculated from the geometric size of the particles. A possible explanation to these observations is that there is a combination of surface and volume reaction. When the particles are large, the nuclide penetrates to a depth smaller than the particle size. When the particles become smaller than the penetration depth, their whole volume will be equilibrated and a further increase in the area will not increase the uptake.

If this hypothesis can be proved to be correct the rock barrier may prove to be much better than previously considered. Given time, the penetration in the rock may become much deeper than in the laboratory experiments, where the time scale is weeks. The time scale in the repository is at least hundreds of years. Other explanations are also possible. One explanation might be that for large particles the outer surface consists of a very coarse structure of small grains. If the surface area of the grains determines the effective area, then this will be roughly proportional to, but larger than the area of the large

particle. When the particles become as small as the grains, the area will be equal to the geometric area.

Rancon's investigation of Cesium and Strontium adsorption on Calciumcarbonate rock shows some interesting results regarding the rate of uptake. In a test with Cs and a block of rock the uptake curve has a form which well can be interpreted by diffusion into the block. The very long time needed to reach equilibrium - more than 50 days - also indicates that a volume reaction can have taken place. Rancon also made column experiments where the bed first was saturated with Cs and Sr and then was eluated with pure water. In these experiments only about 10 % of the adsorbed amount could be washed out again. The tail of the Cs washing curve is very long however. This indicates that given time more Cs will come out. Sr seems to be fixed in a stronger way. These results may be interpreted as irreversible reaction, but also partly as a penetration and a volume reaction. When the washing starts the ions will wander out towards the water but also further into the particles in the direction of the unsaturated rock. Hence it may take much longer time to wash out the rock than to saturate it.

This should be further investigated as it can be of great importance.

At present it is assumed that the reaction is a surface reaction and that the equilibrium is reversible. These are both conservative assumptions.

Table 4.2 a and b is a compilation of equilibrium constants for various nuclides, rocks and water compositions from various sources.

Table 4.2 a

Surface equilibrium constants K_a for Cs and different rocks

Investigation	Kind of rock	Water composition mM	$K_a \cdot 10^4$ m		Particle diameter d_p mm	Comments	
Allard (1977a)	Granitic rock	see table	21		~ 0.1	Water 1 Water 2 $\vartheta = 25^\circ\text{C}$ $[\text{Cs}^+] = 10^{-5}\text{M}$ pH = 8	
		4.2 c	43				
Landström (1977)	Granitic gneiss	Ca	0.9	190	~ 0.1	pH = 8	
		Mg	0.4				
		Na	2.0				
		K	0.14				
		Cl	0.31				
		SO_4	0.15				
		HCO_3	3.8				
		SiO_2	0.23				
Vandergraaf 1976 a,b,c	White lake granite			A*	B*	~ 0.3	Room temp. pH = 5.7
		0	270	160			
		0	600	block			
		NaCl 12	200	18·18·3.8			
		NaCl 1.8	390				
		NaCl 2.0	350				
		CaCl ₂ 1.9	330				
		CaCl ₂ 0.9	350				
		0	800	490			
		NaCl 12	330	200			
		NaCl 1.8	800	490			
		NaCl 2.0	800	490			
		CaCl ₂ 0.9	800	490			
		CaCl ₂ 0.9	800	490			
		0	70	23			
NaCl 12	20	6.7					
NaCl 1.8	45	15					
NaCl 2.0	44	15					
CaCl ₂ 1.9	34	12					
CaCl ₂ 0.9	38	13					

A* = K_a from Vandergraaf's report

B = K_a recomputed for geometric surface of particles

Table 4.2 a continued

Investigation	Kind of rock	Water composition mM	$K_a \cdot 10^4$		Particle diameter d_p mm	Comments
			A*	B		
Vandergraaf 1976, c	Albite	0	A*	B	~ 0.3	Room temp
	Feldspar		200	46		
		NaCl 12	67	15		
		NaCl 1.8	110	25		
		NaCl 2.0	110	25		
		CaCl ₂ 1.9	110	25		
		CaCl ₂ 0.9	125	29		
		Hornblende				pH as above
		NaCl 12	51	15		
		NaCl 1.8	53	16		
		NaCl 2.0	53	16		
		CaCl ₂ 1.9	50	15		
	CaCl ₂ 0.9	53	16			
Rancon 1967	Calcium carbonate rock	"Natural water"	7100		> 0.3	pH 7.5

Table 4.2 b

Surface equilibrium constants K_a for Sr and different rocks

Investigation	Kind of rock	Water composition mM	$K_a \cdot 10^4$ m	Particle diameter d_p mm	Comments
Allard (1977a)	Granitic rock	See table 4.2.c	21 27	~ 0.1	Water 1 Water 2 $\vartheta = 25^\circ\text{C}$ pH= 8 [Sr]~ 10^{-5}M
Landström (1977)	Granitic gneiss	Ca 0.9 Mg 0.4 Na 2.0 K 0.14 Sr 0.02 Sn 0.03 Se 0.09 Nd 0.14 NH ₄ 0.25 Cl ⁻ 0.53 SO ₄ ⁻² 0.15 HCO ₃ ⁻ 3.8 SiO ₂ 0.23 NO ₂ ⁻ 0.42 Br ⁻ 0.25	5.1	~ 0.1	pH = 8 [Sr]= ~10 M
Vandergraaf (1977)	White lake granite	0 NaCl 13 mM NaCl 1.8 NaCl 2.0 CaCl ₂ 1.9 CaCl ₂ 0.9	670 240 500 450 90 140	block 18•18•4	Room temp pH = 5.5
Rancon 1967	Calcium carbonate rock	"Natural water"	50	Unknown	pH = 7.5

Table 4.2 c

Compositions of the two synthetic groundwaters proposed by Allard (1977a)

Ion	Water 1	Conc.	Water 2	
	mg/l	mM	mg/l	mM
Na	288	12.53	42	1.83
K	10	0.26	5	0.13
Mg	15	0.62	7.5	0.31
Ca	75	1.87	37.5	0.94
Cl	500	14.10	93	2.62
F	1.5	0.08	0.75	0.04
SO ₄	15	0.16	7.5	0.08
HCO ₃	207	3.28	100	1.64
Tot	1105	35.54 ¹⁾	293	8.92 ¹⁾

¹⁾ mekv/l

The surface equilibrium constants expressed as K_a -values decrease with increasing salt concentration in the water. It was attempted to make a comparison of the data from the different sources. It is seen that for Cesium and Strontium K_a 's differ by about a factor 10 between the different investigations, if the comparison is made at about the same total salt concentration in the water. This is not a large difference in view of the differences in rock and other experimental differences.

Landström (1977) has made measurements of water and nuclide transport in underground rock in Studsvik. He also made laboratory measurements of nuclide interaction with crushed rock. From the in situ data on water transport between the boreholes it was possible to determine a nominal channel width. With this and the laboratory data on K_a , a retention time for the travel of Sr in the rock was calculated. From this a retardation factor of about 3 was computed. This compares well with the factor 6 from the in situ measurements. The details of these computations are given in appendix 1.

This comparison is, however, based on some assumptions which have to be validated. For this further tests on underground rock should be made. Furthermore the adsorption mechanism - surface or volume reaction - should be clarified.

If the assumption can be validated, an indication of possible retardation effects have been computed and are given in Table 4.3 below. Allards (1977a) mass equilibrium data - K_d -values - were used. These were transformed to K_a -values by use of the geometric surface of the crushed rock in the experiments.

Table 4.3
Retardation of various nuclides in rock.

Nuclide	mass-equilibrium constant K_d $\frac{\text{cm}^3}{\text{g}}$	surface equilibrium constant $K_a = \frac{K_d}{a} \cdot \rho_p$ m^3/m^2	ion velocity u_i m/years	retardation factor $k_i = \frac{u_p}{u_i}$	time to travel 1 km $\frac{1000}{u_i}$ years/km	time to decay to 10^{-9} of original activity $30 T_{1/2}$ years
Sr ⁹⁰	8	$0.27 \cdot 10^{-3}$	1.1	27	910	900
Tc ⁹⁹	1	-	31	1	32	$2.1 \cdot 10^5$
I ¹²⁹	1	-	31	1	32	$2 \cdot 10^7$
Cs ¹³⁷	20-100	$0.7-3.4 \cdot 10^{-3}$	< 0.45	70-340	2220	900
R ²²⁶	100	$3.4 \cdot 10^{-3}$	0.09	340	11000	50000
Th ²²⁹	800	$30 \cdot 10^{-3}$	0.01	3000	100000	200000
Np ²³⁷	30	$1 \cdot 10^{-3}$	0.31	100	3000	$60 \cdot 10^6$
Pu ²⁴⁰	100	$3.4 \cdot 10^{-3}$	0.09	340	11000	200000
Pu ²³⁹	100	$3.4 \cdot 10^{-3}$	0.09	340	11000	750000
Am ²⁴¹	5000	$170 \cdot 10^{-3}$	0.0018	17000	550000	13700
Am ²⁴³	5000	$170 \cdot 10^{-3}$	0.0018	17000	550000	800000

$a \approx 70\,000 \text{ m}^2/\text{m}^3$ in crushed rock (from $a = \frac{6}{d_p}$)

From this it is seen that in rock with a mean fissure width $2b$ of $2 \cdot 10^{-5}$ m and a hydraulic gradient i of 0.003 it takes about 30 years for the water to travel 1 km. The permeability of such a rock would be 10^{-8} m/s if the fissure spacing is 0.7 m. Sr takes 910 years and this is sufficient for Sr to decay totally. Cs and Am^{241} also have time to decay totally. Am^{243} only decays to a certain extent. The other nuclides of importance will go through, but many of them will be considerably delayed.

The above analysis is based on a case where there is no dispersion. As the first part of the breakthrough front arrives at about 20 % of the mean breakthrough time Sr^{90} will not have time to decay in this first part.

Computed water and ion velocities in fissures in rock are shown in figure 4.5 with the surface equilibrium constant K_a as parameter. It is seen that when the fissure width decreases, the ion velocity decreases more than the water velocity. Figure 4.6 shows the relation of fissure width and permeability for fissures of equal size with the fissure spacing as parameter. The data in figures 4.5 and 4.6 have been determined with the aid of extended Snow model. The equations are given in appendix 1.

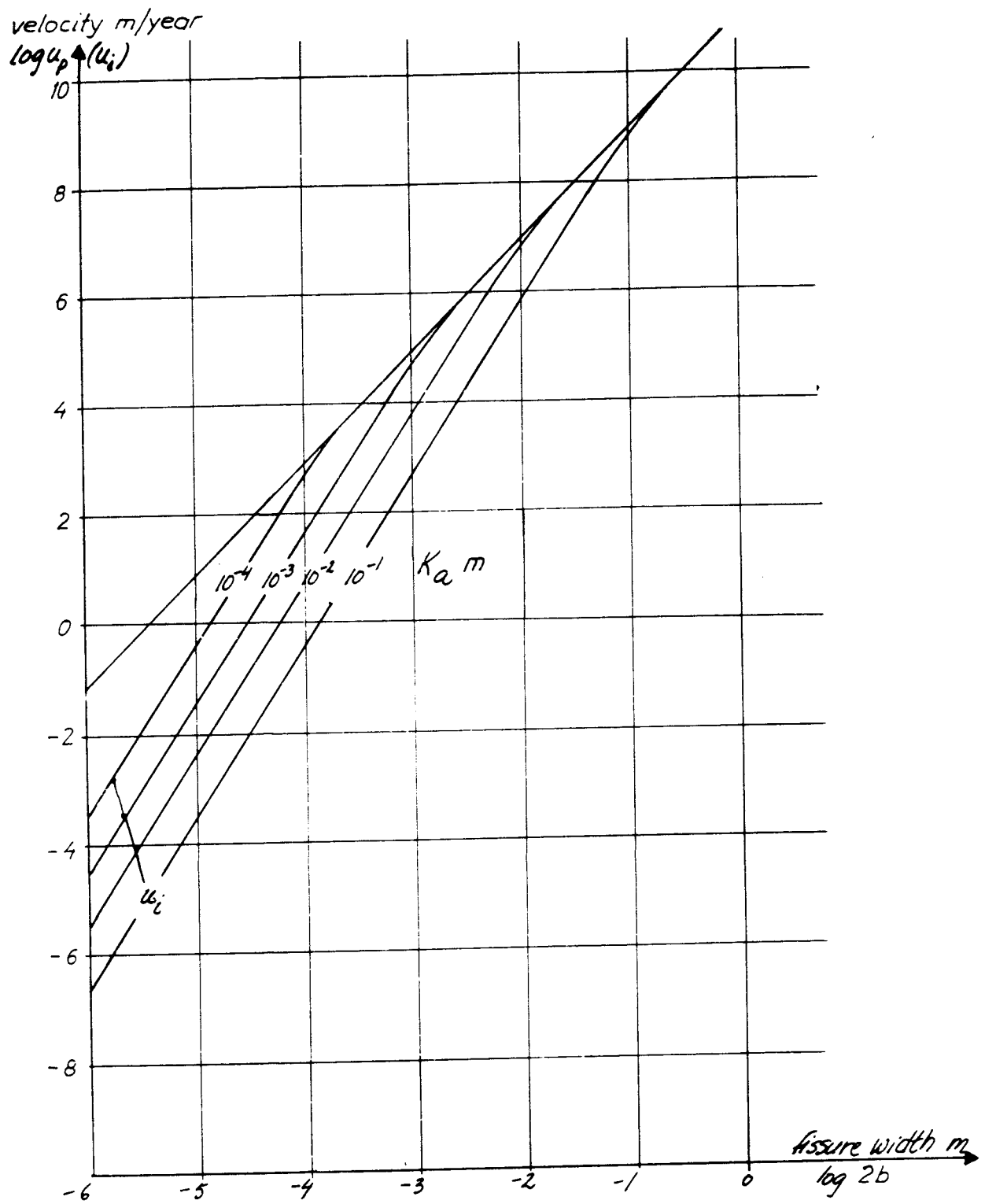


Fig. 4.5 Water and ion velocities in fissures as a function of the fissure width. Surface equilibrium constant as parameter. Based on $i = 0,003$ m/m:

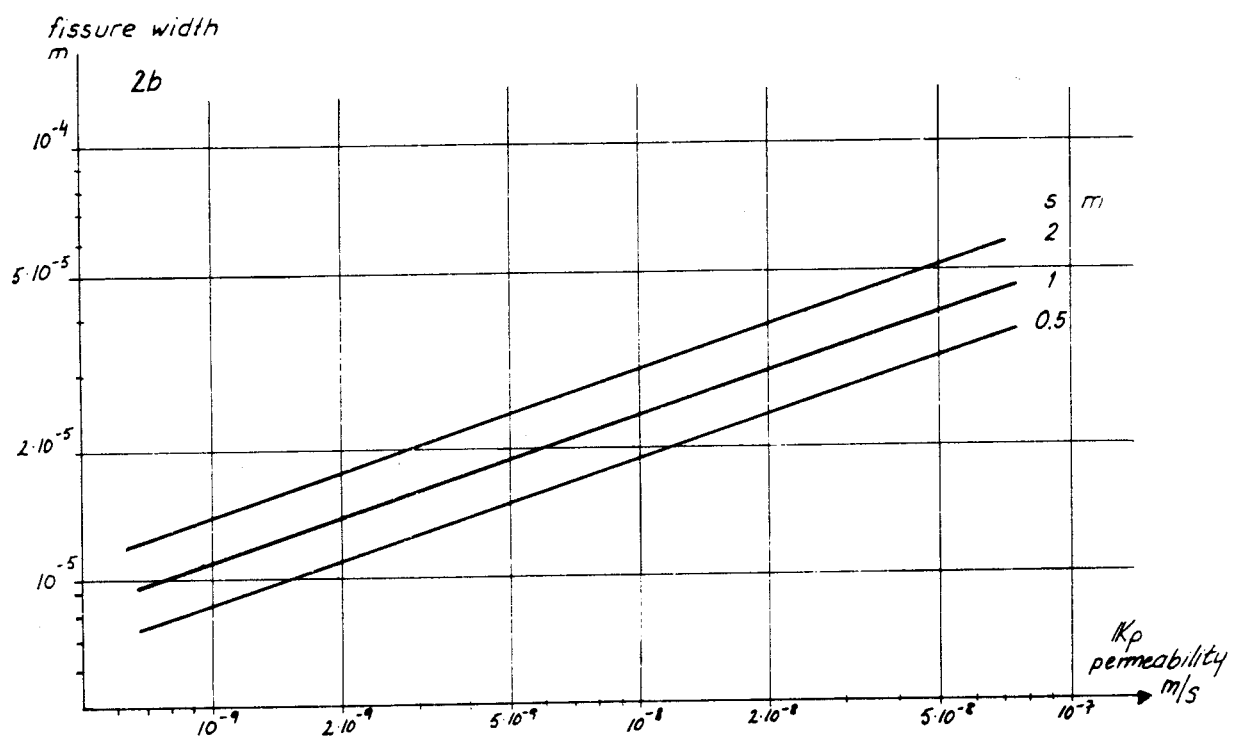


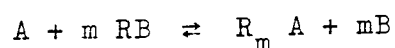
Fig. 4.6 The relation between permeability and fissure width for various fissure spacings, s

4.3 Ion exchange equilibria

4.3.1 Theoretical background

The ion exchange equilibrium is usually described by an equilibrium constant based on the law of mass action.

In the reaction



where m is the ratio of valences of the exchanging ions A and B , an equilibrium constant K_B^A is defined by

$$K_B^A = \frac{y_A}{x_A} \cdot \left(\frac{x_B}{y_B}\right)^m \left(\frac{Q}{C_0}\right)^{1-m}$$

y_A and x_A are the mole fractions of the ion A in the ion exchanger and in the water respectively. C_0 is the total concentration of cations in solution and Q is the total concentration of cations in the ion exchanger. For the exchange of an m -valent ion against a 1-valent, the ratio of the mole fractions in the exchanger and in the solution is given by

$$\frac{y_A}{x_A} = K_B^A \cdot \left(\frac{y_B}{x_B}\right)^m \left(\frac{Q}{C_0}\right)^{m-1}$$

In a multicomponent system where the ion N (1-valent) is abundant in the ion exchanger as well as in the solution, in comparison to the other ions of interest, the equilibrium for ion i may be written

$$\frac{y_i}{x_i} = K_N^i \left(\frac{y_N}{x_N}\right)^{m_i} \left(\frac{Q}{C_0}\right)^{m_i-1} \approx K_N^i \left(\frac{Q}{C_0}\right)^{m_i-1}$$

This is the low concentration case for the exchanging ion. It is applicable to most of the nuclides of interest except

in extreme and improbable cases with very fast solution of the fuel residue. The above expression tells us that for low concentrations of the incoming ions, these will not compete with each other. The equilibrium will be determined by the composition of the salt water and the equilibrium constant of each nuclide in the given surrounding. This expression also indicates that the total salt concentration C_0 is of great importance for multivalent ions.

The equilibrium constant K_N^i is influenced by many factors, the most important of these are: ion exchange material, pH, temperature, concentration of the exchanging ion and the concentration of other ions, positive as well as negative.

In principle it is possible to determine the compositions in an ion exchange system when data for all pairs of ions are known. In practice this is very difficult as the influence of all the mentioned factors on the binary equilibrium data are not sufficiently known. One factor which further complicates the use of literature data for computing equilibria in complex ground water systems, is that many of the nuclides of interest form complexes with the anions. The complexes will have different equilibrium constants from those of the naked ion. Very few data are available on ion exchange equilibria for complexes.

Provided the water composition is known, it is rather easy to measure an overall equilibrium constant which then includes the effects of complexing. Measurements are simplified by the fact that they need only be made at low concentrations of the nuclides. In most cases it will thus be better to measure

measurements than to try to use literature data only.

When the equilibrium constant is known the retardation factor k_i may be determined in a straightforward way.

$$k_i = \frac{q_i}{c_i} (1 - \epsilon_B) \rho_p = (1 - \epsilon_B) \rho_p \left(\frac{Q}{C_0}\right)^m \cdot K_N^i = \frac{u_0}{u_i}$$

ϵ_B denotes the porosity of the ion exchange bed and ρ_p the density of the ion exchange material proper. q_i and c_i are the concentrations in exchanger and in the water respectively. u_0 is the bulk velocity of water and u_i is the velocity of the ion.

4.3.2 Analysis of some data on ion exchange equilibria

Burkholder et al. (1970) give data on retardation factors for most of the interesting nuclides in "Western U.S. desert subsoil", Ames (1960), Amphlett (1956) and Mercer et al. (1963) give data on Cesium and Strontium equilibria with zeolites. Arnek (1977) in addition to Strontium and Cesium has measured equilibria for Europium in some natural and some synthetic zeolites. Ames and Mercer found that of the investigated zeolites the natural zeolite Clinoptilolite was most selective for Cesium, while the synthetic zeolites 4AXW and 13X were the best for Strontium. Arneks data are given in the table 4.4 below. The figures in the table are a relative measure of the equilibrium constant.

Of all the zeolites investigated only Analcime is really bad from the ion exchange point of view. It may be noted that the synthetic zeolite 13X is very much better than the others as regards Eu^{3+} . The same should also apply to the other 3-valent ions such as Am^{3+} in the spent fuel.

Table 4.4
Relative measures of equilibrium constant

Zeolite	Ion	Cs ⁺	Sr ²⁺	Eu ³⁺
Zeolite L(K ⁺)		5	10	-
Zeolite W(K ⁺)		50	10	1
Zeolite F		50	50	5
Mordenite		50	5	1
Phillipsite		50	5	1
Chabasite		50	10	5
Clinoptiliclite		50	10	5
13X		5	50	50
Erionite		50	10	1
Analcime		-	< 0.1	< 0.1

The ion exchangers were in the Na⁺ form originally except the zeolites L and W.

An attempt was made to compute the mass equilibrium constant K_d in a groundwater for some zeolites, using the available literature data. These and experimentally determined K_d values are given in the table 4.5 below. The details of these computations and the literature data used, are given in appendix 2.

Table 4.5

Comparison of measured and computed mass equilibrium values- K_d g/g.

	Cs ⁺		Sr ²⁺		Eu ³⁺	
	measured	Computed	measured	Computed	measured	computed
Clinoptiliclite	2200-5000	430	600-1400	19	1000-20000	3.5
Phillipsite	6800-11000	360	350-3700	150	1000-80000	3.5
Erionite	6200-1400	290	600-21000	200	900-43000	0.5-1.5
Phillipsite	220-21000	590	550-2400	220	930-94000	0.5-1.5

Groundwater composition I. See table 5.1.

The computed K_d -values are much lower than those experimentally found. For Cesium they differ by an order of magnitude, for Strontium the difference is not quite so large. The values for Europium are so different that any comparison seems meaningless. These results emphasize the difficulty in using binary data at low total salt concentrations for predicting equilibria at high salt concentrations.

4.3.3 The influence of anions on ion exchange equilibria

It is well known that many of the nuclides of interest form complexes with the anions present in the water. Sr^{2+} may for example form carbonate- and sulphate complexes. Uranium and Plutonium forms hydroxyl complexes which Americium also does. The complexed species will be larger and will have a lower charge. This will lead to a lower equilibrium constant. Computations of the relative amounts of the various species for the groundwater "1105" (see table 5.1) have been made by Allam (1977a) and are given in his report. These results indicate that about 1 % of the Sr^{2+} is complexed and that practically all Uranium is to be found as various complexes. This is quite in accordance with our experimental data on Uranium which has very small equilibrium constants.

The complexes may vary considerably with the composition of the groundwater. Many different investigators have found rather high equilibrium constants for Strontium and Cesium for various compositions of groundwater, which indicates that these species will retain good equilibrium constants. Uranium and probably Plutonium may have very low equilibrium constants when in the hexavalent form. Americium may also be influenced by complexing.

This indicates a need of further studies on the influence of complexing on the ion exchange equilibria.

5 Experimental work

Many natural and synthetic zeolites were considered. Due to the probable costs of synthetic zeolites we have omitted these and concentrated on the natural zeolites. Of the natural zeolites there are more than 50 which can be used. The choice of the natural zeolites was made by looking at the availabilities. If zeolites are to be used for the ion exchange barriers they will have to be available in the amount of 10-100 thousand tons. Furthermore they will have to be cheap. With these considerations we selected Clinoptilolite, Analcime, Phillipsite, Laumontite, Erionite, Mordenite and Chabasite. A further consideration in choosing zeolites is that they must be stable at elevated temperatures. Of these probably Clinoptilolite and Analcime are the most stable at high temperatures. They can be dehydrated at up to 700°C and will again take up water reversibly. The other zeolites break down at lower temperatures. The nuclides of interest are Cesium, Strontium, Europeum and Uranium. Cesium and Strontium are of interest in themselves, as they are the most dangerous of the nuclides. Europeum will simulate Americium and other three valent ions. Uranium may also give som information on Thorium and Plutonium. We have choosen to make the experiments in simulated ground waters. The composition of the ground waters has been suggested by Allard (1977a). The composition of the ground waters is given in table 5.1 below.

5.1 Equilibrium measurements

The equilibrium measurements are made by contacting a known amount of the zeolite with a known amount of "ground" water, shaking this for a sufficiently long time and measuring the resulting equilibrium. The zeolite was first equilibrated with "ground" water. The measurements have been performed by atomic

Table 5.1

Water compositions

Water	I	II	
	mg/l	mg/l	
Na	288	42	
K	10	5	pH = 8.2-8.3
Mg	15	7.5	
Ca	75	37.5	
Cl	500	93	
F	1.5	0.75	
SO ₄	15	7.5	
HCO ₃	200	100	
Total	1105	293	

absorption spectrophotometry for the ions Cesium and Strontium. Europium has been measured by radioactive methods and Uranium has been measured by light spectrophotometry. Equilibrium measurements have been performed at 20 and 70°C. The zeolites have been ground to particle diameters less than 0.1 mm. These measurements have needed at least one week before equilibrium was established. Even so it is doubtful if a real equilibrium has been reached. The results of these measurements are given in table 5.2 below.

The equilibrium data are given as K_d -values. The measurements have been performed with varying ratios of the amount of zeolite to water. The ratio has been varied by a factor of 100. The primary data of these measurements are given separately in appendix 3. From these data it may be seen that the equilibrium constants are higher for the ground water with a smaller total salt concentration. These are quite expected effects. The values for Uranium are very low. This is probably due to the fact that in the experiments we have oxidizing conditions and

Table 5.2

Measured mass equilibrium constants K_d g/g at 20°C (70°C)

Ion	Cs		Sr	
	I	II	I	II
Water				
Clinoptilolite	2200-5200 (1500-2400) 70°C	16000-40000	600-1400 (4600-6700) 70°C	2300-4000
Chabasite	6800-11000	16000-40000	350-3700	2500-50000
Erionite	6200-14000	11000-22000	600-21000	1500-50000
Mordenite	6900-11000	25000-44000	180-5600	520-15000
Phillipsite	2200-21000	22000-34000	550-2400	3500-15000
Ion	Eu		U	
	I	II	I	II
Water				
Clinoptilolite	1000-30000	4000-60000	0	-
Chabasite	1000-80000	700-110000	6.4	70-86
Erionite	960-43000	9500-110000	3-4	8-20
Mordenite	960-28000	1200-72000	-	5-20
Phillipsite	930-94000	370-120000	2	23-50

thus the Uranium is hexa valent. It will then be strongly complexed with carbonates and other negative ions. The European measurements show the same or nearly the same concentration in the equilibrium experiments. From this it can be concluded that the mechanism in these experiments was not an ion exchange mechanism only. The experiments indicate that there is a precipitation and the solubility has been measured.

Diffusion in particles

The measurement of the diffusivity in the particles is made by a technique very similar to that of the equilibrium measurements. Water

and crushed zeolite are mixed and stirred vigorously. The zeolite has been sieved to a known particle size. Samples are taken at various times and the ion concentration in the water is determined. A concentration time curve such as shown in figure 5.1 below is made. By comparing the experimentally obtained curve with theoretical curves which describe the diffusion in particles as a function of time and particle size, it is possible to determine the diffusivity. Theoretical diffusivity curves are given in Crank (1975). The diffusivity may be regarded as either a diffusion in the water in the pores of the material, or as a diffusion in the solid material itself. The former mechanism is called pore diffusion and the latter solid diffusion. In this case where the equilibrium is linear, pore diffusion and solid diffusion give the same

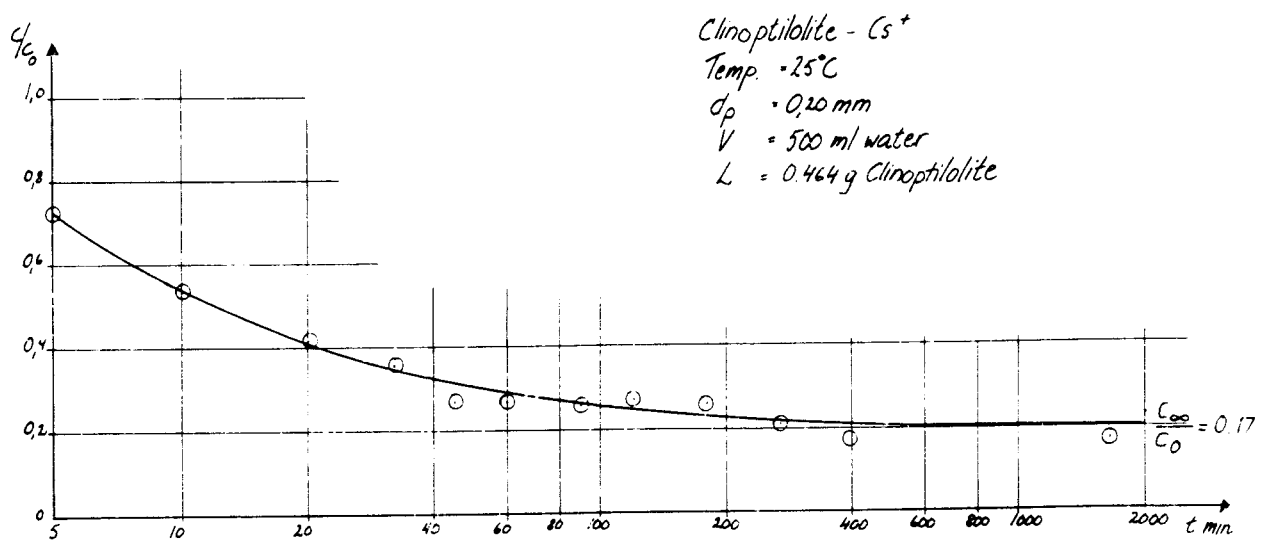


Fig. 5.1 Concentration - time curve for an experiment for determination of the particle diffusivity

shape of the concentration time curves, the difference being that the diffusivities differ by a factor equal to the equilibrium constant. In table 5.3 below the details for the diffusion experiments are given. The evaluated diffusivities are also given in the table. The diffusivities are so high, that the diffusion in the particles will not be a rate determining step under normal circumstances.

5.3 Diffusion in beds

The diffusion in a porous bed may be predicted with fair accuracy provided the diffusivity of the species in water is known. The mechanism of diffusion is a diffusion in the water in the pores between the particles. For the zeolite material which is ground to particles of about 0.1 mm only tortuosity effects and porosity are expected to influence the apparent bed diffusivity. For the clay/quartz material, however, the clay particles are so small that it must be considered if it is not possible that the ions are hindered by the small geometric sizes of the pores. To check this we performed a few experiments, first with zeolites to test the method for determining the diffusivity in a bed and then with the clay material which has been proposed by Pusch (1977). As the clay material will expand with great pressure when it is wetted, the casing for containing the bed had to be made strong. It consists of a teflon block with a cavity. In this cavity the bed is contained by a lid of a glass filter which is screwed on tight. The block is then placed in a glass vessel with a stirrer. The technique for determining the diffusivity in the bed is very similar to the technique described previously for determining the diffusivity in the particles. The bed is now a large one-sided particle. The details of the experiments together with the resulting diffusivities are given in table 5.4 below. The diffusivity for the bed with zeolites is

Table 5.3

Data for the particle diffusivity experiments with Clinoptilolite

Experiment nr	1	2	3	4	5	6
ion	Sr	Sr	Sr	Cs	Cs	Cs
c_o initial conc mg/l	4.7	4.7	4.7	9	9	9
ϑ temperature °C	25	70	70	25	70	70
d_p particle diameter mm	0.2	0.2	0.2	0.2	0.2	0.2
c_∞ equilibrium conc mg/l	0.38	0.15	0.05	0.17	0.29	0.29
K_d "- constant cm^3/g	2060	4600	6700	5260	2200	3280
$t_{1/2}$ half time s	7200	2220	522	510	516*	552*
D_p diffusivity m^2/s	$2.2 \cdot 10^{-12}$	$37 \cdot 10^{-12}$	$32 \cdot 10^{-12}$	$1.2 \cdot 10^{-10}$	$4.7 \cdot 10^{-10}$	$4.9 \cdot 10^{-10}$
L amount of material g	2.76	0.614	1.417	0.464	0.556	0.514
V "- water g	500	500	500	500	500	500

$$\rho_p \approx 1.2 \text{ g/cm}^3$$

* time to reach 70 % of equilibrium.

Table 5.4
Data for the bed diffusivity experiments

Experiment nr	1	2
Material	Clinoptilolite	Clay 10 %; quartz 90 %
ion	Sr ²⁺	Sr ²⁺
c_0 initial concentration	mg/l	5.0
ϑ temperature	°C	5.13
d_p particle diameter	mm	25
c_∞ equilibrium concentration	mg/l	0.04-0.07
K_d "- constant	cm ³ /g	0.091
$t_{1/2}$ half time	s	290
D_B^e diffusivity	m ² /s	2.76·10 ⁵
$\frac{V_p}{L \rho_v}$ amount of water to material	m ³ /m ³	1.1·10 ⁻¹⁰
z_0 bed depth	mm	1.3·10 ⁻¹⁰
		24.75
		14.2
		5
		5

quite what was expected. The diffusivity for the bed with the clay is of the same magnitude and it can thus be concluded that there are no spacial effects in the clay material from the diffusion point of view. In both cases the diffusion may be described as a pore diffusion.

In the above experiments the bed was chosen so deep, that the time determining mechanism is the diffusion in the bed and not diffusion in the particles. The criterion for this is given by Ruckenstein et al (1971).

$$\frac{D_p \epsilon_p}{r_o^2} > 100 \frac{D_b \epsilon_B}{z_o^2}$$

The experimental bed is shown in figure 5.2 below.

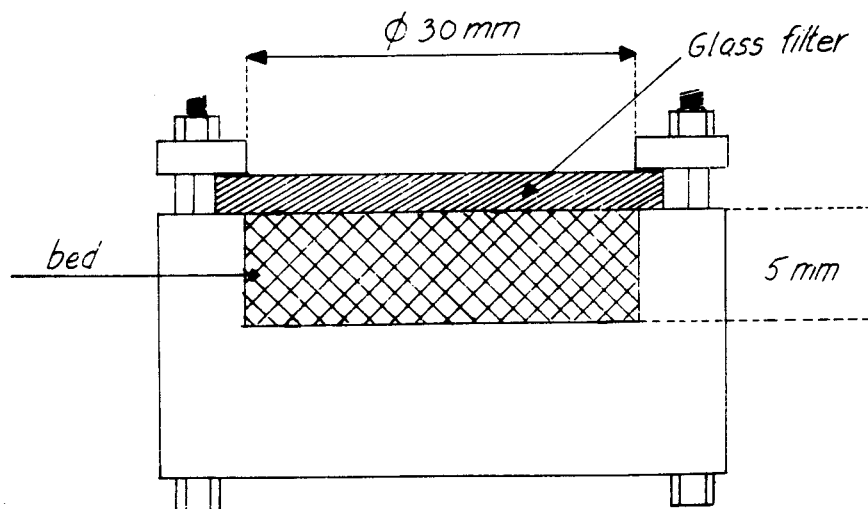


Fig. 5.2 Device for forming the bed in bed diffusivity experiments

The filling material has many duties, the main duty being to protect the capsule. A secondary duty is to retard any leaking radionuclides in their transport towards the surrounding rock and the flowing groundwater. The rock itself also acts as a safeguarding barrier. Besides the obvious positive effect of having a large distance from human activities, the rock protects the buried material mechanically and also by retarding many of the radionuclides by chemical interaction.

The filling material must be mechanically, thermally and chemically stable in the environment of the repository. There seems to be no doubt that the proposed clay/quartz mixture has sufficient mechanical and thermal stability. The same can be said of the zeolites. The chemical stability of these materials also seems to be very good. Many zeolites are formed under conditions similar to those to be expected in the repository.

Mechanical protection of the capsules from movements in the rock is discussed by Jakobson and Pusch (1977) in connection with clay and quartz. The quartz particles make this material very incompressible and rather strong stresses must be taken up by the capsule. If the quartz was exchanged for some porous, brittle material, this would compress under the stresses and the capsule would have to stand less stress. Many zeolites have a rather brittle structure and this property could be chosen to suit the needs of mechanical protection. The drawback of using zeolites instead of quartz is that zeolites may cement after a long time and thus not refill any crack which may have

formed in the filling material. Also zeolites have much lower heat conductivity. On the plus side however, the zeolites have a much higher ion exchange capability than the clay/quartz mixture. The zeolites are from 10 to more than 50 times better ion exchangers and thus will retard many of the radionuclides by this much longer time after a leak has occurred. The lower heat conductivity of the zeolites may be compensated for by diluting the radioactive material, which probably is expensive, or by wetting the zeolites with water. Zeolites as a filling material would increase the permeability as compared to the clay/quartz mixture and thus the water flow through the filling material. The increase in water flow will be very small if the holes of the repository can be oriented perpendicular to the hydraulic gradient. Due to this effect a crack in a cemented filling material will not give rise to a strong increase in water flow, if the rock itself is not seriously defaulted. For the short distance of a meter or less, which is considered for barrier thickness, the transport of matter due to flow is much less than the transport due to diffusion. A moderate increase in the water velocity will thus not increase the transport of nuclides or other reacting species. See 4.1.

The effects discussed above give no way of making a clearcut choice between the filling materials. At present more emphasis has been put on the clay/quartz partly due to the fact that more is known of this material and how to handle it. There are however some difficulties in handling the clay mixture which will not be present if zeolites are used. If no clay is mixed with the zeolites, these may be handled wet or dry and the silicose risk is totally eliminated as there is no quartz present. If clay is mixed with the zeolite, the mixture cannot

be wetted very much during handling, but it will have a lower permeability than zeolites only.

The main gain by using zeolites is that they have a very strong nuclide retarding effect. Using the clay/quartz mixture the barrier must be at least 3 times as thick as a zeolite barrier, to have same nuclide retarding effect, see 4.1. The zeolite barrier may be further improved by using mixtures of natural zeolites or even using some very selective synthetic zeolites. In the table below the thickness necessary to retard some nuclides 30 halflives is given for the clay and the Clinoptilolite alternatives.

It is evident that a 0.2 m clay barrier has practically no nuclide retarding effect, whereas a zeolite barrier this thick will stop Sr and Cs totally and probably also Am²⁴¹. It should be stressed that a doubling of the barrier depth will increase its efficiency by a factor four. The retarding effects is proportional to the square of depth in this diffusion controlled case. The data for Radium applies only to that Radium which starts its travel at the beginning of the

Table 6.1

Barrier depth in meters to retard some radionuclides
30 halflives.

Nuclide	10 % clay + 90 % quartz	clinoptilolite
Sr ⁹⁰	1	0.2
Cs ¹³⁷	1	0.1
Ra ²²⁶	40	1.5
Am ²⁴¹	1	0.1-0.7
Am ²⁴³	5	0.5-2.5

barrier and not that which is produced by decay in the barrier.

The barrier also has to protect the capsule from oxidizing agents, excess acidity or basicity and other agents which may seriously degrade the capsule materials. Of these species probably only metallic ions and some other cations will be retarded more by zeolites than by clay. The diffusion of noninteracting species has the same velocity in both barriers.

Costs of the natural zeolites are probably somewhat higher than for the clay-quartz mixture, but don't seem to be prohibitive.*

Zeolites as filling material form a good barrier for many of the important nuclides by their high ion retarding capability. They would form an additional independent barrier. The clay/quartz mixture has a lower permeability on the other hand. Flow does not seem to be important for the transport through the barrier however, as diffusion is the rate determining step, at the water velocities to be expected, see figure 4.2. This applies to ions as well as such oxidizing agents as oxygen.

With the present knowledge there is no clearcut choice between the clay/quartz mixture and the zeolites as a filling material. A risk analysis may give a better indication on the need for an ion exchange barrier.

6.2 The rock as a barrier for nuclide transport

The rock retards the transport of the nuclides in two ways. Due to the very low permeability of the rock, the water transport is very slow and it will take a very long time for the

* In 10 000 ton lots the f o b price is about \$ 100/ton, in 100 000 ton lots it is \$ 75/ton when ground to less than 100 mesh (< 0.1 mm). If bought in the form it is mined, the price is \$ 60/ton.

water to reach the ground level. The second effect is due to the interaction of many of the nuclides with the rock substance.

6.2.1 Water flow

Very little is published on the flow of water in rock at great depths. There are some data available for depths down to a few hundred meters. With these data it is possible to get only a very rough idea of how frequent the fissures are. Also a rough determination of the fissure widths may be made from the variation of the permeability. Nothing in these data is in direct contradiction to what could be extracted from the tracer runs in Studsvik. This however does not prove that the model used in describing the fissured rock is generally applicable. Much more data on actual water flow in rock must be collected and analysed before any firm conclusions may be drawn. The model used here may be a good starting point.

With this warning in mind, we may speculate somewhat on the consequences if the model and the data were applicable. The fissure width distribution obtained from the Studsvik runs indicate that the residence time distribution of the water is very wide. The first water will arrive at roughly one third or less of the time it takes for the mean to arrive. This may be also expressed in another way. If the permeability of the rock is measured and a mean velocity computed, some 5 % of the water will travel nearly three times as fast.

An attempt was made to determine the dispersion from the correlations valid for porous media of sand type. These expressions give dispersion values which are lower by more

than an order of magnitude. Moreover "normal" dispersion will not give so long a tail as was observed in the Studsvik runs. This also indicates that radial dispersion probably is not the same as in other porous media. If radial dispersion is as large as is indicated in the Studsvik runs, this may lead to a considerable dilution of the radionuclides. This may in some cases be advantageous.

6.2.2 Retardation of radionuclides in rock

Many of the nuclides interact with the rock. The mechanisms of interaction are unknown to a large extent. They include adsorption, ion exchange, precipitation, "irreversible" reaction and probably other mechanisms also. All these effects have been lumped into one overall parameter - the equilibrium "constant". It has been assumed that the wetted surface of the rock determines the amount of interaction. The equilibrium constant therefore is expressed as a surface equilibrium constant. Many experimental results reported in the literature support this, but there are some indications that at least some reactions may occur below the surface also. This is a point of importance, because if the volume of the rock may be utilized for the retarding reactions, very high retardation factors may be achieved if penetration times are sufficiently long. There should be plenty of time available for the nuclides to penetrate deep into the interior of the rock proper in the real repository.

Due to the surface reaction assumption, the dispersion of the retarded nuclides should be even larger than for water. From the analysis of the Studsvik runs it was seen that the first 5% of the nuclide arrives at about one fifth of the mean arrival of the nuclide. This means that the retardation factor is not fully utilized. On the other hand, for a surface

reaction mechanism, the retardation factor is inversely proportional to the fissure width. It may be expected that the fissures will become smaller the deeper the repository is. The nuclide velocity thus may become very small at large depths.

The rock may be an effective barrier for Cs¹³⁷ and Am²⁴¹. Many other nuclides including Sr⁹⁰ will also be considerably delayed.

6.3 Suggestions for further investigations

If zeolites are to be used as filling material, a detailed study should be made on Clinoptilolite, which at present seems to be the best choice. Detailed studies on the equilibria of Cs, Sr, Am, Ra, Pu, U and Th should be made. Special emphasis should be put on the complex formation in various probable water compositions. The reaction mechanisms should also be investigated more thoroughly.

The same kind of investigation could be of interest for the clay/quartz filling. This is interesting only if the barrier thickness of about one meter or more is considered.

The same type of investigation should be made on rock. In addition to this the possibility of reaction in depth should be cleared.

A good description of the fissures in rock should be made. This must be coupled to rather extensive experimental work, to confirm the model for ion retardation. In situ or simulated in situ runs are of great importance for such confirmation.

7 Notation

In some cases, other units have been used in the text than those indicated here. In such cases this has been clearly indicated.

a	specific surface	$\frac{\text{m}^2 \text{ particle}}{\text{m}^3 \text{ particle}}$
b	half width of channel	m
C_o	total concentration of ions in liquid	mol/m^3
c	concentration in liquid	$\text{kg}/\text{m}^3 \text{ liquid}$
c_o	feed concentration	"-
c_∞	equilibrium concentration	"-
D_B	diffusivity in bed	m^2/s
D_p	pore diffusivity in particle	"-
D_r	radial dispersion coefficient in bed	"-
D_x	axial dispersion coefficient in bed	"-
g	gravitational constant	m/s^2
i	hydraulic gradient	m/m
K	volume equilibrium constant	$\frac{\text{m}^3 \text{ liquid}}{\text{m}^3 \text{ particles}}$
K_a	surface equilibrium constant	$\frac{\text{m}^3 \text{ liquid}}{\text{m}^2 \text{ particle}}$
K_d	mass equilibrium constant	$\frac{\text{m}^3 \text{ liquid}}{\text{kg particles}}$
K_p	permeability	m/s
K_B^A	mass action equilibrium constant	-
k_i	retardation factor $\frac{u_o}{u_i}$	-
k_i^1	retardation factor $\frac{u_p}{u_i}$	-
L	mass of solid phase	kg
L_B	volume of bed $L_B = L/(1-\epsilon_B)/\rho_p$	$\text{m}^3 \text{ bed}$
Q_o	total concentration of ions in ion exchanger	mol/m^3
q	concentration in solid phase	$\text{kg}/\text{kg particle}$
q_B	"- bed $q_B = q_p(1-\epsilon_B) + c\epsilon_B$	$\text{kg}/\text{m}^3 \text{ bed}$

r_o	radius of particles	m
s	fissure spacing	m
$T_{1/2}$	half life of nuclide	s
t	time	s
\bar{t}	mean retention time	s
$t_{2\bar{b}}$	retention time in a fissure of width $2\bar{b}$	s
t_{K_p}	retention time computed from permeability measurements	s
$t_{1/2}$	time to reach halfway to equilibrium	s
u_i	velocity of ion "i"	m/s
u_o	bulk velocity	m/s
u_p	velocity in pores $u_p = u_o/\epsilon_B$	m/s
V	mass of liquid	kg
x_A	mole fraction in liquid	-
y_A	mole fraction in ion exchanger	-
z	depth in bed	m
z_o	"- of bed	m
ρ_p	particle density	kg/m ³
ϑ	temperature	°C
ϵ_B	bed porosity	-
ϵ_p	particle porosity	-
ν	viscosity	m ² /s
σ	standard deviation of fissure widths	m
θ_w	relative retention time of water $t/t_{2\bar{b}}$	-
θ_{w,K_p}	relative retention time of water t/t_{K_p}	-
θ_N	relative retention time of nuclide $\frac{t}{t_{2\bar{b}} k_i^1}$	-
θ_{N,K_p}	relative retention time of nuclide $\frac{t}{t_{K_p} k_i^1}$	-

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Flow and adsorption in fractured rock - Analysis of the
Studsvik experiments.

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Flow and adsorption in fractured rock - Analysis of the Studsvik experiments

An attempt has been made to interpret the in situ measurements made by Landström et al. at Studsvik 1977. A model based on the concept that the rock is fractured and that nuclides adsorb on the surfaces was made.

Water velocity

A very often used method for determining the water velocity in a porous medium is by use of the Darcy equation

$$u_p = \frac{K_p i}{\epsilon_B}$$

K_p is called the permeability, u_p is the mean velocity in the pores and ϵ_B is the porosity of the medium. This is a lumped parameter expression of the simplest kind. It gives no information on the velocity distribution or the retention time distribution. It thus will not be able to tell when the nuclide first arrives at a spot.

The very simple model which we have made is an extension of the Snow model. Snow (1968) assumed that the rock is divided into parallel slabs, leaving small flat channels between these. The velocity in such a channel may be determined from laminar flow theory.

$$u_p = \frac{g}{12\nu} \cdot (2b)^2 i$$

g is the gravitational constant, ν is the kinematic viscosity, $2b$ is the channel width and i is the hydraulic gradient. Given a spacing of the channels the porosity may be determined and also the permeability K_p . The equations are given in a separate table below.

Table A 1.1

Equations relating various factors for flow of a fluid
in fractured rock.

General relations

$$K_p = \frac{u_p \epsilon}{i} \quad \text{permeability}$$

$$u_o = u_p \epsilon \quad \text{bulk velocity}$$

$$k_i^1 = \frac{u_p}{u_i} = 1 + \frac{K}{\epsilon_B} (1 - \epsilon_B) \quad \text{retardation factor based on pore velocity}$$

$$k_i^1 = 1 + \frac{a K_a}{\epsilon_B} (1 - \epsilon_B)$$

$$k_i^1 = 1 + \frac{\rho K_d}{\epsilon_B} (1 - \epsilon_B)$$

$$k_i = \frac{u_o}{u_i} = k_i^1 \cdot \epsilon_B \quad \text{retardation factor based on bulk velocity}$$

Special relations for a rock with parallel fractures of equal width.

$$K_p = \frac{g}{12v} \epsilon_B^3 s^2$$

$$\epsilon_B = \frac{2b}{s} \quad \text{porosity}$$

$$a = \frac{2}{s} \quad \text{specific area}$$

$$u_p = \frac{g}{12v} (2b)^2 i \quad \text{fluid velocity in fracture}$$

$$u_i = \frac{g}{12v} \cdot \frac{(2b)^3}{2K_a} \cdot i \quad \text{ion velocity when } K_a \gg b$$

$$u_i = \frac{g}{12v} \cdot \frac{(2b)^3}{(2b+2K_a)} \cdot i$$

If the channels don't have the same widths, the velocities will be different in the various channels. As the flow rate in a channel is proportional to the cube of its width, the large channels will be very important for the transport of the nuclides. If the frequency of the channel widths is known, the residence time distribution may be computed. Conversely if the model really gives a good description of the fissured rock, the frequency of different fissures could be determined from residence time data. This would then give valuable information for determining the adsorption on the fissure walls.

The velocity of the nuclides

Those nuclides which interact with the wall will move slower than the water. The retardation factor k_{ij}^1 may be determined from the equilibrium constant and the channel width. If $\epsilon_B \ll 1$ which may be assumed for the rock

$$k_{ij}^1 = 1 + \frac{2K_{ai}}{2b_j} = \frac{u_{pj}}{u_{ij}}$$

K_{ai} is the surface equilibrium constant for nuclide "i"
 $2b_j$ is the channel width of channel "j". u_p and u_i are the water and nuclide velocities respectively. For readily adsorbing species or when $K_a > b_j$ the nuclide velocity can be written

$$u_{ij} = \frac{\epsilon}{12v} \frac{(2b_j)^3}{2K_a} \cdot i$$

The nuclide velocity is proportional to the cube of the channel width. If the frequency of the width of the fissures is known, the residence time distribution of the nuclides can be determined.

Analysis of the experiments in Studsvik

The Studsvik experiments were performed by giving a tracer pulse in one borehole and observing when and how the tracer arrived downstream in two other boreholes. The measurements were made at about 30 m below the water surface. The distances between the holes were 22 and 51 m respectively. The residence time distribution of the water was measured by using a tracer pulse of radioactive Br^{82} , Sr^{85} and some other nuclides were used to study the adsorption and retardation. Only the Sr data will be used here. Sr was retarded by about a factor 6 in both the 22 m and the 51 m paths.

In the receiving borehole in the 51 m path, there was a pump which kept the hole empty. This makes it difficult to interpret the data as the hydraulic gradient is not known with certainty.

Using the model described above, a normal distribution was assumed for the channel width. The mean width and the standard deviation were determined by fitting the experimental and the computed residence time distributions. The tracer response curves from the Studsvik runs are shown in figure A 1.1 below. The circles are experimental values and the curve is computed by use of the model.

Data for the experiments and the evaluated mean channel widths and their standard deviation are given in table A 1.2.

Table A 1.2

Pathlength	22 m
Mean residence time	35 h
Pore velocity	$1.75 \cdot 10^{-4}$ m/s
Hydraulic gradient	0.11 m/m
Mean pore width	0.063 mm
Standard deviation	0.021 mm

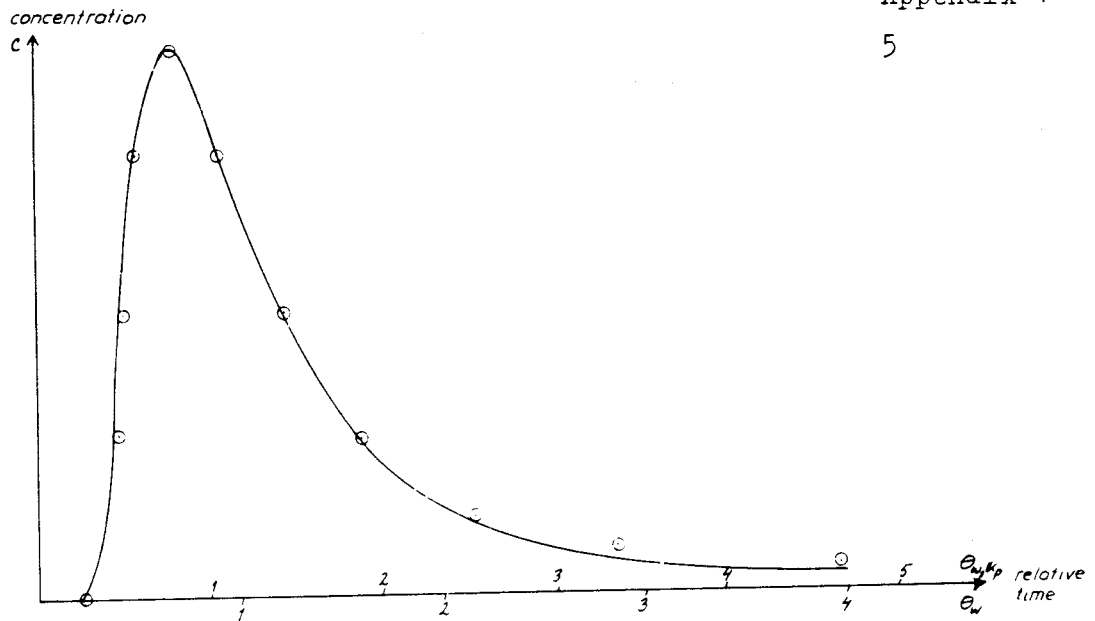


Fig. A.1.1 Comparison of theoretical and experimental retention time distributions for water

With these data the tracer response curve for a nuclide with a large retardation factor was computed. The results are shown in figure A 1.2. The computed and experimental results compare well as far as the shape of the curves is concerned. The measured and computed concentrations have been normalized at the peak. The measured concentration was somewhat lower than the computed. A more detailed comparison would be meaningless as the radial dispersion was considerable in the experiments. The model does not take this in account.

The relative times θ_{N, K_p} and θ_{W, K_p} in the figures are related to the time it would take if all channels had the same width.

This width is chosen such that it would give the permeability which could be measured. This fracture width is somewhat ($\sim 10\%$) larger than the mean width in the normal distribution. The relative times θ_N and θ_W are related to the time of travel in the channel of mean width in the normal distribution. The figure A 1.3 shows the breakthrough of a step input. 5% of the step concentration is reached already after 20% of the mean time expressed as $\theta_{N,K}$. At the mean time the concentration has reached about 80%^D of the input level.

The retardation factor of 6 which was determined from the comparison of Br and Sr tracer tests in the rock, also compares well with what can be determined from laboratory determinations on equilibrium constants. With the relation between the retardation factor and surface equilibrium constant, retardation factors of 6 and 3 were determined from the Allard (1977) and Landström data respectively. The specific surface

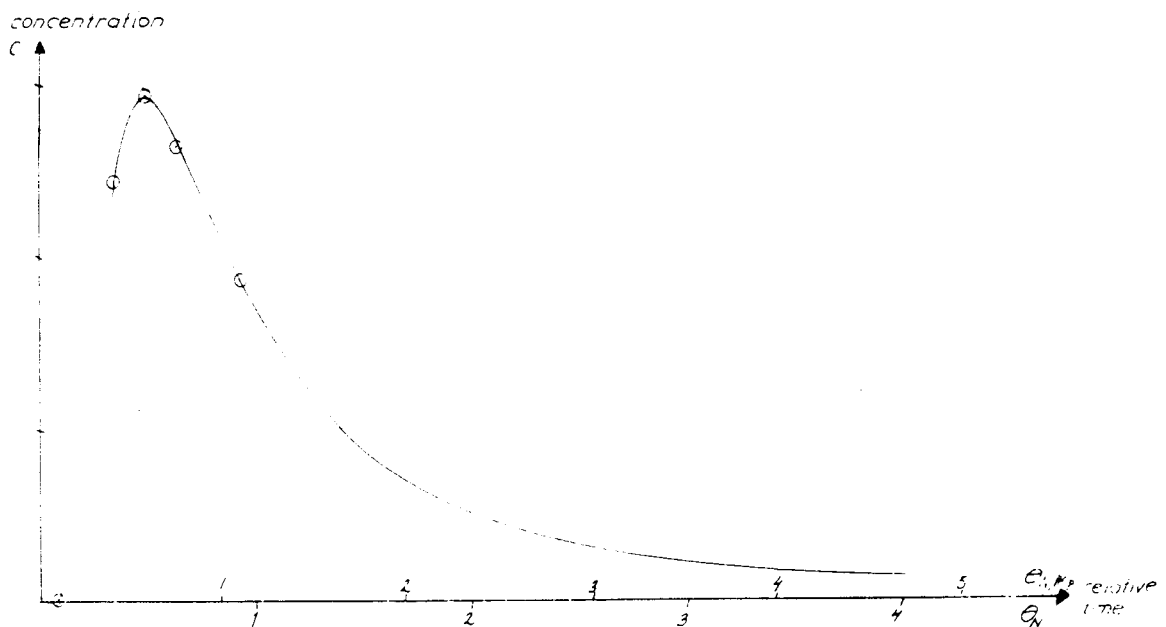


Fig. A.1.2 Comparison of theoretical and experimental retention time distributions for Strontium

of the crushed rock particles used for determining the K_a -values were computed by assuming that the particles are spheres and that the outer surface is the only active surface. The relation between K_d - and K_a -values is given below

$$K_a = \frac{\rho}{a} \cdot K_d$$

and

$$a = \frac{6}{d_p} \quad \text{for spherical particles}$$

The laboratory and in situ results compare well. The very limited in situ data available are not sufficient to confirm the validity of the model used in these comparisons, nor are the data sufficient to validate the use the geometric surface to describe the active adsorption surface.

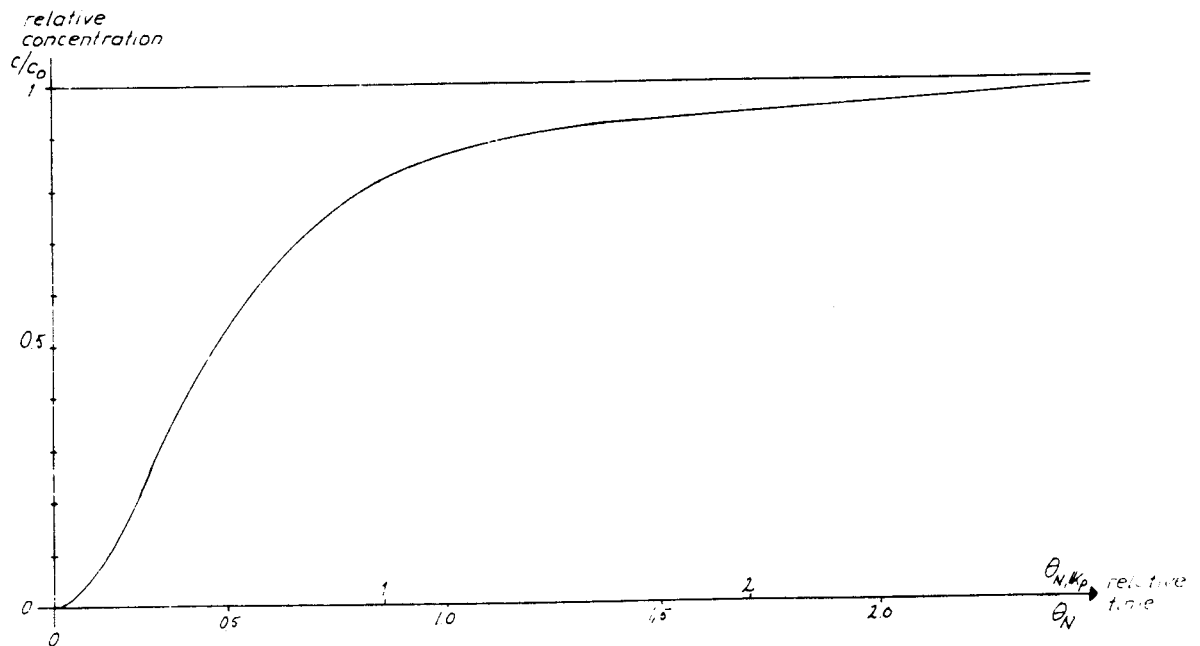


Fig. A.1.3 Breakthrough curve in rock for a nuclide with large retardation factor. Times are related to mean breakthrough times

The results indicate that it might be possible to use very simple laboratory measurements for determining equilibrium data for the rock. They also indicate that the model used for describing the fissures in the rock might be useful for predicting not only the mean breakthrough time but also the first arrival of the nuclides.

Due to the importance of this barrier and the fact that the early part of the breakthrough may arrive at about one fifth of the time of the mean, it is proposed that a further study is made. This should include the in situ or simulated in situ experiments of more nuclides and an attempt to correlate actual fissures in the rock to the breakthrough curve. It may also be worthwhile to make a more thorough study of the modelling of rock fissures. The above model indicates that there is no radial dispersion, which is not true. Radial dispersion may be much more important in rock than in other porous media of the sand type. A very simple calculation assuming a cube type structure of the rock indicated that if the cubes are oriented diagonally in relation to the hydraulic gradient, the radial and the axial dispersions are of the same magnitude. This would give a very strong and beneficial diluting effect.

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Computed equilibria of some zeolites regarding Cs, Sr and Eu

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- 1 Definitions of basic equations
- 2 Method of calculation
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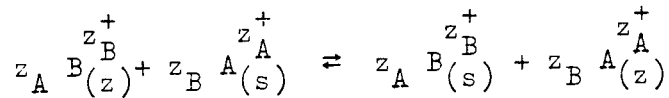
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1

Definitions of basic equations

The ion exchange process may be represented by the following equation:



z_A = charge of cation A

z_B = charge of cation B

Subscripts z and s refer to the zeolite and solution.

The selectivity coefficient is defined by the following relationship: (1)

$$k_B^A = \frac{(q_A/c_A)^{z_B}}{(q_B/c_B)^{z_A}} = \left(\frac{y_A}{x_A}\right)^{z_B} \left(\frac{x_B}{y_B}\right)^{z_A} \left(\frac{Q}{c_0}\right)^{z_B - z_A}$$

where

Q = total capacity of the ion exchanger

c_0 = total concentration in the solution

The thermodynamic equilibrium constant k_a is defined by: (2)

$$k_a = k_B^A \frac{\gamma_B^{z_A}}{\gamma_A^{z_B}} \cdot \frac{f_A^{z_B}(z)}{f_B^{z_A}(z)}$$

γ_A, γ_B = ionic activity coefficients of the ions in the solution

$f_A(z), f_B(z)$ = activity coefficients of A and B in the zeolite

The free energy of exchange ΔG^0 is given by: (2)

$$\Delta G^0 = - \frac{RT}{z_A z_B} \ln k_a.$$

The most commonly used selectivity coefficient in ion-exchange theory is however defined as:

$$(k_B^A)^I = \frac{(y_A/x_A)^{z_B}}{(y_B/x_B)^{z_A}}$$

where: $x_A = \frac{c_A}{c_o}$

$$y_A = q_A/Q$$

c_o = total concentration in the solution (meq/l)

c_A = concentration of A in the solution (meq/l)

Q = total capacity of the ion exchanger (meq/g zeolite)

q_A = amount of A in the ion exchanger (meq/g zeolite)

2 Method of calculation

- a) k_a is estimated from Breck's data (2) if experimental data is not available
- b) k_B^A -values for Strontium, Cesium, Europium for different types of zeolites are obtained from the Department of Inorganic chemistry (3)
- c) The method of calculation of multicomponent ion exchange is too lengthy to describe here and the reader is referred to references (4), (5) and author's quarterly reports.

3 Assumptions

3.1 Composition of ground-water

It is assumed that the ground water has the following composition: (7)

N_a^+	288	mg/l	F^-	1.5	mg/l
K^+	10	mg/l	Cl^-	500	mg/l
Mg^{2+}	15	mg/l	SO_4^{2-}	200	mg/l
Ca^{2+}	75	mg/l	HCO_3^-	200	mg/l

Total 1105 mg/l
pH \approx 8.2

3.2 Equilibrium data

It is assumed that all equilibrium data obtained from the Department of Inorganic chemistry are correct and the following equations

$$k_B^A = \left(\frac{y_A}{x_A}\right)^{z_B} \left(\frac{x_B}{y_B}\right)^{z_B} \left(\frac{Q}{c}\right)^{z_B - z_A}$$

or

$$\left(k_B^A\right)^I = k_B^A \left(\frac{c}{Q}\right)^{z_B - z_A}$$

are used to calculate $\left(k_B^A\right)^I$.

Furthermore k_B^A is also assumed to be constant.

These assumptions have been tested using the equilibrium data obtained from literature (8) and the data from the Department of Inorganic chemistry (3). The agreements between these equations and the experimental data are found to be good.

Another relationship is also used:

$$(k_B^A)^{z_C} (k_C^B)^{z_A} (k_A^C)^{z_B} = 1$$

for all zeolites.

4 Results of the calculation

The results of the calculation are shown on the following pages of this section.

Composition of ground-water and the selectivity coefficients of the different ions are given on pages 9 and 10.

4.1 Clinoptilolite ($Q_c = 2 \text{ meq/g}$)

Equilibrium data for Cesium, Strontium and Europeum. Equilibrium constants are obtained from the Department of Inorganic chemistry (3) and Breck (2) ("Zeolite Molecular Sieves").

a) Cesium:

$$\frac{q \text{ (meq/g)}}{c \text{ (meq/g solution)}} = 432.8$$

b) Strontium:

$$\frac{q \text{ (meq/g)}}{c \text{ (meq/g solution)}} = 18.9$$

c) Europeum:

$$\frac{q \text{ (meq/g)}}{c \text{ (meq/g solution)}} = 3.5$$

4.2 Chabazite

Capacity: $Q_c = 2.6 \text{ meq/g}$

Equilibrium data:

a) Cesium:

$$\frac{q \text{ (meq/g ion exchanger)}}{c \text{ (meq/g solution)}} = 359.2$$

b) Strontium:

$$\frac{q(\text{meq/g zeolite})}{c(\text{meq/g solution})} = 153.05$$

c) Europium:

$$\frac{q(\text{meq/g zeolite})}{c(\text{meq/g solution})} = 61.85$$

4.3 Erionite

Capacity $Q_c = 2.2$ meq/g zeolite

Equilibrium data:

a) Cesium:

$$\frac{q(\text{meq/g zeolite})}{c(\text{meq/g solution})} = 294.6$$

b) Strontium:

$$\frac{q(\text{meq/g zeolite})}{c(\text{meq/g solution})} = 196.0$$

c) Europium:

$$\frac{q(\text{meq/g zeolite})}{c(\text{meq/g solution})} = 0.0044$$

4.4 Phillipsite

Estimated capacity = 3 meq/g

Equilibrium data:

a) Cesium:

$$\frac{q(\text{meq/g zeolite})}{c(\text{meq/g solution})} = 586.5$$

b) Strontium:

$$\frac{q(\text{meq/g zeolite})}{c(\text{meq/g solution})} = 224.3$$

c) Europium:

$$\frac{q(\text{meq/g zeolite})}{c(\text{meq/g solution})} = 0.014$$

5 Equilibrium data used

It should be mentioned here that experimental data for Ca^{2+} and Mg^{2+} at the total concentration of 18 meq/l are usually not available. However these can be estimated from Breck's data at another level of concentration and the order of affinity.

a) Clinoptilolite $Q = 2 \text{ meq/g}$

Ion i	x_i	Selectivity coeffts $(k_{\text{Mg}^{2+}}^i)^I$	Source of data
Cs^+	0.01	150	Breck (2)
K^+	0.0144	66.67	Koon & Kaufman (9)
Na^+	0.6854	16.67	(estimated)
Sr^{2+}	0.01	2.7	Inorganic chemistry (3)
Ca^{2+}	0.21073	1.38	(estimated)
Mg^{2+}	0.06948	1.0	

also

$$(k_{\text{Na}^+}^{\text{Eu}^{3+}})^I = 0.0144 \quad \text{Inorganic chemistry (3)}$$

$(k_{\text{Mg}^{2+}}^i)^I$'s and $(k_{\text{Na}^+}^{\text{Eu}^{3+}})^I$ are calculated

at $C_o = 18 \text{ meq/l}$

b) Chabazite $Q = 2.6 \text{ meq/g}$

Ion	x_i	$(k_{\text{Na}^+}^i)^I$	Source of data
K^+	0.0144	14.85	Breck (2)
Cs^+	0.01	3.3	Inorganic chemistry (3)
Ca^{2+}	0.21073	1.9	Estimated
Sr^{2+}	0.01	1.865	Inorganic chemistry (3)
Mg^{2+}	0.06948	1.500	Estimated
Na^+	0.68540	1.0	

also

$$\left(\frac{k_{\text{Na}^+}^{\text{Eu}^{3+}}}{k_{\text{Na}^+}^{\text{Na}^+}} \right)^{\text{I}} = 0.035$$

Inorganic chemistry(3)

$\left(\frac{k_{\text{Na}^+}^{\text{i}}}{k_{\text{Na}^+}^{\text{Na}^+}} \right)^{\text{I}}$'s are calculated at $C_0 = 18 \text{ meq/g}$

c) Erionite:

$$Q = 2.2 \text{ meq/g}$$

Ion	x_i	$\left(\frac{k_{\text{Na}^+}^{\text{i}}}{k_{\text{Na}^+}^{\text{Na}^+}} \right)^{\text{I}}$	Source of data
K^+	0.0144	10.6	Breck's data (2)
Ca^{2+}	0.21073	4.5	Estimated
Sr^{2+}	0.01	4.406	Inorganic chemistry(3)
Mg^{2+}	0.06948	4.30	Estimated
Cs^+	0.01	4.0	Inorganic chemistry(3)
Na^+	0.6854	1.0	

also

$$\left(\frac{k_{\text{Na}^+}^{\text{Eu}^{3+}}}{k_{\text{Na}^+}^{\text{Na}^+}} \right)^{\text{I}} = 1.63 \cdot 10^{-4}$$

Inorganic chemistry(3)

d) Phillipsite

$$\text{Estimated capacity} = 3 \text{ meq/g}$$

Ion	x_i	$\left(\frac{k_{\text{Mg}^{2+}}^{\text{i}}}{k_{\text{Mg}^{2+}}^{\text{Mg}^{2+}}} \right)^{\text{I}}$	Source of data
K^+	0.0144	237.7	Breck (2)
Cs^+	0.01	22.85	Inorg. chem (3)
Sr^{2+}	0.01	6.17	Inorg. chem (3)
Ca^{2+}	0.21073	1.653	Estimated
Na^+	0.68539	1.43	Estimated
Mg^{2+}	0.6948	1.0	

also

$$\left(\frac{k_{\text{Na}^+}^{\text{Eu}^{3+}}}{k_{\text{Na}^+}^{\text{Na}^+}} \right)^{\text{I}} = 1.2 \cdot 10^{-4}$$

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Equilibrium measurements with various zeolites

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Equilibrium measurements with various zeolites

Tables

Cs^+ and the zeolites Clinoptilolite, Chabasite, Erionite,
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U and the zeolites Clinoptilolite, Chabasite, Erionite,
Mordenite, Phillipsite

Equilibrium measurements with various zeolites

These experiments were performed at the department of inorganic chemistry by Erik Lindgren and Bodil Steby during the summer 1977. The results are given in the attached tables. A condensed table of results is given in table 5.2 in the main report.

The zeolites Clinoptilolite, Chabasite, Mordenite, Erionite, Phillipsite were used. The zeolites were first equilibrated with the synthetic groundwaters. The necessary amount of water was determined by analysing the effluent from a fixed bed. The groundwaters I and II with total salt concentrations 1105 and 293 mg/l were used, see table 5.1 in the main report. Five different amounts of zeolite were used for each ion and water. (1.00, .30, .10, .03 and .01 g). The water volume used was 30 ml. Original concentrations of the ions were: Cs-14.7 mg/l, Sr-5.00 mg/l and U about 10 mg/l. The water-zeolite mixture was shaken for 7-8 days in a thermostated room. The temperature was kept at 20°C. The water was filtered and the solution was analysed in an atomic absorption spectrophotometer.

Uranium was analysed by a light spectrophotometric method.

Europium could not be measured by atomic absorption spectrophotometry as the solubility was much lower than expected. Radioactive measurements were used.

At the start of the experiments the Eu solution probably was supersaturated, but no precipitation could be observed. More than a week later a precipitation had formed. Because of this two different equilibrium constants have been calculated. One- K_a was determined using the original concentration 22090 counts/minute and 16709 counts/minute respectively. The second- K_b is based on the activity of the filtered

solution: 59830 counts/10 minutes and 85744 counts/10 minutes respectively.

A fast test with Clinoptilolite and filtered solution for two hours gave values which are similar to the K_b -values. This indicates that the carbonate is formed rather fast and that the K_b -values are the more correct.

To investigate the time necessary to reach equilibrium a test was run on the concentration in the solution after different times. The result of this test is shown in the figure below.

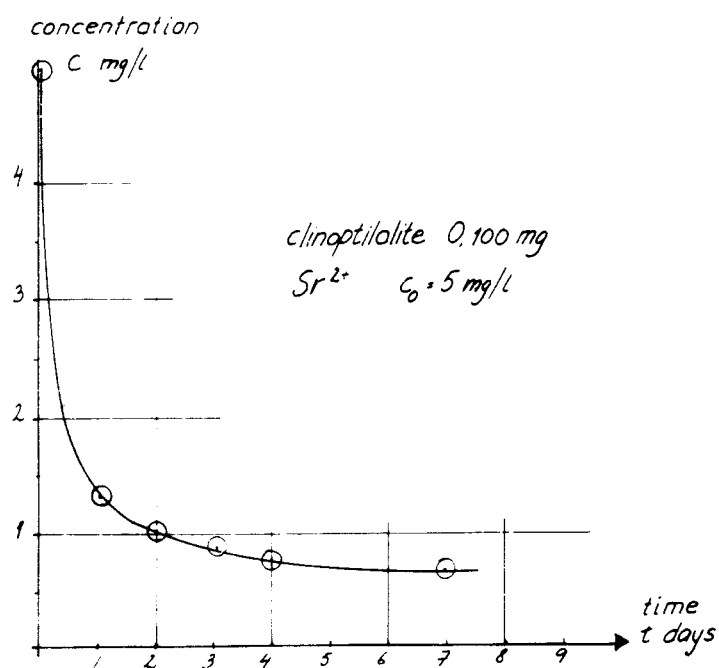


Fig. A.3.1 Concentration versus time in one equilibrium experiment

Results for Cesium

Experimental conditions

C₀ Cs⁺: 14,7 mg/l

Water : I = total salt content 1105 mg/l

II = "- 293 "-

Temp : 20°C

Time : 8 days

Volume: 30 ml

Ion exchanger: Clinoptilolite

Amount g	Final concentration (mg/l)	$\frac{\text{K}}{\text{mekv/g zeolite}}$ $\frac{\text{mekv/g solution}}{\text{mekv/g zeolite}}$
I	0.9999	2.2·10 ³
	0.3023	4.8·10 ³
	0.1008	5.2·10 ³
	0.0313	4.07·10 ³
	0.0093	5.09·10 ³
II	1.0004	> 4·10 ³
	0.3017	> 1·10 ⁴
	0.1008	> 4·10 ⁴
	0.0309	2.8·10 ⁴
	0.0104	1.64·10 ⁴

Cs⁺ - Chabasite

	Amount (g)	Final concentration (mg/l)	$\frac{\text{K}}{\text{mekv/g zeolite}}$ $\frac{\text{mekv/g solution}}$
I	1.0010	< 0.2	> $2.2 \cdot 10^3$
	0.2997	0.2	$7.2 \cdot 10^3$
	0.1022	0.4	$1.1 \cdot 10^4$
	0.0296	1.2	$1.14 \cdot 10^4$
	0.0103	4.4	$6.82 \cdot 10^3$
II	0.9995	< 0.1	> $4 \cdot 10^3$
	0.2997	< 0.1	> $1 \cdot 10^4$
	0.1017	< 0.1	> $4 \cdot 10^4$
	0.0319	0.5	$2.7 \cdot 10^4$
	0.0098	2.3	$1.65 \cdot 10^4$

Cs⁺ - Erionite

	Amount (g)	Final concentration (mg/l)	$\frac{\text{K}}{\text{mekv/g zeolite}}$ $\frac{\text{mekv/g solution}}$
I	0.9987	< 0.2	> $2.2 \cdot 10^3$
	0.3008	< 0.2	> $7.2 \cdot 10^3$
	0.1014	0.3	$1.4 \cdot 10^4$
	0.0320	1.3	$9.66 \cdot 10^3$
	0.0096	4.9	$6.25 \cdot 10^3$
II	0.9997	< 0.1	> $4 \cdot 10^3$
	0.3005	< 0.1	> $1 \cdot 10^4$
	0.0998	0.2	$2.2 \cdot 10^4$
	0.0297	0.8	$1.8 \cdot 10^4$
	0.0098	3.3	$1.06 \cdot 10^4$

Cs- Mordenite

	Amount (g)	Final concentration (mg/l)	K $\frac{\text{mekv/g zeolite}}{\text{mekv/g solution}}$
I	1.0016	< 0.2	$> 2.2 \cdot 10^3$
	0.2994	0.2	$7.3 \cdot 10^3$
	0.0997	0.4	$1.1 \cdot 10^4$
	0.0290	1.3	$1.07 \cdot 10^4$
	0.0092	4.7	$6.94 \cdot 10^3$
II	1.0009	< 0.1	$> 4 \cdot 10^3$
	0.3008	< 0.1	$> 1 \cdot 10^4$
	0.1006	0.1	$4.4 \cdot 10^4$
	0.0317	0.5	$2.7 \cdot 10^4$
	0.0098	1.6	$2.51 \cdot 10^4$

Cs- Phillipsite

	Amount (g)	Final concentration (mg/l)	K $\frac{\text{mekv/g zeolite}}{\text{mekv/g solution}}$
I	1.0003	0.2	$2.2 \cdot 10^3$
	0.2996	0.2	$7.3 \cdot 10^3$
	0.1031	0.2	$2.1 \cdot 10^4$
	0.0298	0.8	$1.7 \cdot 10^4$
	0.0109	3.0	$1.07 \cdot 10^4$
II	1.0002	< 0.1	$> 4 \cdot 10^3$
	0.2999	< 0.1	$> 1 \cdot 10^4$
	0.1007	0.2	$2.2 \cdot 10^4$
	0.0313	0.4	$3.4 \cdot 10^4$
	0.0092	1.3	$3.36 \cdot 10^4$

Sr- Chabazite

	Amount (g)	Final concentration (mg/l)	K $\frac{\text{mekv/g zeolite}}{\text{mekv/g solution}}$
I	1.0016	0.04	$3.7 \cdot 10^3$
	0.2998	0.37	$1.25 \cdot 10^3$
	0.1015	1.22	$9.16 \cdot 10^2$
	0.0297	3.22	$5.58 \cdot 10^2$
	0.0096	4.49	$3.55 \cdot 10^2$
II	1.0014	< 0.01	> $1.5 \cdot 10^4$
	0.2994	< 0.01	> $5.0 \cdot 10^4$
	0.0998	0.14	$1.04 \cdot 10^4$
	0.0301	1.00	$3.99 \cdot 10^3$
	0.0114	2.57	$2.488 \cdot 10^3$

Sr- Erionite

	Amount (g)	Final concentration (mg/l)	K $\frac{\text{mekv/g zeolite}}{\text{mekv/g solution}}$
I	1.0024	0.07	$2.1 \cdot 10^3$
	0.3004	0.40	$1.15 \cdot 10^3$
	0.1009	1.48	$7.07 \cdot 10^2$
	0.0326	2.83	$7.06 \cdot 10^2$
	0.0091	4.23	$6.00 \cdot 10^2$
II	1.0011	< 0.01	> $1.5 \cdot 10^4$
	0.2999	< 0.01	> $5.0 \cdot 10^4$
	0.1010	0.31	$4.49 \cdot 10^3$
	0.0300	1.69	$1.96 \cdot 10^3$
	0.0107	3.24	$1.523 \cdot 10^3$

Sr- Mordenite

	Amount (g)	Final concentration (mg/l)	K $\frac{\text{mekv/g zeolite}}{\text{mekv/g solution}}$
I	1.0018	0.08	$1.8 \cdot 10^3$
	0.3025	0.75	$5.62 \cdot 10^3$
	0.1020	2.35	$3.32 \cdot 10^2$
	0.0300	3.86	$2.95 \cdot 10^2$
	0.0109	4.69	$1.82 \cdot 10^2$
II	0.9995	0.01	$1.5 \cdot 10^4$
	0.3021	0.09	$5.4 \cdot 10^3$
	0.0989	1.06	$1.13 \cdot 10^3$
	0.0293	3.15	$6.01 \cdot 10^2$
	0.0104	4.24	$5.17 \cdot 10^2$

Sr- Phillinsite

	Amount (g)	Final concentration (mg/l)	K $\frac{\text{mekv/g zeolite}}{\text{mekv/g solution}}$
I	1.0003	0.10	$1.5 \cdot 10^3$
	0.3011	0.20	$2.4 \cdot 10^3$
	0.0999	1.02	$1.17 \cdot 10^3$
	0.0317	2.67	$2.26 \cdot 10^2$
	0.0111	4.15	$5.4 \cdot 10^2$
II	1.0000	< 0.01	> $1.5 \cdot 10^4$
	0.3033	0.08	$6.1 \cdot 10^3$
	0.1013	0.10	$1.4 \cdot 10^4$
	0.0335	0.60	$6.57 \cdot 10^3$
	0.0128	2.00	$3.52 \cdot 10^3$

Results for Europeum

Experimental conditions:

Activity at start I a) 30/6, not filtered , 22090/min
 Ib) 13/7, filtered , 59830/10 min
 IIa) 30/6, not filtered , 16709/min
 IIb) 13/7, filtered , 85744/10 min

Water I total salt concentration 1105 mg/l
 II "- 293 "-

Temp: 20°C

Time: 8 days

Volume : 30 ml

Eu- Clinoptilolite

	Amount (g)	Activity in solution (counts /10 min 3 ml)	K_a counts /min, [$\frac{g \text{ zeolite}}{\text{counts /min,}} $] g solution	K_b
I	1.0007	1683	$3.9 \cdot 10^3$	$1.0 \cdot 10^3$
	0.3021	2565	$8.4 \cdot 10^3$	$2.2 \cdot 10^3$
	0.1005	2572	$2.5 \cdot 10^4$	$6.6 \cdot 10^3$
	0.0333	2926	$6.7 \cdot 10^4$	$1.8 \cdot 10^4$
	0.0111	5103	$1.1 \cdot 10^5$	$2.9 \cdot 10^4$
II	0.3017	2202	$7.4 \cdot 10^3$	$3.8 \cdot 10^3$
	0.1024	2945	$1.6 \cdot 10^4$	$8.2 \cdot 10^3$
	0.0340	2868	$5.0 \cdot 10^4$	$2.5 \cdot 10^4$
	0.0124	3382	$1.2 \cdot 10^5$	$5.9 \cdot 10^4$

Eu- Chabazite

	Amount (g)	Activity in solution (counts /10 min, 3 ml)	K_a	K_b
I	1.0000	1666	$3.9 \cdot 10^3$	$1.0 \cdot 10^3$
	0.3019	1922	$1.1 \cdot 10^4$	$3.0 \cdot 10^3$
	0.1008	2089	$3.1 \cdot 10^4$	$8.2 \cdot 10^3$
	0.0294	2172	$1.0 \cdot 10^5$	$2.7 \cdot 10^4$
	0.0099	2173	$3.0 \cdot 10^5$	$8.0 \cdot 10^4$
II	1.0015	3417	$1.4 \cdot 10^3$	$7.2 \cdot 10^2$
	0.3015	2393	$6.8 \cdot 10^3$	$3.5 \cdot 10^3$
	0.1015	2300	$2.1 \cdot 10^4$	$1.1 \cdot 10^4$
	0.0302	1880	$8.7 \cdot 10^4$	$4.4 \cdot 10^4$
	0.0101	2183	$2.2 \cdot 10^5$	$1.1 \cdot 10^5$

Eu- Epidote

	Amount (g)	Activity in solution (counts/10 min 3 ml)	K_a	K_b
I	1.0027	1806	$3.6 \cdot 10^3$	$9.6 \cdot 10^2$
	0.3031	2000	$1.1 \cdot 10^4$	$2.9 \cdot 10^3$
	0.1001	1913	$3.4 \cdot 10^4$	$9.1 \cdot 10^3$
	0.0320	2202	$9.3 \cdot 10^4$	$2.4 \cdot 10^4$
	0.0105	3746	$1.6 \cdot 10^5$	$4.3 \cdot 10^4$
II	1.0030	2624	$1.9 \cdot 10^3$	$9.5 \cdot 10^2$
	0.2995	1816	$9.1 \cdot 10^3$	$4.6 \cdot 10^3$
	0.1021	1805	$2.7 \cdot 10^4$	$1.4 \cdot 10^4$
	0.0303	2510	$6.5 \cdot 10^4$	$3.3 \cdot 10^4$
	0.0102	2246	$2.2 \cdot 10^5$	$1.1 \cdot 10^5$

Eu- Mordenite

	Amount (g)	Activity in solution $\left(\frac{\text{counts}}{10 \text{ min}, 3 \text{ ml}}\right)$	K_a	K_b
I	1.0016	1805	$3.6 \cdot 10^3$	$9.6 \cdot 10^2$
	0.2998	2008	$1.1 \cdot 10^4$	$2.9 \cdot 10^3$
	0.1021	1919	$3.4 \cdot 10^4$	$8.9 \cdot 10^3$
	0.0294	2163	$1.0 \cdot 10^5$	$2.7 \cdot 10^4$
	0.0115	5066	$1.1 \cdot 10^5$	$2.8 \cdot 10^4$
II	1.0009	2153	$2.3 \cdot 10^3$	$1.2 \cdot 10^3$
	0.3026	5001	$3.2 \cdot 10^3$	$1.6 \cdot 10^3$
	0.1021	2025	$2.4 \cdot 10^4$	$1.2 \cdot 10^4$
	0.0294	2256	$7.4 \cdot 10^4$	$3.8 \cdot 10^4$
	0.0115	2979	$1.4 \cdot 10^5$	$7.2 \cdot 10^4$

Eu- Phillipsite

	Amount (g)	Activity in solution $\left(\frac{\text{counts}}{10 \text{ min}, 3 \text{ ml}}\right)$	K_a	K_b
I	0.9996	1862	$3.5 \cdot 10^3$	$9.3 \cdot 10^2$
	0.2997	2365	$9.2 \cdot 10^3$	$2.4 \cdot 10^3$
	0.0995	2035	$3.2 \cdot 10^4$	$8.6 \cdot 10^3$
	0.0325	2013	$1.0 \cdot 10^5$	$2.6 \cdot 10^4$
	0.0096	1931	$3.5 \cdot 10^5$	$9.4 \cdot 10^4$
II	1.0020	6483	$7.4 \cdot 10^2$	$3.7 \cdot 10^2$
	0.3016	2280	$7.2 \cdot 10^3$	$3.6 \cdot 10^3$
	0.1020	2624	$1.8 \cdot 10^4$	$9.3 \cdot 10^3$
	0.0320	2366	$6.5 \cdot 10^4$	$3.3 \cdot 10^4$
	0.0093	2298	$2.3 \cdot 10^5$	$1.2 \cdot 10^5$

Results from a fast test with a filtered solution

The Eu-solution was 14 days old. After filtration it had
the activity 37186 counts/10 min, 3 ml

Ion exchanger: Clinoptilolite

Water : I = total salt concentration 1105 mg/l

Time : 2 h

Temp : 20°C

Volume: 30 ml

Amount (g)	Activity in solution K $\left(\frac{\text{counts}}{10 \text{ min, } 3 \text{ ml}}\right)$	$\left[\frac{\text{counts/min, g zeolite}}{\text{counts/min, g solution}}\right]$
0.9985	3866	$2.6 \cdot 10^2$
0.1003	4955	$1.9 \cdot 10^3$
0.0090	13199	$6.0 \cdot 10^3$

Results for Uranium

Experimental conditions:

C U : 10 mg/l

Water I = total salt content 1105 mg/l

II = total salt content 293 mg/l

Temp: 20°C, Time: 8 days, Volume: 30 ml

		Amount (g)	Final concentration [mg/l]	K $\frac{\text{mekv/g zeolite}}{\text{mekv/g solution}}$	
Clinoptilolite I		1.0000	9.7	0	
		0.3008	10.0	-	
		0.1017	9.4	9.4	Within ana- lytical errors
		0.0300	9.7	0	
		0.0092	9.7	0	
II	1.0008	9.6	0.3		
	0.3002	9.6	1.0		
	0.1004	9.6	3.1	Within ana- lytical errors	
	0.0295	9.6	11		
	0.0098	9.5	64		
Chabazite I		1.0001	8.0	6.4	
		0.3001	9.7	0	
		0.1015	9.5	6.2	Within ana- lytical errors
		0.0292	9.7	0	
		0.0098	9.7	0	
II	1.0003	2.5	86.4		
	0.3008	5.7	70.0		
	0.1011	7.8	72.3		
	0.0307	9.1	64.4		
	0.0109	9.5	57.9		

		Amount (g)	Final concentration K [mg/l]	$\frac{\text{mekv/g zeolite}}{\text{mekv/g solution}}$
Erionite	I	1.0011	8.8	3.1
		0.3004	9.3	4.3
		0.0996	9.7	0
		0.0298	9.7	0
		0.0097	9.8	-
	II	1.0000	7.5	8.8
		0.3007	7.7	26
		0.0996	9.7	0
		0.0299	9.1	66
		0.0098	9.7	0
Mordenite	I	1.0011	9.6	0.3
		0.2995	9.5	2.1
		0.0998	9.7	0
		0.0302	9.4	32
		0.0097	9.7	0
	II	1.0003	8.2	5.5
		0.3001	9.0	7.8
		0.0997	9.0	23
		0.0303	9.3	43
		0.0102	9.3	123

		Amount (g)	Final concentration [mg/l]	K	
				$\frac{\text{mekv/g zeolite}}{\text{mekv/g solution}}$	
Phillipsite	I	0.9994	9.1	2.0	
		0.3001	9.4	3.2	
		0.1001	9.6	3.1	
		0.0309	9.7	0	
		0.0104	10	-	
	II	1.0011*	9.9*		
		0.2996	7.9	23	
		0.1007	8.3	50	
		0.0307	9.3	42	
		0.0109	9.3	120	
Blank	I	0	9.7		
	II	0	9.7		
orig. solution (~ 10 mg/l)	I	-	9.7		
	II	-	9.7		

* The original solution was yellow and as the analysis is made on a yellow complex this may have influenced the results.

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