TECHNICAL
REPORT

95-12

Literature survey of matrix diffusion theory and of experiments and data including natural analogues

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ERRATA

Please replace tables and pages in accordance with enclosed errata sheet.

Yours sincerely,

Birgitta Hörnfeldt

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Errata

SKB TR-95-12 " Literature survey of matrix diffusion theory and of experiments and data including natural analogues" by Yvonne Ohlsson and Ivars Neretnieks

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Due to an error in Microsoft Word version 6.0 for Macintosh, resulting in incorrect conversion from Microsoft Excel, the exponents formatted as scientific notation are reduced by one. Please replace the tables 5.2, 5.6, 5.7, 5.8, 5.9, 5.11, 5.12, 5.13, 5.14, 5.15, 5.16, 5.17, in SKB-TR-95-12 (Literature survey of matrix diffusion theory and of experiments and data including natural analogues) with the ones enclosed.

It should be noted that the same error occurs in the following versions of Microsoft Word:

- Microsoft Word for Windows, versions 6.0, 6.0a, and 6.0c
- Microsoft Word for Windows NT, versions 6.0
- Microsoft Word for the Macintosh, versions 6.0, and 6.0.1
- Microsoft Word for Windows 95, versions 7.0

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p. 39 Ch. 5.1.1.1, line 8: "D_e-values in the range $(1.7\text{-}220)\cdot 10^{-12}$" should be "$D_e$-values in the range $(1.7\text{-}220)\cdot 10^{-14}$"

p.46 Ch. 5.1.2.2, line 12: " D_e-values were $1.9\cdot 10^{-16}$ - $4.4\cdot 10^{-14}$ for granites and $5.0\cdot 10^{-17}$ - $1.9\cdot 10^{-14}$ m^2/s for gneiss." should be " D_e-values were $5.0\cdot 10^{-17}$ - $4.4\cdot 10^{-14}$ for granites and $5.0\cdot 10^{-16}$ - $2.0\cdot 10^{-14}$ m^2/s for gneiss."

Eq. 3.8: q_s should be q_n

Eq. 2.28 and 2.29: The resistivity denoted R should be denoted R_l. This also applies to the text in Ch. 2.1.6.

Ch. 3.2.2, eq. 3.8: The radius of the sphere, R, should be denoted R_{sph}.

Also enclosed:

p. 6 - 7 (Ch. 2.1.4)
p.82-83 (Notations)

where D_a is the apparent diffusion coefficient, which takes into account the effect of retardation and α is the capacity factor ($\alpha=\varepsilon+\rho K_d$), which measures the capacity of the porous material to transport and store the diffusing species.

The retardation in the rock matrix is sometimes expressed with the retardation coefficient, R, which is sometimes defined as

$$R = \frac{\varepsilon + \rho K_d}{\varepsilon_t} \qquad (2.10)$$

R is a measure of the extent of retardation and has a value that ranges from unity to very large values, depending on the degree of sorption. The expression for Fick's law diffusion of sorbing species can also be expressed in a more general manner, allowing for non-linear sorption as well:

$$\frac{\partial}{\partial t}\left(\varepsilon C_p + \rho C_r\right) = D_p \varepsilon_t \frac{\partial^2 C_p}{\partial x^2} \qquad (2.11)$$

where C_r is the number of moles of solute in the solid phase per unit mass of porous medium. Instantaneous sorption is assumed. We illustrate the case for a Freundlich isotherm:

$$C_r = K C_p^{\beta} \qquad (2.12)$$

where K and β are constants, and β is the Freundlich exponent. The distribution ratio, K_d, is defined as the ratio of C_r to C_p and is then given by:

$$K_d = \frac{C_r}{C_p} = K C_p^{\beta-1} \qquad (2.13)$$

Combining the equations results in:

$$\frac{\partial C_p}{\partial t}\left(\varepsilon + \rho K\ \beta C_p{}^{\beta-1}\right) = \frac{\partial C_p}{\partial t}\left(\varepsilon + \rho K_d \beta\right) = D_e \frac{\partial^2 C_p}{\partial x^2} \qquad (2.14)$$

and rearranging equation (2.14):

$$\Rightarrow \qquad \frac{\partial C_p}{\partial t} = \frac{D_e}{\left(\varepsilon + \rho K_d \beta\right)} \cdot \frac{\partial^2 C_p}{\partial x^2} = \frac{D_e}{\alpha} \frac{\partial^2 C_p}{\partial x^2} \qquad (2.15)$$

where in this case α is equal to $\varepsilon + \rho K_d \beta$. If sorption is linear then β is equal to 1 and K_d is independent of concentration. The expression then turns into equation (2.8) again.

2.1.5 Surface Diffusion

If transport can take place in the sorbed but mobile phase the flow rate in the adsorbed phase will be:

$$N_S = -D_S \varepsilon_S \frac{\partial C_S}{\partial x} \qquad (2.16)$$

As sorption is fast, equilibrium is assumed to exist between C_s and C_p. ε_s is the hypothetical volume fraction of water at the pore surfaces where the "sorbed" ions are concentrated. The equilibrium relation is:

$$\varepsilon_s C_s = \rho K_d C_p \qquad (2.17)$$

then the total transport rate under steady state will be the sum of the pore diffusion and surface diffusion transport:

Rock	*Water*	*Cond*	*Conc [NaCl]* (*M*)	D_e (m^2/s)	D_a (m^2/s)	ε (%)	D_e/D_a (%)	*Ref*
Gneiss	Synthetic "Hästholmen"		0.0044	9.60E-14				Lehikoinen 1992
Gneiss			0.7	8.50E-14				
Gneiss			1	7.60E-14				
Tonalite	Allard	Aerobic		2.3-7.0 E-13	5.3-17 E-11		0.2-1	Puukko 1993
Tonalite	Romuvaara	Aerobic		1.4-1.5 E-12	1.1 E-10		1.3	
Tonalite	Allard	Anaerobic		4.5-17 E-13				
Tonalite	Romuvaara	Anaerobic		3.4-22 E-13				
Granite	Allard	Aerobic		1.5-6.9 E-13	3.3-9.1 E-11		0.8-1.1	
Granite	Romuvaara	Aerobic		2.6-4.5 E-13				
Granite	Allard	Anaerobic		2.3-7.2 E-13				
Granite	Romuvaara	Anaerobic		1.4-11 E-13				
Gneiss	Allard	Aerobic		1.7-27 E-14	7.8-550 E-12		0.05-0.45	
Gneiss	Olkiluoto	Aerobic		3.2 E-13	2.3 E-10		0.14	
Gneiss	Allard	Anaerobic		6.2-50 E-14				
Gneiss	Olkiluoto	Anaerobic		1.2-2.0 E-13	1.4-30 E-11		0.07-0.84	
Finnsjön Granite	Synthetic GW			1.80E-13		0.18-0.91		Skagius 1986
Finnsjön Granite	Distilled water			1.30E-13		0.18-0.91		
Mäntsälä plutonic rock	Allard			5.40E-13	3.20E-10	0.20	0.17	Kaukonen 1993
Mäntsälä plutonic rock	Allard			9.40E-14	2.58E-11	0.20	0.36	
Syyry plutonic rock	Syyry Ground water			5.80E-14	3.48E-11	0.26-0.43	0.17	
Syyry plutonic rock	Syyry Ground water			5.70E-14	5.17E-11	0.26-0.43	0.11	
Syyry plutonic rock	Syyry Ground water			9.10E-14	3.92E-11	0.26-0.43	0.23	
Sodankylä vulcanite	Allard			6.35E-13	2.05E-10	0.27	0.31	
Sodankylä vulcanite	Allard			2.68E-13	1.08E-10	0.27	0.25	
Sodankylä vulcanite	Allard			3.67E-13	1.20E-10	0.27	0.31	

Table 5.2 Literature data, tritiated water

Rock	*Water*	D_e (m^2/s)	ε (%)	α (%)	F_f	*Ref*	*comments*
Granite		4.03E-14	3.4			Eriksen 1985	Disc thickness: 0.14 cm
Granite		2.94E-14	2.4				Disc thickness: 0.21 cm
Granite		2.94E-14	2.3				Disc thickness: 0.28 cm
Finnsjön granite	Distilled water with [Uranine]=9.9 g/l	2.30E-15	0.06			Skagius, Neretnieks 1983	
Gabbro		<4.0e-16					
Gabbro		<2.8e-16					
Finnsjön granite	Distilled water with [Uranine]=10 g/l	2.20E-15	0.06	0.02	5.00E-06	Skagius, Neretnieks 1985	
		5.30E-15	0.09-0.21	0.02	1.20E-05		
Migmatite Studsvik		2.30E-14	0.18-0.22	0.22	5.10E-05		
Granite Gideå		1.30E-14	0.15-0.17	0.11	2.90E-05		
		1.30E-14	0.16-0.19	0.12	2.90E-05		
Gneiss Gideå		3.20E-15	0.11-0.12	0.11	7.10E-06		
Gneiss Svartberget		9.30E-15	0.08-0.12	0.07	2.07E-05		
		9.60E-15	0.08-0.11	0.07	2.13E-05		
Migmatite granite		6.90E-14	0.22-0.33	0.30	1.53E-04		
		5.20E-14	0.30-0.38	0.94	1.16E-04		
biotite gneiss (from Svartboberget)		7.80E-14	0.30-0.38	0.52	1.73E-04		
		6.00E-14	0.23-0.32	0.62	1.33E-04		
Biotite gneiss (From Fjällveden)		3.60E-15	0.17-0.24	0.02	8.00E-06		
		3.90E-15	0.19-0.24	0.04	9.00E-06		

Table 5.6 Literature data, uranin

Rock	*Water*	*Cond*	*Contact time (days)*	*Conc (M)*	*D_a (m^2/s)*	*Ref*	*Comments*
Finnsjön granite	Synthetic		355	1.00E-08	2.30E-14	Ittner 1988	Am-241, rock tablets 2x2x2 cm
Finnsjön granite	Synthetic		263	1.00E-08	2.80E-14		
Finnsjön granite	Synthetic	pH=8.4	877	1.00E-09	3.90E-16		
Studsvik granite	Synthetic		85	1.00E-08	7.10E-16		
Stripa granite	Synthetic	pH=8.6	665	1.00E-09	1.00E-15		
Stripa granite	Synthetic	pH=8.9	1202	1.00E-09	3.80E-15		

Table 5.7 Literature data, americium

Rock	*Water*	*Cond*	*Tc-conc (M)*	*Contact time*	*D_a (m^2/s)*	*Ref*	*comments*
Rapakivi granite	granitic gw	oxic	6.20E-06	1/2 y	7.90E-15	Suksi et al 1989	Tc-99 as NH_4TcO_4
Rapakivi granite		oxic	6.20E-06	1 y	2.30E-13		
Rapakivi granite		anoxic	7.70E-06	1/2 y	2.30E-14		
Rapakivi granite		anoxic	7.70E-06	1 y	2.40E-15		
Tonalite	granitic gw	oxic	6.20E-06	1/2 y	6.00E-14		
Tonalite		oxic	6.20E-06	1 y	1.80E-15		
Tonalite		anoxic	7.70E-06	1/2 y	1.70E-14		
Tonalite		anoxic	7.70E-06	1 y	2.30E-15		
Finnsjön granite	Synthetic	oxic	1.00E-06	349d	3.00E-13	Ittner et al 1988	TcO_4^-
Finnsjön granite				349d	1.90E-14		
Finnsjön granite				85d	4.50E-14		
Finnsjön granite				167d	1.10E-13		
Finnsjön granite				349d	2.20E-14		
Studsvik granite				167d	2.20E-14		
Stripa granite				257d	2.05E-13		
Stripa granite				167d	2.20E-14		
Finnsjön granite	Synthetic	oxic	<1.00E-6	85d	1.50E-12	Torstenfelt et al 1982	TcO_4^-

Table 5.14 Literature data, technetium

Rock	*Water*	*Cond*	*U-conc (M)*	*Cont. time*	*D_a (m^2/s)*	*Ref*	*comments*
Rapakivi granite	granitic gw	oxic	4.20E-06	1 y	5.20E-14	Suksi 1989	U-233 as $UO_2(NO_3)_2$
Rapakivi granite	granitic gw	anoxic	4.30E-06	1/2 y	4.20E-14		
Rapakivi granite	bentonite gw	anoxic	4.00E-06	1/2 y	1.80E-14		
Rapakivi granite	granitic gw	anoxic	4.30E-06	1 y	1.30E-14		
Rapakivi granite	bentonite gw	anoxic	4.00E-06	1 y	2.00E-14		
Porphyritic granite	granitic gw	oxic	4.20E-06	1 y	5.70E-14		
Granodiorite	granitic gw	oxic	4.20E-06	1/2 y	3.60E-14		
Tonalite	granitic gw	anoxic	4.30E-06	1 y	1.10E-14		
Tonalite	bentonite gw	anoxic	4.00E-06	1 y	5.30E-14		

Table 5.15 Literature data, uranium

Rock	*Water*	*Cond*	*Conc (M)*	*Contact time*	D_a (m^2/s)	*Ref*	*comments*
Finnsjön granite	synthetic	aerobic	1.00E-09	854d	1.60E-15	Ittner 1988	Pu-239
Stripa granite	synthetic	aerobic	1.00E-09	858d	1.20E-15		
Stripa granite	synthetic	aerobic	1.00E-09	646d	1.50E-15		
Rapakivi granite	granitic gw	oxic	1.80E-14	1 y	2.40E-14	Suksi 1989	Pu-236 as $Pu(NO_3)_4$
Rapakivi granite	granitic gw	anoxic	4.70E-14	1 y	2.70E-15		
Porphyritic granite	granitic gw	oxic	1.80E-14	1 y	4.10E-15		
Granodiorite	granitic gw	oxic	1.80E-14	1 y	2.70E-15		
Tonalite	granitic gw	oxic	1.80E-14	1/2 y	1.10E-14		
Tonalite	granitic gw	oxic	1.80E-14	1 y	5.40E-15		
Tonalite	granitic gw	anoxic	4.70E-14	1 y	3.50E-15		

Table 5.16 Literature data, plutonium

Rock	*Water*	*Cond*	*Conc (M)*	D_e (m^2/s)	ε (%)	*Ref*	*Comments*
Inada granite	0.1M KCl	pH=4, 25°C	0.1	1.90E-13	0.7	Yamaguchi 1993	Ba(+2),
				2.10E-13			multi-tracer test,
				2.50E-13			$D_{(bulk)}$=8.48E-10 m^2/s
				2.90E-13			
				3.00E-13			
				3.50E-13			
Inada granite	0.1M KCl	pH=4, 25°C	0.1	3.00E-13	0.7	Yamaguchi 1993	Be(+2),
							$D_{(bulk)}$=5.85E-10 m^2/s
				3.30E-13			multi-tracer test
Inada granite	0.1M KCl	pH=4, 25°C	0.1	1.90E-13	0.7	Yamaguchi 1993	Mg+2
				1.90E-13			$D_{(bulk)}$=7.05E-10 m^2/s
				2.30E-13			multi-tracer test
				2.40E-13			
				2.90E-13			
				3.00E-13			
				3.30E-13			
				3.60E-13			

Table 5.17 Literature data, barium, beryllium, magnesium

Rock	*Water*	*Cond*	*Cont. time*	*Conc (M)*	D_e (m^2/s)	D_a (m^2/s)	*e* (%)	*Ref*	*Comments*
Inada granite	Deionized water	30°C, pH4.2				8.00E-14	0.8	Idemitsu et al 1991	D_{fa}= 2.00E-11
		30°C, pH6.1				4.00E-14			8.00E-12
		30°C, pH7.6				8.00E-14			2.00E-11
		30°C, pH9.3				8.00E-14			2.00E-11
Inada granite	0.1M KCl	pH=4, 25°C			1.60E-13		0.7	Yamaguchi et al 1993	$D_{(bulk)}$ =6.99E-10 m^2/s
					2.10E-13				
					2.20E-13				
					2.50E-13				
					2.60E-13				
					3.10E-13				
					3.40E-13				
					3.50E-13				
Tonalite	synthetic G W, ion strength 0.0085		6 m	7.60E-10	1.20E-14	5.40E-17		Pinnioija 1985	D.c.c
			12 m	7.10E-09		4.80E-16		Muuronen 1985	D.c.c
			12 m	3.50E-09		8.30E-16		Suksi 1987	N.f.s. unfilled
			6 m	3.50E-09		1.11E-14		Suksi 1987	N.f.s. filled
mica gneiss	synthetic G W, ion strength 0.0085		12 m	7.10E-09		8.50E-17		Suksi 1987	D.c.c
			12 m	3.50E-09		7.50E-16		Suksi 1987	N.f.s. unfilled
Rapakivi granite	synthetic G W, ion strength 0.0085		12 m	7.10E-09		5.00E-16		Suksi 1987	D.c.c
			6 m	3.50E-09		3.90E-16		Suksi 1987	N.f.s. unfilled
			12 m	3.50E-09		9.60E-16		Suksi 1987	N.f.s. unfilled
			6 m	3.50E-09		1.85E-15		Suksi 1987	N.f.s. filled
			12 m	3.50E-09		7.50E-16		Suksi 1987	N.f.s. filled

D.c.c = drill core cup, N.f.s = natural fissure surface

Table 5.8 Literature data, cobalt

Rock	*Water*	*Condition*	*Cs conc (M)*	*D_e (m^2/s)*	*D_a (m^2/s)*	*ε (%)*	*Ref*	*Comments*
Tonalite	Allard	Aerobic			(1.7-5.7)E-14		Puukko et al 1993	
	Romuvaara	Aerobic			(5.6-17)E-14			
Granite	Allard	Aerobic			(6.5-1800)E-15			
	Romuvaara	Aerobic			2.60E-14			
Gneiss	Allard	Aerobic			(3.1-6.7)E-15			
	Olkiluoto	Aerobic			2.60E-15			
Mäntsälä plutonic rock	Allard				1.15E-14		Kaukonen et al 1993	D_a values were derived from diffusion profiles.
Mäntsälä plutonic rock	Allard				4.70E-15			
Syyry plutonic rock	Syyry Ground water				1.68E-14			
Syyry plutonic rock	Syyry Ground water				2.72E-14			
Sodankylä vulcanite	Allard				1.90E-14			
Sodankylä vulcanite	Allard				2.08E-14			
Inada granite	Deionized water	30°C, pH4.3			3.00E-14	0.8	Idemitsu et al 1992	D_{fa}=1.00E-11 m^2/s
		30°C, pH6.0			6.00E-14	0.8		1.00E-11
		30°C, pH7.7			5.00E-14	0.8		1.00E-11
		30°C, pH9.4			5.00E-14	0.8		1.00E-11
		40°C, pH4.2			5.00E-14	0.8		1.50E-11
		56°C, pH4.2			7.00E-14	0.8		3.00E-11
Finnsjön granite	Synthetic				5.00E-12		Ittner et al 1988	Cs-137
Finnsjön granite					1.20E-13			
Finnsjön granite					2.20E-13			
Finnsjön granite					8.30E-14			
Finnsjön granite					1.40E-13			
Studsvik granite	Synthetic				5.90E-14			
Studsvik granite					3.50E-14			
Studsvik granite					1.10E-13			
Stripa granite	Synthetic				1.80E-13			
Stripa granite					2.40E-14			
Stripa granite					3.40E-14			
Stripa granite					2.50E-14			

Table 5.9 Literature data, cesium

Rock	*Water*	*Cond*	*Cs-conc (M)*	D_e *(m^2/s)*	D_a *(m^2/s)*	ε *(%)*	*Ref*	*Comments*
Finnsjön granite	Synthetic Allard			8.50E-13		0.3-0.5	Skagius et al 1982	0.100-0.120 mm*
Finnsjön granite				2.80E-12				0.200-0.250 mm
Finnsjön granite				3.80E-12				0.375-0.43 mm
Finnsjön granite				3.70E-11				1.0-1.5 mm
Finnsjön granite				1.20E-11				2.0-3.0 mm
Finnsjön granite				1.60E-11				4.0-5.0 mm
Stripa granite				2.90E-13				0.100-0.120 mm
Stripa granite				9.80E-13				4.0-5.0 mm
Tonalite	synthetic G W, ion strength 0.0085	3 m cont.time			2.00E-15		Suksi 1987	D.c.c, Cs-134
		6 m			1.50E-15			D.c.c
		12 m			7.20E-15			D.c.c
Rapakivi granite		6 m			3.40E-14			D.c.c
mica gneiss		12 m			4.70E-16			D.c.c
Tonalite		12 m	5.00E-07		3.70E-15			N.f.s. unfilled
		3 m	5.00E-07		3.20E-14			N.f.s. filled
		12 m	5.00E-07		1.00E-15			N.f.s. filled
Mica gneiss		12 m	5.00E-07		3.30E-15			N.f.s. unfilled
		12 m	5.00E-07		3.80E-15			N.f.s. filled
Rapakivi granite		12 m	5.00E-07		1.2E-15			N.f.s. unfilled
		3 m	5.00E-07		2.70E-14			N.f.s. filled
		12 m	5.00E-07		1.20E-15			N.f.s. filled
Finnsjö granite	Synthetic GW**	132 d cont. time			2.10E-13		Torstenfelt (1982)	Cs-137,
Studsvik granite		132 d			7.90E-14			
Stripa granite		132 d			9.50E-14			
Stripa granite		85 d			3.10E-13			Ref sample, polished
Finnsjö granite	Synthetic GW**				1.30E-13		Torstenfelt (1983)	Cs-137,
Studsvik granite					1.70E-13			
Stripa granite					5.30E-14			
Stripa granite					5.80E-14			Ref sample, polished

* Particle size fraction

** Synthetic groundwater representative of the waters at the sampling locations

Table 5.9 Literature data, cesium

Rock	*Water*	*Cont. time*	Cs-*Conc (M)*	D_e (m^2/s)	D_a (m^2/s)	ε *(%)*	K_d (m^3/kg)	β	*Ref*	*Comments*
Darley Dale sandstone	Simulated GW		1.9E-5	4.50E-11		10	44±3	1	Smith 1990	Linear sorpt. model
				2.31E-11			1.29±0.06	0.550		non-linear model
				2.57E-11			3.4±3.4	0.705		non-linear model
				4.60E-11			40±10	1.00		non-linear model
Stripa granite				1.00E-12			1.1	0.66	Skagius 1986	granite pieces
				1.00E-12			3.9	0.66	Skagius 1982	granite particles
Finnsjö granite				1.60E-12			9.8	0.54	Skagius 1986	granite pieces
				1.60E-11			30	0.54	Skagius 1982	granite particles
Finnsjö granite				1.00E-12			6.1	0.54	Skagius 1986	Granite pieces, simultaneous sorption (Cs, Sr)
Finnsjö granite		132 d		2.70E-10	2.10E-13		0.49		Torstenfelt 1982	Cs-137
Studsvik granite		132 d		2.30E-10	7.90E-14		1.11			
Stripa granite		132 d		3.80E-10	9.50E-14		0.15			
Stripa granite		85 d		1.20E-10	3.10E-13		0.15			Ref sample, polished

Table 5.9 Literature data, cesium

Rock	*Water*	*Cond*	*Cont. time*	*Ni-Conc (M)*	D_e *(m^2/s)*	D_a *(m^2/s)*	ε *(%)*	*Ref*	*Comments*
Inada granite	0.1M KCl	pH=4, 25°C		0.1	1.9E-13		0.7	Yamaguchi 1993	$D_{(bulk)}$ =6.79E-10, multi component experiment
					2.0E-13				
					2.4E-13				
					2.5E-13				
					2.9E-13				
					3.0E-13				
					3.4E-13				
					3.6E-13				
Rapakivi granite	synthetic G W, ion strength 0.0085		12 m			1.60E-16		Suksi 1987	D.c.c
Tonalite			6 m			8.60E-16			N.f.s. filled
Tonalite			12 m			4.00E-16			N.f.s. filled
Rapakivi granite			12 m			3.40E-16			N.f.s. unfilled
Rapakivi granite			6 m			1.39E-15			N.f.s. filled
Rapakivi granite			12 m			4.10E-16			N.f.s. filled

Table 5.11 Literature data, nickel

Rock	*Water*	*Cond*	*Np-Conc (M)*	*Cont. time*	*D_e (m^2/s)*	*D_a (m^2/s)*	*Ref*	*comments*
Tonalite	Allard	Aerobic	(1.8-3.6)E-10		1.80E-14		Puukko et al 1993	
Tonalite	Allard	Aerobic	(1.8-3.6)E-10		2.50E-14	1.90E-12		
Tonalite	Romuvaara	Aerobic	(1.8-3.6)E-10		4.60E-14	2.80E-12		
Tonalite	Allard	Anaerobic	(1.8-3.6)E-10		7.70E-15			
Rapakivi granite	Allard	anoxic	7.80E-05	1/2 y		9.60E-14	Suksi et al 1989	Np-237 as $Np(NO_3)_5$
Rapakivi granite		anoxic	7.80E-05	1 y		1.40E-14		
Porphyritic granite		oxic	6.70E-05	1 y		3.00E-13		
Tonalite		oxic	6.70E-05	1/2 y		4.30E-14		
Tonalite		oxic	6.70E-05	1 y		2.70E-14		
Tonalite		anoxic	7.80E-05	1 y		2.10E-14		
Finnsjön granite	Synthetic GW*		1.00E-08	866 d		3.30E-15	Ittner et al 1988	Np-237
Stripa granite			1.00E-08	654 d		4.10E-15		

*Synthetic groundwater representative of the groundwaters from the sampling locations

Table 5.12 Literature data, neptunium

Rock	*Water*	*Cond*	*Conc (M)*	*D_e (m^2/s)*	*D_a (m^2/s)*	*ε %*	*α*	*Ref*	*Comments*
Inada granite	Deionized water	30°C, pH4.3			4.00E-14	0.8		Idemitsu 1991	D_{fa}=1.00E-11
		30°C, pH6.0			4.00E-14				4.00E-12
		30°C, pH7.7			5.00E-14				1.00E-11
		30°C, pH9.4			4.00E-14				1.00E-11
Inada granite	0.1M KCl	pH=4, 25°C	0.1M $Sr(NO_3)_2$	2.00E-13		0.7	0.019	Yamaguchi 1993	$D_{(bulk)}$ =7.94E-10
				2.10E-13			0.002		$D_{(bulk)}$ =7.94E-10
				2.60E-13			0.022		$D_{(bulk)}$ =7.94E-10
				2.60E-13			0.003		$D_{(bulk)}$ =7.94E-10
				3.10E-13			0.019		$D_{(bulk)}$ =7.94E-10
				3.60E-13			0.014		$D_{(bulk)}$ =7.94E-10
	Deionized water	pH5.5, 25°C	0.1M $Sr(NO_3)_2$	3.20E-12			2.4		
				9.50E-12			1.5		
				1.70E-11			1.7		
Darley Dale sandstone	Distilled water			1.40E-10		10	51	Bradbury 1986*	
				1.20E-10		10	59		
Cenomanian sample	Ground water	pH=7.0		1.10E-10		8.1	7	Lang 1986*	
Anhydrite	Simulated ground water			1.30E-12		0.5	0.5	Bradbury 1986*	
				1.30E-12		0.5	0.8		
Upper magnesian limestone	Simulated ground water			7.40E-12		22	1.3	Bradbury 1986*	
				5.90E-12		22	1.3		
Biotite gneiss	Distilled water			1.00E-13		0.2	0.12	Skagius 1988*	
Finnsjön granite				4.50E-13				Skagius 1982	0.100-0.120 mm**
Finnsjön granite				1.60E-12					0.200-0.250
Finnsjön granite				3.50E-12					0.375-0.43
Finnsjön granite				4.40E-12					1.0-1.5
Finnsjön granite				1.10E-11					2.0-3.0
Finnsjön granite				2.40E-11					4.0-5.0
Stripa granite				1.10E-14					0.100-0.120
Stripa granite				1.00E-12					4.0-5.0

Table 5.13 Literature data, strontium

Rock	*Water*	*Cond*	*Conc (M)*	*D_e (m^2/s)*	*D_a (m^2/s)*	*ε (%)*	*α*	*Ref*	*Comments*
Stripa granite				1.30E-12		0.31-0.34		Skagius 1986	
Finnsjön granite				2.20E-12		0.18-0.91			
Finnsjön granite	Synthetic				4.90E-13			Ittner 1988	Sr-90
Stripa granite	Synthetic				2.70E-14				
Studsvik granite	Synthetic				2.40E-14				
Darley Dale sandstone	Simulated ground water		[Sr]=1.4e-5, [I]=1.3e-10, [Cs]=1.9e-5M	1.50E-10		10	150	Smith 1990	
Tonalite	synthetic G W, ion strength 0.0085	6 m cont time			5.10E-14			Suksi 1987	D.c.c, Sr-90
		12 m			1.40E-14				D.c.c
Mica gneiss		6 m			1.70E-14				D.c.c
		12 m			6.60E-16				D.c.c
Rapakivi granite		6 m			3.50E-14				D.c.c
		12 m			1.10E-14				D.c.c
Tonalite		3 m			3.50E-14				N.f.s. unfilled
		12 m			2.30E-14				N.f.s. unfilled
		3 m			5.40E-14				N.f.s. filled
		12 m			1.60E-14				N.f.s. filled
Mica gneiss		3 m			9.10E-14				N.f.s. unfilled
		12 m			3.70E-15				N.f.s. filled
Rapakivi granite		3 m			8.60E-14				N.f.s. unfilled
		12 m			3.80E-14				N.f.s. unfilled
		3 m			2.10E-13				N.f.s. filled
		12 m			1.10E-13				N.f.s. filled

*Reviewed by Yamaguchi 1993

**Particle size Fraction

Table 5.13 Literature data, strontium

7. NOTATIONS

A	Area	m^2
C	Concentration	$mole/m^3$
C_0	Initial concentration	$mole/m^3$
C_1	Inlet concentration	$mole/m^3$
C_2	Outlet concentration	$mole/m^3$
C_r	Concentration in the rock	$mole/kg$
C_p	Concentration in the pore water	$mole/m^3$
C_s	Concentration in the sorbed phase	$mole/m^3$
D	Diffusivity	m^2/s
D_p	Pore diffusivity	m^2/s
D_w	Diffusion coefficient of substance in (infinitely diluted) water	m^2/s
D_s	Diffusivity in the sorbed state	m^2/s
D_a	Apparent diffusivity	m^2/s
D_e	Effective diffusivity	m^2/s
F_f	Formation factor	-
K_a	Distribution coefficient	m^3/m^2
K_d	Mass distribution coefficient	m^3/kg
L	Sample thickness	m
L(%)	The percent radionuclide left in solution after sorption	%
x	Distance	m
M	Total amount of solute in solid after time t	$mole/kg$
M_∞	Total amount of solute in solid after infinite time	$mole/kg$
N	Rate of transfer per unit area	$mole/s,m^2$
N_{pore}	Rate of transfer in the pore per unit area	$mole/s,m^2$
N_s	Rate of transfer in the sorbed phase per unit area	$mole/s,m^2$
Q	Total amount of diffusing substance in time, t	$mole/m^2$
q	Amount of ion sorbed onto the rock	$mole/kg$
R	Retardation factor	-
R_l	Resistivity in a liquid	Ωm
R_{sph}	Radius of spherical particle	m
R_p	Resistivity in the pore fluid	Ωm
r	Radius	m
S(%)	The percent sorbed radionuclide on the sample surface	%
t	Time	s

V	Volume	m^3
α	Rock capacity factor	-
β	Freundlich exponent	-
δ_D	Constrictivity	-
ε	Total porosity	-
ε_t	Transport porosity	-
ε_δ	Storage porosity	-
ε_s	Sorption porosity	-
κ	Electrical conductivity in liquid	$(\Omega m)^{-1}$
κ_p	Electrical conductivity in pore liquid	$(\Omega m)^{-1}$
ρ	Density	kg/m^3
τ^2	Tortuosity	-
τ	Relaxation time	s

LITERATURE SURVEY OF MATRIX DIFFUSION THEORY AND OF EXPERIMENTS AND DATA INCLUDING NATURAL ANALOGUES

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Literature Survey of Matrix Diffusion Theory and of Experiments and Data Including Natural Analogues

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Keywords: *Matrix diffusion, surface diffusion, anion exclusion, natural analogues, adsorption, diffusivity, radionuclide, radioactive waste*

ABSTRACT (ENGLISH)

Diffusion theory in general and matrix diffusion theory in particular has been outlined, and experimental work has been reviewed. Literature diffusion data has been systematised in the form of tables and data has then been compared and discussed. Also natural analogues supporting matrix diffusion theory and pore connectivity, have been briefly reviewed and discussed. Strong indications of surface diffusion and anion exclusion have been found, and natural analogue studies and "in-situ"-experiments suggest pore connectivity in the scale of metres. Matrix diffusion, however, mostly seem to be confined to zones of higher porosity extending only a few centimetres into the rock. Surface coating material do not seem to hinder sorption or diffusion into the rock.

ABSTRACT (SWEDISH)

Matrisdiffusion har behandlats utförligt. Teori och experimentella tekniker gås igenom, och litteraturdata har samlats i tabeller vilka sedan jämförts och diskuterats. Även naturliga analogier vilka stöder matrisdiffusionteori och ett sammanhängande porsystem, studeras och diskuteras översiktligt. Starka indicier från flera undersökningar tyder på att ytdiffusion och "anion exclusion" äger rum, och genom naturliga analogistudier har man funnit sammanhängande porsystem i meterskala. Matrisdiffusion har dock i de flesta fall varit begränsat till ett område med förhöjd porositet och som sträcker sig endast några centimeter in i berget. Material avsatt på sprickytan tycks varken hindra sorption eller diffusion in i bergmatrisen.

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SUMMARY

Radionuclides escaping from a radioactive waste repository would constitute a danger to the biosphere, unless they have decayed to non-hazardous levels. Diffusion into the porous rock, matrix diffusion, can withdraw the radionuclides from the water flow in fractures and thereby retard them. It is of great importance to understand matrix diffusion and related phenomena, for safety assessment of the repository.

Natural analogue studies can make important contributions for the validation of matrix diffusion theory and experimental results. Studies of saltwater profiles and uranium series disequilibrium are useful tools for validation of pore connectivity and matrix diffusion.

Much laboratory work has been carried out and experimental methods for determinations of sorption and diffusion data can generally be considered reliable. Evaluation of the results have in some cases been difficult, due to unexpectedly high or low diffusivities. High diffusivities of sorbing species have been interpreted as diffusion in the sorbed state, and taking surface diffusion into account in describing diffusion has given good fittings to experimental values. The phenomenon seems to disappear at high ionic strengths, suggesting that other species occupy the sorption sites. For anionic species low diffusivities are due to electrostatic repulsion, since the rock pore walls are negatively charged. Also this phenomenon decreases with increasing ionic strength.

Laboratory results have been questioned due to the small samples usually used, where the contribution of dead-end pores could affect diffusivities. Other matters that could influence results are the sampling procedure, which could produce new fissures, and also the fact that the sample is de-stressed, possibly irreversibly.

Diffusivities and sorption coefficients have been found to be of the same magnitude or larger in most fissure coating materials, compared to in unaltered rock. The coatings do not seem to block the pores of the underlying unaltered rock. From natural analogues, absence of matrix diffusion has been suggested to be due to clogging of the pores by secondary minerals formed during shearing. Natural analogue studies and *in-situ* experiments have indicated pore connectivity on the scale of metres. In most studies, however, matrix diffusion seems to be limited to weathered or altered zones, only extending a few centimetres into the rock. Quantitative interpretations of concentration profiles have been reported, but unknown initial and boundary conditions, as well as possibly other transport mechanisms than matrix diffusion being active over the long time scale, makes it difficult to obtain unambigious data from natural analogues.

In this literature survey diffusion theory in general and matrix diffusion in particular have been outlined. Experimental methods and literature data as well as natural analogues have been reviewed. Literature diffusion data has been systematised in tables with the aim to facilitate comparison, and the phenomena surface diffusion and anion exclusion are discussed.

1 INTRODUCTION AND BACKGROUND

Deep knowledge about transport mechanisms occurring in rock is essential to achieve a reliable safety assessment of deep geologic repositories for spent radioactive fuel. In the Swedish concept copper canisters containing the radioactive waste will be placed in excavated holes in tunnels in the bedrock, about 500 metres under the ground surface. The canisters will be embedded in water-saturated bentonite clay and the tunnels will be back-filled with a mixture of bentonite and sand.

Radionuclides escaping from such a repository would constitute a danger to the biosphere if it is reached before the activity of the radionuclides have decayed to a non-hazardous level. The nuclides escaping from the canister have to migrate through the dense bentonite before they reach the bedrock. In water conducting fractures in the bedrock the nuclides can then be transported towards the biosphere.

Some radionuclides sorb onto the rock surfaces or to surface coating material and some do not. The latter would therefore reach the surface faster. The rock is full of micropores which make up a three-dimensional pore system. If the nuclides diffuse into these micropores they would be withdrawn from the waterflow that could carry them up to the biosphere, and they would be delayed by sorption onto much larger internal surfaces and by longer diffusion paths, and thereby be given more time to decay. This retardation mechanism is known as matrix diffusion and has been studied intensively in, for example, Sweden, Finland, Switzerland, the United Kingdom and Canada for more than ten years.

Old fissures in the bedrock are often covered with coating materials produced by contact with moving groundwater and resulting in weathering and alteration or zones of precipitation and crystallisation products from the ground water. Porosities of granites and gneisses are around 0.1 - 1 % (Skagius 1986), the lower values apply to gneiss. Porosities of fissure coating material and altered zones are generally higher, up to 8 - 10 % in some cases (Skagius 1986). Knowledge of transport properties in the coatings are also of importance, because the nuclides have to be transported through this coating layer before they reach the underlying rock.

To validate the theories and the experimental results evidence from nature is valuable, especially due to the long time scales involved. At natural analogue sites all over the world conditions and processes, similar to those at a repository for radioactive waste, are studied to achieve better knowledge about the long term events and to validate the models used in the safety assessment.

The importance of matrix diffusion is illustrated in Figure 1, by projected breakthrough curves for some radionuclides in a decay chain at a long distance from the leakage point. Curves for surface sorption and surface sorption plus matrix diffusion are shown, and the effect is obviously important.

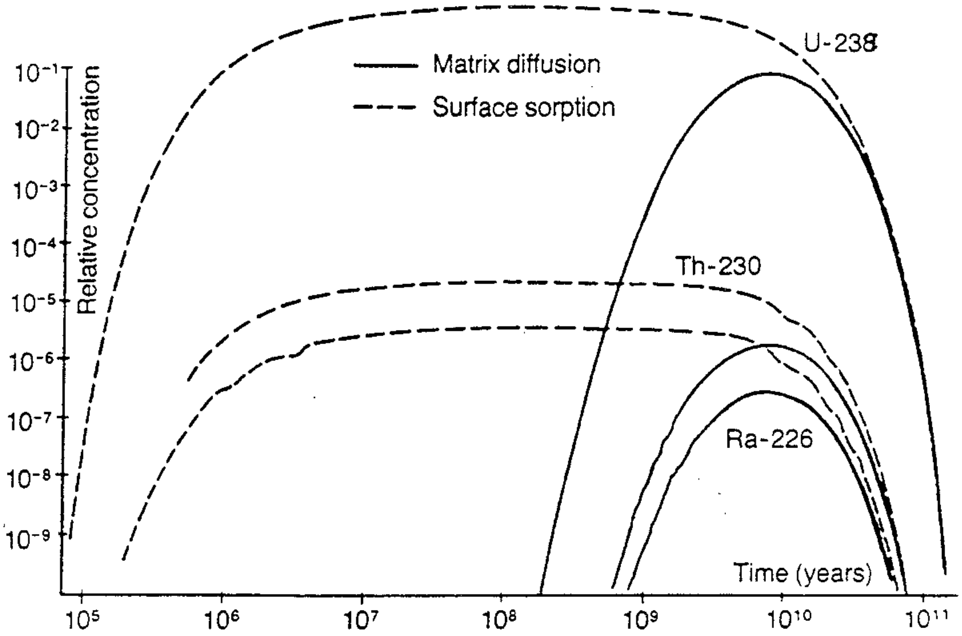

Figure 1.1 The effect of matrix diffusion on breakthrough at a distant point from the repository. $D_p=10^{-12}$ m^2/s. (Birgersson et al., 1988)

In this literature report, diffusion theory in general and diffusion in porous rock in particular, are outlined. Experimental work done in the area of matrix diffusion and related phenomena, and experimental data are reviewed and discussed. An attempt has been made to systematise reviewed experimental data, which are presented in tables to facilitate comparison. Natural analogue studies are briefly reviewed and discussed.

2 THEORY

2.1 THEORY AND EQUATIONS

2.1.1 Fick's Laws of Diffusion

Fick's first law of diffusion states that the substance diffuses in the direction of decreasing concentration :

$$N = -D\frac{\partial C}{\partial x} \quad (2.1)$$

where N is the rate of transfer per unit area, D is the diffusivity and C the concentration of the diffusing species.

When the transport is instationary and the solute accumulates or is depleted from the system, Fick's second law and the law of conservation of mass describes transport and accumulation.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad (2.2)$$

This equation is usually used for diffusion in solids or stationary liquids and for equimolar counter-diffusion in gases. The solutions to problems described by Fick's second law may often be found in the monographs of Crank (1975) and of Carslaw and Jaeger (1959).

2.1.2 Diffusion in a Pure Liquid

For a substance diffusing in pure water Fick's first law is described by:

$$N = -D_w \frac{\partial C}{\partial x} \quad (2.3)$$

where D_w is the diffusivity of the substance in pure water.

2.1.3 Diffusion in Porous Media

In porous media dissolved solutes move by diffusion in the pore water. The tortuosity of the pores increases the diffusion path. The diffusion is thus hindered by the tortuosity and the constrictivity of the pores. Therefore the pore diffusivity will be less than in unconfined water:

$$D_p = D_w \frac{\delta_D}{\tau^2} \quad (2.4)$$

where δ_D is the constrictivity, τ^2 the tortuosity and D_p the pore diffusivity, and Fick's first law will become:

$$N = -D_p \, \varepsilon \frac{\partial C_p}{\partial x} \quad (2.5)$$

where ε is the porosity of the material and C_p the solute concentration in the pore water. However, ε is made up of a transport porosity, ε_t, and a storage porosity, ε_d.

$$\varepsilon = \varepsilon_t + \varepsilon_d \quad (2.6)$$

The transport porosity is made up by the pores that are utilised in transporting the substance in the x-direction. Storage porosity refers to pores that have a dead end, and therefore contribute little or nothing to the transport, but can affect the capacity to hold the dissolved species. Therefore only the transport porosity will be used for transport and equation (2.7) should be written:

$$N = -D_p \varepsilon_t \frac{\partial C_p}{\partial x} \qquad (2.7)$$

$D_p \varepsilon_t = D_e$, and is called the effective pore diffusivity. The porosity of the pore system of Swedish granites and gneisses varies between 0.06 % and 1 % (Skagius and Neretnieks 1986) for the rock matrix.

2.1.4 Diffusion of Sorbing Species in Porous Media

If there is sorption of the diffusing species onto the porous material surface and transport is instationary, assuming that transport only takes place in the pore water, the diffusion coefficient is constant (i.e. sorption is linear) and that sorption is reversible, Fick's second law can be expressed as follows:

$$\frac{\partial C_p}{\partial t}(\varepsilon + \rho K_d) = D_p \varepsilon_t \frac{\partial^2 C_p}{\partial x^2} \qquad (2.8)$$

where K_d is the mass distribution coefficient and equal to C_r/C_p where C_r is the concentration of the species in the rock. For linear sorption, $\varepsilon + \rho K_d$ is constant.

Equation (2.8) can be rearranged as follows:

$$\frac{\partial C_p}{\partial t} = \frac{D_p \varepsilon_t}{\varepsilon + \rho K_d} \frac{\partial^2 C_p}{\partial x^2} = \frac{D_e}{\alpha} \frac{\partial^2 C_p}{\partial x^2} = D_a \frac{\partial^2 C_p}{\partial x^2} \qquad (2.9)$$

where D_a is the apparent diffusion coefficient, which takes into account the effect of retardation and α is the capacity factor ($\alpha=\varepsilon+\rho K_d$), which measures the capacity of the porous material to transport and store the diffusing species.

The retardation in the rock matrix is sometimes expressed with the retardation coefficient, R, which is sometimes defined as

$$R = \frac{\varepsilon + \rho K_d}{\varepsilon_t} \qquad (2.10)$$

R is a measure of the extent of retardation and has a value that ranges from unity to very large values, depending on the degree of sorption. The expression for Fick's law diffusion of sorbing species can also be expressed in a more general manner, allowing for non-linear sorption as well:

$$\frac{\partial}{\partial t}\left(\varepsilon C_p + \rho C_r\right) = D_p \varepsilon_t \frac{\partial^2 C_p}{\partial x^2} \qquad (2.11)$$

where C_r is the number of moles of solute in the solid phase per unit mass of porous medium. Instantaneous sorption is assumed. We illustrate the case for a Freundlich isotherm:

$$C_r = K C_p^{\beta} \qquad (2.12)$$

where K and β are constants, and β is the Freundlich exponent. The distribution ratio, K_d, is defined as the ratio of C_r to C_p and is then given by:

$$K_d = \frac{C_r}{C_p} = K C_p^{\beta-1} \qquad (2.13)$$

Combining the equations results in:

$$\frac{\partial C_p}{\partial t}\left(\varepsilon + \rho K\,\beta C_p^{\,\beta-1}\right) = \frac{\partial C_p}{\partial t}\left(\varepsilon + \rho K_d \beta\right) = D_e \frac{\partial^2 C_p}{\partial x^2} \qquad (2.14)$$

and rearranging equation (2.14):

$$\Rightarrow \qquad \frac{\partial C_p}{\partial t} = \frac{D_e}{\left(\varepsilon + \rho K_d \beta\right)} \cdot \frac{\partial^2 C_p}{\partial x^2} = \frac{D_e}{\alpha} \frac{\partial^2 C_p}{\partial x^2} \qquad (2.15)$$

where in this case α is equal to $\varepsilon + \rho K_d \beta$. If sorption is linear then β is equal to 1 and K_d is independent of concentration. The expression then turns into equation (2.8) again.

2.1.5 Surface Diffusion

If transport can take place in the sorbed but mobile phase the flow rate in the adsorbed phase will be:

$$N_s = -D_s \varepsilon_s \frac{\partial C_s}{\partial x} \qquad (2.16)$$

As sorption is fast, equilibrium is assumed to exist between C_s and C_p. ε_s is the hypothetical volume fraction of water at the pore surfaces where the "sorbed" ions are concentrated. The equilibrium relation is:

$$\varepsilon_s C_s = \rho K_d C_p \qquad (2.17)$$

then the total transport rate under steady state will be the sum of the pore diffusion and surface diffusion transport:

$$N_{tot} = N_{pore} + N_s = -D_p\varepsilon_t\frac{\partial C_p}{\partial x} - D_s\varepsilon_s\frac{\partial C_s}{\partial x} \qquad (2.18)$$

resulting in:

$$N_{tot} = -\left(D_p\varepsilon_t + D_s\varepsilon_s\frac{dC_s}{dC_p}\right)\frac{\partial C_p}{\partial x} \qquad (2.19)$$

If the equilibrium is linear the effective pore and the surface diffusivity can be expressed as an effective diffusivity:

$$D_e = D_p\,\varepsilon_t + \rho\,K_d\,D_s \qquad (2.20)$$

giving:

$$N_{tot} = -D_e\frac{\partial C_p}{\partial x} \qquad (2.21)$$

where D_e now includes the effect of surface diffusion in addition to pore diffusion. For instationary transport Fick's second law will become:

$$\varepsilon\frac{\partial C_p}{\partial t} + \varepsilon_s\frac{\partial C_s}{\partial t} = \frac{\partial}{\partial x}\left(D_s\varepsilon_s\frac{\partial C_s}{\partial x} + D_p\varepsilon_t\frac{\partial C_p}{\partial x}\right) \qquad (2.22)$$

If D_s is not concentration dependent and if C_s is in linear equilibrium with C, the expression above reduces to:

$$\frac{\partial C_p}{\partial t}(\varepsilon+\rho K_d)=\frac{\partial^2 C_p}{\partial x^2}\left(D_s\rho K_d+D_p\varepsilon_t\right) \quad (2.23)$$

Rearranging results in:

$$\frac{\partial C_p}{\partial t}=\frac{D_s\rho K_d+D_p\varepsilon_t}{(\varepsilon+\rho K_d)}\frac{\partial^2 C_p}{\partial x^2} \qquad (2.24)$$

If both sides are multiplied by $D_p\varepsilon_t$, and the expression is rearranged the following equation is derived:

$$\frac{\partial C_p}{\partial t}=D_p\frac{\varepsilon_t\left(D_s\rho K_d+D_p\varepsilon_t\right)}{(\varepsilon+\rho K_d)D_p\varepsilon_t}\frac{\partial^2 C_p}{\partial x^2} \quad (2.25)$$

and the retardation factor, R, is then defined as:

$$R=\frac{(\varepsilon+\rho K_d)D_p\varepsilon_t}{\varepsilon_t\left(D_s\rho K_d+D_p\varepsilon_t\right)} \qquad (2.26)$$

If $D_s\rho K_d >> D_p\varepsilon_t$, and $\varepsilon << \rho K_d$ then the retardation factor is reduced to:

$$R=\frac{D_p}{D_s} \qquad (2.27)$$

This means that if the magnitudes of the pore diffusivity and the surface diffusivity are the same, i.e. if $D_p \approx D_s$, then R will be equal to 1, and there would be no retardation even though there is sorption.

2.1.6 Comparison Between Diffusion and Electrical Conductivity

Both the diffusivity and the electrical conductivity are dependent on ionic mobility. Ionic mobilities, determined by electrical conductivity measurements, can therefore be used to calculate diffusivities. Diffusion can be compared with the ability of charged particles to conduct electricity. Electricity is transferred or conducted by means of the charged particles, and the electrical current is proportional to the potential gradient with the proportionality constant k (electrical conductivity) in the same manner as the diffusion of a substance is proportional to a concentration gradient with the diffusivity, D, as proportionality constant.

In a non-conductive porous material electrical conduction will only occur in the fluid in the pores. Tortuosity and constrictivity of the pores cause the electrical conductivity to be smaller than in an unconfined liquid. A relation between these properties is then given by:

$$\frac{\kappa_p}{\kappa} = \frac{R_l}{R_p} = \frac{\varepsilon_t \, \delta_D}{\tau^2} = Ff \qquad (2.28)$$

where κ_p and κ denote the electrical conductivity in the fluid in the pores and in an open liquid filled space respectively. In the same manner R_l denotes the resistivity. Combining this expression with equation (2.4) gives:

$$\frac{D_p \varepsilon_t}{D_w} = \frac{\varepsilon_t \, \delta_D}{\tau^2} = \frac{R_l}{R_p} \qquad (2.29)$$

This relation is valid when there is neither surface diffusion nor surface conduction.

2.1.7 The Influence of Dead-End Pores

A corrected form of Fick's second law, given by Hemingway et al. (1983), takes into account that some of the pores are dead-ended.

$$\alpha^{t}\frac{\partial C}{\partial t}=D_{e}\nabla^{2}C-\alpha^{*}\frac{\partial C^{*}}{\partial t} \quad (2.30)$$

$$\frac{\partial C^{*}}{\partial t}=\frac{1}{\tau}\left(C-C^{*}\right) \quad (2.31)$$

where α^t is the capacity factor of the through-transport pores, C^* is the concentration in dead-end pores, α^* is the capacity factor of the dead-end pores and τ is the relaxation time. Hemingway et al. (1983) also give the solution to the equation.

3 EXPERIMENTAL DETERMINATION AND INTERPRETATION OF DIFFUSION AND SORPTION DATA

3.1 THROUGH DIFFUSION EXPERIMENTS WITH NON-SORBING OR WEAKLY SORBING SPECIES

The rate of transport through a rock sample can be investigated by through-diffusion experiments. The mass transport is followed by continuous sampling as the solute moves from a solution with a high concentration towards one with a lower concentration. This can be done by letting the two sides of a thin rock sample be in contact with solutions of different concentrations, by fixing the sample in a hole in a plate and attaching two chambers containing the solutions to each side (Skagius and Neretnieks 1986, Bradbury and Green 1985). Puukko et al. (1993) let the migrating species diffuse from a spiked solution in a drilled-out cup in a rock cylinder through the rock into an outer reservoir containing a lesser concentration of the species. The mass flow was followed by repeated sampling of the water in the outer reservoir.

3.1.1 Interpretation of D_e and ε.

Skagius and Neretnieks (1986) determined the flow rates, N, of non-sorbing species through rock plates by making a linear regression of the experimental data, and then calculating the effective diffusivity using eq. 3.1:

$$N = -D_e \frac{\partial C}{\partial x} = D_e \frac{(C_1 - C_2)}{L} \qquad (3.1)$$

where L is the thickness of the plate and C_1 and C_2 the concentrations on each side of the plate.

Analytical solutions to both methods described in section 3.1 are given by Crank (1975). If the outlet concentration is negligible compared to the inlet concentration in the first case, and the inlet concentration is constant with time, the following equation results:

$$\frac{Q}{LC_1} = \frac{D_e t}{L^2} - \frac{\varepsilon}{6} - \frac{2\varepsilon}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-\frac{D_e n^2 \pi^2 t}{L^2 \varepsilon}\right) \qquad (3.2)$$

Q = total amount of diffusing substance that has passed through the sample in time, t, [mole/m^2]
C_1 = inlet concentration [mole/m^3]
L = thickness of the sample [m]
ε = total porosity of the rock sample
$D_e = D_p \varepsilon_t$ = effective diffusivity [m^2/s]

as time, t, approaches infinity the expression approaches the line:

$$Q = \frac{C_1 D_e}{L} t - \frac{C_1 L \varepsilon}{6} \qquad (3.3)$$

In the concentration-time curve the slope of the straight line is equal to $C_1 D_e / L$, and the intercept on the time axis is $L^2 \varepsilon / 6 D_e$ at time t, meaning that D_e and ε (when there is no sorption) can be determined. The solutions on both sides of the sample can also be circulated in tubes from a sampling unit to the rock surface and back to the sampling unit. The concentration of the species is measured in samples taken in the sampling unit. D_e is determined from the slope as described above, but the intercept on the time axis also includes the time it takes for transport from the rock surface to the sampling unit. The transport time is though rather short compared to the breakthrough time, and the intercept on the time axis is mainly due to the porosity of the rock sample (Skagius 1986).

In the second case, Puukko et al (1993) calculated effective diffusivities in diffusion from a cylindrical tube with the inner radius a and the outer radius b. At steady state, with the boundary conditions $C=C_1$ at r=a, for all t, and $C=C_2$ at r=b, for all t, Fick's second law results in the following expression:

$$Q = \frac{2\pi D_e (C_2 - C_1) t}{\ln b - \ln a} \qquad (3.4)$$

When C_2-C_1=C_0,

$$D_e = \frac{Q}{t}\frac{(\ln a - \ln b)}{2\pi C_0} \qquad (3.5)$$

When the cumulative mass flow, Q, is plotted against time, t, the effective diffusivity can then be calculated from the slope of the straight line.

3.1.2 Interpretation of D_a

Puukko et al. (1993) also calculated the apparent diffusion coefficient from the same Q versus t curve. The intercept, L, with the time axis of the asymptote to the curve, gives the time lag. With the same boundary and initial conditions, the intercept will be:

$$L = \frac{b^2 - a^2 + \left(a^2 + b^2\right)\cdot \ln(a/b)}{4D_a \cdot \ln(a/b)} \qquad (3.6)$$

The diffusivity calculated from this expression would then be the apparent diffusion coefficient, D_a. The relation between the effective diffusion coefficient and the apparent diffusion coefficient for material of low porosity is the following:

$$D_e = D_a(\varepsilon + K_d\rho) \qquad (3.7)$$

Where K_d is the mass distribution coefficient. The ratio D_e/D_a expresses the effective porosity.

3.2 SORBING SPECIES

When a solute sorbs onto a solid surface at least three interactions can be involved (Skagius 1986) namely physical, chemical and electrostatic adsorption. Physical adsorption is due to van der Waal's forces and is rapid and reversible. This is the major sorption mechanism for hydrolysed and complexed metal ions such as actinides. Physical adsorption is quite independent of solute concentration and ion strength. Chemical adsorption is due to chemical bonding between solute and surface. It is a slow and irreversible reactant-specific mechanism. Electrostatic adsorption occurs by ion exchange caused by electrostatic Coulomb forces. Ion exchange depends on the surface and the composition of the solution, and is reversible.

In sorption studies the distribution coefficient, K_a (= $C_{surface}/C_{solution}$), describes the fast sorption onto the external surface of the rock sample. K_a is therefore generally measured after short contact times (days - weeks). Suksi et al. (1987,1989) and Pinnioja et al. (1985) did such measurements but also used a somewhat modified distribution coefficient, K_a*. This coefficient was determined after longer contact times, but did not take into account the increase of contact area due to penetration into the rock. After the experiment, penetration depth was determined and K_d-values (m^3/kg) were calculated.

Suksi et al (1987,1989) injected the tracer solution into drill core cups of tonalite, mica gneiss and Rapakivi granite, which were sealed with rubber stoppers. The use of the rock itself as the spiking vessel results in avoiding extra adsorption to the walls of the plastic vessels normally used. The radioactivity of the spiking solutions was between 11 and 37 kBq in 10 ml of synthetic groundwater. Experiments with sections of drillcores of the same rock types, containing natural fissure surfaces, were also carried out. The walls of the drillcore samples where covered with a paint to confine the contact of radioactive tracer solution to the natural fracture surface. Contacting was carried out in 150 ml or 300 ml vessels with caps. Both types of experiments where carried out under atmospheric oxygen conditions. Contact times varied from one week to nineteen months. Diffusion depth was taken as the depth where nuclide concentration was 0.001 x initial nuclide concentration (detection limit).

Skagius, Svedberg and Neretnieks (1982) studied sorption of strontium and cesium on granite. Rock pieces were crushed and graded into different size fractions by sieving. The fractions were washed with distilled water and then dried at approximately 80°C for 24 h. They were then contacted with synthetic Allard water to obtain equilibrium between water and rock material. Each solid fraction was mixed with groundwater spiked with strontium or cesium or both. The concentration decrease in the solution was followed by atomic absorption spectrometry, and when a concentration decrease was no longer seen, equilibrium between solid and liquid was assumed. Distinction was made between sorption on external and inner surfaces. The "total sorption coefficient" measured was plotted versus the reciprocal diameter of the particles, giving the internal sorption as the particles grew larger and the outer surface area became less important, and the external sorption from the inclination of the plotted curve. A Freundlich sorption isotherm was then fitted to the experimental results, giving the Freundlich exponent telling whether sorption is linear or non-linear.

Aksoyoglu, Bajo and Mantovani (1991) did batch sorption experiments with I-131, Br-82, Sr-85, Na-22 and Cs-137 on crushed particles (<250 μm or < 63 μm) of Grimsel mylonite. The particles were conditioned with natural ground water before adding the nuclides. For rock-water conditioning and some of the sorption experiments dialysis bags with a pore size of 2.4 nm were used for efficient phase separation of solids and solutions. Ions could pass freely through the interface of the bags and particles (above 2.4 nm) remained inside the bags. The bags, containing mylonite and water, were placed and equilibrated in a groundwater-filled container. Then the bags were placed in polyethylene bottles which contained spiked ground water. The bottles were shaken manually only once a day, to avoid disturbing the system by creating fresh rock surfaces. This was found to be insufficient, however, to attain equilibrium in a reasonable time wherefore continuous agitation was used in later experiments. Desorption experiments were carried out by replacing the solutions in the bottles with unspiked ground water. For non- or weakly sorbing I-131 and Br-82 dialysis bags were not used. Solution samples were instead filtered through a 0.45 μm one-way filter.

When diffusion takes a very long time instationary methods are used. This can be accomplished by indiffusion of tracers in tablets and crushed particles of rock samples, immersed in traced solutions (Skagius 1986). The decrease of the tracer concentration in the solution is then used to determine the transport properties and the final steady state to determine equilibrium sorption.

Ittner et al (1988) used small rock tablets covered with a thin resin on all sides except for one, and submerged into synthetic ground water spiked with a radioactive tracer element. After a contact time of three months up to three years, thin layers of the rock were ground off and analysed radiometrically, giving a concentration profile of the element in the rock.

Suksi et al (1989) equilibrated drill core samples with synthetic ground water for two months, and then spiked them for 6-18 months. Sorption was followed monthly by taking small samples from the spiked solutions and measuring the radioactivity by liquid scintillation counting. The tracer solution was then removed and the solutions were analysed, and the rock specimens were rinsed and dried. The drill core samples were cut in frozen form to avoid elution of the migrated but non- or weakly sorbed activity with the water used as coolant in the sawing. The samples were kept for several days in a freezer before they were cut up with a diamond-bladed rock saw. Profiles were examined by auto-radiography to estimate the diffusion pathways of the elements.

3.2.1 Autoradiography

The rock sample is placed on a photographic film for exposure, and the autoradiographic study shows the migration pathways of the tracer in the rock by comparing photographs of the surfaces.

3.2.2 Interpretation of D_a

If the crushed particles mentioned above are treated as porous bodies of spherical shape and the equilibrium isotherm is linear, an analytical solution to the diffusion equation (Crank 1975) is suggested by Skagius for the determination of D_a.

$$\frac{M}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha\,(\alpha+1)\,\exp\,(-D_a\,q_n^2\,t/R_{sph}^2)}{9+9\alpha+q_n^2\,\alpha^2} \qquad (3.8)$$

where

M = the total amount of solute in sphere after time t
M_∞ = total amount of solute in sphere after infinite time
R_{sph} = radius of sphere

and the q_n values are the non-zero roots of :

$$\tan q_n = \frac{3q_n}{3+\alpha q_n^2} \qquad (3.9)$$

and

$$\alpha = \frac{V}{mK_d} \qquad (3.10)$$

where V is the volume of the spiked solution. A mass balance gives the concentration, C, in the solution after time t:

$$\frac{C}{C_0} = 1 - \frac{M}{M_\infty}\left(\frac{mK_d / V}{1 + mK_d / V}\right) \qquad (3.11)$$

D_a can then be evaluated by matching one of the expressions to experimental data. If the equilibrium is non-linear, numerical solutions to the diffusion equation must be used.

Ittner et al. (1988) and Suksi et al. (1987, 1989) used the analytical solution for the case of a linear isotherm and constant concentration in the solution during the experiment, Crank (1975):

$$\frac{C_p(x,t)}{C_0} = \operatorname{erfc}\left(\frac{x}{2\sqrt{D_a t}}\right) \qquad (3.12)$$

where C_0 is the concentration in the pore water in the first thin layer at the surface of the solid, C is the concentration at the distance x from the surface, t is the diffusion time in seconds and erfc the error function complement (= 1-erf). If z in erfc(z) is plotted against x, the slope of the lines gives D_a from $z = x/2\sqrt{D_a t}$ where t is known.

3.2.3 Determination of Sorption Coefficients

Suksi et al (1987) suggested the following expression to calculate the distribution coefficient, K_a, from in-diffusion experiments:

$$K_a = \frac{S(\%) / A}{L(\%) / V} \qquad (3.13)$$

where S(%) and L(%) are the percent sorbed radionuclide on sample surface and percent radionuclide left in solution respectively, A is the surface area of the sample and V the volume of solution. However, they used a modified distribution coefficient, K_a^*, which only accounted for the geometric surface area and not the increase in contact area due to penetration into the rock or the roughness of the rock material.

Mass distribution coefficients, K_d, were then calculated using the K_a^*-values.

$$K_d = \frac{K_a^* A}{V_r \rho} \quad (3.14)$$

where A is the geometric surface area of sample being in contact with the solution, and V_r the maximum volume of the rock sample being in contact with the solution, ($V_r = A \cdot$penetration depth). ρ is the density of the rock.

3.2.4 Simultaneous Diffusion-Sorption Experiments

Smith (1990) studied diffusion and sorption of I-125, Sr-85 and Cs-137 in a disc of Darley Dale Sandstone, with a diameter of 25 mm and a thickness of 5 mm. The method allows the parameters D_e, K_d and β (the Freundlich exponent) to be determined from a non-steady state system, and shorter duration of the experiment is needed. That the sorption coefficient is obtained makes it unnecessary to make separate sorption experiments, and size distribution as well as water to rock ratio problems are avoided. The water used was ”simulated groundwater” prepared by "equilibrating" distilled water with crushed rock over a 5-month period and then filtering it before use.

3.2.4.1 Interpretation of D_e and Freundlich Isotherms

Regression models were fitted to experimental data, with the effective diffusivity and the sorption coefficient as linear regression parameters, and adding the Freundlich parameter as well for non-linear sorption. The diffusion equation:

$$\frac{\partial C}{\partial t} = \frac{D_e}{\alpha}\frac{\partial^2 C}{\partial x^2} \tag{3.15}$$

where $\alpha = \varepsilon + \rho K_d$, must be solved for each nuclide.

For non-sorbing or linearly sorbing species, K_d is not a function of nuclide concentration, and the following solution is obtained for equation (3.15), with the boundary conditions $C=C_0$ at $x=0$ and, $C=0$ at $x=L$:

$$\frac{CVL}{AC_0} = D_e t\left[1 - \frac{\alpha L^2}{6} - \frac{2\alpha L^2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-\frac{D_e n^2 \pi^2 t}{L^2 \alpha}\right)\right] \tag{3.16}$$

For the non-sorbing species, $K_d=0$ and the porosity of the rock could be calculated. For sorbing species eq (3.16) must be solved for K_d-values that are concentration dependent, and the Freundlich isotherm is used for sorption. This is done by numerical intergrations, giving D_e, K_d and β (Freundlich parameter) as regression parameters when fitted to numerical data.

3.2.5 Diffusion in the Sorbed State

Yamaguchi, Sakamoto and Senoo (1993) made through-diffusion experiments with strontium in Inada granite. Drill cores were sawed into 5 mm thick circular plates, 40 mm in diameter. The porosity of the granite, measured by a water saturation method, was (0.68 ± 0.03)% and the pore sizes varied from 10 nm to 10 µm. Two solutions were used. The first one was 0.1 M KCl solution with the adjusted pH 4. The other solution was deionized water with a pH of 5.5. At high K-concentration the sorption sites are occupied by K, and Sr is hardly sorbed. Then diffusion should be due to only pore diffusion. In deionized water sorption sites are available to Sr, and the effective diffusivity should be the same if there was still only pore diffusion. However, the effective diffusivity was forty times larger than in 0.1 M KCl. One explanation to the higher diffusivity could be that diffusion coefficients in bulk solution become smaller at high ionic strength, but this should give a decrease of no more than 30 % according to the authors. Therefore the difference in effective diffusivity could not be explained only by the difference in ionic strength. The diffusion of Sr^{2+} in bulk solution is smaller than that of I^-. Effective diffusion coefficient of Sr in granite, however, was much greater than for I^-. If diffusion of the sorbed nuclides was assumed to be the explanation and a linear sorption isotherm was used, the following expressions were derived:

$$\varepsilon\frac{\partial C}{\partial t}+\rho\frac{\partial q}{\partial t}=D_p\varepsilon\frac{\partial^2 C}{\partial x^2}+D_s\rho\frac{\partial^2 q}{\partial x^2} \qquad (3.17)$$

where D_s is the surface diffusion coefficient, ε is the total porosity ($\varepsilon \approx \varepsilon_t$), and q is the amount of ion sorbed onto rock, $q= K_dC$, giving:

$$\alpha\frac{\partial C}{\partial t}=\left(D_p\varepsilon+D_s\rho K_d\right)\frac{\partial^2 C}{\partial x^2} \qquad (3.18)$$

where $\alpha = \varepsilon + \rho K_d$. Then the effective diffusion coefficient can be identified as:

$$D_e = D_p\varepsilon + D_s\rho K_d \qquad (3.19)$$

In the study D_e is shown to clearly depend on the sorptivity, ρK_d. At high sorptivities D_e was proportional to the sorptivity and at low sorptivities there was no dependency, indicating that at high sorptivities diffusion of sorbed Sr may significantly affect the effective diffusivity. The conclusion is that at high sorptivities D_e corresponds to the second term of eq (3.20), whereas at low sorptivities the first term is dominant. At low sorptivities D_e should then be:

$$D_e \approx D_p \varepsilon = D_w \varepsilon \frac{\delta_D}{\tau^2} \qquad (3.20)$$

and then D_e could be estimated based on $\varepsilon\delta_D/\tau^2$ or the formation factor of the granite.

3.3 ELECTRICAL CONDUCTIVITY MEASUREMENTS

Electrical conductivity measurements in salt-water-saturated rock samples have been used as an alternative method to determine the formation factor from which it is possible to determine the effective diffusivity, D_e (Skagius and Neretnieks 1986). The samples are saturated with salt solution and placed between two electrodes. The resistivity in the saturated sample is calculated by the measured resistance and the dimension of the sample.

3.3.1 Interpretation of D_e

By using the resistivity from the experiment described above in the following relation, the formation factor, F_f, is obtained:

$$\frac{\kappa_p}{\kappa} = \frac{R}{R_p} = \frac{\varepsilon_t \delta_D}{\tau^2} = Ff \qquad (3.21)$$

From the formation factor the effective diffusivity is finally obtained through:

$$F_f = \frac{D_p \varepsilon_t}{D_w} = \frac{D_e}{D_w} \qquad (3.22)$$

Another expression, Archie's law, for the formation factor was given by Parkhomenko 1967 (reviewed by Valkiainen 1992) for dense, igneous rocks and metamorphosed sedimentary rocks:

$$F_f = 0.71 \cdot \varepsilon^{1.58} \qquad (3.23)$$

3.4 POROSITY AND PORE CONNECTIVITY

The porosity of a rock sample can be determined from diffusion experiments as described in chapter 5.1.1. There are also more direct ways of measuring porosity, for example by measuring the difference in weight between the sample vacuum-dried and the sample saturated with water, the water saturation method. Another method is the direct method, where the bulk volume of the porous sample is first measured. The voids are then in some way destroyed, and the volume of only the solids can be measured. Other methods are described in "Porous Media, Fluid Transport and Pore Structure" by F.A.L. Dullien (1979).

The pore connectivity was examined by Bradbury and Green (1986) by electrical resistivity measurements. Drill cores were saturated with an aqueous electrolyte (3 M NaCl) and the resistivity of the core was measured and compared to the resistivity of the electrolyte. Formation factors were thereafter calculated using equation (3.21).

4 NATURAL ANALOGUES

Matrix diffusion has been studied in laboratory scale, and diffusivities and sorption characteristics of rock materials have been determined. Pore connectivity has been confirmed both under mechanical stress in laboratory and in "*in-situ*" tests under natural conditions. Still evidence for matrix diffusion over the time scales relevant for repository safety is needed. This is sought from natural systems where the processes studied have been occurring over geological time scales. The pore connectivity and the availability of the pore system to species in the groundwater has been studied in systems where land up-lift has changed the groundwater composition from saline to fresh in water conducting fractures and therefore an outleaching process has started from the rock. Remobilisation and transport of naturally occurring uranium in rock close to water conducting fractures, and interactions between oxygen and fracture surface resulting in a redox front moving into the rock, are other examples of natural analogue systems studied.

To obtain quantitative data from the natural systems is difficult due to not known or changing conditions over the time scales involved, or due to not known actual time scale. A concentration profile could origin in many processes, occurring in series or parallel to each other. Also qualitative data can be questioned, for the same reasons.

4.1 URANIUM SERIES DISEQUILIBRIUM

Nuclide migration in rock can be indicated by disequilibrium in the decay chain (U-238) - (U-234) - (Th-230). Radioactive equilibrium is established between the nuclides after about 1.7 Ma if the system is closed, meaning that the respective ratios U-234/U-238, Th-230/U-234 and Th-230/U-238 become equal to unity. If weathering or water circulation affects the system then U-238 and U-234 could become mobile while Th-230 is (assumed) immobile and the ratios mentioned above will be less then or more than one depending on whether there is an excess or depletion of U-238 and/or U-234.

Isotopic variation of uranium has been recognised as being produced by two mechanisms (Smellie et al 1986):
1) Selective leaching of U-234 itself, 2) the direct alpha recoil transfer of a U-234 precursor (i.e. Th-234), and a combination of these processes. For selective leaching to occur, U-234 atoms must be more susceptible to leaching and removal than U-238 atoms. This is facilitated by lattice damage resulting from the radioactive decay of U-238. The resultant daughter atoms will be located in weakly bonded or interstitial sites, and oxidation of the daughter (i.e. U-234)

to the 6+ valence state as a result of the recoil within the lattice, will render it more vulnerable to removal by water. Direct alpha recoil of Th-234 can occur from near the surface of a mineral grain into the intergranular pore water, thereafter it is trapped and decays to U-234. This results in the enrichment of U-234 in water and a U-234 depletion in the mineral. An additional mechanism is the process of daughter product emplacement from pore waters containing dissolved U-238 and U-234. Subsequent decay of these radionuclides result in the recoiling nuclides of Th-230, Th-234, Pa -234, and U-234 being adsorbed or embedded in particulate matter at the solid-liquid interface. After sufficient geological time, this mechanism results in solids which are enriched in U-234 and Th-230 relative to U-238. How recently the migration has occurred is determined from the half-lives of the nuclides involved.

Naturally occurring uranium and thorium are used as representative analogues of the actinides. The daughter nuclides in the U-238 and Th-232 decay chains have chemical properties and half-lives such that the degree of equilibrium between parent-daughter pairs can be used to provide information about rock-water interactions. Such studies can indicate the degree of radionuclide mobility and can provide information on the rates of processes occurring over time intervals of up to 1 Ma. Disequilibrium measurements may help to evaluate the effective addition or removal of uranium within the near vicinity of an open, water-bearing fracture zone (Smellie et al 1986).

Chemical extraction of rocks containing uranium, to remobilise and separate uranium phases, provide a useful analytical method for evaluating the mass transfer and *in-situ* fixation of uranium in geochemical cycling. Study of the distribution of uranium series nuclides in the surroundings of uranium mineralization gives knowledge about the fixation mechanisms of uranium during dispersion.

The behaviour of all actinides in geochemical surroundings is strongly dependent on the oxidation state of the element. For uranium, the most common oxidation states in natural groundwater (neutral or slightly alkaline waters) in deep bedrock are U(IV) and U(VI). At reduced conditions uranium occurs mainly in the form of U(IV)-compounds, which has a low solubility at reduced conditions and the uranium concentration is therefore rather low in these groundwater. At more oxidised conditions, U(VI)-compounds will be the main compounds occurring, and due to the higher solubility of U(VI), the concentration of uranium in the groundwater will be higher, and the uranium transport is thereby facilitated.

Latham (1991) interpreted uranium profiles and U-234/U-238 activity ratios as they varied with distance into the rock at a granite fracture wall using a simple diffusion-sorption model. Samples were taken from El Berrocal in Spain, Kråkemåla in Sweden and from Manitoba in Canada. The model assumes a linear reversible isotherm. The purpose was to estimate long term

K_d-values for uranium migration in granite close to fractures. Estimated K_d-values were between 0.1 and 10 m^3/kg.

4.2 NATURAL ANALOGUE SITES

4.2.1 Böttstein

Böttstein is a natural analogue study site located in central northern Switzerland. Investigations have there been carried out involving examination of drillcores from a borehole drilled to about 1500 meters. The sample for examination was taken from 618 m depth. The Böttstein granite is typically coarse-grained and rich in biotite. The drillcore used was chosen from a fracture intersection which was suspected to be water conducting. The selected sample consisted of 7 cm of pegmatite in contact with 13 cm of biotite-rich granite. The sampled core section indicated significant uranium depletion, while thorium seemed to be immobile. The U-234/U-238 ratio is unity for most of the core length although close to the fracture a small enrichment can be seen. The Th-230/U-234 ratio is a little more than one except close to the fracture where a significant decrease occurs. This suggests solution to rock transfer of Th-230 produced by the decay of U-234 in solution. The fluid flow is probably faster through the Kråkemåla (Section 4.2.3) core explaining the differences in the Th-230/U-234 ratio. Uranium and rare earth elements showed mobilisation at distances ranging from 3 to 20 cm from the fracture surface, but the degree of uranium mobilisation is less than for Kråkemåla granite. Investigations of iron oxidation states indicated a fairly uniform degree of oxidation throughout the rock types (granite and pegmatite) (Smellie et al 1986).

4.2.2 Grimsel

The Grimsel test site in Switzerland consists of granitic rock. The main uranium- and thorium-bearing mineral phases are allanite, thorite, zircon and apatite. In drillcores, different elements showed mobilisation at distances ranging from 3 to 20 cm from the fracture surface. The uranium and thorium distributions varies irregularly and there is no obvious relation between uranium and thorium, suggesting that the uranium and thorium contents are controlled by minerals which are distinctly uranium or thorium bearing. The isotopic data shows secular equilibrium for the uranium daughters measured. This could be due to that the fracture is not water-conducting, or because there are no groundwater interactions at this depth (Smellie et al. 1986).

Alexander et al. (1990) investigated transport of radionuclides in rock samples adjacent to a water-bearing fracture, by uranium series disequilibrium studies. Calculations indicate that transport of Ra-226 in the vicinity of the fracture can be described by matrix diffusion. Comparison between field data and laboratory studies and simple model calculations suggest that the near-fracture transport can be described by matrix diffusion, even though the rock matrix shows numerous amount of microfractures that could be water-bearing. Pore diffusivity was calculated from the expression:

$$x \approx \sqrt{\frac{D_p}{R_p} t} \quad (4.1)$$

where $R_p = 1 + K_d \rho (1 - \varepsilon)/\varepsilon$. Using the K_d-value 0.1 m^3/kg, the rock density 2700 kg/m^3, the porosity 0.007 and the time $1.6 \cdot 10^3$ y and $8 \cdot 10^3$ y, pore diffusivities of $(1.4 - 6.9) \cdot 10^{-10}$ were obtained. The obtained diffusivities were similar to those assumed in the Nagra safety assessment base case. In this work the authors suggest that characterisation of the extent of connected porosity around relevant fissures would be more cost-effective than attempts to improve diffusion measurement methods. This origins in the lack of sensitivity with respect to the diffusion coefficient, used to describe matrix diffusion, that was observed.

4.2.3 Kråkemåla

Smellie et al. (1986) examined a drillcore from Kråkemåla in Sweden. The drillcore, coarse grained Götemar granite, showed some alteration through all the length but more intense alteration adjacent (3-5 cm) to the fracture surface. There were also some mineral-coating on the surface. Considering the major length of the drill core (i.e. excluding the fracture edge) the isotope data shows depletion of both U-234 and Th-230 relative to U-238. This means that throughout the granite the loss of U-234 has been occurring over at least one million years by solid to solution alpha-recoil processes. The granite close to the fracture zone is characterised by enrichment of all four isotopes. These fall off rapidly over a distance of 1-3 cm into the granite. The U-234/U-238 ratio is about 2.29 at the near surface, and about 0.86 in the major part of the core. The source to the enhanced concentrations could be either uranium leached from the granite (as indicated by the U-234 /U-238 ratio in the rest of the core), or from uranium transported in solution within the fracture migrating into the water-saturated rock. If the former process is responsible, then uranium migration over at least 40 cm is occurring whereas a constraint of about 3 cm can be applied if the latter process is taking place.

The thorium and REE (together with Ta, Cs and Sc) behaviour suggests that thorium has remained relatively immobile throughout the history of the granite, and its irregular pattern reflects the pattern of the dominant thorium bearing mineral monazite, which is of primary origin. In a closed chemical system uranium distribution would be the same as the thorium pattern. The Th-230/U-234 and Ra-226/Th-230 equilibrium and U-234/U-238 disequilibrium suggest that the process involved is either continuos or else indicates a time scale long enough to allow re-equilibration of Th-230 with U-234 and Ra-226 with Th-230 but short enough to maintain U-234 disequilibrium with U-238, i.e. a time scale of about 10^6 years. Uranium is in comparison easily mobilised and leached from granite if the system is open to fluid flow. Deeper into the rock U and Th shows this similar distribution wherefore this part probably has retained its original uranium and thorium profile. Absence of the similarity of the profiles within the initial part of the drillcore indicates leaching and it can be seen that monazite in this part has been partially altered. At the fracture surface, however, U has been enriched markedly suggesting that in the groundwater/fracture system uranium accumulation is taking place rather than leaching.

The mechanism giving rise to uranium deposition at and near the fracture could be due to any or all of: a) precipitation at a boundary between differing physico-chemical conditions, b) sorption on the fracture filling minerals, and c) solution to solid recoil transfer.

4.2.4 Cornwall

Blocks of granite (1.5*1*0.6m) were immersed in salt water and used to construct wavebreaks in Falmouth, Cornwall, in 1956. The idea of the experiments by Jeffries (1987) was to examine trace element profiles due to migration into or out from the granite block in the sea-water. Reference samples not immersed in water, were taken from the same area as the blocks, to determine the original levels of tracer before any immersion in sea-water. Cl^-, Br^-, SO_4^{2-} - and F^--ions were leached out and Cl^- and Br concentrations were 15 to 40 times higher than those in the fresh granite samples. SO_4^{2-} and F^- profiles had maxima at depths 11-14 cm into the block, which were interpreted to be caused by weathering of the rock which contains minerals with these species.

Diffusivities calculated from chloride and bromide concentration profiles were at least a factor of three higher than measured in the laboratory. Some of the intrusion of the salt water may have been caused by capillary suction, because the rock had been at least partly dried before immersion in the sea, but the assessed apparent diffusivities were found not to be unreasonable.

4.2.5 East Bull Lake

In East Bull Lake, Ontario, Pinto Coelho (1987) studied matrix diffusion close to a mineralised vein. The depths to which percolating groundwater had leached out the elements uranium, thorium, neodynium, lanthanum, bromine, strontium and barium as chemical analogues of plutonium, neptunium, cerium, americium, iodine and radium, were measured. The depths in the rock where redistribution of elements could be seen varied between 32 and 65 mm and was taken as a measure of the matrix diffusion depth. Greater redistribution occurred closer to the vein. The major elements were leached from the rock to the depth of 50 mm.

Miller et al 1994 suggest that the resulting depths should be treated with caution because important information is missing. The duration of fluid flow and the maximum fluid temperature are unknown. The probably higher temperatures could have enhanced the diffusion depth, and the depths given by Pinto Coelho (1987) might be maximum depths, but also this is speculative because of the unknown boundary conditions.

4.2.6 El Berrocal

Blocks and cores from El Berrocal granite were examined by Heath et al. (1992) in order to determine the extent to which diffusion of natural radionuclides has taken place from fractures into the rock matrix, and the microstructural control of diffusion. The results indicate that matrix diffusion might be limited to a zone extending only a few centimetres into the rock, and that the deeper part of the rock is not available for matrix diffusion.

There was clear evidence of water movement through the fractures from which the samples were taken. There was high concentration of uranium in the water and deep matrix diffusion might have been expected to occur. Such diffusion did not take place, however, and penetration of uranium into the rock seemed to be limited to a clearly defined zone close to the fracture surface. In the higher of the two cores examined diffusion was limited to 35 mm, and in the lower sample some 80 mm into the rock. The zone where diffusion had taken place had been altered and beyond this zone of enriched uranium content there was depletion of uranium extending up to 100 mm into the rock.

The conclusion was that enhanced uranium mobility exists adjacent to the fracture due to microscopical changes in the rock and that this zone extends only a few centimetres from the fracture.

4.2.7 Kamlunge

In the test site of Kamlunge in northern Sweden, Smellie et al (1988) studied a section of granitic rock extending from a single water conducting fracture in an environment of oxidising groundwater. Hydrothermal alteration extends 2 to 3 cm into the rock, and there an enrichment of uranium and thorium can be seen. The whole rock section has been affected by uranium loss over a time period of about 10^4-10^5 years, and a connected porosity over at least 10 cm is indicated. The conditions during this time have probably been reducing. Porosity and diffusivity measurements showed no significant differences between altered and fresh rock portions. The porosity was about 0.1 %.

4.2.8 Marysvale

The natural analogue site in Marysvale, Utah, USA, consists of a hydrothermal uranium deposit enclosed in granitoid country rock. The ore deposit is considered a natural analogue to a radioactive waste canister emplaced in a granitic repository environment. Two episodes of alteration were recognised in the study. Greater retention was found in the studied rock than in laboratory measurements. Possible reasons for this discrepancy were suggested such as greater amount of microfractures, secondary mineral formation within micro cracks, time and temperature dependence of K_d, oxidation state of nuclide and preferential sorption/reduction by chlorite and pyrite. Apparent diffusivities derived for the rock matrix were 10^{-19}- 10^{-16} m^2/s and distribution coefficients 1 - 10^2 m^3/kg i.e. orders of magnitude greater than expected from laboratory measurements (Shea 1984).

4.2.9 Palmottu

The Palmottu natural analogue study site comprises a small U-Th mineralisation in Nummi-Pusula in south-western Finland. From C-14 dating it has been found that Lake Palmottu was isolated from the Baltic Sea approximately 9000 years ago. The main component of the ore at Palmottu is crystalline uraninite, which makes it resemble the composition of spent radioactive fuel. The uraninite has been altered under anoxic conditions, which are the conditions in deep bedrock repositories for radioactive waste. The migration behaviour of radionuclides in crystalline rock can be studied because of the alteration process, that has released and mobilised uranium and its daughter elements. Both oxic and anoxic conditions has been investigated because of the change from oxic conditions at the surface to anoxic conditions deeper in the bedrock. The validation of matrix diffusion is based on comparing measured and simulated concentration profiles (Rasilainen et al 1994).

Evidence for uranium penetration beyond the alteration zone, 16-20 cm from the fracture, has been obtained. Uranium enrichment from water containing uranium, to altered rock around the water carrying fracture seems to effectively retard or immobilise uranium. In the zone close to the fracture, a loss of U-234 can be observed due to α-recoil and the interconnected pores that allow U-234 to be transferred to the aqueous phase and transported from the site.

Radioactive disequilibrium between uranium isotopes deeper in the rock has also been found. The U-234/U-238 activity ratio increases from around 0.6 near the fracture up to 1.3-1.8 deeper in the rock indicating transport of U-234 towards the rock and the conclusion has been drawn that the interconnected porosity extends at least 20 cm from the fracture.

On unaltered rock the effect of uranium penetration from groundwater into the rock was studied by means of a 17 cm rock core with both fracture surfaces covered by calcite. Migration routes formed paths that closely followed grain boundaries and micro cracks. Fracture calcite separated from both the ends of the core show a clear but opposite disequilibrium state.

Rasilainen and Suksi (1994) have tried to validate the matrix diffusion concept by interpreting measured uranium series profiles around water-carrying fissures. Simulated distribution curves, based on general matrix diffusion theory, were fitted to the measured distribution of uranium series elements in rock samples, by quantifying the matrix properties and then adjusting the time scale to get a curve fit. There was a rough agreement between measured and simulated profiles, but there were serious difficulties in fitting the model to all measurements. Large K_d values were needed in the simulations and raised doubts that matrix diffusion was responsible for the observed enrichment in the rock. Using sorption isotherms instead of the simple K_d concept was suggested. Because of high concentrations, the sorption sites available might have been saturated. If boundary conditions and matrix properties are quantified, the diffusion time can be deduced. Matrix properties can be measured but are difficult due to the small amount of rock material. Even if boundary conditions and matrix properties are defined, the initial condition and time scale would still be unknown. To reduce the number of unknowns, the initial condition can be determined by examining pore water concentrations. It was concluded that there is a need for further sorption studies.

Suksi et al (1994) and Rasilainen et al (1994) concluded that diffusion could not be the only explanation to the concentration profiles in the samples, but the active role of diffusion is indicated. They suggest an older phenomenon to be responsible for the immobile bulk enrichment closest to the fracture upon and beyond which concentration is superimposed by matrix diffusion. The depth of the concentration profile into the virgin rock can be seen as the minimum depth of the connected pore network. None of the samples that have been examined have exhibited radioactive equilibrium, and the most distant sample point has been located 16 cm from the fracture. Earlier sorption experiments have assumed the extracted radioactivity to have been sorbed activity. The bulk enrichment is dominating close to the fracture and if this cannot be modelled, the concentration distribution is not very useful for quantitative matrix diffusion validation. Techniques to separate the effects of young and old processes causing concentration profiles are being developed.

In the simulations the code FTRANS has been used, in which four factors need to be quantified. The fourth parameter can, however, be adjusted if the three others are quantified. The factors needed are boundary conditions, initial conditions, matrix properties and time. The boundary conditions can also be time-dependent. The time factor cannot be measured directly, and is therefore used as a fitting parameter. Consequently there is a need for independent evidence of time scales.

When sorption isotherms are used, non-linearity is introduced in a strictly linear equation. FTRANS solves this by piece-wise approximation in space and time. A constant K_d-value is calculated for every nuclide in every element during every time step. Linear interpolation is used between K_d and concentrations.

4.2.10 Poços de Caldas

Romero et al. (1992) investigated the formation of redox fronts at Poços de Caldas, Brazil. Water migrates into the rock by water inflow into fissures and by molecular diffusion into the porous rock matrix, and oxygen oxidises the pyrite in the rock which produces very sharp redox fronts. This can be clearly seen because of colour changes between the originally grey rock and the oxidised reddish rock. In some water bearing fractures where there are small channel apertures in the rock walls, the rock surrounding those channels has been affected to a depth of tens of cm or more resulting in red oxidised rock. This was explained by diffusion of oxygenated water into the rock matrix.

The behaviour of natural decay series radionuclides and stable elements at the existing redox front was investigated at the Osami Utsumi uranium mine (MacKenzie et al 1991). The generally greater mobility of U(VI) and Ra than of U(IV), Th and Pa in groundwater was confirmed, and there was clear evidence of enrichment and deposition of uranium a few cm into the reduced side of the redox front within the last $3 \cdot 10^5$ years. At the oxidised side uranium deposition was also occurring, probably by incorporation in iron oxides, even though uranium would be predicted to be soluble in an oxidising environment. There was evidence of significant enrichment and retention in the oxidised rock for up to $7 \cdot 10^5$ years. The distribution of uranium and other elements at the redox fronts indicated that long-term advective flow has occurred parallel to the direction of the fronts, with dissolution at the front and diffusion of the dissolved species into both the reduced and the oxidised rock.

Thorium was preferentially enriched on the reduced side of the redox fronts. Deeper into the mine the effect was lesser. This was in consistence with the decreasing thorium transport with increasing length of the flow path of the groundwater. The effect for uranium is the opposite resulting in greater separation of uranium from thorium with greater lengths of flow paths.

Preferential loss of U-234 from the solid phase due to alpha recoil effects and resulting in enhanced mobility of the daughter isotope occurs both in the reduced and the oxidised rock. The importance to consider this effect in far-field situations is stressed. The higher mobility of U-234 compared to that of Th-230 produced *in-situ*, despite that both are susceptible to alpha recoil loss to solution, was significant.

The redox fronts act as retardation zones because of the enrichment of many elements, but could in a large time scale provoke the breakthrough of a front containing enhanced radionuclide concentrations in the near surface zone due to the propagation of the front.

4.2.11 Alligator Rivers

Uranium ore bodies in the Alligator Rivers region in the Northern Territory of Australia have been studied with the aim to collect field data and to identify and quantify processes which occur on both short and geological time scales. The Alligator Rivers natural analogue site consist of four major uranium deposits namely Jabiluka, Ranger, Koongarra and Nabarlek (Duerden et al. 1987). All effects identified through the Alligator Rivers analogue study, with the possible exception of colloid transport, lead to underestimation of long-term retardation when sorption coefficients measured over short time scales are used (Airey 1987).

4.2.11.1 Jabiluka

A quarts-chlorite-mica schist drillcore intersecting a calcite-filled fracture at the Jabiluka uranium deposit in the Alligator Rivers Region in Australia, was studied by uranium series disequilibrium data. The core sample showed no weathering. The data showed enrichment of uranium at the fracture surface and that the groundwater interaction with the rock extended a few cm into the rock (Nightingale 1988, in Brandberg et al. 1993).

4.2.11.2 Koongarra

The primary mineralisation in the Koongarra deposit, in the Alligator Rivers Region in Australia, comprises uraninite veins within a zone of partly weathered quarts-chlorite schist. The degree of uranium migration from a water-conducting fissure into the rock matrix was studied in rock samples. Enrichment of uranium was present in the fissure coating material, but very little migration into the fresh rock was observed. Penetration of uranium seemed to increase with the degree of alteration and weathering, which could be observed in a concentration profile extending a few mm into the rock. U-234 migrated more slowly than U-

238. The α-activity profile from fracture surface into fresh rock showed an exponential decrease to a distance of about 180 µm from the fissure. I-129 was found to be leached preferentially from the ore relative to U during weathering of the primary ore body examined. Also Tc-99 had much higher mobility than uranium.

A one-dimensional model to calculate U-234/U-238 and Th-230/U-234 activity ratios was compared with measured gradients in drill core samples. Best fit was obtained when Th-230 was considered to be the least mobile species (Duerden et al. 1987).

4.2.12 Hästholmen

About 5000 years ago the island of Hästholmen, situated off the coast of the Gulf of Finland, started to rise from the Baltic Sea. The rate of the postglacial land uplift is about 3 mm per year. A layer of fresh groundwater is now floating on top of the saline layer due to infiltrated rainwater into the ground. The bedrock consisting of coarse-grained granite has been studied for suitability as an underground repository for radioactive waste.

Lehikoinen et al (1992) investigated non-fractured core sections of several meters selected between two water-bearing fractures. The water in the fractures was fresh infiltrated rainwater of low salinity, and it was assumed that it had been flowing in the fracture for 1000 years. The sections selected were sampled at intervals of about one metre, each originally containing old saline water. The pore water from the samples was extracted with ion-exchanged water and the contents of chloride and sulphate were determined. The salinity of the pore water was indicated by the anion concentrations determined, and the regions with decreasing concentration of anions were interpreted as being caused by matrix diffusion. Due to this result it was concluded that the pore system is open and connected for at least one meter over the time period studied. The apparent diffusion coefficient, giving a reasonable fit to the profiles, was determined to $2 \cdot 10^{-9}$ m^2/s. The effective diffusivity calculated was then about $1 \cdot 10^{-12}$ m^2/s, and that is about one order of magnitude higher than expected from laboratory measurements. The model used was, however, one-dimensional. The study shows that regions with gradually decreasing salinity can still be found indicating matrix diffusion in the scale of meters.

4.3 DISTRIBUTION OF PA-231 AND RA-226 IN ROCK - AN INDICATOR OF ROCK MATRIX DIFFUSION.

In a three-year study, summarised by Saarinen and Suksi (1995), Pa-231 and Ra-226 were studied to support the findings of uranium movement in rock. The short-lived nuclides were chosen in order to observe more recent radionuclide movement. With the same purpose a rock sample from a young uranium phase in rock matrix, was studied. Rock samples close to water conducting fractures in the vicinity of a uranium deposit were examined.

The observed mobility of Pa-231 and Ra-226 indicate that accumulated uranium does not "clog" the rock pores. U-234 was released from the U accumulation and transported through the altered zone deeper into the virgin rock.

Recent uranium penetration was observed in one rock sample which indicated uranium accumulation 10,000 - 33,000 years ago. An apparent diffusivity of $6 \cdot 10^{-15}$ was calculated from the sample uranium distribution.

None of the samples analysed showed radioactive equilibrium which gives a measure of the minimum depth of connected pore system. In this case the most distant sample point from the fracture surface was 12 cm, and the pore system may extend much further than that.

Apparent diffusivities estimated for Ra-226 from movements about 20 mm in the rock were 10^{-15}-10^{-14} m^2/s which is higher than average values measured for U. This suggests radium transport in the sorbed state.

Calcite coatings on rock samples did not seem to have hindered radionuclide transport. Sorption was found to be higher on altered rock, and since rock alteration seems to change with time, transport and sorption properties also change over long periods.

5 LITERATURE DATA

In the literature vast amount of diffusivity and sorption data can be found. It is, however, difficult to compare data due to different, and sometimes vaguely pronounced, experimental conditions. Therefore it has been attempted in this report to systemize reported data in the form of tables. This has been done for diffusivity data, but not yet for sorption data.

Neretnieks (1979) presented a table of expected D_a-ranges for non-sorbing and sorbing nuclides which is useful for comparison of experimental data.

$K_d \rho$	D_a Low value (m^2/s)	D_a High value (m^2/s)
$\varepsilon_p = 0.004\text{-}0.009$	$0.6 \cdot 10^{-10}$	$10 \cdot 10^{-10}$
1	$0.24 \cdot 10^{-12}$	$9 \cdot 10^{-12}$
100	$0.24 \cdot 10^{-14}$	$9 \cdot 10^{-14}$
10000	$0.24 \cdot 10^{-16}$	$9 \cdot 10^{-16}$

Table 5.1. Expected apparent diffusivities, D_a (m^2/s), in granite for non-sorbing ($K_d\rho = \varepsilon_p$), weakly sorbing ($K_d\rho = 1$), intermediately sorbing ($K_d\rho = 100$), and strongly sorbing ($K_d\rho = 10000$), nuclides (Neretnieks 1979)

Brandberg and Skagius (1991) in compiling data for the SKB 91 study suggested an effective diffusivity value, D_e, of $1 \cdot 10^{-13}$ m^2/s, and a pore diffusivity of $2 \cdot 10^{-11}$ m^2/s based on measurements in Finnsjön rock. These values were proposed for all elements, sorbing and non-sorbing, and for both fresh and saline reference water. The suggested transport porosity, ε_t (or ε_p in the notation used in the study), was 0.5%.

The diffusivity of ions in both fresh and saline mobile water at infinite dilution is proposed to be $2 \cdot 10^{-9}$ m^2/s (Brandberg and Skagius 1991).

Diffusivities and sorption have been found to be larger in fissure coating materials and do not seem to block the pores of the underlying virgin rock (Saarinen and Suksi 1995).

5.1 NON-SORBING SPECIES

5.1.1 Neutral Species

Neutral non-sorbing species diffusing in a porous medium are not retarded by sorption and are not affected by the charged pore walls. Therefore the whole pore volume is available for diffusion, and diffusivities are high and not affected by ionic strength. Porosities calculated from diffusion experiments are generally in good agreement with values from water saturation methods and other porosity determination methods, because of the availability of the whole pore space to the tracers. Tritiated water is often used as a neutral tracer in diffusion experiments.

5.1.1.1 Tritiated Water, HTO

The bulk phase diffusivity of HTO used in the calculations of Skagius and Neretnieks (1986), was $2.4 \cdot 10^{-9}$ m^2/s. The effective diffusivities determined in Finnsjön granite were $(13\text{-}18)\cdot 10^{-14}$ m^2/s. The porosity was determined in crushed rock material and in larger samples. The porosity for the crushed material was 0.91 % and for larger samples 0.18-0.21 %. Lehikoinen et al. (1992) reported values between $7.6\cdot 10^{-14}$ m^2/s and $9.6\cdot 10^{-14}$ m^2/s in gneiss samples in solutions with NaCl-concentrations between 0.0044 and 1 M. Kaukonen et al. (1993) determined effective diffusivities in acidic rock to lay in the range of $(0.57\text{-}6.35)\cdot 10^{-13}$ m^2/s and Puukko et al. (1993) reported D_e-values in the range $(1.7\text{-}220)\cdot 10^{-14}$ m^2/s the lower values corresponding to gneiss, and values for tonalite and granite being an order of magnitude higher.

The ratio of apparent to effective diffusivities were approximately equal to measured porosities in the determinations of Kaukonen et al. (1993). In the work or Puukko et. al. (1993), however, estimation of the porosity from apparent and effective diffusivities were, in many samples, only realistic if water was regarded as a sorbing species, with a mass distribution ratio of $5 \cdot 10^{-6}$ m^3/kg, giving a retardation factor of 5.

Rock	Water	Cond	Conc [NaCl] (M)	D_e (m^2/s)	D_a (m^2/s)	ε (%)	D_e/D_a (%)	Ref
Gneiss	Synthetic "Hästholmen"		0.0044	9.60E-14				Lehikoinen 1992
Gneiss			0.7	8.50E-14				
Gneiss			1	7.60E-14				
Tonalite	Allard	Aerobic		2.3-7.0 E-13	5.3-17 E-11		0.2-1	Puukko 1993
Tonalite	Romuvaara	Aerobic		1.4-1.5 E-12	1.1 E-10		1.3	
Tonalite	Allard	Anaerobic		4.5-17 E-13				
Tonalite	Romuvaara	Anaerobic		3.4-22 E-13				
Granite	Allard	Aerobic		1.5-6.9 E-13	3.3-9.1 E-11		0.8-1.1	
Granite	Romuvaara	Aerobic		2.6-4.5 E-13				
Granite	Allard	Anaerobic		2.3-7.2 E-13				
Granite	Romuvaara	Anaerobic		1.4-11 E-13				
Gneiss	Allard	Aerobic		1.7-27 E-14	7.8-550 E-12		0.05-0.45	
Gneiss	Olkiluoto	Aerobic		3.2 E-13	2.3 E-10		0.14	
Gneiss	Allard	Anaerobic		6.2-50 E-14				
Gneiss	Olkiluoto	Anaerobic		1.2-2.0 E-13	1.4-30 E-11		0.07-0.84	
Finnsjön Granite	Synthetic GW			1.80E-13		0.18-0.91		Skagius 1986
Finnsjön Granite	Distilled water			1.30E-13		0.18-0.91		
Mäntsälä plutonic rock	Allard			5.40E-13	3.20E-10	0.20	0.17	Kaukonen 1993
Mäntsälä plutonic rock	Allard			9.40E-14	2.58E-11	0.20	0.36	
Syyry plutonic rock	Syyry Ground water			5.80E-14	3.48E-11	0.26-0.43	0.17	
Syyry plutonic rock	Syyry Ground water			5.70E-14	5.17E-11	0.26-0.43	0.11	
Syyry plutonic rock	Syyry Ground water			9.10E-14	3.92E-11	0.26-0.43	0.23	
Sodankylä vulcanite	Allard			6.35E-13	2.05E-10	0.27	0.31	
Sodankylä vulcanite	Allard			2.68E-13	1.08E-10	0.27	0.25	
Sodankylä vulcanite	Allard			3.67E-13	1.20E-10	0.27	0.31	

Table 5.2 Literature data, tritiated water

5.1.2 Anionic Species

Anions are generally non-sorbing in repository rock environments due to their negative charge. Therefore they have high diffusivities and they have been used to determine rock porosities. Most often, depending on the composition of the solution, determined porosities are found lower than values from, for example, water saturation methods. This has been explained as anion exclusion, i.e. the negatively charged ion does not have access to the whole pore space because of electrostatic repulsion at the negatively charged pore walls, and the measured porosity is an "effective porosity". Another explanation is that some pores are more available than other pores.

5.1.2.1 Iodide

Diffusion of iodine has been studied intensely, and generally in the more important highly soluble form, which is as the iodide ion, I^-. The other valence state, (V), corresponds to IO_3^-. I^- is considered a non-sorbing ion due to its negative charge. Some sorption experiments have, however, been done and the non-sorptive behaviour on rocks has been confirmed. The bulk phase diffusivity of I^- used in the calculations of Skagius and Neretnieks (1985), was $1.6 \cdot 10^{-9}$ m^2/s.

Ittner et al. (1988) reported apparent diffusivities of $(1.5 - 3.2) \cdot 10^{-14}$ m^2/s for diffusion of iodide in granite tablets.

Skagius and Neretnieks (1985) determined effective diffusivities of iodide in 0.1 and 1 M NaI solutions in granites and other rocks to be $(1\text{-}70) \cdot 10^{-14}$ m^2/s.

Bradbury and Green (1986) determined effective diffusivities in granite samples. In "fresh" rock D_e-values were $(2\text{-}160) \cdot 10^{-14}$ m^2/s and $(4.5\text{-}64) \cdot 10^{-13}$ m^2/s for weathered zones in Cornish Carnmenellis granite samples. For Canadian granite effective diffusivity values of $(2.5 - 16) \cdot 10^{-13}$ m^2/s were reported. An effective diffusivity value of $5 \cdot 10^{-13}$ m^2/s was suggested to be a good estimate for Swedish, Canadian and UK granites.

Smith et al. (1990) calculated an effective diffusivity of $2.4 \cdot 10^{-11}$ m^2/s for diffusion of I-125 and determined the porosity to be 10 %, using a solution of simulated groundwater spiked with a mixture of I-125, Sr-85 and Cs-137, and regarding I-125 as a non-sorbing tracer.

Suksi et al. (1987) aimed to determine apparent diffusivities in drill core cups and filled and unfilled natural fracture surfaces of tonalite, mica gneiss and Rapakivi granite samples. No concentration profile of iodine could be measured, with the method used, and no diffusion coefficients were calculated.

Suksi et al. (1987) obtained K_d-values of $(0.4\text{-}3.1)\cdot 10^{-3}$ m^3/kg for diffusion of iodide in drillcore cups and filled as well as unfilled natural fractures of tonalite, granite and gneiss after 6 months contact time. They also reviewed determinations by some other authors and found K_d-values to be around 10^{-3} m^3/kg. Aksoyoglu et al. (1991) found no detectable sorption of I-131 on mylonite.

Rock	Water	D_e (m^2/s)	D_a (m^2/s)	ε (%)	α (%)	F_f	Ref	Comments
Finnsjön Granite (younger granite)	0.1 M NaI in distilled water	2.60E-13		0.4-0.6	0.37	1.62E-04	Skagius 1985	Porosities are determined by two methods
		3.20E-13		0.5-0.6	0.32	2.00E-04		
		4.40E-13		0.4-0.55	0.26	2.75E-04		
		2.50E-13		0.4	0.38	1.56E-04		
		2.70E-13		0.3-0.4	0.34	1.69E-04		
		2.26E-13		0.24-0.34	0.34	1.41E-04		
		2.20E-13		0.19-0.31	0.36	1.38E-04		
		2.40E-13		0.25-0.3	0.28	1.50E-04		
		2.48E-13		0.21-0.3	0.41	1.55E-04		
		2.50E-13		0.19-0.27	0.37	1.56E-04		
		2.65E-13		0.26-0.27	0.47	1.66E-04		
		2.53E-13		0.26-0.28	0.41	1.58E-04		
		2.47E-13		0.21-0.30	0.37	1.54E-04		
		2.44E-13		0.23-0.29	0.32	1.52E-04		
		2.35E-13		0.24-0.4	0.34	1.47E-04		
		2.48E-13		0.25-0.35	0.37	1.55E-04		
		4.40E-13		0.26-0.37	0.65	2.75E-04		
Granite Finnsjön	0.1 M NaI in distilled water	7.10E-14		0.1-0.2	0.27	4.40E-05		
		4.10E-14		0.1-0.2	0.18	2.60E-05		
	1 M NaI in distilled water	8.40E-14		0.14	0.3	5.20E-05		
		7.00E-14		0.11	0.2	4.40E-05		
Stripa granite	1 M NaI in distilled water	1.60E-13		0.3	1.05	1.00E-04		
		1.30E-13		0.27	0.21	8.10E-05		
Karlshamn gneiss	1 M NaI in distilled water	1.30E-13		0.32	0.74	8.10E-05		
Karlshamn gneiss	0.1 M NaI in distilled water	4.80E-14		0.26	0.27	3.00E-05		
Magmatite Studsvik	1 M NaI in distilled water	1.20E-13		0.17-0.21	0.3	7.50E-05		
	0.1 M NaI in distilled water	2.00E-13		0.17-0.22	0.3	1.25E-04		

Table 5.3 Literature data, iodide.

Rock	Water	D_e (m^2/s)	D_a (m^2/s)	ε (%)	α (%)	F_f	Ref	Comments
Gideå granite	0.1 M NaI in	1.00E-13		0.12-0.17	0.14	6.20E-05	Skagius 1985	
	distilled water	1.30E-13		0.12-0.18	0.14	8.10E-05		
		9.00E-14		0.11-16	0.14	5.60E-05		
		1.10E-13		0.11-17	0.14	6.90E-05		
Gideå gneiss	0.1 M NaI in distilled water	1.80E-14		0.06-0.07	0.05	1.12E-05		
Svartberget granite	0.1 M NaI in	1.90E-14		0.07	0.07	1.19E-05		
	distilled water	3.50E-14		0.07-0.09	0.12	2.19E-05		
Svartberget migmatite	0.1 M NaI in	6.60E-13		0.2-0.25	1.14	4.12E-04		
granite	distilled water	3.40E-13		0.29-0.36	0.58	2.12E-04		
		2.60E-13		0.26-0.3	0.28	1.62E-04		
Garnet holding biotite	0.1 M NaI in	1.50E-13		0.21-0.34	0.26	9.40E-05		
gneiss	distilled water	3.60E-13		0.28-0.32	0.92	2.25E-04		
Fjällveden biotote	0.1 M NaI in	7.20E-14		0.1-0.26	0.36	4.50E-05		
gneiss	distilled water	7.40E-14		0.1-0.29	0.15	4.60E-05		
Finnsjön granite	synthetic GW		1.90E-14				Ittner et al 1988	I-125
Stripa granite			3.20E-14				Ittner et al 1988	I-125
Studsvik granite			1.50E-14				Ittner et al 1988	I-125
Darley Dale sandstone	Simulated GW [Sr]=1.4e-5, [I]=1.3e-10, [Cs]=1.9e-5M	2.40E-11		10			Smith 1990	

Table 5.3 Literature data, iodide.

Rock	*Water*	D_e (m^2/s)	D_a (m^2/s)	ε (%)	α (%)	F_f	*Ref*	*Comments*
Cornish Carnmenellis granite		6.40E-12			6.5		Bradbury 1986	s1(0)
		2.10E-13			0.3			s1(20)
		3.10E-14			0.04			s1(5)
		4.50E-13			0.28			s2(0)
		2.50E-13			0.33			s2(5)
		1.30E-12			0.16			s3(0)
		5.60E-14			0.057			s3(5)
		5.60E-14			0.065			s3(10)
		8.60E-14			0.08			s3(15)
		7.70E-14			0.096			s3(25)
		1.50E-14			1.9			s4(0)
Canadian granites		5.70E-13			0.4			
		4.70E-13			0.29			
		2.80E-13			0.18			
		2.50E-13			0.28			
		4.80E-13			0.28			
		1.60E-12			0.93			
		6.60E-13			-			
Granite**		1.32E-12			-			(0)
		8.30E-13			0.58			(1.5)
		9.90E-13			-			(1.5)
		7.50E-13			-			(3)
		7.50E-12			0.88			(7.5)

** Samples taken from a fissure containing core

s1(0) = sample 1 including the fissure surface

s1(20)= 20 cm from the fissure surface

Table 5.3 Literature data, iodide.

5.1.2.2 Chloride

Kumpulainen and Uusheimo (1989) made diffusion measurements and electrical resistivity measurements in granite and gneiss samples. The NaCl-concentration was 0.004 M in the diffusion measurements and 1M in the electrical resistivity measurements. D_e-values from the diffusion measurements were $(0.06\text{-}0.72)\cdot 10^{-14}$ m^2/s and for electrical resistivity measurements $(2.4\text{-}14.2)\cdot 10^{-14}$ m^2/s. Calculations using measured diffusivities gave diffusion porosities (D_e/D_a) of 0.010-0.033 %, while water saturation methods resulted in values one to two orders of magnitude greater.

Lehikoinen et al. (1992) reported effective diffusivities in the same rock samples as used by Kumpulainen and Uusheimo. Effective diffusivities were compared when NaCl-concentration changed from 0.0044 M to 1M and again to 0.0044 M. D_e-values increased about one order of magnitude when the 1 M solution was used and decreased again for the last 0.0044 M solution. D_e-values were $5.0\cdot 10^{-17}$ - $4.4\cdot 10^{-14}$ for granites and $5.0\cdot 10^{-16}$ - $2.0\cdot 10^{-14}$ m^2/s for gneiss. In new gneiss samples D_e-values varied from $1.4\cdot 10^{-14}$ to $2.8\cdot 10^{-14}$ m^2/s when NaCl-concentration varied between 0.0044 and 1M. Fitting a dead-end porosity model to the experimental outleaching profiles from Rapakivi granite samples, gave the D_e-values $(2\text{-}5)\cdot 10^{-14}$ m^2/s for NaCl-concentrations between 0.001 and 1M.

Rock	*NaCl-conc* (*M*)	D_e (*m^2/s*)	D_a (*m^2/s*)	F_f	ε %	α %	*Ref*	*Comments*
gneiss 1	0.004	2.40E-15	1.00E-11			0.024*	Kumpulainen 1989	diffusion experiments
gneiss 2		6.00E-16	5.40E-11			0.001*		
gneiss 3		1.10E-15	1.80E-11			0.006*		
gneiss 1	1	7.20E-14		4.87E-05				El. resistivity measurements
gneiss 2		8.30E-14		5.61E-05				
gneiss 3		5.90E-14		3.96E-05				
Granite 1	0.004	2.60E-15	8.00E-12			0.032*		diffusion experiments
Granite 2		7.20E-15	1.10E-11			0.065*		
Granite 3		6.00E-16	6.30E-11			0.001*		
Granite 1	1	1.14E-13		7.68E-05				El. resistivity measurements
Granite 2		1.42E-13		9.07E-05				
Granite 3		2.40E-14		1.62E-05				

Changing the NaCl-conc between 0.0044 and 1 M in the same rock sample.

Rock	*NaCl-conc* (*M*)	D_e (*m^2/s*)	D_a (*m^2/s*)	F_f	ε %	α %	*Ref*	*Comments*
Gneiss 1	0.0044	2.60E-15				0.024*	Lehikoinen 1992	
Gneiss 1	1	2.00E-14						
Gneiss 1	0.0044	5.00E-16						
Gneiss 2	0.0044	7.00E-16				0.001*		
Gneiss 2	1	1.50E-14						
Gneiss 2	0.0044	4.00E-16						
Gneiss 3	0.0044	1.20E-15				0.006*		
Gneiss 3	1	1.90E-14						
Gneiss 3	0.0044	1.90E-15						
Granite 1	0.0044	2.90E-15				0.032*		
Granite 1	1	1.90E-14						
Granite 1	0.0044	1.90E-16						
Granite 2	0.0044	8.10E-15				0.065*		
Granite 2	1	4.40E-14						
Granite 2	0.0044	9.80E-15						
Granite 3	0.0044	6.00E-16				0.001*		
Granite 3	1	6.00E-15						
Granite 3	0.0044	5.00E-17						

New gneiss samples:

Rock	*NaCl-conc* (*M*)	D_e (*m^2/s*)	D_a (*m^2/s*)	F_f	ε %	α %	*Ref*	*Comments*
Gneiss 5	0.0044	1.4E-14					Lehikoinen 1992	
Gneiss 6	0.7	2.8E-14						
Gneiss 7	1	2.2E-14						

Fitting a dead-end porosity model to the experimental outleaching profiles from rapakivi granite samples the following results were obtained:

Rock	*NaCl-conc* (*M*)	D_e (*m^2/s*)	D_a (*m^2/s*)	F_f	ε %	α %	*Ref*	*Comments*
Rapakivi granite	1	4E-14				0.1	Lehikoinen 1992	
	0.1	5E-14				0.06		
	0.01	3E-14				0.06		
	0.001	2E-14				0.04		

* Porosities calculated from diffusivities D_e/D_a by Kumpulainen (1989)

Table 5.4 Literature data, chloride

5.1.2.3 Bromide

No diffusivities in rock has been found in the literature but sorption on mylonite has been studied by Aksoyoglu et al. (1991), but no sorption of Br-82 was observed.

5.1.2.4 Cr-EDTA

Skagius and Neretnieks (1983) determined effective diffusivities of Cr-EDTA in granites to be $0.7 \cdot 10^{-14}$ m^2/s and less than $7.5 \cdot 10^{-16}$ m^2/s in Gabbro. In free water at 25°C the diffusivity was $4.2 \cdot 10^{-10}$ m^2/s. In 1985 they reported effective diffusivities of $(6\text{-}49) \cdot 10^{-15}$ m^2/s for granite and gneiss.

Porosities determined by two methods, the water saturation method and the leaching method, gave values between 0.1 and 0.4 %. Porosities determined from concentration versus time graphs gave generally lower values, 0.03-0.13 %, and one value of 0.29 % which was more in accordance with those from the "direct" measurements.

Rock	*Water*	*Cr-EDTA-Conc (g/l)*	ε *(%)*	α *(%)*	D_e *(m^2/s)*	F_f	*Ref*
Finnsjön granite	distilled water	10			6.90E-15	1.60E-05	Skagius 1983
gabbro					<7.5E-16	<0.18e-5	
gabbro					<8.2E-16	<0.19e-5	
Studsvik migmatite			0.19	0.032	9.50E-15	2.30E-05	
			0.18	0.004	4.90E-15	7.50E-06	
Finnsjön granite	distilled water	8	0.10-0.22	0.04	6.20E-15	1.50E-05	Skagius1985
Studsvik migmatite			0.16-0.21	0.03	9.40E-15	2.20E-05	
Gideå granite			0.15-0.17	0.11	1.30E-14	2.90E-05	
			0.16-0.19	0.12	1.30E-14	2.90E-05	
Svartboberget migmatite granite.			0.28-0.36	0.29	4.90E-14	1.17E-04	
			0.22-0.34	0.13	2.90E-14	6.90E-05	
Garnetholding biotite gneiss.			0.24-0.32	0.13	2.50E-14	7.10E-05	
			0.29-0.34	0.06	3.00E-14	7.10E-05	
Biotite gneiss			0.27-0.33	0.08	6.00E-15	1.40E-05	

Table 5.5 Literature data, Cr-EDTA

5.1.2.5 Uranin

Skagius and Neretnieks (1983, 1985) determined effective diffusivities of uranin in granites and other rocks to be $0.23 \cdot 10^{-14}$ m^2/s. In free water at 25°C the diffusivity was $4.5 \cdot 10^{-10}$ m^2/s. Effective diffusivities in discs of granite was also determined by Eriksen (1985) to be $(2.9-4.0) \cdot 10^{-14}$ m^2/s. In this case the porosity of the granite was 2-3 % i.e. about an order of magnitude larger than that of the rocks used by Skagius and Neretnieks.

Rock	*Water*	D_e (m^2/s)	ε (%)	α (%)	F_f	*Ref*	*comments*
Granite		4.03E-14	3.4			Eriksen 1985	Disc thickness: 0.14 cm
Granite		2.94E-14	2.4				Disc thickness: 0.21 cm
Granite		2.94E-14	2.3				Disc thickness: 0.28 cm
Finnsjön granite	Distilled water with	2.30E-15	0.06			Skagius, Neretnieks 1983	
Gabbro	[Uranine]=9.9 g/l	<4.0e-16					
Gabbro		<2.8e-16					
Finnsjön granite	Distilled water with	2.20E-15	0.06	0.02	5.00E-06	Skagius, Neretnieks 1985	
	[Uranine]=10 g/l	5.30E-15	0.09-0.21	0.02	1.20E-05		
Migmatite Studsvik		2.30E-14	0.18-0.22	0.22	5.10E-05		
Granite Gideå		1.30E-14	0.15-0.17	0.11	2.90E-05		
		1.30E-14	0.16-0.19	0.12	2.90E-05		
Gneiss Gideå		3.20E-15	0.11-0.12	0.11	7.10E-06		
Gneiss Svartberget		9.30E-15	0.08-0.12	0.07	2.07E-05		
		9.60E-15	0.08-0.11	0.07	2.13E-05		
Migmatite granite		6.90E-14	0.22-0.33	0.30	1.53E-04		
		5.20E-14	0.30-0.38	0.94	1.16E-04		
biotite gneiss (from		7.80E-14	0.30-0.38	0.52	1.73E-04		
Svartboberget)		6.00E-14	0.23-0.32	0.62	1.33E-04		
Biotite gneiss (From		3.60E-15	0.17-0.24	0.02	8.00E-06		
Fjällveden)		3.90E-15	0.19-0.24	0.04	9.00E-06		

Table 5.6 Literature data, uranin

5.2 SORBING SPECIES

Diffusion of sorbing species is generally slower than for non-sorbing species due to sorption on mineral surfaces in the rock pores. For some cations, however, unexpectedly high diffusivities have been obtained. This has been suggested to be due to transport in the sorbed state much like the surface diffusion phenomena observed on metal surfaces. The diffusivities generally decrease with increasing ionic strength, to a value that is suggested to be due to pure pore diffusion. The sorption sites are in this case saturated by for example Na^+ or K^+. Sorption is generally concentration dependent and is linear or non-linear. Non-linear sorption can be described by a sorption isotherm, for example the Freundlich or the Langmuir isotherm. Sorption can also be linear in one concentration range while it is non-linear in another. Sorption mechanisms were described in chapter 3.

Suksi et al. (1987) did sorption experiments on natural filled and unfilled fracture surfaces and in drill core cups. Sorption was more effective on natural fracture surfaces than on freshly drilled core samples. After one week the sorption tendency of radionuclides on the rock samples was: K_a (Cs) > K_a(Co) > K_a(Am) > K_a(Ni) > K_a(Sr) > K_a(I). In general, filling material (except calcite) increased sorption.

5.2.1 Americium

Americium sorbs strongly on geologic materials and has a low solubility in groundwater. The large ion radius prevents deep penetration into the mineral lattice (Suksi et al. 1987). Ittner et al. (1988) reported the D_a-values (3.90-280) 10^{-16} m^2/s of Am-241 in Swedish granites. Suksi et al. (1987) could not observe any diffusion of Am-241 in drill core cups and filled and unfilled natural fracture surfaces of tonalite, mica gneiss and Rapakivi granite samples after one years' contact time.

Haakanen and Hölttä (1992) reviewed reported sorption coefficients. For Finnish minerals K_d-values between 0.33 and 9.6 m^3/kg have been obtained.

Rock	*Water*	*Cond*	*Contact time (days)*	*Conc (M)*	*D_a (m^2/s)*	*Ref*	*Comments*
Finnsjön granite	Synthetic		355	1.00E-08	2.30E-14	Ittner 1988	Am-241, rock tablets 2x2x2 cm
Finnsjön granite	Synthetic		263	1.00E-08	2.80E-14		
Finnsjön granite	Synthetic	pH=8.4	877	1.00E-09	3.90E-16		
Studsvik granite	Synthetic		85	1.00E-08	7.10E-16		
Stripa granite	Synthetic	pH=8.6	665	1.00E-09	1.00E-15		
Stripa granite	Synthetic	pH=8.9	1202	1.00E-09	3.80E-15		

Table 5.7 Literature data, americium

5.2.2 Cobalt

For Inada granite Idemitsu et al. (1992) reported D_a-values in deionized water, and distinguished between diffusion in the matrix and a higher diffusion in fissures of a few microns width. The evaluated values for matrix diffusion were $(4\text{-}8)\cdot10^{-14}$ m^2/s, and for the fissure diffusion $(0.8\text{-}2)\cdot10^{-11}$ m^2/s. Yamaguchi et al. (1993) reported the D_e-values $(1.60\text{-}3.50)\cdot10^{-13}$ m^2/s in 0.1 M KCl. Suksi et al. (1987) determined apparent diffusivities of Co-60 in drill core cups and filled and unfilled natural fracture surfaces of tonalite, mica gneiss and Rapakivi granite samples to be $(8.5\text{-}96)\cdot10^{-17}$ m^2/s after one years' contact time in synthetic groundwater with the ionic strength 0.0085.

Sorption has been found to decrease with increasing ionic strength, but it has not been shown that cation exchange is the governing sorption mechanism. Sorption coefficients were reviewed by Suksi et al. (1987) to lay in the range 0.14-0.16 m^3/kg (McKinley, Nikula). In their own determinations K_d-values were 0.01-0.1 m^3/kg for sorption in drill core cups of tonalite, gneiss and granite. On filled and unfilled natural fracture surfaces K_d-values of 0.02-0.9 m^3/kg were reported. All values were measured after one years' contact time with spiked synthetic ground water.

Rock	*Water*	*Cond*	*Cont. time*	*Conc (M)*	*D_e (m^2/s)*	*D_a (m^2/s)*	*e (%)*	*Ref*	*Comments*
Inada granite	Deionized water	30°C, pH4.2				8.00E-14	0.8	Idemitsu et al 1991	D_{fa}= 2.00E-11
		30°C, pH6.1				4.00E-14			8.00E-12
		30°C, pH7.6				8.00E-14			2.00E-11
		30°C, pH9.3				8.00E-14			2.00E-11
Inada granite	0.1M KCl	pH=4, 25°C			1.60E-13		0.7	Yamaguchi et al 1993	$D_{(bulk)}$ =6.99E-10 m^2/s
					2.10E-13				
					2.20E-13				
					2.50E-13				
					2.60E-13				
					3.10E-13				
					3.40E-13				
					3.50E-13				
Tonalite	synthetic G W, ion strength 0.0085		6 m	7.60E-10	1.20E-14	5.40E-17		Pinnioija 1985	D.c.c
			12 m	7.10E-09		4.80E-16		Muuronen 1985	D.c.c
			12 m	3.50E-09		8.30E-16		Suksi 1987	N.f.s. unfilled
			6 m	3.50E-09		1.11E-14		Suksi 1987	N.f.s. filled
mica gneiss	synthetic G W, ion strength 0.0085		12 m	7.10E-09		8.50E-17		Suksi 1987	D.c.c
			12 m	3.50E-09		7.50E-16		Suksi 1987	N.f.s. unfilled
Rapakivi granite	synthetic G W, ion strength 0.0085		12 m	7.10E-09		5.00E-16		Suksi 1987	D.c.c
			6 m	3.50E-09		3.90E-16		Suksi 1987	N.f.s. unfilled
			12 m	3.50E-09		9.60E-16		Suksi 1987	N.f.s. unfilled
			6 m	3.50E-09		1.85E-15		Suksi 1987	N.f.s. filled
			12 m	3.50E-09		7.50E-16		Suksi 1987	N.f.s. filled

D.c.c = drill core cup, N.f.s = natural fissure surface

Table 5.8 Literature data, cobalt

5.2.3 Cesium

Cs is strongly sorbing and occurs in the form Cs^+, which does not form stable complexes with anions usually found in ground water. Sorption on geologic material is mainly by cation exchange, dependent on pH and ionic strength of water, and has been found to be non-linear and reversible (Aksoyoglu et al. (1991), Suksi et al. (1987)). Aksoyoglu also found that at least two different types of sorption sites might be involved in sorption, depending on if the cesium uptake is high or low, and that there could be competition between cesium and potassium for the available sorption sites. Migration into the rock matrix follows pathways constituted by high-capacity minerals (mainly biotite, hornblende and chlorite) in grains or in microfissures (Torstenfelt et al. 1983). Cesium did not sorb significantly on calcite, which decreased K_a-values, in the experiments of Pinnioja et al. (1985). Surface coating materials do not prevent migration into the underlying rock, and fracture minerals act as good sorption surfaces to cesium (Torstenfelt et al. 1983). The diffusivity of Cesium in synthetic groundwater was determined by Skagius and Neretnieks, 1986, to be $2.4 \cdot 10^{-9}$ m²/s, which is 1.5-2 times greater than for the corresponding strontium salt.

Apparent diffusivities, D_a, under oxic conditions have been calculated from in-diffusion experiments in many investigations. Puukko et al. (1993) and Suksi et al. (1987) reported D_a values for Cs-134 between $1 \cdot 10^{-15}$ and $17 \cdot 10^{-14}$ m²/s for tonalite, $0.47 \cdot 10^{-15}$ and $180 \cdot 10^{-14}$ m²/s for granite and $(2.6\text{-}6.7) \cdot 10^{-14}$ m²/s for gneiss. The experiments of Kaukonen et al. (1993) resulted in $(0.47\text{-}2.72) \cdot 10^{-14}$ m²/s for basic rocks (plutonic rocks and vulcanite) and Ittner et al. (1987) and Torstenfelt et al. (1982,1983) reported values for Cs-137 in granite between $(2.4\text{-}22) \cdot 10^{-14}$ m²/s and $(5.3\text{-}31) \cdot 10^{-14}$ m²/s, respectively. Idemitsu et al. (1992) distinguished between diffusion in the matrix and a higher diffusion in fissures of a few microns width in deionized water. Determinations gave $D_{a(matrix)}$-values of $(3\text{-}7) \cdot 10^{-14}$ m²/s, and $D_{a(fissure)}$ -values of $(1\text{-}3) \cdot 10^{-11}$ m²/s for Cs-134 diffusion in granite.

Skagius and Neretnieks (1982) reported an effective diffusivity of $(3\text{-}160) \cdot 10^{-13}$ m²/s in granite particle fractions. In 1986 they obtained effective diffusivities of $(1\text{-}2) \cdot 10^{-12}$ m²/s in pieces of granite. Smith et al. (1990) calculated an effective diffusivity of $(2.3\text{-}2.6) \cdot 10^{-11}$ m²/s for diffusion of Cs-137 in Darley Dale Sandstone with a porosity of 10 %, using a solution of simulated groundwater spiked with a mixture of I-125, Sr-85 and Cs-137.

Torstenfelt et al. (1982) used K_d-values 0.150-1.110 m³/kg, obtained in batch measurements (with a contact time of one day), to calculate effective diffusivities from measured apparent diffusivities.

Distribution coefficients of 0.8-1.9 m^3/kg for rocks in low-salinity ground water and 0.1-0.3 m^3/kg in more alkaline waters were obtained by Kaukonen et al. (1993). In the experiments of Aksoyoglu et al. (1991) sorption coefficients varied between 21 and 3800 ml/g on mylonite.

The Freundlich exponent has been determined to be 0.54 - 0.66 by Skagius et al. (1982). For Cs concentrations between $2 \cdot 10^{-9}$ and $1.3 \cdot 10^{-4}$ M the Freundlich exponent was 0.588-0.603 in the sorption experiments of Aksoyoglu et al. (1991). An increase of the potassium concentration lead to decreased sorption of Cs, suggesting competition between Cs and K for available sites.

Rock	*Water*	*Condition*	*Cs conc (M)*	*D_e (m^2/s)*	*D_a (m^2/s)*	*ε (%)*	*Ref*	*Comments*
Tonalite	Allard	Aerobic			(1.7-5.7)E-14		Puukko et al 1993	
	Romuvaara	Aerobic			(5.6-17)E-14			
Granite	Allard	Aerobic			(6.5-1800)E-15			
	Romuvaara	Aerobic			2.60E-14			
Gneiss	Allard	Aerobic			(3.1-6.7)E-15			
	Olkiluoto	Aerobic			2.60E-15			
Mäntsälä plutonic rock	Allard				1.15E-14		Kaukonen et al 1993	D_a values were derived from diffusion profiles.
Mäntsälä plutonic rock	Allard				4.70E-15			
Syyry plutonic rock	Syyry Ground water				1.68E-14			
Syyry plutonic rock	Syyry Ground water				2.72E-14			
Sodankylä vulcanite	Allard				1.90E-14			
Sodankylä vulcanite	Allard				2.08E-14			
Inada granite	Deionized water	30°C, pH4.3			3.00E-14	0.8	Idemitsu et al 1992	D_{fa}=1.00E-11 m^2/s
		30°C, pH6.0			6.00E-14	0.8		1.00E-11
		30°C, pH7.7			5.00E-14	0.8		1.00E-11
		30°C, pH9.4			5.00E-14	0.8		1.00E-11
		40°C, pH4.2			5.00E-14	0.8		1.50E-11
		56°C, pH4.2			7.00E-14	0.8		3.00E-11
Finnsjön granite	Synthetic				5.00E-12		Ittner et al 1988	Cs-137
Finnsjön granite					1.20E-13			
Finnsjön granite					2.20E-13			
Finnsjön granite					8.30E-14			
Finnsjön granite					1.40E-13			
Studsvik granite	Synthetic				5.90E-14			
Studsvik granite					3.50E-14			
Studsvik granite					1.10E-13			
Stripa granite	Synthetic				1.80E-13			
Stripa granite					2.40E-14			
Stripa granite					3.40E-14			
Stripa granite					2.50E-14			

Table 5.9 Literature data, cesium

Rock	*Water*	*Cond*	*Cs-conc* *(M)*	D_e *(m^2/s)*	D_a *(m^2/s)*	ε *(%)*	*Ref*	*Comments*
Finnsjön granite	Synthetic Allard			8.50E-13		0.3-0.5	Skagius et al 1982	0.100-0.120 mm*
Finnsjön granite				2.80E-12				0.200-0.250 mm
Finnsjön granite				3.80E-12				0.375-0.43 mm
Finnsjön granite				3.70E-11				1.0-1.5 mm
Finnsjön granite				1.20E-11				2.0-3.0 mm
Finnsjön granite				1.60E-11				4.0-5.0 mm
Stripa granite				2.90E-13				0.100-0.120 mm
Stripa granite				9.80E-13				4.0-5.0 mm
Tonalite	synthetic G W, ion strength 0.0085	3 m cont.time			2.00E-15		Suksi 1987	D.c.c, Cs-134
		6 m			1.50E-15			D.c.c
		12 m			7.20E-15			D.c.c
Rapakivi granite		6 m			3.40E-14			D.c.c
mica gneiss		12 m			4.70E-16			D.c.c
Tonalite		12 m	5.00E-07		3.70E-15			N.f.s. unfilled
		3 m	5.00E-07		3.20E-14			N.f.s. filled
		12 m	5.00E-07		1.00E-15			N.f.s. filled
Mica gneiss		12 m	5.00E-07		3.30E-15			N.f.s. unfilled
		12 m	5.00E-07		3.80E-15			N.f.s. filled
Rapakivi granite		12 m	5.00E-07		1.2E-15			N.f.s. unfilled
		3 m	5.00E-07		2.70E-14			N.f.s. filled
		12 m	5.00E-07		1.20E-15			N.f.s. filled
Finnsjö granite	Synthetic GW**	132 d cont. time			2.10E-13		Torstenfelt (1982)	Cs-137,
Studsvik granite		132 d			7.90E-14			
Stripa granite		132 d			9.50E-14			
Stripa granite		85 d			3.10E-13			Ref sample, polished
Finnsjö granite	Synthetic GW**				1.30E-13		Torstenfelt (1983)	Cs-137,
Studsvik granite					1.70E-13			
Stripa granite					5.30E-14			
Stripa granite					5.80E-14			Ref sample, polished

* Particle size fraction

** Synthetic groundwater representative of the waters at the sampling locations

Table 5.9 Literature data, cesium

Rock	*Water*	*Cont. time*	Cs-*Conc* *(M)*	D_e *(m^2/s)*	D_a *(m^2/s)*	ε *(%)*	K_d *(m^3/kg)*	β	*Ref*	*Comments*
Darley Dale sandstone	Simulated GW		1.9E-5	4.50E-11		10	44±3	1	Smith 1990	Linear sorpt. model
				2.31E-11			1.29±0.06	0.550		non-linear model
				2.57E-11			3.4±3.4	0.705		non-linear model
				4.60E-11			40±10	1.00		non-linear model
Stripa granite				1.00E-12			1.1	0.66	Skagius 1986	granite pieces
				1.00E-12			3.9	0.66	Skagius 1982	granite particles
Finnsjö granite				1.60E-12			9.8	0.54	Skagius 1986	granite pieces
				1.60E-11			30	0.54	Skagius 1982	granite particles
Finnsjö granite				1.00E-12			6.1	0.54	Skagius 1986	Granite pieces, simultaneous sorption (Cs, Sr)
Finnsjö granite		132 d		2.70E-10	2.10E-13		0.49		Torstenfelt 1982	Cs-137
Studsvik granite		132 d		2.30E-10	7.90E-14		1.11			
Stripa granite		132 d		3.80E-10	9.50E-14		0.15			
Stripa granite		85 d		1.20E-10	3.10E-13		0.15			Ref sample, polished

Table 5.9 Literature data, cesium

5.2.4 Sodium

Fitting a dead-end porosity model to the experimental outleaching profiles from Rapakivi granite Lehikoinen et al. (1992) achieved effective diffusivities of (8-100)·10^{-14} m^2/s in NaCl-concentrations of 0.001-1 M giving the lowest diffusivities for the highest concentrations.

Rock	*NaCl-Conc.* *(M)*	*De* *(m^2/s)*	*Ref.*
Rapakivi granite	1	8E-14	Lehikoinen et al. 1992
	0,1	3E-13	
	0,01	4E-13	
	0,001	1E-12	

Table 5.10 The effect of salinity on diffusivity

Aksoyoglu et al. (1991) did sorption and desorption experiments with sodium on mylonite. At concentrations much below natural levels, no concentration dependence was observed. In desorption with the bulky exchanging complex AgTU desorption coefficients were much lower than in sorption. This was suggested to be due to that some exchangeable internal Na sites were not accessible, which could have caused the slow kinetics. Sorption was slow and steady state had not been reached within 49 days, when the experiments were ended. The steady-state sorption coefficient was suggested to be 3.0 - 3.5 ml/g.

5.2.5 Nickel

Yamaguchi et al. (1993) achieved D_e values of $(1.9\text{-}3.6)\cdot 10^{-13}$ m^2/s in Inada granite and 0.1 M KCl-solution. Suksi et al. (1987) measured apparent diffusivities for indiffusion of Ni-63 in drill core cups, and filled and unfilled natural fracture surfaces of tonalite, mica gneiss and Rapakivi granite samples. The experiments were carried out in synthetic groundwater with the ionic strength 0.0085. The D_a-values $(1.6\text{-}4.1)\cdot 10^{-16}$ m^2/s were achieved.

Andersson et al. (1983) measured sorption of nickel on granite and obtained K_d-values of 0.4 m^3/kg. A conservative value of 0.2 m^3/kg was suggested in the KBS-programme due to the similarities between nickel and cobalt. Suksi et al. (1987) reported K_d-values 0.021-0.13 m^3/kg for sorption on drill core cups of granite, gneiss and tonalite, and after 19 months contact time. For natural fracture surfaces, filled and unfilled, values were 0.4-12.1 m^3/kg.

Rock	*Water*	*Cond*	*Cont. time*	*Ni-Conc (M)*	D_e *(m^2/s)*	D_a *(m^2/s)*	ε *(%)*	*Ref*	*Comments*
Inada granite	0.1M KCl	pH=4, 25°C		0.1	1.9E-13		0.7	Yamaguchi 1993	$D_{(bulk)}$ =6.79E-10, multi component experiment
					2.0E-13				
					2.4E-13				
					2.5E-13				
					2.9E-13				
					3.0E-13				
					3.4E-13				
					3.6E-13				
Rapakivi granite	synthetic G W, ion strength 0.0085		12 m			1.60E-16		Suksi 1987	D.c.c
Tonalite			6 m			8.60E-16			N.f.s. filled
Tonalite			12 m			4.00E-16			N.f.s. filled
Rapakivi granite			12 m			3.40E-16			N.f.s. unfilled
Rapakivi granite			6 m			1.39E-15			N.f.s. filled
Rapakivi granite			12 m			4.10E-16			N.f.s. filled

Table 5.11 Literature data, nickel

5.2.6 Neptunium

Suksi et al. (1989) reported apparent diffusivity values of $(2.7\text{-}4.3)\cdot 10^{-14}$ m^2/s for tonalite and $3.0\cdot 10^{-13}$ m^2/s for porphyritic granite under oxic conditions. Under anoxic conditions the corresponding D_a -values lay in the range $(1.4\text{-}9.6)\cdot 10^{-14}$ m^2/s.

Puukko et al. (1993) made diffusion experiments in tonalite under anaerobic and aerobic conditions. Under aerobic conditions D_e-values were $(1.8\text{-}2.5)\cdot 10^{-14}$ m^2/s and D_a $1.9\cdot 10^{-12}$ m^2/s in Allard water. In Romuvaara-water and aerobic conditions D_e were $4.6\cdot 10^{-14}$ m^2/s and D_a $2.8\cdot 10^{-12}$ m^2/s. Under anaerobic conditions and in Allard water, D_e were $7.7\cdot 10^{-15}$ m^2/s, i.e. about the same under reducing as under oxidising conditions.

Ittner et al. 1988 reported apparent diffusivities of $(3.3 - 4.2)\cdot 10^{-15}$ for Np-237 in Finnsjön and Stripa granite.

As compared to the cation exchange sorption of cesium and strontium on high-capacity minerals, neptunium sorption (also mostly on high-capacity minerals) is predominantly due to physical sorption and therefore these minerals act as transport pathways into the rock to a much less extent than for cesium and strontium (Ittner et al. 1988).

Suksi et al. (1989) describes the aqueous behaviour of Np and reported that under oxidising conditions the pentavalent state of Np is dominating in the form of NpO^{2+} at pH below 7-8 or as NpO_2HCO_3. Under reducing water condition then Np primarily exists in the oxidation state IV, probably mainly as $Np(OH)_4$ as the dominant aqueous species. In contradiction to this Puukko et al. (1993) claimed that under anoxic conditions the Np in the water phase still consists of Np(V), but the sorbed Np is in the reduced Np(IV) state. They found sorption of Np on rocks to be very low under oxic conditions when K_d was calculated from D_e/D_a, $\varepsilon=0.3$ % and $\rho=2700$ kg/m^3. Under reducing conditions sorption was as high as 95-99 %. Precipitation was observed in all cases, but much more under anoxic conditions. In a review (by Suksi et al., 1989) of previous studies a K_d-value of 1 m^3/kg is suggested by McKinley and Haderman (1984) to be realistic for reducing conditions, and 0.1 m^3/kg for oxidising conditions.

Kaukonen et al. (1993) found sorption to be the same on basic and acidic rock under oxic and anoxic conditions. K_d-values showed some tendency to increase with decreasing bicarbonate concentration. Under oxic conditions with a bicarbonate concentration of 123 ppm the values varied between 0.016 and 0.072 m^3/kg, the highest value applying to Mäntsälä plutonic rock. For granite and tonalite the values were in the range 0.03-0.05 m^3/kg. Under anoxic conditions the values 0.9-1.8 m^3/kg were obtained. The higher values under anoxic conditions were explained by reduction to Np(IV) and formation of the strongly sorbing $Np(OH)_4$. No concentration dependence of sorption was observed under anoxic conditions. Hakanen and Hölttä (1992) suggest in a review report for TVO that 0.002 m^3/kg would be a conservative K_d value for granite while a realistic value would be 0.005 m^3/kg. For tonalites and mica gneisses a realistic value would be 0.01 m^3/kg.

Rock	*Water*	*Cond*	*Np-Conc (M)*	*Cont. time*	*D_e (m^2/s)*	*D_a (m^2/s)*	*Ref*	*comments*
Tonalite	Allard	Aerobic	(1.8-3.6)E-10		1.80E-14		Puukko et al 1993	
Tonalite	Allard	Aerobic	(1.8-3.6)E-10		2.50E-14	1.90E-12		
Tonalite	Romuvaara	Aerobic	(1.8-3.6)E-10		4.60E-14	2.80E-12		
Tonalite	Allard	Anaerobic	(1.8-3.6)E-10		7.70E-15			
Rapakivi granite	Allard	anoxic	7.80E-05	1/2 y		9.60E-14	Suksi et al 1989	Np-237 as $Np(NO_3)_5$
Rapakivi granite		anoxic	7.80E-05	1 y		1.40E-14		
Porphyritic granite		oxic	6.70E-05	1 y		3.00E-13		
Tonalite		oxic	6.70E-05	1/2 y		4.30E-14		
Tonalite		oxic	6.70E-05	1 y		2.70E-14		
Tonalite		anoxic	7.80E-05	1 y		2.10E-14		
Finnsjön granite	Synthetic GW*		1.00E-08	866 d		3.30E-15	Ittner et al 1988	Np-237
Stripa granite			1.00E-08	654 d		4.10E-15		

*Synthetic groundwater representative of the groundwaters from the sampling locations

Table 5.12 Literature data, neptunium

5.2.7 Strontium

The diffusivity of strontium in synthetic groundwater was determined by Skagius and Neretnieks (1986), to be $1 \cdot 10^{-9}$ m^2/s. Most determinations give diffusivities in rock too large to only be due to pore diffusion. The main sorption mechanism is by ion exchange on high capacity minerals and sorption decreases with increasing ionic strength.

Idemitsu et al. (1992) suggested that part of the diffusion was due to diffusion in the matrix and part to diffusion in fissures of a few microns width. Apparent diffusivities from "matrix diffusion" were $(4\text{-}5) \cdot 10^{-14}$ m^2/s and from "fissure diffusion" $(4\text{-}10) \cdot 10^{-12}$ m^2/s in Inada granite with deionized water.

Yamaguchi et al. (1993) reported effective diffusion coefficients, D_e, (also in Inada granite) of $(2.0\text{-}3.6) \cdot 10^{-13}$ m^2/s in 0.1M KCl solution and $(0.32\text{-}1.7) \cdot 10^{-11}$ in deionized water. They also reviewed earlier measurements.

Skagius et al. (1982) determined effective pore diffusivities of $(0.011\text{-}24) \cdot 10^{-12}$ m^2/s in granite particles. In 1986 they reported an effective diffusivity of $(1\text{-}2) \cdot 10^{-12}$ m^2/s in pieces of granite.

Ittner et al. (1988) reported apparent diffusivities of $(2.4\text{-}49) \cdot 10^{-14}$ m^2/s for diffusion of Sr-90 in granite under oxic conditions.

Smith et al. (1990) calculated an effective diffusivity of $14.8 \cdot 10^{-11}$ m^2/s for diffusion of Sr-85 in Darley Dale sandstone with a porosity of 10 %, using a solution of simulated groundwater spiked with a mixture of I-125, Sr-85 and Cs-137. The sorption isotherm was assumed to be linear, which gave a good fit to experimental values.

Suksi et al. (1987) calculated apparent diffusivities for Sr-90 that were $(6.6\text{-}2100) \cdot 10^{-16}$ m^2/s with the highest values for filled natural fracture surfaces of granite and the lowest for drill core cups of mica gneiss.

For mylonite particles (<63µm) distribution coefficients of 0.11 m^3/kg were obtained by Aksoyoglu et al. (1991) after contacting during 20-40 days using both solution activities and cation exchange methods for determination. For larger particles (<250 µm) values of $66.9 \cdot 10^{-3}$ m^3/kg for a contact time of 34 days, were obtained. For nuclide concentrations much below the natural levels in ground waters, sorption coefficients did not seem to be affected by different nuclide concentrations, indicating that isotopic exchange takes place in this concentration range.

Suksi et al. (1987) reported the K_d-values 0.001-0.01 m^3/kg, 0.006-0.025 m^3/kg, and 0.002-0.2 m^3/kg for 15 months contact time in drill core cups, 12 months in unfilled natural fractures and 12 months in filled natural fractures respectively. Rock types used were tonalite, granite and gneiss. They also reviewed earlier determinations like the results of Allard et al. that were 0.006-0.016 m^3/kg for crushed granite, and Vandergraaf's results 0.0006-0.06 m^3/kg for granite.

In the experiments of Skagius et al. (1982) the Freundlich exponent for strontium was evaluated to be 0.93-1.07 for sorption on granites (i.e. approximately linear). Yamaguchi et al. also used linear sorption which gave good fit to experimental data.

Smith (1990) determined the distribution coefficient from diffusion experiments in a solution of simulated groundwater spiked with a mixture of I-125, Sr-85 and Cs-137 and assuming a linear adsorption isotherm. Ordinary batch-sorption tests were also performed. K_d was determined to be 0.06 m^3/kg in diffusion experiments and 0.05 m^3/kg, with a water to rock ratio of 20:1, and 0.10 m^3/kg, with a water to rock ratio of 3:1, in batch-sorption tests on rock coupons.

Rock	*Water*	*Cond*	*Conc* *(M)*	D_e (m^2/s)	D_a (m^2/s)	ε %	α	*Ref*	*Comments*
Inada granite	Deionized water	30°C, pH4.3			4.00E-14	0.8		Idemitsu 1991	D_{fa}=1.00E-11
		30°C, pH6.0			4.00E-14				4.00E-12
		30°C, pH7.7			5.00E-14				1.00E-11
		30°C, pH9.4			4.00E-14				1.00E-11
Inada granite	0.1M KCl	pH=4, 25°C	0.1M $Sr(NO_3)_2$	2.00E-13		0.7	0.019	Yamaguchi 1993	$D_{(bulk)}$ =7.94E-10
				2.10E-13			0.002		$D_{(bulk)}$ =7.94E-10
				2.60E-13			0.022		$D_{(bulk)}$ =7.94E-10
				2.60E-13			0.003		$D_{(bulk)}$ =7.94E-10
				3.10E-13			0.019		$D_{(bulk)}$ =7.94E-10
				3.60E-13			0.014		$D_{(bulk)}$ =7.94E-10
	Deionized water	pH5.5, 25°C	0.1M $Sr(NO_3)_2$	3.20E-12			2.4		
				9.50E-12			1.5		
				1.70E-11			1.7		
Darley Dale sandstone	Distilled water			1.40E-10		10	51	Bradbury 1986*	
				1.20E-10		10	59		
Cenomanian sample	Ground water	pH=7.0		1.10E-10		8.1	7	Lang 1986*	
Anhydrite	Simulated ground water			1.30E-12		0.5	0.5	Bradbury 1986*	
				1.30E-12		0.5	0.8		
Upper magnesian limestone	Simulated ground water			7.40E-12		22	1.3	Bradbury 1986*	
				5.90E-12		22	1.3		
Biotite gneiss	Distilled water			1.00E-13		0.2	0.12	Skagius 1988*	
Finnsjön granite				4.50E-13				Skagius 1982	0.100-0.120 mm**
Finnsjön granite				1.60E-12					0.200-0.250
Finnsjön granite				3.50E-12					0.375-0.43
Finnsjön granite				4.40E-12					1.0-1.5
Finnsjön granite				1.10E-11					2.0-3.0
Finnsjön granite				2.40E-11					4.0-5.0
Stripa granite				1.10E-14					0.100-0.120
Stripa granite				1.00E-12					4.0-5.0

Table 5.13 Literature data, strontium

Rock	Water	Cond	Conc (M)	D_e (m^2/s)	D_a (m^2/s)	ε (%)	α	Ref	Comments
Stripa granite				1.30E-12		0.31-0.34		Skagius 1986	
Finnsjön granite				2.20E-12		0.18-0.91			
Finnsjön granite	Synthetic				4.90E-13			Ittner 1988	Sr-90
Stripa granite	Synthetic				2.70E-14				
Studsvik granite	Synthetic				2.40E-14				
Darley Dale sandstone	Simulated ground water		[Sr]=1.4e-5, [I]=1.3e-10, [Cs]=1.9e-5M	1.50E-10		10	150	Smith 1990	
Tonalite	synthetic G W, ion strength 0.0085	6 m cont time			5.10E-14			Suksi 1987	D.c.c, Sr-90
		12 m			1.40E-14				D.c.c
Mica gneiss		6 m			1.70E-14				D.c.c
		12 m			6.60E-16				D.c.c
Rapakivi granite		6 m			3.50E-14				D.c.c
		12 m			1.10E-14				D.c.c
Tonalite		3 m			3.50E-14				N.f.s. unfilled
		12 m			2.30E-14				N.f.s. unfilled
		3 m			5.40E-14				N.f.s. filled
		12 m			1.60E-14				N.f.s. filled
Mica gneiss		3 m			9.10E-14				N.f.s. unfilled
		12 m			3.70E-15				N.f.s. filled
Rapakivi granite		3 m			8.60E-14				N.f.s. unfilled
		12 m			3.80E-14				N.f.s. unfilled
		3 m			2.10E-13				N.f.s. filled
		12 m			1.10E-13				N.f.s. filled

*Reviewed by Yamaguchi 1993

**Particle size Fraction

Table 5.13 Literature data, strontium

5.2.8 Technetium

Bradbury, Lever and Kinsey (1982) reported the effective diffusivity of Tc-99 in granite (assuming a porosity of 0.7 %) to be $7 \cdot 10^{-13}$ m^2/s and α to be 0.15. Suksi et al. (1989) measured apparent diffusivities in tonalite and gneiss. D_a-values varied from $1.8 \cdot 10^{-15}$ to $2.3 \cdot 10^{-13}$ m^2/s under oxic conditions and from $2.3 \cdot 10^{-15}$ to $2.3 \cdot 10^{-14}$ m^2/s under anoxic conditions. Ittner et al. (1988) reported D_a-values $(1.9\text{-}30) \cdot 10^{-14}$ for Swedish granites under oxidising conditions. Torstenfelt et al. (1982) found an effective diffusivity of $1.5(\pm 0.8) \cdot 10^{-12}$ m^2/s in granites assuming no sorption .

Under aerobic conditions technetium is in the highly soluble form TcO_4^- (Tc(+VII)), which is stable in the whole pH-range 0-14 (Suksi et al. 1989). Under reducing conditions the form is $TcO(OH)_2$ in ground waters, and the solid phase probably TcO_2 (Hakanen and Hölttä 1992). For crushed Finnish rock K_d values range from 0 to $7 \cdot 10^{-7}$ m^3/kg.

Values reviewed by Hakanen and Hölttä for anoxic conditions ranged from 0.20 to 1.00 m^3/kg. $5 \cdot 10^{-2}$ m^3/kg was proposed as a conservative K_d. Suksi et al. (1989) also reviewed earlier measurements of Allard et al., Vandergraaf, Meyer, McKinley and Hadermann, and Koskinen. Under reducing conditions sorption well above zero has been observed especially on iron containing minerals, fracture filling materials and inclusions. McKinley and Hadermann achieved K_d-values of 0.25 m^3/kg for sorption under reducing conditions and 0.005 m^3/kg under oxidising conditions.

Rock	*Water*	*Cond*	*Tc-conc (M)*	*Contact time*	*D_a (m^2/s)*	*Ref*	*comments*
Rapakivi granite	granitic gw	oxic	6.20E-06	1/2 y	7.90E-15	Suksi et al 1989	Tc-99 as NH_4TcO_4
Rapakivi granite		oxic	6.20E-06	1 y	2.30E-13		
Rapakivi granite		anoxic	7.70E-06	1/2 y	2.30E-14		
Rapakivi granite		anoxic	7.70E-06	1 y	2.40E-15		
Tonalite	granitic gw	oxic	6.20E-06	1/2 y	6.00E-14		
Tonalite		oxic	6.20E-06	1 y	1.80E-15		
Tonalite		anoxic	7.70E-06	1/2 y	1.70E-14		
Tonalite		anoxic	7.70E-06	1 y	2.30E-15		
Finnsjön granite	Synthetic	oxic	1.00E-06	349d	3.00E-13	Ittner et al 1988	TcO_4^-
Finnsjön granite				349d	1.90E-14		
Finnsjön granite				85d	4.50E-14		
Finnsjön granite				167d	1.10E-13		
Finnsjön granite				349d	2.20E-14		
Studsvik granite				167d	2.20E-14		
Stripa granite				257d	2.05E-13		
Stripa granite				167d	2.20E-14		
Finnsjön granite	Synthetic	oxic	<1.00E-6	85d	1.50E-12	Torstenfelt et al 1982	TcO_4^-

Table 5.14 Literature data, technetium

5.2.9 Uranium

In natural waters uranium occurs in the three oxidation states IV, V and VI. Under oxidising conditions uranium exists as uranyl ion, UO_2^{2+}, i.e. oxidation state VI. Under reducing conditions U^{4+} is the main form. In the presence of carbonate, $UO_2(CO_3)_3^{4-}$ and at high carbonate concentrations $(UO_2)_3(CO_3)_6^{6-}$ dominate. Fe(II) in magnetite, pyrite and silicate minerals reduces uranium predominantly to oxidation state IV at intermediate or low total carbonate concentrations (Suksi et al., 1989).

Suksi et al. (1989) reported apparent diffusivities of U-233 (as UO_2 $(NO_3)_2$ in tonalite and granite of $(3.6\text{-}5.7)\cdot10^{-14}$ m^2/s under oxic conditions, $(1.1\text{-}4.3)\cdot10^{-14}$ m^2/s in granitic groundwater and anoxic conditions and $(1.8\text{-}5.3)\cdot10^{-14}$ m^2/s in bentonite water and anoxic conditions. The proposed value is $5\cdot10^{-14}$ m^2/s for oxic conditions and $1\cdot10^{-15}$ m^2/s for reducing conditions.

Sorption is low under oxidising conditions, and high under reducing conditions. In the review of Hakanen and Hölttä (1992) conservative K_d -values of $1\cdot10^{-3}$ m^3/kg for granites and $3\cdot10^{-3}$ m^3/kg for tonalites and gneisses were proposed, as well as the corresponding realistic values, $5\cdot10^{-3}$ and $1\cdot10^{-2}$ m^3/kg under oxidising conditions. Under reducing conditions values of 0.8 - 2 m^3/kg have been measured and as a conservative value for all rocks 10^{-1} m^3/kg was proposed, and a realistic value of 1 m^3/kg (Hakanen and Hölttä, 1992) . Kaukonen et al. (1993) made sorption experiments on plutonic rock and vulcanite under oxic and anoxic conditions. K_d-values decreased slightly with increasing uranium concentration for the Mäntsälä plutonic rock samples and distinctly for Syyry plutonic rock, while for Sodankylä vulcanite no changes occurred. Decreasing bicarbonate concentration resulted in clear increase of the distribution coefficients of Mäntsälä and Syyry samples. Under anoxic conditions no concentration dependence was observed in the uranium concentration range 10^{-10}-10^{-7} M. K_d-values were 0.64-2.55 m^3/kg for Syyry plutonic rock and 0.79-1.63 m^3/kg for Sodankylä vulcanite.

Rock	*Water*	*Cond*	*U-conc (M)*	*Cont. time*	*D_a (m^2/s)*	*Ref*	*comments*
Rapakivi granite	granitic gw	oxic	4.20E-06	1 y	5.20E-14	Suksi 1989	U-233 as $UO_2(NO_3)_2$
Rapakivi granite	granitic gw	anoxic	4.30E-06	1/2 y	4.20E-14		
Rapakivi granite	bentonite gw	anoxic	4.00E-06	1/2 y	1.80E-14		
Rapakivi granite	granitic gw	anoxic	4.30E-06	1 y	1.30E-14		
Rapakivi granite	bentonite gw	anoxic	4.00E-06	1 y	2.00E-14		
Porphyritic granite	granitic gw	oxic	4.20E-06	1 y	5.70E-14		
Granodiorite	granitic gw	oxic	4.20E-06	1/2 y	3.60E-14		
Tonalite	granitic gw	anoxic	4.30E-06	1 y	1.10E-14		
Tonalite	bentonite gw	anoxic	4.00E-06	1 y	5.30E-14		

Table 5.15 Literature data, uranium

5.2.10 Plutonium

Under oxic groundwater conditions plutonium is tetravalent or pentavalent and occur as $Pu(OH)_4$ or $Pu(OH)_5^-$. Under reducing conditions the oxidation state is probably trivalent and the species are $PuCO_3^+$, Pu^{3+} and $PuOH^{2+}$ (Suksi et al. 1989).

Suksi et al. (1989) measured apparent diffusivities in granite and gneiss. D_a-values varied from $2.7\cdot10^{-15}$ to $2.4\cdot10^{-14}$ m^2/s under oxic conditions, and were $2.7\cdot10^{-15}$ m^2/s in Rapakivi granite and $3.5\cdot10^{-15}$ m^2/s for tonalite under anoxic conditions.

Ittner et al. (1988) reported apparent diffusivities in Swedish granites to be $(1.2\text{-}1.6)\cdot10^{-15}$ m^2/s in synthetic ground water.

Plutonium is very strongly sorbed on solid surfaces and precipitation is believed to be responsible to part of the high distribution coefficients. Values of K_d in the range 0.1 - 5 m^3/kg have been reported, the higher value corresponding to reducing ground waters from the measurements of McKinley et al. (1984) (In Suksi et al. 1989). Hakanen and Hölttä (1992) proposed a conservative value under reducing condition of 0.5 m^3/kg and a realistic value of 2 m^3/kg.

Rock	*Water*	*Cond*	*Conc (M)*	*Contact time*	*D_a (m^2/s)*	*Ref*	*comments*
Finnsjön granite	synthetic	aerobic	1.00E-09	854d	1.60E-15	Ittner 1988	Pu-239
Stripa granite	synthetic	aerobic	1.00E-09	858d	1.20E-15		
Stripa granite	synthetic	aerobic	1.00E-09	646d	1.50E-15		
Rapakivi granite	granitic gw	oxic	1.80E-14	1 y	2.40E-14	Suksi 1989	Pu-236 as $Pu(NO_3)_4$
Rapakivi granite	granitic gw	anoxic	4.70E-14	1 y	2.70E-15		
Porphyritic granite	granitic gw	oxic	1.80E-14	1 y	4.10E-15		
Granodiorite	granitic gw	oxic	1.80E-14	1 y	2.70E-15		
Tonalite	granitic gw	oxic	1.80E-14	1/2 y	1.10E-14		
Tonalite	granitic gw	oxic	1.80E-14	1 y	5.40E-15		
Tonalite	granitic gw	anoxic	4.70E-14	1 y	3.50E-15		

Table 5.16 Literature data, plutonium

5.2.11 Protactinium

Under aerobic conditions Pa(IV) is easily oxidised to Pa(V) by dissolved oxygen. Hakanen and Hölttä (1992) proposed the conservative K_d-value for rocks under reducing and aerobic conditions $1 \cdot 10^{-2}$ m^3/kg, and a realistic value $1 \cdot 10^{-1}$ m^3/kg. No diffusion data in rocks has been found in this study.

5.2.12 Barium, Beryllium and Magnesium

For diffusion of Ba^{+2}, Be^{+2}, and Mg^{+2} in Inada granite Yamaguchi et al. (1993) reported D_e-values $(1.90\text{-}3.50) \cdot 10^{-13}$ m^2/s, $(3.00\text{-}3.30) \cdot 10^{-13}$ m^2/s and $(1.9\text{-}3.6) \cdot 10^{-13}$ m^2/s respectively in 0.1 M Kcl-solution.

Rock	*Water*	*Cond*	*Conc (M)*	*D_e (m^2/s)*	*ε (%)*	*Ref*	*Comments*
Inada granite	0.1M KCl	pH=4, 25°C	0.1	1.90E-13 2.10E-13 2.50E-13 2.90E-13 3.00E-13 3.50E-13	0.7	Yamaguchi 1993	Ba(+2), multi-tracer test, $D_{(bulk)}$=8.48E-10 m^2/s
Inada granite	0.1M KCl	pH=4, 25°C	0.1	3.00E-13 3.30E-13	0.7	Yamaguchi 1993	Be(+2), $D_{(bulk)}$=5.85E-10 m^2/s multi-tracer test
Inada granite	0.1M KCl	pH=4, 25°C	0.1	1.90E-13 1.90E-13 2.30E-13 2.40E-13 2.90E-13 3.00E-13 3.30E-13 3.60E-13	0.7	Yamaguchi 1993	Mg+2 $D_{(bulk)}$=7.05E-10 m^2/s multi-tracer test

Table 5.17 Literature data, barium, beryllium, magnesium

5.3 POROSITY AND EXTENSION OF MICRO PORES

Fracture surfaces are often more porous than the underlying rock, which in fresh fractures can be due to contribution of residual porosity. The underlying rock can be altered and change gradually into the intact rock. The porosity decreases rapidly when the depths into the rock exceeds grain dimensions (Valkiainen 1992).

Brandberg and Skagius (1991) reviewed mean porosities reported for different rock types (Table 5.3). They suggested the transport porosity 0.5% for all Swedish rocks.

Rock	porosity (%)
Aplitegranite	0.55
Gneissgranite	0.12
Gneiss	0.23
Granodiorite	0.23
Granite	0.50

Table 5.18 Porosities of some rocks.

Bradbury and Green (1986) found pore connectivity to exist over metre distances. In smaller samples (less than 5 cm in length) the formation factor is higher than in larger samples (5-120 cm) where it is constant. This might be explained by the contribution of dead-end porosity that is less important in larger samples. Most experiments have been made on small samples of fresh, "good", rock, wherefore it was pointed out that results might be affected by dead-end pores which are of more importance in small samples. Weathering effects at the surfaces did not prevent diffusion into the rock matrix. If there have been any differences in diffusion properties between weathered zones and "good" rock, diffusivities have been greater in weathered zones. A porosity of 0.5 % for granite was suggested as a good estimation for Canadian, Swedish and UK granites.

The extension of the micro pore system in undisturbed rock has been examined by Birgersson (1988) at the 360 m level in the Stripa mine in Sweden. Non-sorbing tracers migrated at least 400 mm into the rock (the measuring limit) during three months to 3.5 years. There were large differences in migration depths into the rock for samples taken fairly close to each other. Fissure coatings and filling material did not hinder the migration into the underlying rock. That has also been found by Torstenfelt et al. (1982,1983), Skagius (1986), Suksi et al. (1987) and Saarinen et al. (1995).

The pore size generally shows a wide distribution. For Inada granite Yamaguchi et al. (1993) reported pore sizes between 10 nm and 10 µm, and a total porosity of 0.7% (determined by the water saturation method).

5.4 EFFECT OF LARGE ROCK OVERBURDEN

Bradbury and Green (1986) found that a confining pressure (up to 16 MPa appr. 500m depth) reduced diffusion rates with a factor 2. Skagius and Neretnieks (1985) presented results suggesting that rock samples are not essentially damaged when taken from its natural surrounding (destressed), and that the porosity remains open under the pressure studied although diffusivities in laboratory samples are 2-5 times higher than under "*in-situ*" conditions.

Birgersson (1988) found diffusivities and hydraulic conductivity obtained from *in-situ* measurements to compare well to laboratory results. Large differences in diffusivities and hydraulic conductivity were found in samples located just a few centimetres apart.

5.5 DISCUSSION OF LITERATURE DATA

5.5.1 Non-Sorbing Neutral Species

Reported effective diffusivities determined for tritiated water are in the range $(1\text{-}7)\cdot 10^{-13}$ m^2/s for granite in both Finnish and Swedish determinations. Values reported for gneiss are about one magnitude smaller and do not vary significantly with ionic strength and with changes from anaerobic to aerobic conditions. This is what would be expected from non-sorbing neutral species, which are not affected by exclusion or sorption phenomena. into a porous media should ideally exhibit high diffusivities and only be hindered by the porous structure compared to diffusion in bulk solutions. Determinations of porosity from the diffusion experiments are therefore in accordance with porosities calculated from diffusivities.

5.5.2 Non-Sorbing Anionic Species

5.5.2.1 Anion Exclusion

Anions diffusing in a porous media seem to be hindered not only by the tortuosity and the constrictivity of the media, but also by electrostatic repulsion when the pore walls are negatively charged. This means that the anion does not have access to the whole pore volume and the effective porosity is less than for a non-charged or a positively charged species. Therefore, porosities calculated from diffusion experiments, with for example I^- or Cl^-,are generally lower than values obtained from water saturation methods or electrical resistivity measurements. In strong electrolytic solutions, however, the anion exclusion effect seems to be absent.

In determinations of α from concentration versus time curves, Skagius and Neretnieks (1985) found α for iodide to be in fair agreement with measured porosities, and in some cases even higher. The agreement and the I^- diffusivities did not seem to be affected by changes in NaI-concentrations between 0.1 M and 1.0 M. The ionic strength was, however, high in both solutions used, compared to that in natural groundwater, wherefore the effect of anion exclusion probably was absent even with the lower concentration.

Kumpulainen and Uusheimo (1989) made diffusion measurements using a Cl-36 tracer and electrical resistivity measurements in granite and gneiss samples. Effective diffusivities differed one to two orders of magnitude with the methods giving higher values for electrical resistivity measurements. Diffusion porosities were calculated using the measured diffusivities giving values lower than expected from the water saturation method. The small effective porosities appear to be caused by anion exclusion. The differences in diffusivities could be due to that NaCl-concentration was 0.004 M in the diffusion measurements and 1M in the electrical resistivity measurements.

In the experiments of Lehikoinen et al. (1992) clear increases in diffusivities were obtained for the 1 M NaCl-solution compared to the 0.0044 M solution for diffusion in gneiss and granite. Good agreement when fitting a dead-end porosity model to experimental data was achieved. Effective diffusivities as well as rock capacity factors of Cl increased with increasing NaCl-concentration which was seen as an effect of anion exclusion and steric effects. Anion exclusion was, though, not always observed in the comparisons between Cl and HTO diffusion. A reason suggested for this was that in some cases a single pore might dominate as transport path wherefore anion exclusion could not be observed.

Smith (1990) determined effective diffusivities of I^-, Sr^{2+} and Cs $^{2+}$ in Darley Dale sandstone with a porosity of 10%, using time dependent solutions to the governing equations. The effective diffusivity of Sr was found to be more than six times larger than that of I. The larger value for Sr was suggested to origin in effects of anion exclusion and/or ion diameter. However, it was not within the scope of the study to explain this phenomenon.

For Cr-EDTA and uranin porosities calculated from fittings to break-through curves have been reported (Skagius and Neretnieks, 1985) to be lower than values from porosities determined by the water-saturation method or by the leaching method. This phenomenon was interpreted to origin in less availability of some pores to diffusion processes. Effective diffusivities of Cr-EDTA are in the same range, which corresponds to their almost equal diffusivities in free water.

According to Gutierrez (reviewed in Lehikoinen et al., 1992) there was no anion exclusion in the rocks studied using tritiated water and Cl-36. The porosity of the granite was quite high, 4.7 %, and it was suggested that ion exclusion would not be of importance in these large pores. If this is correct, then the results of Smith mentioned above should be due to other mechanisms than anion exclusion because of the even higher porosity of the sandstone than of granite.

5.5.3 Sorbing Species

In many investigations surprisingly high diffusivities in rock have been found for sorbing species, especially for strontium and cesium. At high ionic strengths, however, the phenomenon seems to disappear. This behaviour has been interpreted as diffusion in the sorbed state (Neretnieks 1994, Yamaguchi 1993, Lehikoinen 1992, Suksi 1987 and others). At high ionic strengths sorption sites are occupied by cations like Na or K, and there is no or little sorption of the species in question and therefore no diffusion in the sorbed state.

Skagius et al. (1982,1985,1986) compared effective diffusivities from electrical resistivity measurements in salt water saturated rocks, with diffusivities obtained for non-sorbing as well as sorbing species. There was fair agreement with the results from non-sorbing species (iodide, Cr-EDTA and uranin), but effective diffusivities of cesium and strontium were more than ten times higher than expected from the results of non-sorbing species and electrical resistivity measurements. This was seen as an effect of surface diffusion. Including both pore diffusion and surface diffusion to the diffusion model greatly improved fittings to experimental data. The effect of surface diffusion was greater in the case of cesium.

The diffusion coefficients calculated by Suksi et al. (1987) were for Sr and Cs too high to only be due to pore diffusion. Diffusion in the sorbed state, surface diffusion, was suggested to be the explanation for the high diffusion of these species.

If the results of Smith (1990) for effective diffusion of I^-, Sr^{2+} and Cs^{2+} in Darley Dale sandstone are again considered, and if the indications that anion exclusion is of small importance in highly porous rocks are correct, then the more than six times higher diffusivity for Sr than that of I might be due to surface diffusion.

Yamaguchi, Sakamoto and Senoo (1993) found strong indications of surface diffusion for strontium and also developed a model taking into account both pure pore diffusivity and diffusivity due to diffusion in the sorbed state. The equation consisted of two parts, one due to pure pore diffusion which dominates when sorption is low, and one part due to surface diffusion and becomes important at high sorptive conditions. In the study D_e was shown to clearly depend on the sorptivity, ρK_d. At high sorptivities D_e was proportional to the sorptivity and at low sorptivities there was no dependency, indicating that at high sorptivities diffusion of sorbed Sr may significantly affect the effective diffusivity. The conclusion is that at high sorptivities D_e corresponds to the second term of eq (3.19), whereas at low sorptivities the first term is dominant. At low sorptivities D_e should then be:

$$D_e \approx D_p \varepsilon = D_v \varepsilon \frac{\delta}{\tau^2} \qquad (5.1)$$

and then D_e could be estimated based on $\varepsilon\delta_D/\tau^2$ or the formation factor of the granite. This was tested in multi-tracer experiments in 0.1M KCl with Ba, Be, Co, Mg, Ni and Sr and the proportional relationship between D_e and D_v was confirmed to be valid for divalent cations. The effective diffusion coefficient of Sr at low sorptivities was expressed as:

$$D_e = 2.1 \cdot 10^{-10}\, \varepsilon^{1.3} \qquad (5.2)$$

For I^-, effective diffusivity in rocks has been expressed as:

$$D_e = 6.4 \cdot 10^{-10}\,\varepsilon^{1.3} \qquad (5.3)$$

which is three times larger than for Sr. In bulk solution the diffusion coefficient of I^- is about 2.5 times larger than that of Sr^{2+}, suggesting that the difference in D_e at low sorptivities is reasonable. The general expression for the effective diffusion coefficient of Sr presented in the study was:

$$D_e = 2.1 \cdot 10^{-10}\,\varepsilon^{1.3} + 3.5 \cdot 10^{-12}\,\rho K_d \qquad (5.4)$$

Similar diffusion experiments by Idemitsu et al. (1992) also in Inada granite with the nuclides Cs, Sr and Co in deionized water, but here the high diffusivities were not explained by surface diffusion. The penetration profiles showed a steep slope close to the surface and less inclination deeper into the rock. This was explained by two diffusion paths. One by ordinary matrix diffusion in submicro pores and one by diffusion in fissures of a few microns. The submicron pore network made up approximately 80% of the total porosity of the rock. Apparent diffusivities were determined to be 10^{-11}-10^{-12} m^2/s through the fissure, and 10^{-14} m^2/s through the pore network for all three nuclides. pH-changes (4.3 - 9.4) and temperature changes (30 - 56°C) had no significant influence on diffusivities. The apparent matrix diffusivities were in the same range as diffusivities from many other determinations.

The reviewed diffusivities for cobalt in rock show large variations. The experimental conditions are quite different, however. Due to the large differences no reliable conclusions can be drawn from comparisons, and this discussion is only of speculative character. The experimental solutions vary from deionized water (Idemitsu) through synthetic groundwater (Pinnioija, Muuronen, Suksi), with the ionic strength 0.0085, to 0.1 M KCl-solutions (Yamaguchi) in the different investigations. For the synthetic groundwater apparent diffusivities are very low for all three rock types used (tonalite, mica gneiss and Rapakivi granite), compared to those in Inada granite. The experiments in deionized water were carried out and interpreted by Idemitsu et al. (1991) in the manner described above. If the model describes the diffusion correctly then the apparent diffusivities due to matrix diffusion are in the range $(4\text{-}8) \cdot 10^{-14}$ m^2/s. The apparent diffusivities in synthetic groundwater were generally one to three orders of magnitude smaller. Sorption has been reported to decrease with ionic strength, which could cause lower diffusivities if there was surface diffusion. However, sorption was found to be quite high in the synthetic groundwater used. Compared to diffusivities obtained in 0.1 M Kcl, and assuming a sorption coefficient of 0.1 m^3/kg and a rock density of 2500 kg/m^3, the effective diffusivities in synthetic groundwater would be of the same magnitude. This suggests absence of surface diffusion, because diffusivities in the KCl-solution case would be due to only pore diffusion if the sorption seats were occupied by K^+, and should be much lower than in the synthetic ground water case. If the same calculations were made in the deionized water-case, assuming a sorption coefficient of 0.1 m^3/kg and a rock density of 2500 kg/m^3, very high effective diffusivities would be obtained, and this would instead suggest that surface diffusion was occurring.

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In the diffusion experiments of Lehikoinen et al. (1992) described above effective diffusivities of Na showed a behaviour opposite to that of Cl, with decreasing diffusivity and rock capacity factor with increasing NaCl-concentration. This was suggested to origin in surface diffusion that would be important at low salt concentrations (when diffusivity is high even compared to HTO-diffusivity) while at high salt concentrations pure pore diffusion would account for the diffusivity.

6 DISCUSSION

A large amount of diffusion and sorption data is available in the literature. Diffusivities can differ quite a lot between samples taken from the same sampling location fairly close to each other, wherefore tests will finally be needed from the chosen location for a final repository for spent nuclear waste. More determinations of diffusivities in general are therefore not really worth the cost, but instead the experimental work should be directed towards deeper understanding of the different phenomena affecting diffusion and sorption. Also more evidence from *in-situ* tests and natural analogues would be desirable.

The results from experimental determinations have been questioned due to for example the small samples generally used in laboratory determinations, which could result in to high diffusivities due to the contribution from residual porosity which is less important in larger samples.

Fissure coating material do not seem to hinder diffusion into the underlying rock, but instead diffusivities and sorption is mostly greater for these materials.

To achieve greater reliability in safety assessment modelling deeper knowledge about processes like anion exclusion and surface diffusion is needed. The effect of anion exclusion is clear from the experiments reviewed in this study. In samples of greater porosity the effect seems to be absent. This would probably be due to that this phenomenon would be of less importance in larger pores. In this literature review high diffusivities for Cs^+, Sr^{2+}, Na^+ and possibly also for Co^{2+} in many studies suggest that surface diffusion is occurring. For strontium this is shown very convincingly in the model developed by Yamaguchi (1993) where both pore diffusion and surface diffusion were taken into account and gave good fit to experimental data. In some studies diffusivities of strontium or cesium are compared to diffusivities of anions, and conclusions are based on these comparisons. This makes it difficult to distinguish between the two phenomena mentioned, and results from a non-sorbing non-anionic species would have been useful for the evaluation. Porosity determinations have sometimes been made from diffusion experiments with anionic species, and it is important to not use these values as the true porosity, but instead as an effective diffusivity for the specific anion used.

Another doubt that has been expressed regarding the credibility of laboratory experiments is that the laboratory samples have been destressed and the pore system might be more open than under real conditions at repository depths. "*In-situ*" experiments and laboratory experiments under mechanical stress have shown that the pore system is open and connected also under natural conditions at repository depths, when the rock is under great stress implied by the mass of the bedrock.

Also natural analogues support that the pore system is open and connected, at least in the scale of centimetres to tens of centimetres. Diffusivities derived from concentration profiles are, however, questioned due to unknown initial and boundary conditions. Diffusion mostly seems to be confined to altered zones of the rock. The degree of alteration might be of importance to the movement of uranium. Different kinds of fractures could also be of importance. Suksi and Ruskiniemi (1992) (in Brandberg et al. 1993) found no evidence of matrix diffusion in samples with shear fractures and suggested that the pores were sealed by secondary minerals formed during shearing.

The high apparent diffusivities estimated for Ra-226 by Saarinen et al (1995) compared to average values measured for U were interpreted as possible transport of radium in the sorbed state. Evidence of surface diffusion from natural analogues would be valuable, and more studies are necessary for verification.

7. NOTATIONS

A	Area	m^2
C	Concentration	$mole/m^3$
C_0	Initial concentration	$mole/m^3$
C_1	Inlet concentration	$mole/m^3$
C_2	Outlet concentration	$mole/m^3$
C_r	Concentration in the rock	mole/kg
C_p	Concentration in the pore water	$mole/m^3$
C_s	Concentration in the sorbed phase	$mole/m^3$
D	Diffusivity	m^2/s
D_p	Pore diffusivity	m^2/s
D_w	Diffusion coefficient of substance in (infinitely diluted) water	m^2/s
D_s	Diffusivity in the sorbed state	m^2/s
D_a	Apparent diffusivity	m^2/s
D_e	Effective diffusivity	m^2/s
F_f	Formation factor	-
K_a	Distribution coefficient	m^3/m^2
K_d	Mass distribution coefficient	m^3/kg
L	Sample thickness	m
L(%)	The percent radionuclide left in solution after sorption	%
x	Distance	m
M	Total amount of solute in solid after time t	mole/kg
M_∞	Total amount of solute in solid after infinite time	mole/kg
N	Rate of transfer per unit area	$mole/s,m^2$
N_{pore}	Rate of transfer in the pore per unit area	$mole/s,m^2$
N_s	Rate of transfer in the sorbed phase per unit area	$mole/s,m^2$
Q	Total amount of diffusing substance in time, t	$mole/m^2$
q	Amount of ion sorbed onto the rock	mole/kg
R	Retardation factor	-
R_l	Resistivity in a liquid	Ωm
R_{sph}	Radius of spherical particle	m
R_p	Resistivity in the pore fluid	Ωm
r	Radius	m
S(%)	The percent sorbed radionuclide on the sample surface	%
t	Time	s

V	Volume	m^3
α	Rock capacity factor	-
β	Freundlich exponent	-
δ_D	Constrictivity	-
ε	Total porosity	-
ε_t	Transport porosity	-
ε_δ	Storage porosity	-
ε_s	Sorption porosity	-
κ	Electrical conductivity in liquid	$(\Omega m)^{-1}$
κ_p	Electrical conductivity in pore liquid	$(\Omega m)^{-1}$
ρ	Density	kg/m^3
τ^2	Tortuosity	-
τ	Relaxation time	s

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