

Sorption of Cs, I and actinides in concrete systems

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

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SORPTION OF Cs, I AND ACTINIDES
IN CONCRETE SYSTEMS

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ABSTRACT

Samples of seven different concretes were prepared (Standard Portland cement of two kinds; sulphate resistant, blast furnace slag, high alumina, fly ash and silica cements) and the corresponding pore waters were analyzed. Batch-wise distribution studies were performed in the various concrete/pore water systems, as well as for three old concrete samples from a hydro power station dam (more than 60 years old), for the elements Cs, I, Th, U, Np, Pu and Am at trace concentration levels.

Generally the sorption of Cs was low, and somewhat higher for I. All the actinides, including U and Np in their hexa- and pentavalent states, respectively, were strongly sorbed on the cement phase.

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SUMMARY

Samples of 7 different concretes (Standard Portland cement of two types, sulphate resistant cement, blast furnace slag cement, high alumina cement, fly ash cement and silica cement) were prepared, and the pore waters were analyzed in the concretes, after storing the samples under water for a minimum of 14 months. Three samples from old concrete constructions (hydro power station dams) were collected and characterized with respect to the pore water composition.

Batch-wise distribution studies were performed for the elements Cs, I, Th, U, Np, Pu and Am at trace concentration levels, using crushed concrete (stored under water for a minimum of 12 months) as solid sorbents and with artificial pore waters as aqueous phases.

Generally the sorption of cesium was lower (by 1-2 orders of magnitude in terms of the distribution coefficients) than in a rock system (high salinity and low exchange capacity in the cement phase).

For iodine, a considerably higher sorption was observed on concrete than on most rock systems, possibly due to a partial oxidation to IO_3^- at high pH under oxic conditions.

The sorption of americium (trivalent) and thorium (tetravalent) was similar in concrete and rock systems.

For neptunium (pentavalent) and uranium (hexavalent) the distribution coefficients were much higher in concrete than in most rocks (by 1-2 orders of magnitude). This could illustrate the role of carbonates in natural waters that normally dominate the solution chemistry of actinides in their higher oxidation states (forming anionic low-sorbing species).

Plutonium, which possibly could be oxidized to the hexavalent state at pore water pH, had a sorption similar to that of Th(IV), but also within the upper range of sorption data for U(VI).

The differences between the various concretes were generally minor in terms of their sorbing capacity. Most important parameters affecting the sorption were the time (increased sorption with time during several months in most systems) and pH (decreasing sorption with increasing pH in the penta- and hexavalent actinide systems). The addition of TBP or ethanol amine (2 weight % with respect to the amount of concrete) had no significant effect on the sorption of the actinides.

1. INTRODUCTION

Concrete is a possible conditioning, encapsulation and over-pack material in connection with long-term storage of radioactive waste, particularly low and medium level wastes (1, 2). Low and medium level waste consist mainly of the following categories:

- o waste from normal nuclear reactor operations (operational waste)
- o waste from fuel reprocessing other than the high-level waste (reprocessing waste)
- o waste from decommissioning of nuclear reactors (decommissioning waste)

Operational waste contains ion exchange resins, various concentrates and solids, as well as technological waste. The dominating radionuclides in this waste are activation products (e.g. ^{60}Co), some fission products (e.g. ^{90}Sr , ^{137}Cs) and minor quantities of actinides (e.g. $^{239,240}\text{Pu}$, $^{241,243}\text{Am}$). Many of these waste categories will be incorporated in concrete.

Reprocessing waste could contain ion exchange resins, as well as precipitates, degradation products, diluents etc. from the solvent extraction processes and also various kinds of technological waste. Important radionuclides in this waste are activation products (e.g. ^{14}C , ^{60}Co), some fission products (^{90}Sr , ^{99}Tc , ^{129}I , ^{137}Cs and others) and substantial quantities of actinides ($^{235,236,238}\text{U}$, ^{237}Np , $^{238-242}\text{Pu}$, $^{241,243}\text{Am}$). Concrete, as well as bitumen, are possible conditioning materials for these waste categories.

Decommissioning waste, which will contain activation products (^{14}C , ^{60}Co , $^{59,63}\text{Ni}$ and others) as well as minor amounts of fission products and actinides, will largely be incorporated in concrete.

The release of radionuclides in concrete waste forms or in waste categories that have been encapsulated in concrete will largely be diffusion controlled, as long as the concrete is intact. The nuclide transport will be highly affected by the chemical conditions in the concrete (pore water composition, cement and ballast composition) as well as by the chemical retardation (sorption) of the radionuclides when contacting the solid cement matrix.

The actinides may dominate the biological hazards from these wastes already after some 10^3 - 10^4 years and onwards.

Studies of the sorption of I and Cs as well as the actinides Th, U, Np, Pu and Am on various types of concrete under representative pore water conditions are described in this report.

2. CONCRETE SYSTEMS

2.1. Concrete chemistry

Concrete can be described as a porous solid with waterfilled pores. The solid consists mainly of two parts (3,4):

- o a continuous phase; the cement paste
- o a particle phase; aggregates added to the cement, usually 65-75 % of the total volume.

The aggregates are completely surrounded by the continuous cement paste matrix.

Portland cement, largely made from lime, quartz sand and clay, can be described as a mixture of essentially

tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$	45-65 %
dicalcium silicate, $2\text{CaO} \cdot \text{SiO}_2$	10-30 %
tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$	5-15 %
tetracalcium aluminate ferrite, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	5-12 %
gypsum, CaSO_4	< 5 %

By the reaction with water a formation of a continuous solid phase occurs, which contains hydrates such as

- calcium silicate hydrate, $(1.5-2)\text{CaO} \cdot \text{SiO}_2 \cdot (1-2)\text{H}_2\text{O}$
- calcium hydroxide, $\text{Ca}(\text{OH})_2$
- calcium aluminate hydrate $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$
- and others.

(A detailed description of cement chemistry, etc., is given in ref 3).

2.2. Cement composition

In this study seven different cement pastes were prepared:

- o Standard Portland cement (SPP); from Cements AB, Slite, Sweden

- o Portland cement, CPA 55 (FPP); a French product, provided by SKBF/KBS, Stockholm, Sweden
- o Sulphate resistant cement (SRP); from Cementa AB, Slite, Sweden
- o Blastfurnace slag cement (MP); a mixture of Standard Portland cement and blastfurnace slag (mainly consisting of calcium silicate), from Cementa AB, Slite, Sweden
- o High alumina cement, Secar 80 (ALP); from Lafarge Fondu International, provided by Titan AB, Upplands Väsby, Sweden
- o Fly ash cement (FAP); prepared from Standard Portland cement with addition of 30 % fly ash
- o Silica cement, Densit (SIP); prepared from Standard Portland cement with addition of 20 % silica fume and 3.2 % naphthalene.

The chemical compositions of the cement pastes are given in Table 1 and 2 (5).

Concretes were prepared with cement, water and ballast and in a few cases additives as follows (weight %; w/c = water/cement ratio):

Standard Portland cement (SPB)

- 32 % Standard Portland, Slite
- 16 % Water, w/c = 0.5
- 52 % Quartz sand, Kebo, 0.1-0.25 mm

Standard Portland cement, French mixture (FPB)

- 62 % Portland cement, CPA 55
- 22 % Water, w/c = 0.36
- 15 % Quartz sand, Fontainbleau, <0.3 mm
- <0.5 % Thinning agent LL923

Sulphate resistant cement (SRB)

- 32 % Sulphate resistant cement, Slite
- 16 % Water, w/c = 0.5
- 52 % Quartz sand, Kebo, 0.1-0.25 mm

Blast furnace slag cement (MB)

- 32 % Slag cement, Slite
- 16 % Water, w/c = 0.5
- 52 % Quartz sand, Kebo, 0.1-0.25 mm

High alumina cement (ALB)

- 32 % Cement, Secar 80, Lafarge
- 16 % Water, w/c = 0.5
- 52 % Quartz sand, Kebo, 0.1-0.25 mm

Fly ash cement (FAB)

- 22 % Standard Portland cement, Slite
- 16 % Water, w/c = 0.5
- 10 % Fly ash
- 52 % Quartz sand, Kebo, 0.1-0.25 mm

Silica cement (SIB)

- 30 % Standard Portland cement, Slite
- 12 % Water, w/c = 0.32
- 8 % Silica fume, Kema Nobel AB, Ljungaverk
- 1.2 % Naphtalene
- 49 % Quartz sand, Kebo, 0.1-0.25 mm

Some old concrete samples were also available for this study:

- o Concrete from inflow tunnel 1 in the hydro power station at Porjus, Sweden (PB). The tunnel has been in operation for about 65 years.
- o Concrete from inflow tunnel G1 in the Oliden hydro power station at Trollhättan, Sweden (TB). The tunnel has been in operation for about 74 years.

The original composition of these concretes, including the choice of ballast material, is not available.

2.3. Pore water composition

Pore waters were obtained from the cement pastes of Table 1, as well as from one of the old concrete samples (Porjus) by applying a high pressure to a cylindrical sample (diameter 45 mm, height 80 mm). By this method 4-10 ml of pore water was obtained at each pressing. All cement samples were stored under water 4-10 months prior to the pore water analyses. A detailed description of the recovery of pore water as well as of the chemical analyses, is given in ref. 5.

Table 1. Chemical composition of the cement pastes (in weight %)

	SPP	FPP	SRP	MP	ALP	FAP ^a	SIP ^a
CaO	63.4	60.3	65.1	47.5	18.2	46.6	50.7
SiO ₂	20.6	25.8	22.9	28.5	-	29.2	35.7
Al ₂ O ₃	4.2	6.8	2.3	7.8	80.5	10.6	3.4
Fe ₂ O ₃	2.1	2.6	3.6	1.4	-	3.7	1.7
MgO	3.4	1.5	3.4	6.9	-	3.1	3.4
K ₂ O	1.1	0.25	-	1.1	-	1.4	0.9
Na ₂ O	0.2	-	-	0.6	-	2.5	2.6
SO ₃	3.2	3.0	2.7	4.3	-	2.5	2.6
Cl	-	-	-	-	-	trace	0.01
ZnO	-	-	-	-	-	-	0.07

^a See Table 2 for the composition of the solid additive

Table 2. Composition of solid additives to the fly ash and silica cements (in weight %)

	Fly ash	Silica fume
CaO	7.3	0.07
SiO ₂	49.2	96
Al ₂ O ₃	25.4	0.23
Fe ₂ O ₃	7.2	0.08
MgO	2.48	0.13
K ₂ O	2.12	0.37
Na ₂ O	0.40	0.20
SO ₃	0.90	-

The chemical composition of the pore waters of SPP, FPP, SRP, MP, ALP, FAP, and SIP is given in Table 3. The data for the pore water of Porjus concrete is shown in Table 4 (6).

Four artificial pore waters, PW1, PW2, PW3, and PW4 were made for the sorption studies, Table 5.

PW1 is representative of pore waters from aged Standard Portland cements (SPP, FPP, MP, FAP and also largely PB).

PW2 corresponds roughly to the pore waters of sulphate resistant cement (SRP) as well as the silica cement (SIP), although these cement types have quite different compositions.

PW3 is representative of the high alumina cement (ALP).

PW4 could represent pore water from a Standard Portland cement which has not been stored under water (see ref. 4).

2.4. Organic agents

Various organics may be present in the concrete in a waste repository with various origin:

- o Additives to the cement, e.g. naphtalene (in SIB), "Thinning agent LL923" (in FPB; composition unknown, but possibly a lignosulphonate product)
- o Organics from the incorporated or encapsulated waste, e.g. decontamination agents (EDTA, citrate, oxalate etc.), solvent extraction reagents or degradation products (organic phosphates and amines), radiolysis products (simple carboxylic acids ?) etc.

The presence of organic complexing agents may have a significant effect on the sorption and mobility of radionuclides in the concrete matrix.

Table 3. Data for the pore waters of fresh concrete samples
(ion concentrations in mg/l)

	SPP	FPP	SRP	MP	ALP	FAP	SIP
Age ^a	10	4	9	10	10	10	9
w/c ^b	0.5	0.36	0.5	0.5	0.5	0.5	0.35
Na	1500	1800	600	3200	4200	1600	300
K	6300	5700	600	6000	100	7500	700
Ca	90	20	470	50	< 1	15	130
Mg	0.2	0.1	0.2	0.1	0.06	0.15	0.1
Al	< 5	30	< 5	5	2800	15	< 5
Si	< 6	6	< 6	< 6	< 6	< 6	< 6
Fe	0.5	0.5	0.5	0.5	0.9	0.7	0.5
Anions ^c	(<300)	(>2000)	(0)	(<400)	(0)	(500-200)	(500-2000)
Eh ^d	0.14	-0.20	0.084	-0.38	0.13	0.11	0.13
pH	13.4	13.2	13.1	13.5	13.3	13.4	12.4

^a Age of cement paste sample before pore water pressing and analysis, months

^b Water/cement ratio

^c Predominantly SO_4^{2-} ; estimated concentration ranges (assuming charge balances and an uncertainty of 0.05 in the pH-measurements). No other anions than OH^- and SO_4^{2-} would be expected in significant concentrations in the pore water (c.f. Figure 5). No sulphate analyses were reported in ref 5.

^d In V; a system in equilibrium with air would give a potential in the range (-0.1) - 0.2 V. In the presence of Fe(II)/Fe(III) a potential of -0.45 V or lower would be expected. Thus, the values for MP is representative of a Fe(II)/Fe(III)-buffered system. Only FPP of the other cement pastes exhibit reducing conditions, indicating the presence of Fe(II).

Table 4. Pore water composition in old concrete samples (Porjus)
(ion concentrations in mg/l)

	a-1	a-2	b-1	b-2
Na	1500	3650	260	100
K	1530	5080	180	90
Ca	92	33	570	480
SO ₄ ²⁻	640	740	250	120
pH	12.9	>13	12.6	12.4

Sample a from an 80 cm long drilling core; a-1 is taken ca 36 cm and a-2 65 cm from the water exposed concrete surface.

Sample b from a 65 cm long drilling core; b-1 is taken ca 35 cm and b-2 55 cm from the water exposed concrete surface.

Table 5. Artificial pore water composition

	PW1		PW2		PW3		PW4	
	mg/l	mM	mg/l	mM	mg/l	mM	mg/l	mM
Na	1600	70	460	20	4100	180	7000	304
K	6300	160	630	16	120	3	12000	307
Ca	40	1	320	8			10	0.25
Al					2700	100	27	2.8
SO ₄ ²⁻							400	4.2
SiO ₂							15	0.26
pH	<13.4		<12.7		<13.3		13.2	

Pore water-concrete combinations:

PW1: SPB, FPB, MB, FAB, PB, TB; PW2: SRB, SIB; PW3: ALB; PW4: FPB, MB, MP

3. EXPERIMENTAL

The sorption of radionuclides on concrete was studied in distribution experiments using a batch technique (see e.g. ref. 7).

3.1. Radionuclides

The following radionuclides were used in the distribution measurements (initial concentrations given):

- o ^{125}I (half-life 60 d); 1.9×10^{-10} M
- o ^{134}Cs (half-life 2.1 y); 4.3×10^{-10} M
- o ^{234}Th (half-life 24.1 d) + ^{232}Th as carrier; 2.0×10^{-10} M
- o ^{233}U (half-life 1.6×10^5 y); 2.2×10^{-7} M
- o ^{235}Np (half-life 410 d) + ^{237}Np as carrier; 1.9×10^{-7} M
- o ^{239}Pu (half-life 2.4×10^4 y); 1.2×10^{-9} M
- o ^{241}Am (half-life 433 y); 2.3×10^{-9} M

Activities were measured using a NaI well-type scintillation counter (gamma) or by liquid scintillation technique (alfa).

3.2. Sorption measurements

The concrete samples, which were stored under water for 12-16 months prior to the experiments, were crushed and sieved in nitrogen atmosphere, and a size fraction of 0.090-0.125 mm was collected. A weighed portion of the selected size fraction was washed and preequilibrated with the corresponding artificial pore water (c.f. Table 5) for a minimum of 1 week. The water was discharged, and fresh pore water of known volume was added for a second preequilibration step of minimum 2 weeks after which a small volume of a radionuclide stock solution was added. Samples of the aqueous phase were withdrawn after various contact times (1 d - 3 months for most of the systems) and pH was measured. The distribution coefficient, K_d , was determined according to

$$K_d = (c_0 - c)V/cm \quad (\text{m}^3/\text{kg}) \quad (1)$$

where c = concentration in the aqueous phase (mol/m^3)
 c_0 = initial concentration in the aqueous phase (mol/m^3)
 V = volume of aqueous phase (m^3)
 m = mass of solid phase (kg).

Organics (tributyl phosphate, TBP, or ethanol amine) were added to the water in a few systems (FPR) to simulate the effect of complexing organics in the concrete (e.g. from reprocessing waste).

Also a series of measurements were performed with different aqueous phases and the same cement phase (FPB; PW1, PW4 or saturated $\text{Ca}(\text{OH})_2$ -solution).

The experimental procedures and conditions etc. are summarized in Table 6.

Table 6. Experimental procedure and conditions in the sorption studies

Solid phase	- Crushed concrete: SPB, FPB, SRB, MB, ALB, FAB, SIB, PB-I, PB-II, TB, MP Minimum age 12 months Size fraction: 0.090-0.125 mm
Water phase	- Artificial pore waters, PW1-PW4 (Table 5) Additives: 2% TBP or 2% ethanol amine (weight % of solid) for a series of FPB-systems Saturated $\text{Ca}(\text{OH})_2$ -solution for a series of FPB-systems
Experimental conditions etc.	- Solid/liquid ratio: 0.90 g/45.0 ml Phase separation: Centrifugation, 17000 rpm, 30 min Temperature: 25 ± 1 °C Atmosphere: Free from CO_2 (glove box) Contact times: (6 h), 1 d, 6 d, 1 week, 6 weeks, 3 months, (6 months)

4. RESULTS

The observed distribution coefficients vs the contact times are illustrated in Figure 1a-f (various concretes with corresponding pore water phases) and in Figure 2a-e (FPB and MB; various water phases and organic additives).

The distribution coefficients after long contact time (100 d) are summarized in Table 7.

Table 7. Distribution coefficients ($\log K_d, m^3/kg$) after long time (100 d).

Concrete	Pore water	Element						
		I	Cs	Th	U	Np	Pu	Am
SPB	PW1	-0.9 \pm 0.1	-3 \pm 0.2 ^a		0.3 \pm 0.2	0.6 \pm 0.5	0.1 \pm 0.2	0.9 \pm 0.1
FPB	PW1	-1.0 \pm 0.1	-3 \pm 0.1		0.2 \pm 0.2	0.7 \pm 0.3	0.1 \pm 0.2	0.9 \pm 0.3
FPB	PW4			0.7 \pm 0.1	-0.6 \pm 0.1	0.7 \pm 0.2	0.7 \pm 0.1	1.6 \pm 0.2
FPB	PW4 ^b			0.6 \pm 0.2	-0.6 \pm 0.1	0.7 \pm 0.2	0.8 \pm 0.1	1.6 \pm 0.1
FPB	PW4 ^c			0.6 \pm 0.2	-0.7 \pm 0.1	0.7 \pm 0.2	0.6 \pm 0.2	1.2 \pm 0.2
FPB	Ca(OH) ₂			0.8 \pm 0.2	0.7 \pm 0.2	1.0 \pm 0.2	1.1 \pm 0.2	1.4 \pm 0.2
SRB	PW2	-0.8 \pm 0.1	-3 \pm 0.3		0.4 \pm 0.3	0.8 \pm 0.5	0.7 \pm 0.2	1.0 \pm 0.3
MB	PW1	-2.5 \pm 0.2	-2.9 \pm 0.1		0.2 \pm 0.2	0.8 \pm 0.2	0.1 \pm 0.2	1.4 \pm 0.3
MB	PW4			0.5 \pm 0.2	-1.0 \pm 0.2	0.5 \pm 0.1	0.6 \pm 0.2	1.3 \pm 0.3
MP	PW4			0.6 \pm 0.2	-0.6 \pm 0.1	0.7 \pm 0.2	0.7 \pm 0.1	1.4 \pm 0.3
FAB	PW1	-1.4 \pm 0.1	-2.9 \pm 0.2		0.2 \pm 0.2	1.0 \pm 0.2	0.1 \pm 0.2	1.4 \pm 0.4
ALB	PW3		-2.9 \pm 0.2		-0.4 \pm 0.2	0.3 \pm 0.4	0.2 \pm 0.2	0.8 \pm 0.2
SIB	PW2	-1.8 \pm 0.1	-2.3 \pm 0.2		0.8 \pm 0.3	0.7 \pm 0.5	1.0 \pm 0.3	1.2 \pm 0.4
PB-I	PW1	-1.6 \pm 0.1	-2.9 \pm 0.2		0.2 \pm 0.2	1.4 \pm 0.5	0.3 \pm 0.1	1.0 \pm 0.3
PB-II	PW1		-2.4 \pm 0.1		-0.2 \pm 0.2	0.6 \pm 0.1	0.3 \pm 0.1	1.3 \pm 0.4
TB	PW1	-1.5 \pm 0.1	-2.6 \pm 0.1		0.1 \pm 0.2	1.5 \pm 0.5	0.4 \pm 0.3	0.4 \pm 0.2

^a Above -2.4 in one batch; see Fig. 1b

^b With TBP

^c With ethanol amine

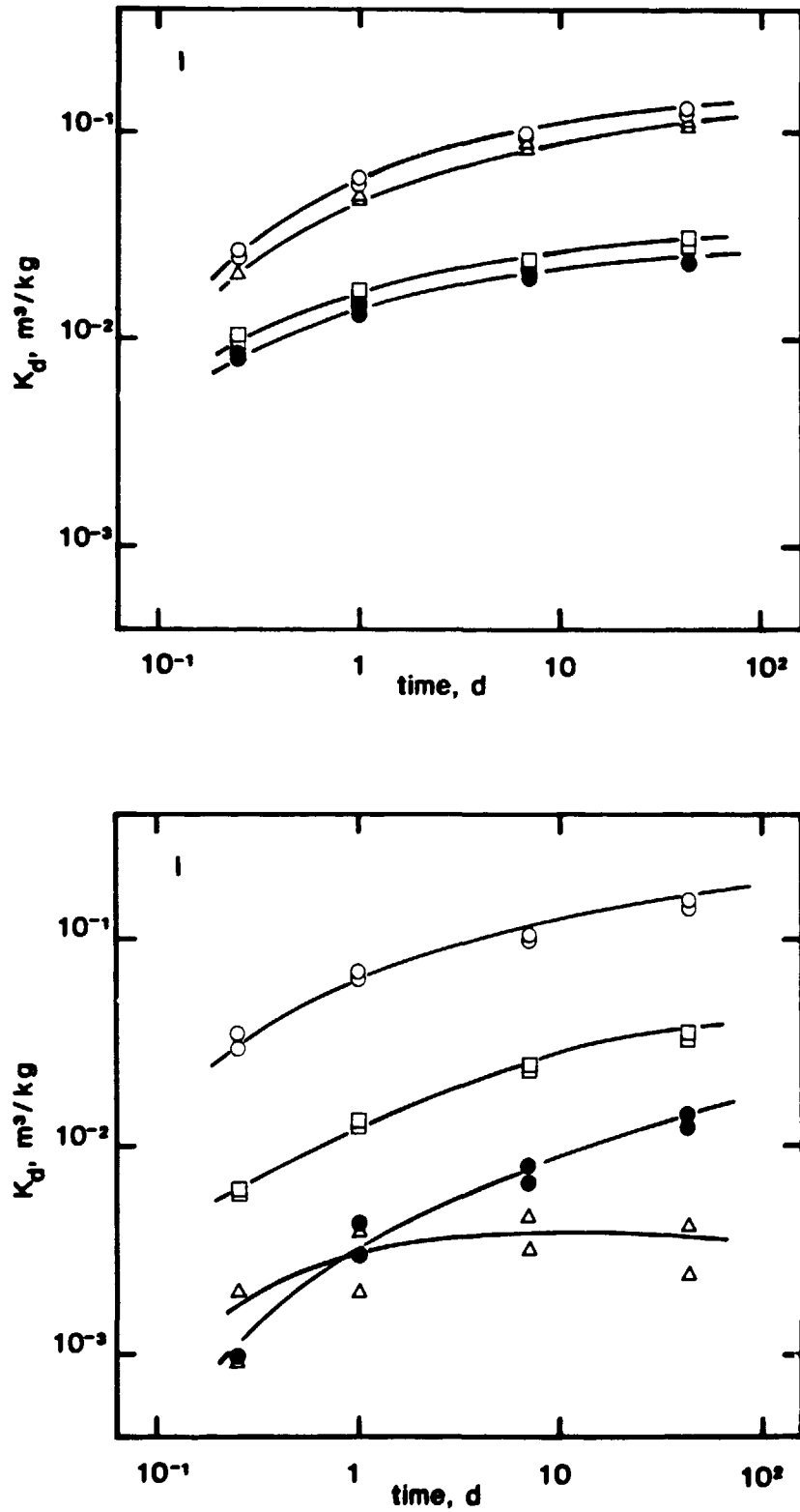


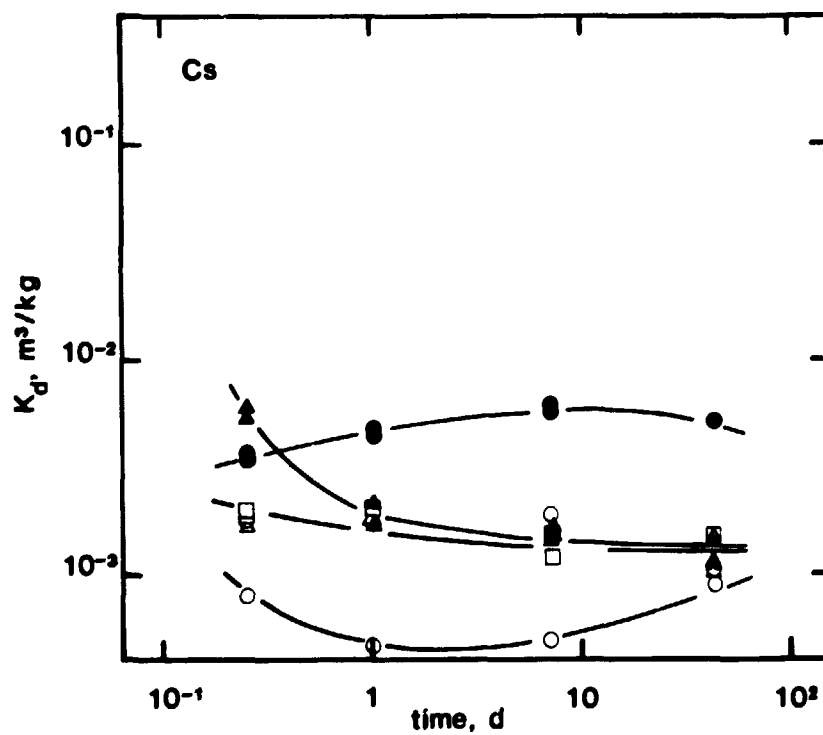
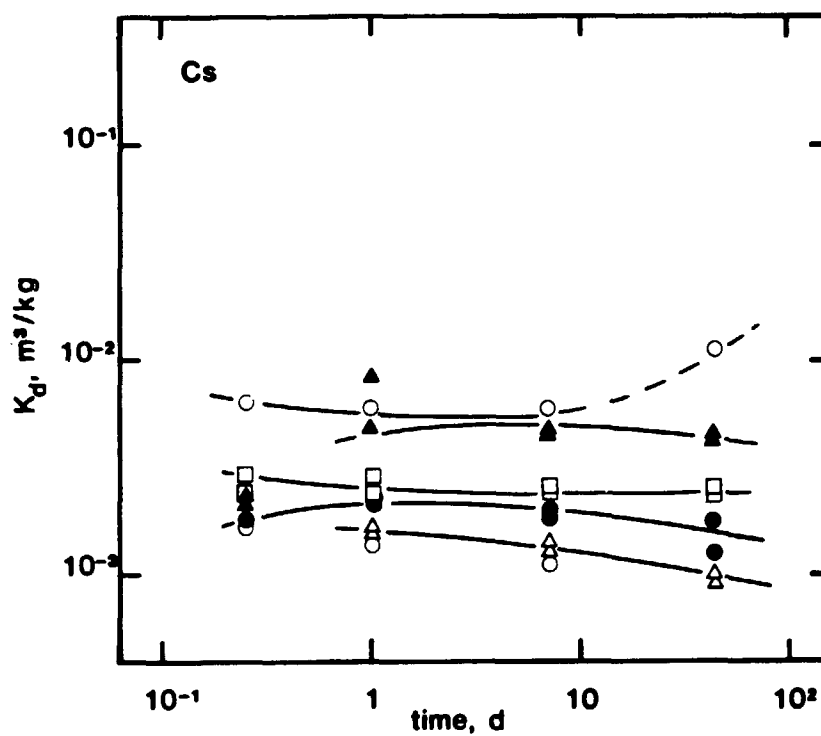
Figure 1. The distribution coefficient (K_d) vs time

a. Iodine

○ SPB, △ FPB, □ TB, ● PB-I, ▲ PB-II (top figure)

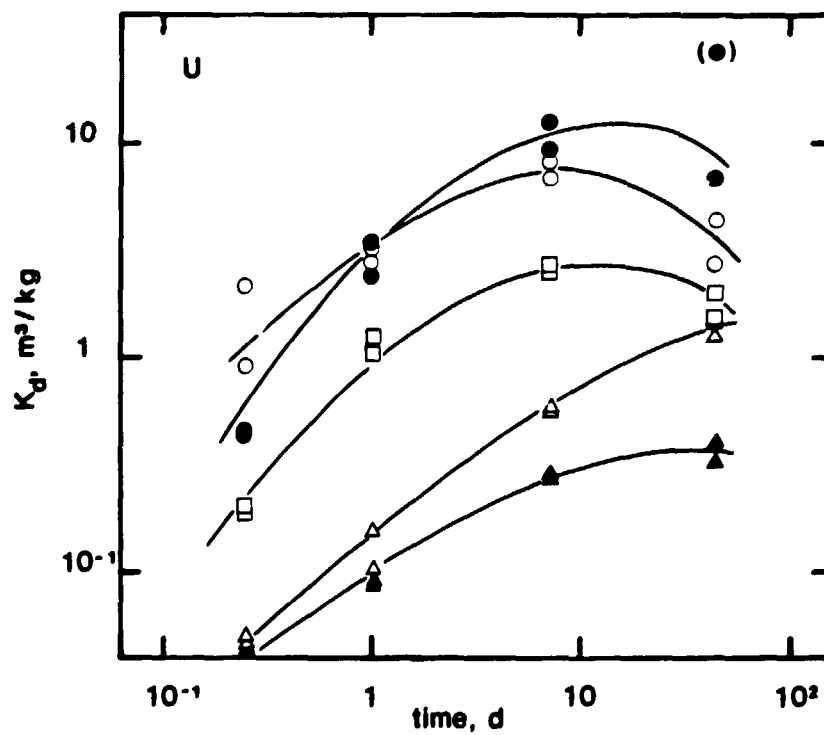
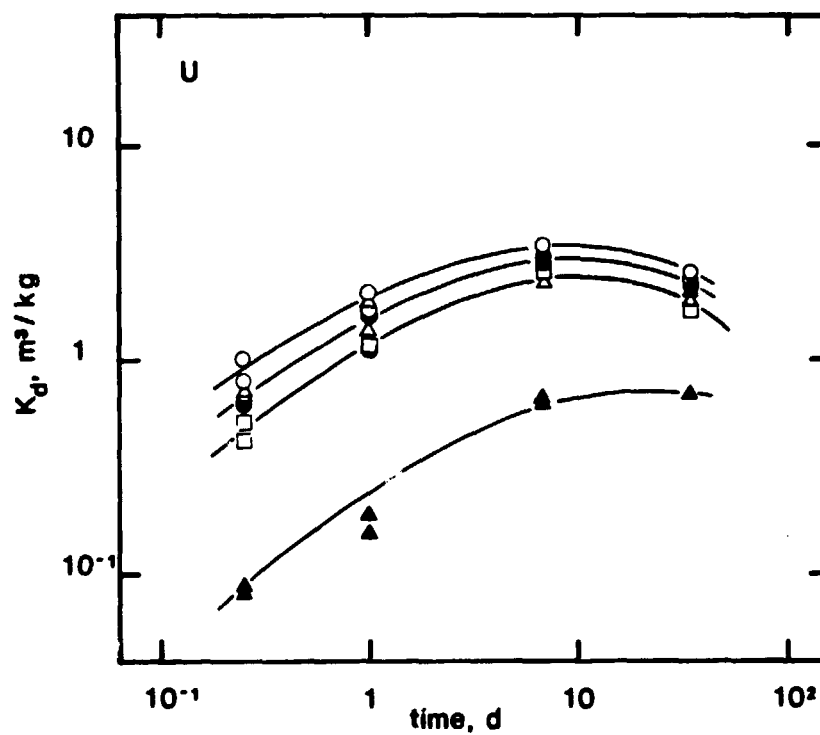
○ SRB, △ MB, □ FAB, ● SIB, ▲ ALB (bottom figure)

PW1-PW3 according to Table 5



b. Cesium

- SPB, △ FPB, □ TB, ● PB-I, ▲ PB-II (top figure)
 ○ SRB, △ MB, □ FAB, ● SIB, ▲ ALB (bottom figure)
 PW1-PW3 according to Table 5

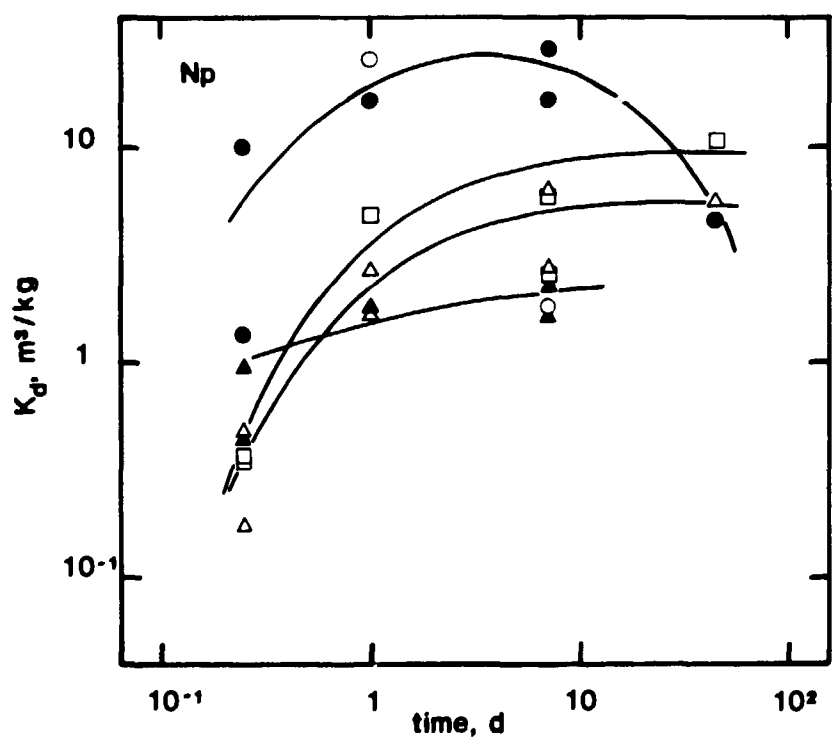
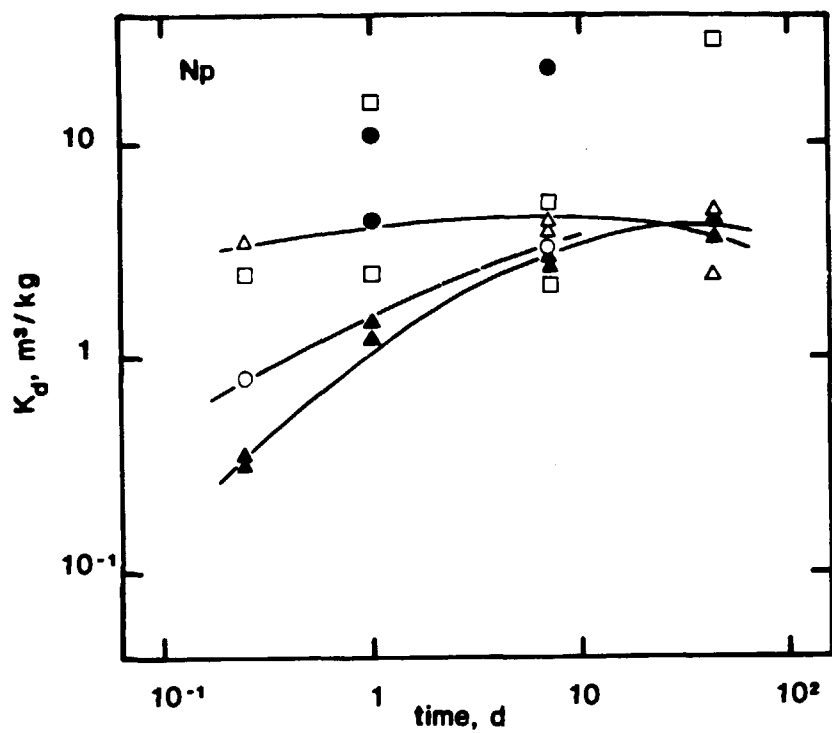


c. Uranium

○ SPB, △ FPB, □ TB, ● PB-I, ▲ PB-II (top figure)

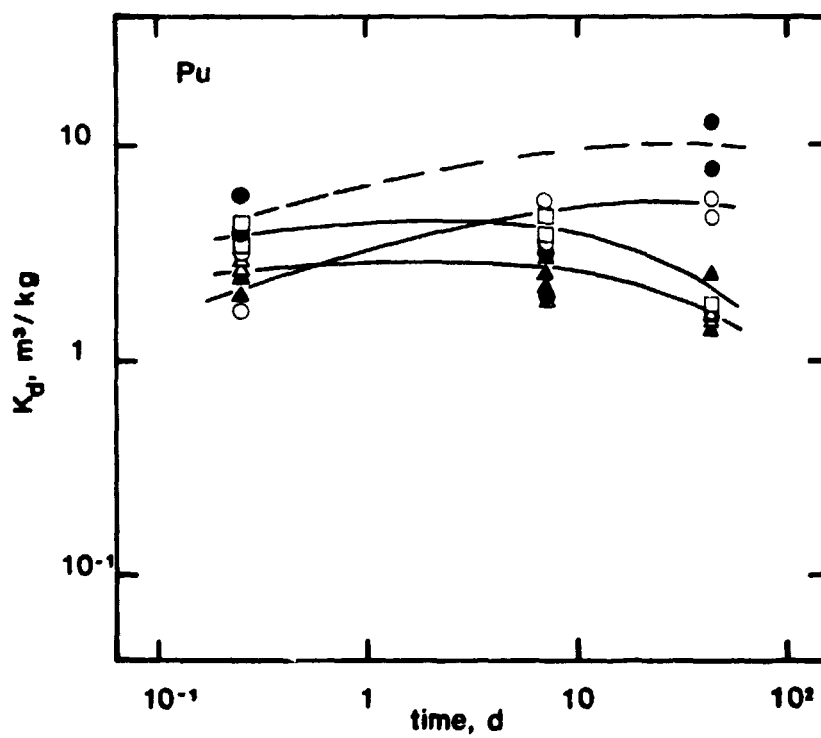
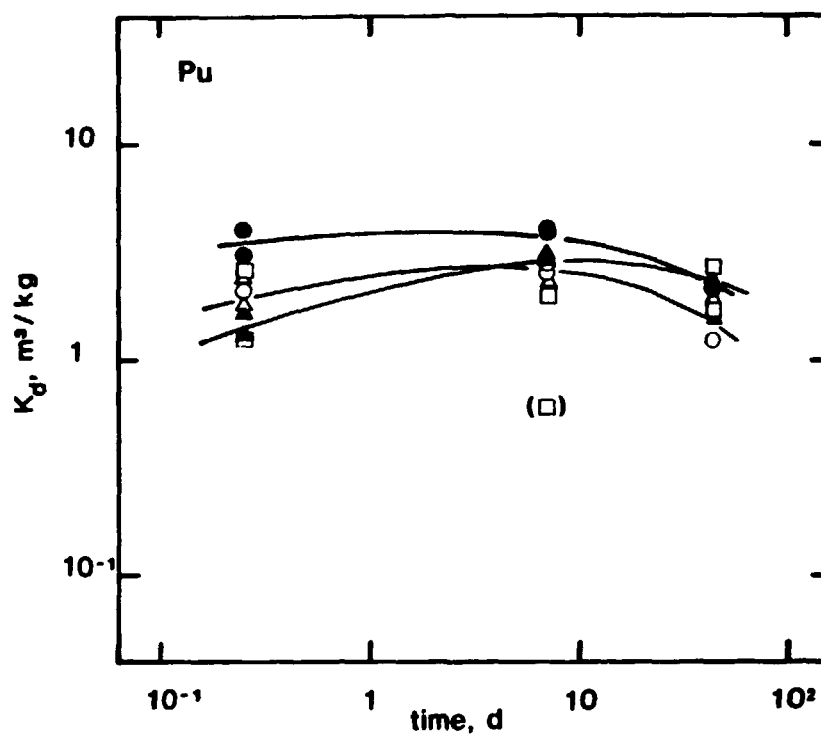
○ SRB, △ MB, □ FAB, ● SIB, ▲ ALB (bottom figure)

PW1-PW3 according to Table 5



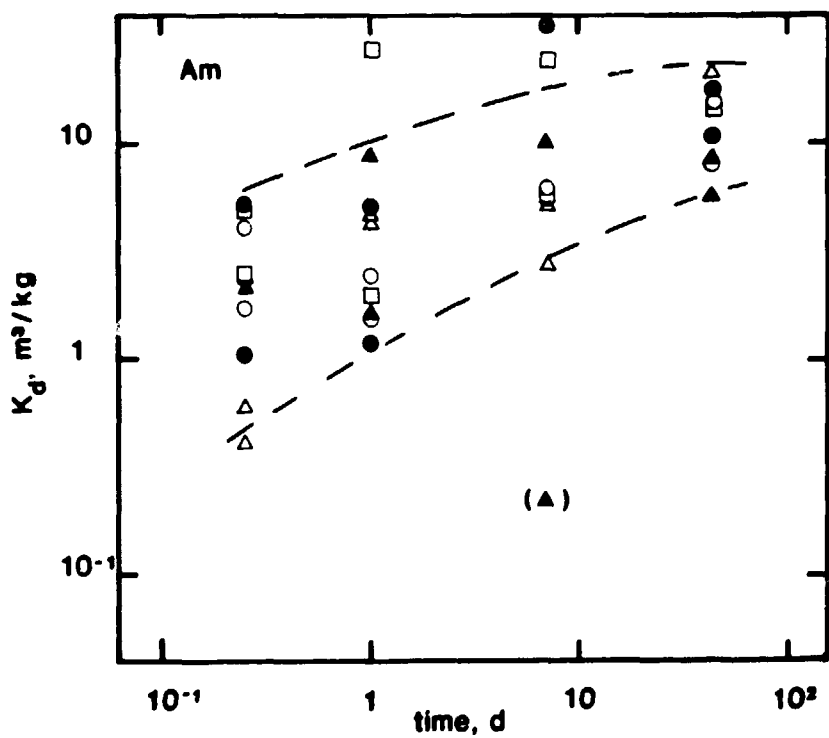
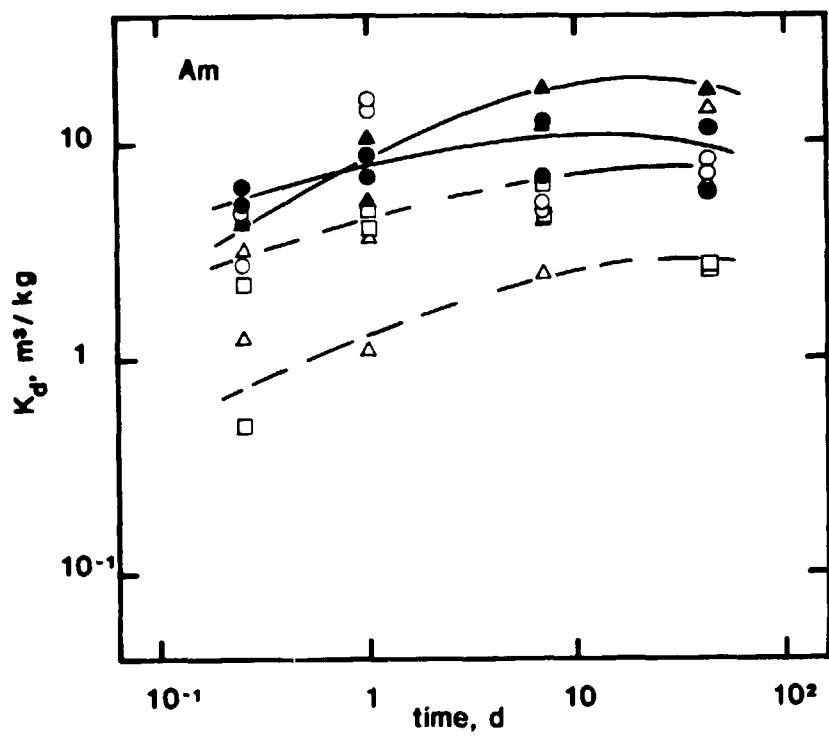
d. Neptunium

- SPB, △ FPB, □ TB, ● PB-I, ▲ PB-II (top figure)
 ○ SRB, △ MB, □ FAB, ● SIB, ▲ ALB (bottom figure)
 PW1-PW3 according to Table 5



e. Plutonium

- SPB, △ FPB, □ TB, ● PB-I, ▲ PB-II (top figure)
 ○ SRB, △ MB, □ FAB, ● SIB, ▲ ALB (bottom figure)
 PW1-PW3 according to Table 5



f. Americium

- SPB, △ FPB, □ TB, ● PB-I, ▲ PB-II (top figure)
 ○ SRB, △ MB, □ FAB, ● SIB, ▲ ALB (bottom figure)
 PW1-PW3 according to Table 5

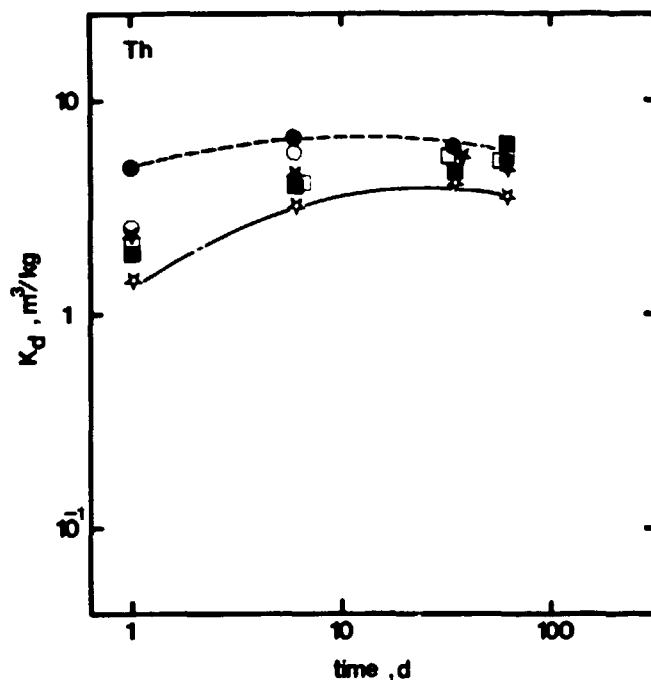
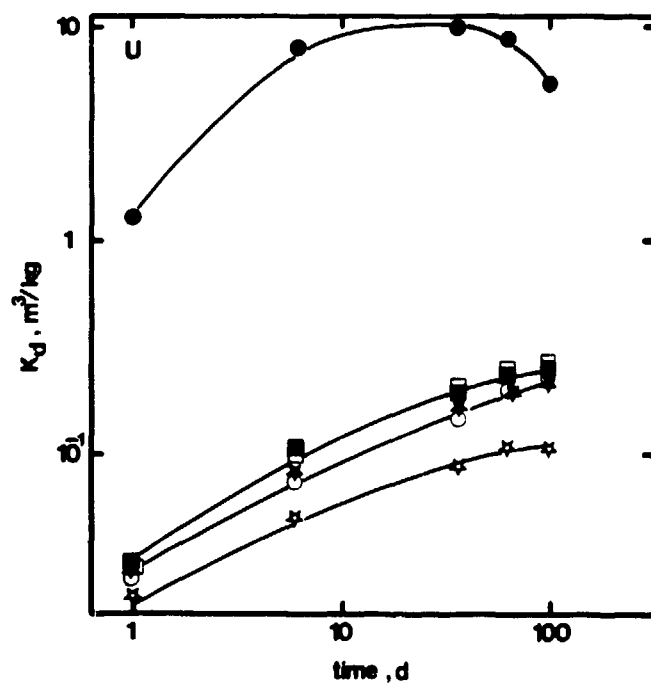


Figure 2. The distribution coefficient (K_d) vs time

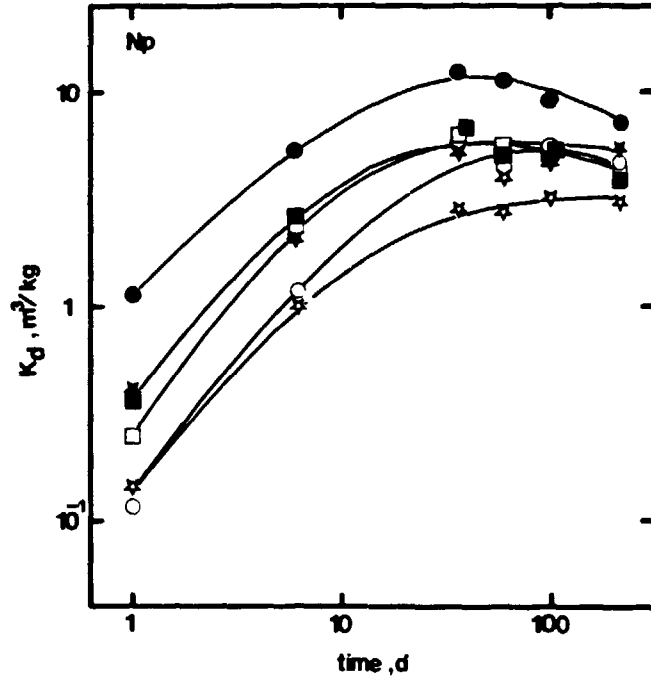
a. Thorium

○ FPB, PW4, ● FPB, $\text{Ca}(\text{OH})_2$ -solution, ■ FPB, PW4+TBP,
 ★ FPB, PW4+amine, ☆ MB, PW4, □ MP, PW4



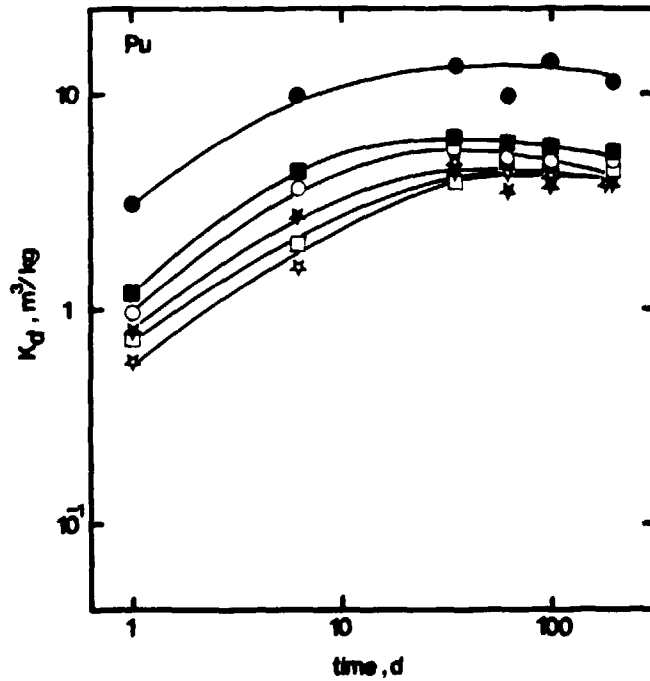
b. Uranium

○ FPB, PW4, ● FPB, $\text{Ca}(\text{OH})_2$ -solution, ■ FPB, PW4+TBP,
 ★ FPB, PW4+amine, ☆ MB, PW4, □ MP, PW4



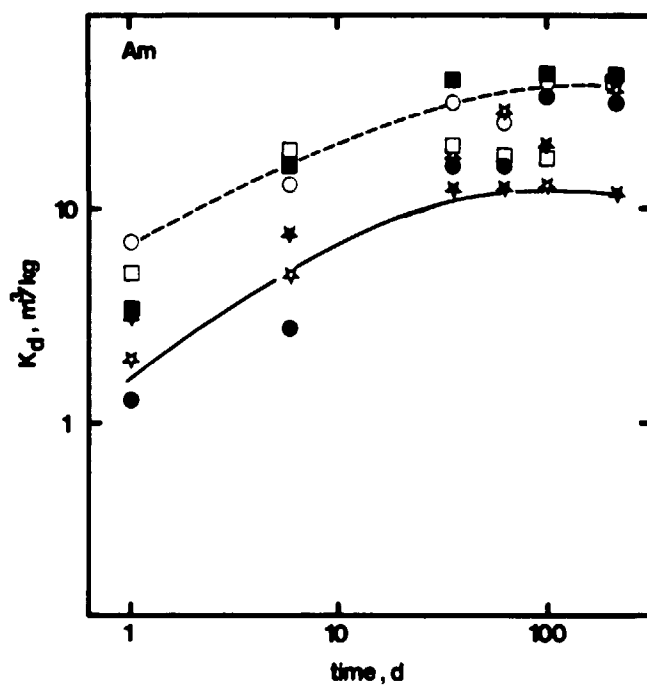
c. Neptunium

○ FPB, PW4, ● FPB, $Ca(OH)_2$ -solution, ■ FPB, PW4+TBP,
 ★ FPB, PW4+amine, ☆ MB, PW4, □ MP, PW4



d. Plutonium

○ FPB, PW4, ● FPB, $Ca(OH)_2$ -solution, ■ FPB, PW4+TBP,
 ★ FPB, PW4+amine, ☆ MB, PW4, □ MP, PW4



e. Americium

○ FPB, PW4, ● FPB, $Ca(OH)_2$ -solution, ■ FPB, PW4+TBP,
 ★ FPB, PW4+amine, ☆ MB, PW4, □ MP, PW4

5. DISCUSSION AND CONCLUSIONS

5.1. Processes in the concrete

The range of distribution coefficients for the elements and concrete systems of this study are illustrated in Figure 3.

As previously observed (4), the sorption of the non-hydrolyzed cation Cs^+ is minor in most concrete systems. This would be expected, since cation exchange is the dominating sorption mechanism for a monovalent cation in most systems (7). This would not favour the uptake of trace amounts of Cs^+ in a pore water system of high salinity and on a sorbent (cement) of low exchange capacity. The variations observed between e.g. different Standard Portland concretes and the old concrete samples may be attributed to the sorptive properties of the ballast materials.

Tri- and tetravalent actinides like Am(III) and Th(IV) are strongly sorbed on all the concretes. For thorium, the dominating species in solution is expected to be $Th(OH)_4$, at the high pH of the pore water, since higher hydrolysis products (e.g. $Th(OH)_5^-$) probably do not exist (8).

Thorium would be close to or possibly exceed the solubility product under the present conditions, considering the low solubility of $Th(OH)_4(s)$ - $ThC_2(s)$. For americium, the hydrolysis products $Am(OH)_3$ - $Am(OH)_4^-$ would dominate, considering the low carbonate concentration of the pore water. The total concentration is well below the solubility product of $Am(OH)_3(s)$. A similar very strong sorption of tri- and tetravalent hydrolyzed actinides is observed in geologic systems at lower pH (9,10).

For the higher oxidation states, represented by Np(V) and U(VI), the sorption is considerably stronger in the concrete-pore water system than observed in most groundwater-rock environments (9,10) (by 1-2 orders of magnitude in terms of distribution coefficients). This can reflect the dominance of hydrolysis products like NpO_2OH (and possibly $NpO_2(OH)_2^-$?) for neptunium and $UO_2(OH)_2$ - $UO_2(OH)_3^-$ for uranium (11).

The formation of highly charged anionic complexes would be of minor importance considering the low total carbonate concentration in the pore water. A formation of polynuclear uranium species such as $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$ at high uranium concentration would still lead to a predominance of highly sorbing species.

A family of fairly ill-defined "uranates" may exist at high pH, such as $\text{U}_2\text{O}_7^{2-}$ or UO_3^- (under reducing conditions) (12). These species would form sparingly soluble complexes with monovalent cations, which could be of importance in a pore water environment.

Plutonium, which is tetra- or pentavalent under oxidic groundwater conditions, exhibit a sorption behaviour similar to that of Th(IV), however with lower distribution coefficient values in certain systems (c.f. Figure 2a and d). Possibly a partial oxidation to the hexavalent state would be feasible in an oxidic cement pore water environment, as illustrated by the Eh/pH-diagram of Figure 4 (13).

The substantial sorption of iodine in the concrete systems is higher than expected, considering the minor sorption on most geologic materials in groundwater systems (14). The predominant iodine species is I^- in natural waters, and it would be expected to dominate also at higher pH in aerated waters if the redox potential can be described by $\text{Eh} = 0.8 - 0.06 \text{ pH}$ (8,12). However, if the slope of the pH-dependence is slightly lower than 0.06 and/or if the potential determining H_2O_2 -production is increased at high pH, the I^-/IO_3^- -potential defined by $\text{Eh} = 1.09 - 0.06 \text{ pH}$ may be exceeded in a pore water environment. An enhanced apparent iodine sorption could then be feasible due to solubility limitations at the high calcium concentration of the pore water.

The differences in sorption between the various types of concrete used in the present study were usually minor with a few exceptions:

- o The aged concretes were better sorbents than fresh ones for cesium, probably reflecting the properties of the ballast.
- o The sorption of iodine was lower in the slag cement (MB) than in the other concretes, possibly reflecting the somewhat lower redox potential in this system.

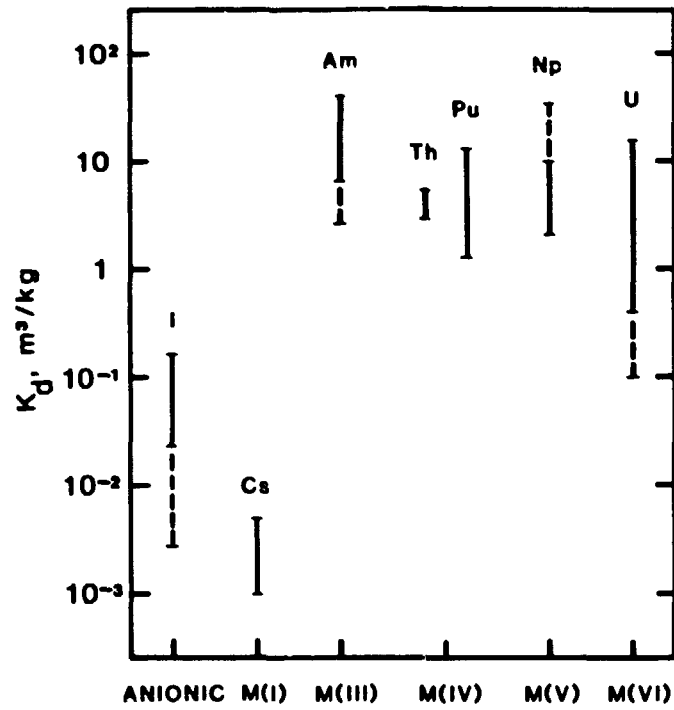


Figure 3. Ranges of observed distribution coefficients (K_d) for the various concrete systems.

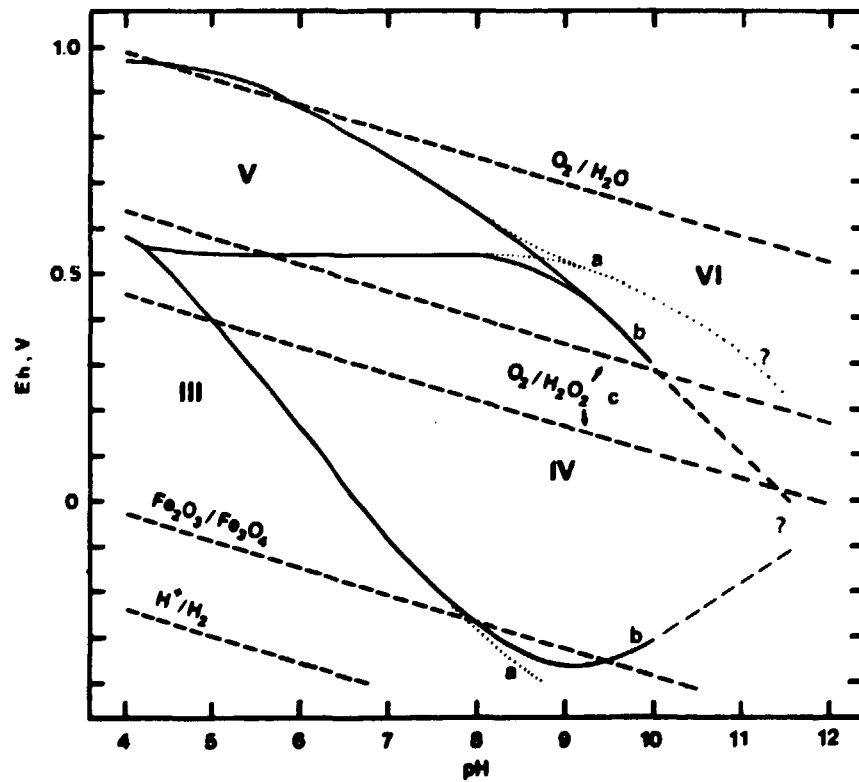


Figure 4. Eh/pH-diagram for plutonium in a groundwater-cement pore water system.

a): System free from CO_3^{2-} .

b): Open system (CO_2 from the air).

c): Probable Eh-range in aerated systems (13).

- o The high alumina concrete (ALB) gave a slightly lower sorption than the other concretes for neptunium and uranium for unknown reasons.
- o Some significant effects due to the pore water composition were noticable (see below).

For most of the systems the distribution coefficients increased with time, reaching a fairly constant level after several months. Exceptions were cesium (fairly constant with time) as well as uranium, plutonium and in some systems neptunium. The general increase of the sorption with time could be due to diffusion into the cement matrix. The decrease with time for uranium and neptunium may indicate changes of the cement phase or slow speciation changes of unknown nature. Also the slight decrease in pH with time could contribute to the enhanced sorption in some systems (c.f. Table 8 and discussion below). Carbonatization should not be important since the experiments were performed in controlled atmosphere. For plutonium a slow oxidation to the hexavalent state, leading to a slightly decreased sorption, could be a possible explanation.

For the actinides in their higher oxidation states (U, Pu and in some systems Np) as well as for iodine the sorption tended to decrease with increasing pH. This could (for the actinides) reflect a speciation change with an increased average negative charge of the species with increasing pH. An increase in pore water salinity (changing from PW1 to PW4 in the French Standard Portland System, FPP), gave a reduced sorption in the uranium system but not in the other actinide systems.

The presence of TBP or ethanol amine had no significant effect on the sorption properties of any of the actinides. These organics are, however, too weak complexing agents to significantly influence the speciation in solution, and no pronounced effects would be expected. The effects of strong complexing organics on the sorption behaviour of particularly the actinides still remains to be studied (using e.g. DTPA or EDTA as complexing agent).

Table 8. Changes of pH after long time (100 d)

Concrete	Pore water ^a	Element						
		I	Cs	Th	U	Np	Pu	Am
SPB	13.4	13.2	13.1		13.4	13.4	13.1	13.4
FPB	13.4	12.8	12.9		13.3	13.3		13.2
FPB	13.2			13.5	13.9	13.6	13.6	13.2
FPB ^b	13.2			13.5	13.8	13.3	13.6	13.4
FPB ^c	13.2			13.5	13.8	13.2	13.6	13.1
FPB ^d	12.5			11.6	12.2	12.0	11.7	11.4
SRB	12.7	12.5	12.5		12.8	12.9	12.6	12.8
MB	13.4	13.2	13.1		13.4	13.4	13.2	13.4
MB	13.2			13.4	13.6	13.2	13.5	13.2
MP	13.2			13.4	13.6	13.2	13.5	13.1
FAB	13.4	13.2	13.1		13.3	13.4	13.1	13.3
ALB	13.3	11.2 ^e	10.8 ^e		12.9	12.9	12.7	12.9
SIB	12.7	12.1	12.1		12.5	12.6	12.3	12.6
PB-I	13.4	13.0	13.0		13.3	13.3	13.0	13.3
PB-II	13.4	13.0	13.0		13.3	13.2	13.0	13.2
TE	13.4	13.0	13.0		13.3	13.3	13.0	13.3

^a Initial pH of the artificial pore water

^b With TBP

^c With ethanol amine

^d Ca(OH)₂

^e Possibly incorrect measurements? There is no obvious chemical or experimental reason why the pore waters of the I- and Cs-systems should have a lower pH than the pore waters of the actinide systems

5.2. Processes in the concrete-groundwater interphase

The concentration ranges for the dominating an- and cations of cement pore waters and groundwaters from crystalline rocks are illustrated in Figure 5. Drastic changes in Na, K, SO_4^{2-} and CO_3^{2-} -concentrations would be expected, as well as in pH. A precipitation of $\text{CaCO}_3(\text{s})$ on the concrete surface in contact with the groundwater must be expected. This calcite layer may affect the dissolution rate of the cement matrix (dissolution of Ca-silicates and diffusion of Ca^{2+}), but can not otherwise be expected to serve as a barrier for the transport of trace element through the interphase.

For cesium a drastically enhanced sorption must be expected in the groundwater system due to

- o lower salinity
- o higher exchange capacity of the solid phases.

For actinides in the trivalent state (Am), another solubility limiting phase may be formed ($\text{Am}_2(\text{CO}_3)_3(\text{s})$ or a mixed Am- CO_3 -OH-phase in the groundwater instead of $\text{Am}(\text{OH})_3(\text{s})$, 8,15). The total solubility will be somewhat lower in the low pH-range and significant fraction of anionic Am-carbonates will be found. This may lead to a slight decrease of the sorption at high pH (above 10) but would have only minor effects at lower pH.

For tetravalent actinides (Th) no major effects due to the changes in the water chemistry will be expected when going from the cement pore water to the groundwater system.

For actinides in the pentavalent state (Np) and particularly the hexavalent state (U) the presence of substantial carbonate concentrations in the groundwater will have a large and drastic influence both on chemical speciation and sorption properties. Solubility limiting phases are likely to be species of a type $\text{Na}_x\text{AnO}_2(\text{CO}_3)_y(\text{s})$, leading to much higher maximum solubilities than for a carbonate free system. Dominating species in solution will be of the type $\text{AnO}_2(\text{CO}_3)_x$, where $x = 1-3$. A decrease of the distribution coefficient by orders of magnitude could be expected when the actinides go from the concrete to the bedrock system.

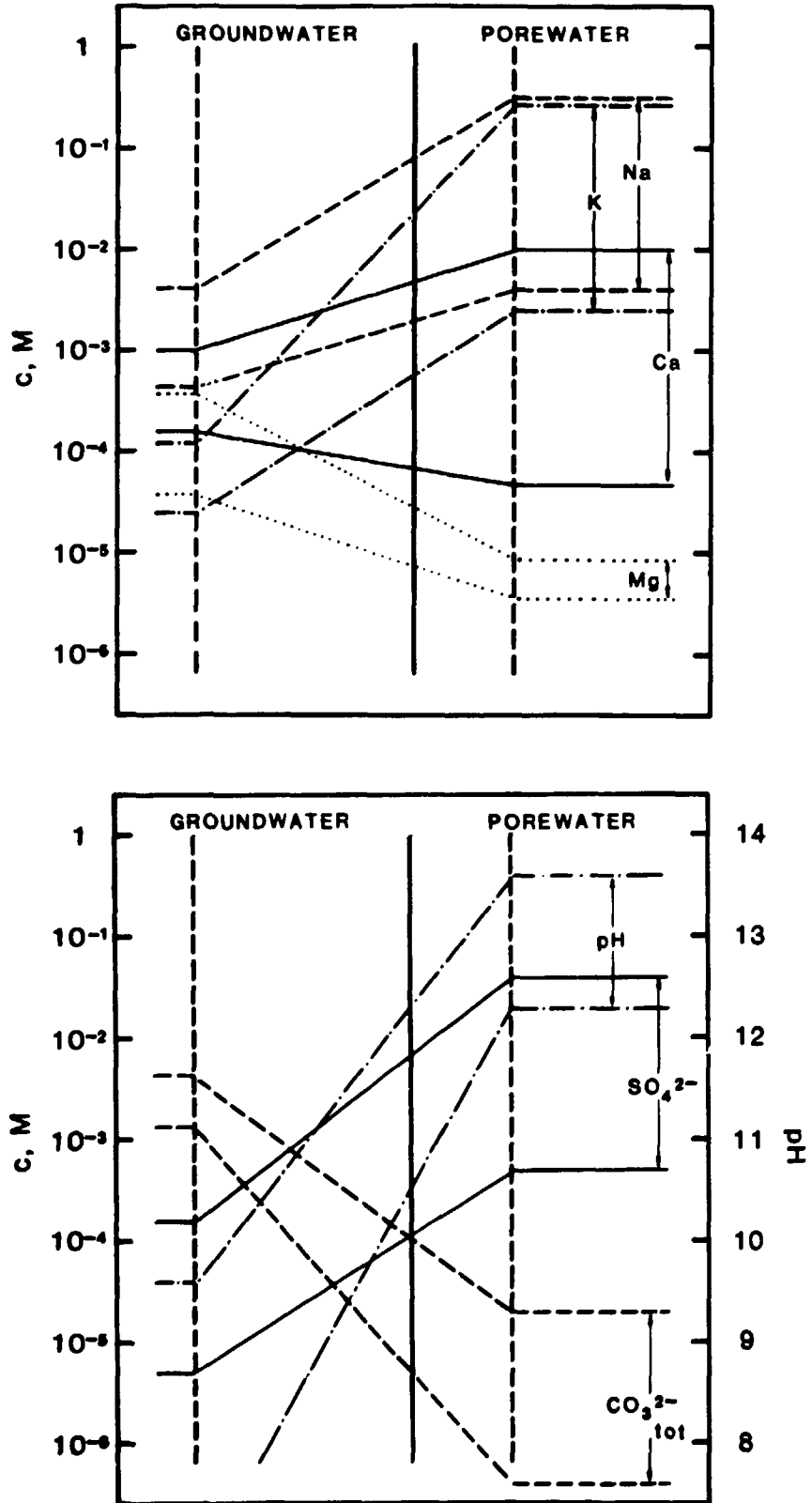


Figure 5. Concentration ranges for the dominating an- and cations in cement pore waters and groundwaters from crystalline rock.

For plutonium the effect of carbonate would be less than for uranium and neptunium, since the higher oxidation states (V or VI) would not prevail in neutral groundwater under non-oxic conditions.

Thus, for the system concrete/pore water - bedrock/groundwater the maximum solubility is expected to be lower and the sorption on the solid phase larger in the concrete for penta- and hexavalent actinides, while the differences between concrete and bedrock would be less significant for the tri- and tetravalent states.

Direct measurements of trace element diffusion in concrete (for Cs, Am and Pu) as well as studies of the release of particulates from a water exposed concrete surface and radionuclide sorption on these particles are in progress.

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