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Sorption and diffusion studies of Cs and I in concrete

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OF Cs AND I IN CONCRETE

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SUMMARY

Concrete has been suggested as a possible encaplulation material for long-term storage of low and medium level radioactive waste. At an underground storage of concrete encapsulated waste, a slow release of radioactive elements into the groundwater by diffusion through the concrete must be considered in the safety analysis. The diffusion may be delayed by sorption reactions on the solid.

A wide range of long-lived radionuclides may be present in the low and medium level radioactive waste. Here, the sorption and diffusion of iodide and cesium in slag cement paste and concrete has been studied. The influence of four different water phases (pore water, groundwater, Baltic Sea water and sea water) as well as the influence of some added species (carbonate, sulphate, and magnesium) has been investigated.

A significant sorption of iodide on cement paste in contact with pore water was observed, indicating that the diffusion may be expected to be retarded in this medium.

For cesium the highest sorption was found for concrete and groundwater. This means that the sorption increases as the concrete is weathered. Low or insignificant sorption was found for the cement paste, indicating that the ballast is responsible for the Cs-sorption.

Carbonatization enhances the Cs-sorption by about a factor of 3.

The diffusivity of Cs in concrete and cement paste was determined to between $2 \cdot 10^{-14}$ and $8 \cdot 10^{-14}$ m^2/s in pore water (where an insignificant sorption was observed).

The choice of ballast as well as addition of suitable "getters" with high sorption of the long-lived radionuclides might decrease the mass transfer rate through the cement.

CONTENTS

1. INTRODUCTION

Concrete has been suggested as a possible encapsulation or overpack material for long-term storage of radioactive waste from nuclear power production, particularly in conjunction with the deposition of low and medium level waste.[1] A storage in underground repositories similar to the concepts suggested for high level waste[2] or unreprocessed fuel[3] may be a possible alternative. The concrete in such a repository will be accessible to groundwater. A slow release of waste elements into the groundwater, largely controlled by the rate of diffusion through the concrete (and through any other secondary barrier such as a clay backfill, if any) must be considered in the safety analysis of such a concept.

The low and medium level waste from nuclear power production might contain a wide range of long-lived radionuclides, such as ^{14}C, ^{59}Ni, ^{90}Sr, ^{99}Tc, ^{129}I, ^{135}Cs, ^{137}Cs, actinides, etc.[4] Although these nuclides would constitute a minor fraction of the initial activity of the waste, their long half-lifes would make them potentially hazardous if released into the groundwater.

A study of the sorption and diffusion of iodide and cesium in slag cement paste and concrete in different aqueous environments is described in this report.

2. MASS TRANSFER IN A CONCRETE BARRIER

2.1. Some properties of cement and concrete

Concrete may be considered as a porous solid mixture of essentially two phases:[5]

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

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

2.1.1. Chemical composition of the cement paste

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

tricalcium silicate, $3CaO \cdot SiO_2$	45-65 %
dicalicium silicate, $2CaO \cdot SiO_2$	10-30 %
tricalcium aluminate, $3CaO \cdot Al_2O_3$	5-15 %
tetracalcium aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	5-12 %
gypsum, $CaSO_4$	< 5 %

By the reaction with water a formation of a continous solid phase occurs, containing hydrates such as

calcium silicate hydrate, $(1.5-2)CaO \cdot SiO_2 \cdot (1-2)H_2O$
calcium hydroxide, $Ca(OH)_2$
calcium aluminate hydrate $4CaO \cdot Al_2O_3 \cdot 13H_2O$
and others.

(A detailed description of cement chemistry, etc is given in ref 5).

2.1.2. Pore water composition and aging processes

Dehydration processes, leading to volume reduction and structure changes, including formation of polysilicates, are possible general aging processes of the cement paste.

Initially the pore water in the cement matrix is a solution of soluble sodium and potassium hydroxides (pH 13-14) with some calcium, magnesium, aluminum, silica and sulphate at ppm-levels. (Dry Portland cement contains 60-67 % CaO, 20-25 % SiO_2, 2.7-7.1 % Al_2O_3, 1.6-3.9 % Fe_2O_3, 1.5-3.8 % MgO, 1.6-3.3 % SO_3, 0.1-1.5 % K_2O and 0.0-0.5 % Na_2O). In an aqueous environment this sodium-potassium hydroxide will be dissolved and transported out of the matrix by diffusion. In a second phase free calcium hydroxide (ca 1 % of the matrix) will dissolve and diffuse out from the cement (pore water pH of 12.6) . The time required for this process would probably be thousands of years. In a third phase a degradation of calcium silicates and aluminates would occur, however with a considerably slower rate. During the whole dissolution and degradation process pH will never be below 10.[6]

The presence of certain agents may have a large influence on the degradation rate of the cement paste. Contact with water of low calcium concentration or low pH would enhance the dissolution of calcium hydroxide. Magnesium and ammonium salts would decrease pH in the paste due to reactions with hydroxyl ions, also leading to an increased degradation rate.

Contact with carbon dioxide or carbonate/hydrogene carbonate would have a sealing effect on the cement paste due to the formation and precipitation of calcium carbonate.

The reaction between sulphate and calcium or aluminates in the paste will cause an expansion and possibly lead to an increased fracturing.[7]

2.2. Transport mechanisms of ions in cement and concrete

Since concrete may be described as a porous solid with water filled pores, a mass transfer by diffusion in these pores can be expected to be the dominating transport mechanism. The overall diffusivity in a porous solid is largely related to the porosity but also to properties such as tortuosity and constrictivity. These parameters of the concrete will, however, change with time during the hydration and aging processes. The apparent overall diffusivity may also be decreased by sorption reactions on the solid surfaces.

Diffusion due to a concentration gradient can in general be described by the following equation (one dimensional diffusion with constant diffusivity):[8]

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \qquad (1)$$

where c = concentration in liquid (mol/m^3)
t = time (s)
D = diffusivity (m^2/s)
x = length (m)

In case of sorption on the solid due to reversible reactions this process can be described by

$$q = K_d c \tag{2}$$

where q = concentration in solid (mol/kg)
K_d = distribution coefficient (m^3/kg)

Assuming that K_d is concentration independent, the diffusion including sorption will be described by:

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} - \rho \frac{dq}{dt} \tag{3}$$

where ρ = density of solid (kg/m^3)
Inserting (2) into (3) gives

$$\frac{dc}{dt} = D/(K_d\rho + 1) \frac{d^2c}{dx^2} \tag{4}$$

Thus, the relation between the overall diffusivity with sorption (D_s) and without sorption (D) on the solid would be given by

$$D = D_s (K_d\rho + 1) \tag{5}$$

i.e. the diffusivity will be decreased by a factor $(K_d\rho + 1)$ due to the sorption.

Non-linear sorption isotherms, giving concentration dependent distribution coefficients, are often observed for the sorption of e.g. cations on geologic media. Concrete may, however, be expected to act largely as an ion exchanger. Thus the sorption process may be regarded as linear as long as the concentration of the interacting ion is low (less than 5-10 % of the total ion exchange capacity).[9]

The overall diffusivity (and mass transfer rate) would in principle be obtainable from the diffusivity in the pure aqueous phase and measurements of the sorption in terms of the distribution coefficient, provided that the porosity, tortuosity and constructivity of the porous solid medium are accurately known. These parameters defining the diffusion paths are, however, not easily determined and consequently, in order to allow a calculation of mass transfer rates, direct measurements of the diffusivity in the solid are required. The influence of chemical parameters such as the composition of the aqueous phase (ionic strength, pH, reacting species) may, however, be studied separately in batchwise distribution studies.

2.3. Parameters of importance for the mass transport in cement

In order to allow predictions and evaluations of mass transfer rates in cement a number of parameters must be specified and their influence on the process be well understood.

2.3.1. Solid phase

The solid concrete consists, as discussed in 2.1, of a cement matrix and a rock ballast. The compositions and properties of both these materials would have considerable effects on the transport process in the concrete and have to be characterized. Since the structure of the cement matrix changes with time, due to crystallization, leaching of some of its components (dehydration) and chemical reactions with species in the water (carbonate, sulphate, magnesium etc), the age and prehistory of the concrete (e.g. way of storing) must be properly selected. As old samples as possible should be used in the experimental studies. The samples should be stored in a carbonate-free environment to avoid unwanted carbonatization and to allow a separate study of the influence of this reaction.

The sorptive properties of the ballast may also affect the mass transfer rate, since the sorption of e.g. non-hydrolyzed cations would be related to the cation exchange capacity of the exposed solid phases.

2.3.2. Liquid phase

The composition of the liquid phase influences the mass transfer properties of ions in the solid concrete through the direct effects of the contact with the solid matrix (leaching, chemical reactions, degradation etc.). If a retardation of a diffusing species is due to ion exchange, variations in pH may be of importance for this process. Ions in the water affecting the complexation or solubility of the transported species would also be of fundamental importance for the mass transport.

3. EXPERIMENTAL

3.1. Choice of radionuclides

The sorption and diffusion of iodide and cesium were studied using ^{131}I (half-life 8.04 d) and ^{134}Cs (half-life 2.06 y). The nuclide concentrations in both batch and diffusion experiments were about 10^{-8} M. No inactive carrier was used.

3.2. Solid and liquid phases

The solid phase was either a concrete made from slag cement or the pure cement paste without ballast. Samples aged 1-2 years (provided by the CBI, The Swedish Cement and Concrete Research Institute) were used in the experiments. All samples had been stored in the absence of air, either in saturated $Ca(OH)_2$-solution or encapsulated in asphalt to avoid carbonatization. The composition of the solid test samples are given in Table 1.

The following aqueous phases were used:

artificial ground water (average granitic groundwater)
artificial ground water with added carbonate (623 mg/l)
artificial ground water with added sulphate (50 mg/l)
artificial ground water with added magnesium (20 mg/l)
artificial Baltic Sea water (average of Swedish East Coast)
artificial sea water (typical of Swedish West Coast)
artificial pore water (two different compositions, c.f. 3.2.1.)

The carbonate, sulphate and magnesium additions correspond to the maximum concentration levels expected in granitic groundwaters.[11]
The sea water and Baltic Sea water were studied because the ground water may be, or may in the future become, contaminated by intruding sea water. All water compositions are given in Table 2.

Table 1. Composition of test samples [10]

No.	Composition [a]	Water/cement ratio	Age [b] (months)
C1	Paste, A	0.35	17
C2	Paste, B	0.35	12
C3	Paste, A	0.40	25
M1	Mortar[c], A	0.40	25
M2	Mortar[c], A	0.60	25

[a] A: 47.6% CaO, 29.3% SiO_2, 7.9% Al_2O_3, 1.3% Fe_2O_3, 4.9% MgO, 3.8% SO_3, 1.0% K_2O, 0.7% S^{2-}. (Na_2O n.d.)

B: 47.3% CaO, 28.5% SiO_2, 7.7% Al_2O_3, 2.0% Fe_2O_3, 4.7% MgO, 2.2% SO_3, 1.1% K_2O, 0.7% Na_2O, 0.7% S^{2-}

[b] Time between preparation and start of sorption/diffusion experiments. C1 and C2 were covered with asphalt during storage and C3, M1, and M2 were stored in sat. $Ca(OH)_2$-sol.

[c] Cement:aggregate = 1:4 (sand, 4 mm)

All experiments, both sample preparations and batch and diffusion measurements, were performed in an inert atmosphere (N_2) to avoid carbonatization of the solid.

3.2.1 Characterization of pore water

By the pressing of crushed cement paste in a tablet press (press load of 20 ton/cm^2), small amounts of the cement pore water were released (0.02 - 0.05 g per batch of 2 - 3 g of paste) (c f Figure 1). The pore water was diluted and analyzed with respect to sodium, potassium, calcium and magnesium (by atomic absorption spectrophotometry) as well as pH (c f Table 3). In the artificial pore waters used some aluminum, sulphate and silicate was added as well at probable concentration levels [12]. The concentrations of these species were too low to be determined accurately in the highly diluted sample solutions, using analysis methods availible.

Two types of pore waters were identified. In the pore water from the cement paste that had been covered with an asphalt layer the sodium and potassium concentrations were 1.4 - 1.8 times higher than in the pore water from the paste stored in saturated $Ca(OH)_2$-solution. Also the hydroxide concentration was significantly higher in the asphalt covered samples.

Table 2. Water composition in the experiments [12]

Ion	SW		BW		GW		PW1		PW2	
	mg/l	mM	mg/l	mM	mg/l	mM	mg/l	mM	mg/l	mM
Na^+	10560	459	4980	216	65	2.84	10000	435	7000	304
K^+	380	9.71	179	4.58	3.9	0.100	22000	563	12000	307
Mg^{2+}	1270	52.3	599	24.7	4.3	0.177				
Ca^{2+}	398	9.93	188	4.68	18	0.448	10	0.250	10	0.250
Sr^{2+}	13.3	0.151	6.3	0.071						
Al^{3+}							75	2.78	75	2.78
F^-	1.4	0.071	0.66	0.033						
Cl^-	18980	535	8950	252	70	1.97				
Br^-	64.5	0.807	30.4	0.381						
HCO_3^-	140	2.29	140	2.29	123	2.01				
SO_4^{2-}	2650	27.6	1250	13.0	9.6	0.100	400	4.17	400	4.17
BO_3^{3-}	24.7	0.420	11.6	0.198						
SiO_2					12	0.206	20	0.343	15	0.258
pH	8		8		8.2		13.9		13.2	

SW = Artificial sea water　I = 1.2
BW = Artificial Baltic water　I = 0.56
GW = Artificial groundwater　I = 0.0084
PW = Artificial pore water

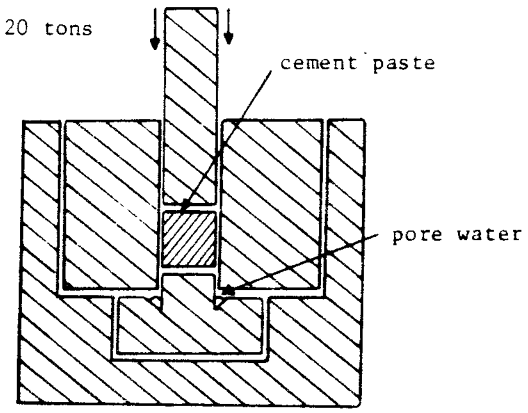


Figure 1. Devise for recovery of pore water by pressing

Table 3. Pore water composition (average of 2-4 samples)

	Concentration, mg/l				
	C1	C2	C3	M1	M2
Na^+	10130	10110	7700	6000	7310
K^+	21910	21350	13465	10245	12110
Ca^{2+}	25	15	19	< 4	19
Mg^{2+}	< 0.3	< 0.3	2	3	4
pH	13.9	13.9	13.4	13.2	12.9

Al: Estimated concentration 10-100 mg/l

Si: Estimated concentration range 10-100 mg/l

SO_4^{2-}: Estimated concentration range 50-500 mg/l

3.3. Batch experiments

The cement pastes and concretes were crushed and a size fraction of 0.063-0.125 mm was collected by sieving. The distribution studies were performed in glass bottles, with a solid/liquid ratio of 11 or 20 g/l (0.5 or 0.9 g solid per 45 ml water). After a pre-equilibration time of 1 week a small aliquot of ^{134}Cs- or ^{131}I-solution was added to the system. After a contact time of 1 day the bottles were centrifuged (1h at 4000g) and samples of the water phase were counted for radioactivity using a NaI-well-type scintillation counter. A new sample was taken after 1 week. Distribution coefficients (mol/kg solid per mol/m^3 liquid) were calculated by comparison with reference bottles without solid sorbents (c f ref. 13).

3.4. Diffusivity measurements

The diffusivity in a solid can be determined either under steady state or non-steady state conditions. Steady state diffusion can be determined by studying the mass transport from one solution to another, separated by a thin slice of the solid. At least 6 months would be required to obtain a steady state condition, assuming a diffusivity of at least 10^{-13} m^2/s for a 3 mm thick concrete slice. Non-steady state diffusion can be studied by analyzing the concentration profile in a solid after a certain contact time with a solution containing the diffusing species (preferably with a geometry allowing diffusion in only one direction).

In this study, only non-steady state diffusion experiments were performed. Test rods with a diametre of 2 cm were sawed from the cement paste and concrete. The rods were covered with an epoxy resin on all sides but one of the planar end surfaces, and fitted into metal tube holders. These holders were made to fit into a specially built grinding device, used for studying concentration profiles in solids. The samples were equilibrated with pore water for 2 weeks and then put into a pore water solution containing the radionuclide. The nuclide concentration in the water was kept constant during the experiment, and the water was stirred to avoid concentration gradients. After a contact time of 2-3 months the concentration of the radionuclide as a function of pentration depth in the solid was analyzed. Layers 0.1-0.2 mm thick were removed from the exposed end surface of the solid by grinding with an abrasive paper, and the dust obtained was fixed on the paper with a cellulose fixative (c f Figure 2).

Two measurements were made on each type of cement paste (C1 - C3) and concrete (M1 - M2). The total activity of each paper was measured with a NaI-well-type scintillation counter.

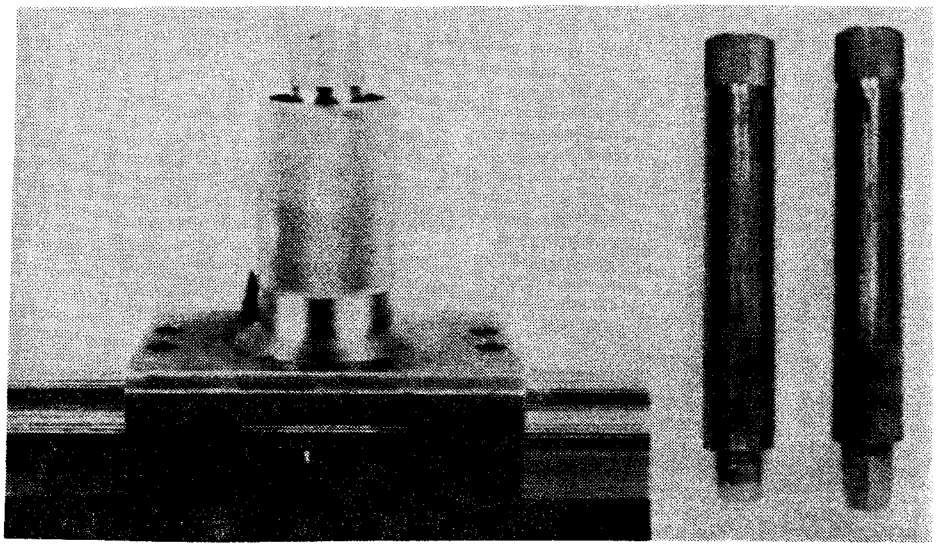


Figure 2. Grinding devise for the study of concentration profiles in solids (left) and concrete samples in holders (right)

4. RESULTS AND DISCUSSION

4.1 Batch measurements

The measured distribution coefficients for cesium and iodide are given in Table 4 and Figure 3. All values are derived from double samples. Estimated maximum systematic errors are given within parantheses.[13]

The highest sorption of iodide is found for cement paste in pore water. Very low sorption was observed in sea water, while it was slightly higher in Baltic Sea water and groundwater. The only added ion that seems to have any significant effect on the sorption is sulphate.

The sorption of cesium on concrete shows a similar qualitative ionic strenght dependence as has been observed for the pure ballast mate-

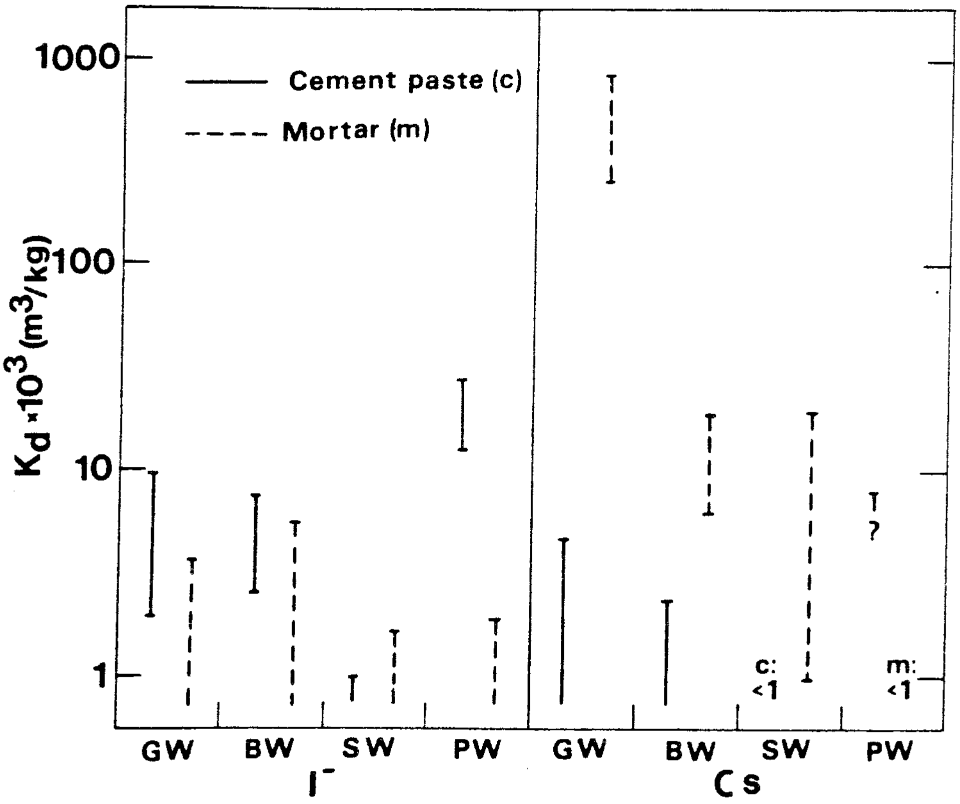


Figure 3. Ranges of distribution coefficients (K_d) for I^- and Cs

Table 4. Distribution coefficients (K_dx10^3, m^3/kg)

Nuclide	Sample	Time	GW [a]	GW+HCO_3^- [b]	GW+SO_4^{2-} [c]	GW+Mg^{2+} [d]	BW [a]	SW [a]	PW 1 [a]	PW 2 [a]
^{131}I	C 1	1 d	5.5(1.7)	2.0(1.8)	9.6(2.0)	9.1(2.0)	6.6(1.7)	0 (1.4)	15 (2.0)	
		7 d	7.4(1.8)	3.0(1.8)	13 (2.1)	7.5(2.0)	7.0(1.8)	0 (1.6)	20 (2.3)	
	C 2	1 d	3.1(1.6)				7.8(1.8)	0.9(1.4)	13 (2.0)	
		7 d	4.9(1.7)				7.7(1.8)	1.1(1.6)	16 (2.2)	
	C 3	1 d	2.8(1.6)				2.7(1.6)	0 (1.4)		13 (2.0)
		7 d	3.2(1.7)				3.3(1.7)			17 (2.2)
	M 1	1 d	0 (1.4)	0 (1.7)			5.6(1.7)	0.5(1.4)		0.2(1.4)
		7 d	0 (1.6)	0 (1.7)			5.7(1.8)	1.7(1.7)		0.7(1.7)
	M 2	1 d	0 (1.4)		3.0(1.8)	2.1(1.8)	0 (1.4)	0 (1.4)		1.3(1.5)
		7 d	0 (1.6)		3.8(1.8)	2.2(1.8)	0.3(1.6)	0 (1.6)		2.2(1.7)
^{134}Cs	C 1	1 d	0 (1.9)	4.1(2.2)	3.6(2.1)	0.3(1.9)	0 (1.9)	0 (1.9)	0 (1.9)	
		7 d	0 (1.9)	4.8(2.2)	3.6(2.1)	0 (1.9)	1.1(2.0)	0 (1.9)	0 (1.9)	
	C 2	1 d	0 (1.9)				0 (1.9)	0 (1.9)	0 (1.9)	
		7 d	0 (1.9)				2.3(2.0)	0 (1.9)	0 (1.9)	
	C 3	1 d	0 (1.9)				0 (1.9)	0 (1.9)		7.7(2.3)
		7 d	0 (1.9)				1.9(2.0)	0 (1.9)		7.5(2.3)
	M 1	1 d	128 (8)	615 (31)			7.4(2.3)	15 (2.6)		0 (1.9)
		7 d	241 (13)	850 (39)			21 (2.7)	20 (2.7)		0 (1.9)
	M 2	1 d	145 (8)		220 (12)	204 (11)	7.8(2.3)	1.2(2.0)		0 (1.9)
		7 d	248 (15)		328 (15)	335 (16)	20 (2.7)	6.4(2.3)		0 (1.9)

[a] Final pH-values:

GW/C	12.2±0.1	
BW/C	10.7±0.2	(9.6 for C 3)
SW/C	9.6±0.1	
PW/C	13.5±0.1	
GW/M	11.6±0.1	
BW/M	9.4±0.4	
SW/M	9.3±0.1	
PW/M	13.4±0.1	

[b] Tot. HCO_3^-: 623 mg/l

[c] Tot. SO_4^{2-}: 50 mg/l

[d] Tot. Mg^{2+}: 20 mg/l

rial[14], i e an increased sorption whth decreasing ionic strength. This is however not the case for the pure cement paste, which shows practically no sorption of cesium at all (except for C3/PW, c f Table 4). Thus the sorption in the concrete seems to be largely due to the ballast. However in the pore water system the sorption is very low. The already high distribution coefficients for the concrete/groundwater systems is still increased by the addition of sulphate or magnesium and in particular, by carbonatization.

Thus, for iodide, the largest retention in intact concrete will occur for a material with as low ballast content as possible. The diffusivity will then be determined only by mechanical properties as porosity, tortuosity and constrictivity. A leaching with groundwater will lead to an increasing retention of cesium in the matrix due to sorption effects.

For cesium the choice of ballast material in the concrete would be of crucial importance for the retaining properties.

An addition of "getters" with high sorption of certain radionuclides might be feasible for improving the properties of concrete as an encapsulation material for low and medium level radioactive waste.

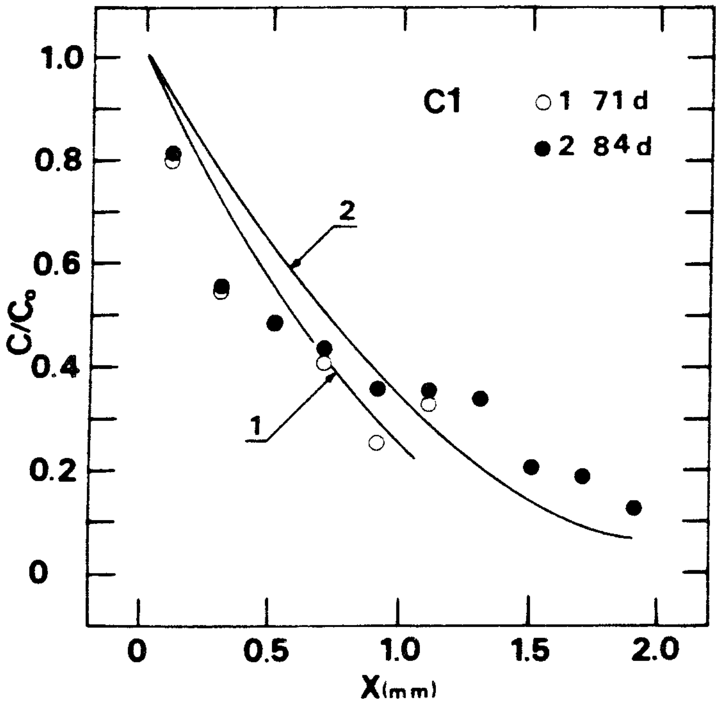
4.2 Diffusivity measurements

The concentration profile in the solid may be expected to follow the equation:

$$\frac{c}{c_o} = \mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (6)$$

which is the solution to eq (1), assuming constant concentration of the diffusing species in the solution and zero initial concentration in the porous solid.

The concentration profiles of ^{134}Cs in the concrete samples obtained by grinding off fragments of 0.1 or 0.2 mm, were curve fitted by the method of least squares to eq (6). The result is shown in Figure 4.



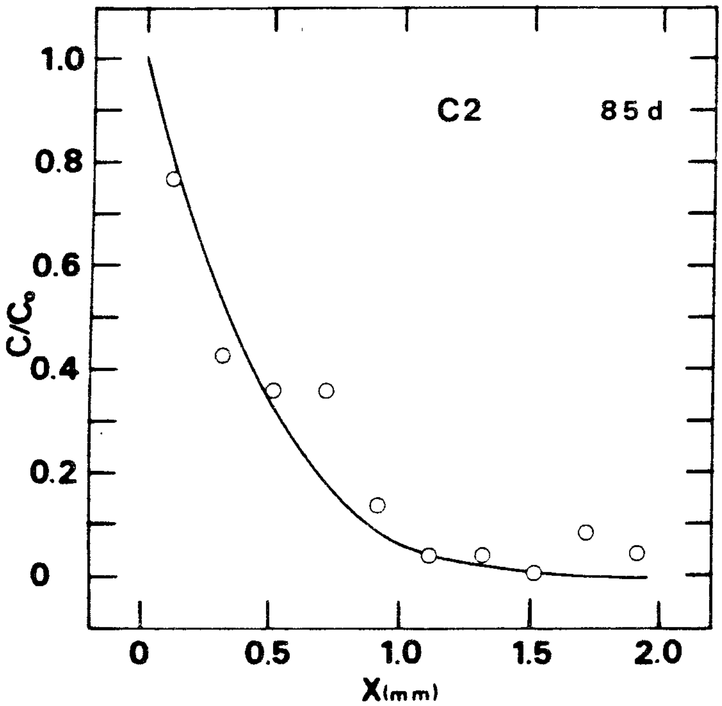
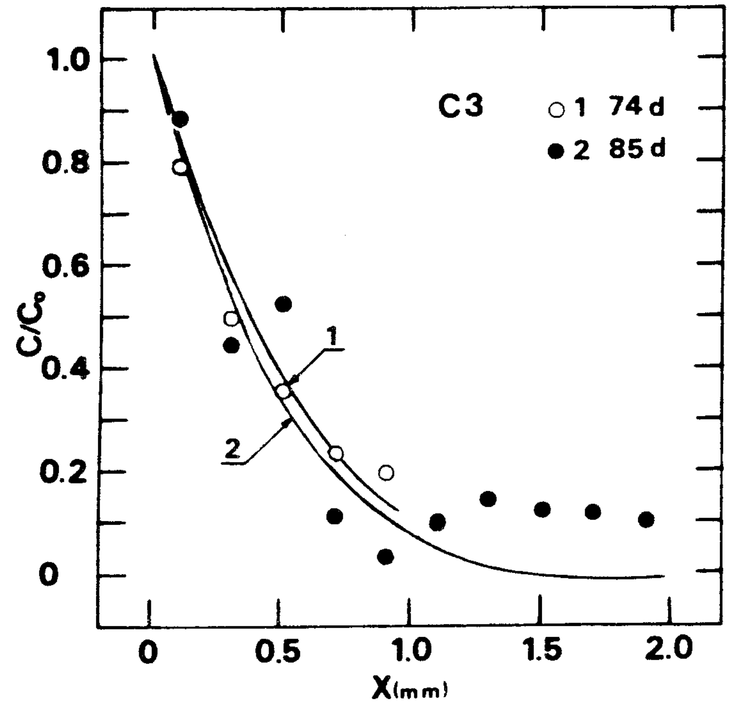


Figure 4. Measured ^{134}Cs concentration profiles (dots) and equation (6) fitted to data (curve)



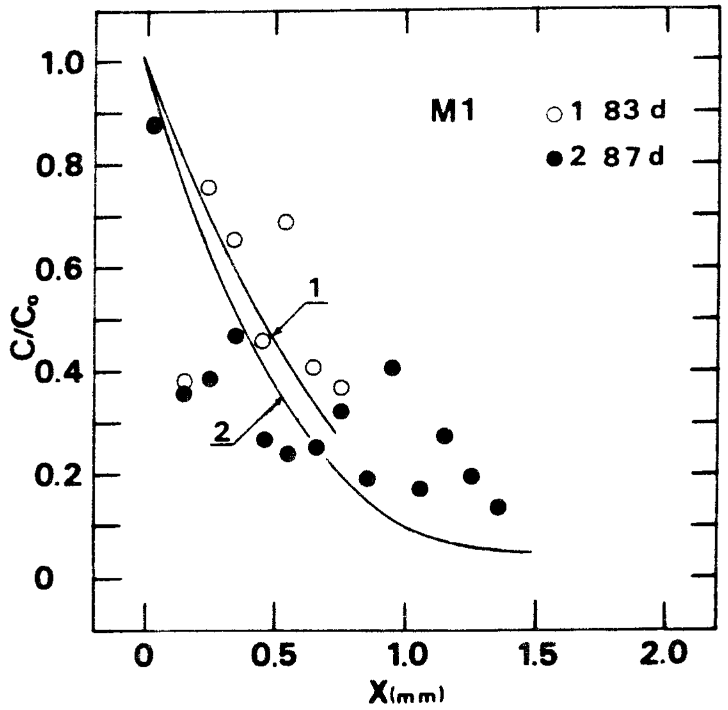


Figure 4 (Continued)

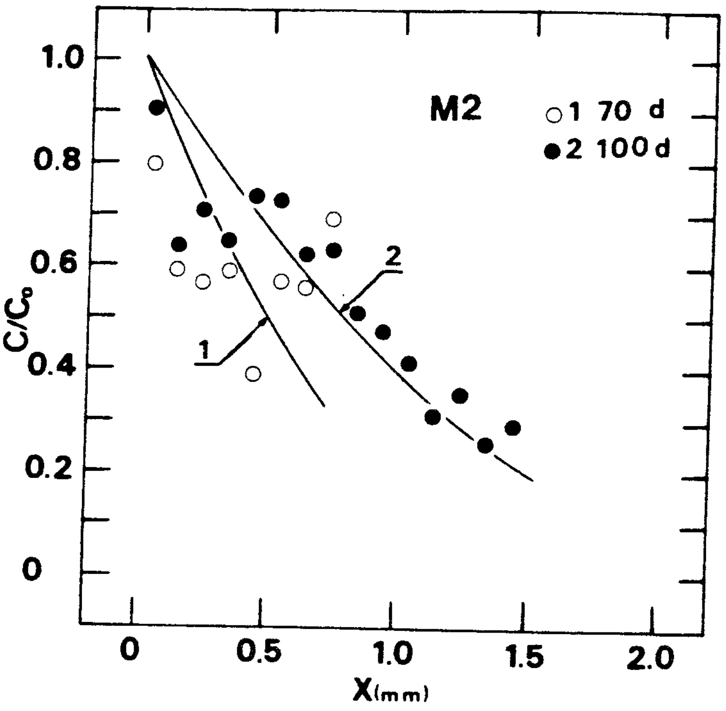


Figure 4 (Continued)

The effort to measure the diffusion of ^{131}I was not successful, due to the low diffusivity and short half life (8.04 d) of this isotope.

The experimentally derived concentration profiles seem to follow the theoretical curve form fairly well. A slight deviation towards too low concentration at low values of x and too high at higher values seem to occur. Effects of this type may be due to a sorption by a non-linear isotherm of the type $q = K c^{1/n}$ (Freundlich), where $1/n > 1$, i e the sorption increases with increasing concentration (unfavourable equilibrium[15]). This leads to a continous spreading of the concentration profile. A consequence of this spreading is that the driving force for mass transfer through the solid is decreasing with time.

To define to what degree the sorption isotherm is unfavourable requires a thorough study of the concentration dependence of the distribution coefficient, preferably in batch measurements. The method used to evaluate the experiments gives the diffusivity with any non-linear effects included. At higher distribution coefficients a lower diffusivity than calculated from eq (6) would actually be the case if an unfavourable sorption isotherm is assumed.

The diffusivities obtained in the experiments, Table 5, are of the same order of magnitude as earlier reported values for Na^+ and Cl^- in slag cement (i e $11 \cdot 10^{-14}$ and $4 \cdot 10^{-14}$ m^2/s in ref 7). In comparison with diffusivities in other porous bodies the values obtained are very low. The main resistance to mass transfer in the cement paste can probably be ascribed to geometric factors such as porosity, tortousity and constrictivity, which causes few, long and narrow diffusion paths through the solid. The measured K_d-values indicate that the retention by sorption may not decrease the diffusivity by more than about one order of magnitude in the samples (cement paste or mortar) studied. This is a little surprising since the distribution coefficients are several orders of magnitude higher for cesium in mortar than in cement paste in groundwater (c f Table 4). On the other hand very low distribution coefficients are obtained both for the cement paste and mortar in pore water.

One of the consequenses of weathering of the concrete in groundwater would be a change of the composition of the water in the vicinity of concrete surfaces (decreasing pH, decreasing ionic strenght). This would tend to increase the sorption of cesium, as well as the presence of Mg^{2+}, SO_4^{2-} or HCO_3^- would increase the sorption, other effects not considered. This increase of the sorption might decrease the diffusivity by up to three orders of magnitude.

Table 5. Diffusivities (D) of Cs obtained from concentration profiles

No.	$D \times 10^{14}$ (m^2/s) Sample 1	Sample 2
C1	6.4	7.0
C2	-	2.0
C3	2.3	1.7
M1	3.5	2.3
M2	3.7	8.1

There is no reason to expect that the diffusivity of iodide, without taking sorption into account, should be higher than that of cesium. Since higher distribution coefficients were observed for iodide than for cesium in pore water, the diffusivity of iodide might initially be one to two orders of magnitude lower than of cesium.

5. CONCLUSIONS

The low diffusivity observed for cesium in slag cement implies that the mass transport rate of cesium through intact slag cement paste or concrete would be very low. Assuming a diffusivity of 10^{-13} m^2/s, it would take 3900 years before the concentration of cesium on one side of a 0.4 m thick concrete wall would reach 1 % of the concentration 9600 years and for 50 % over 50 000 years would be required. Diffusion through a water filled fractured concrete block would of course be much faster. To reach 10 % of the inner concentration outside the block may take less than a year, assuming one major fissure.

The flux of radionuclides (mass/year) through the concrete depends not only on the diffusivity, but also on the concentration gradient obtained. The maximum possible concentration gradient is in principle the concentration inside the concrete divided by the diffusion lenght; assuming that no mass transfer resistance will occur in the surrounding clay buffer. For intact concrete cubes with 1.6 m sides and 0.4 m wall thickness containing Cs-activity of 1 Ci/m^3 inside the walls a maximum yearly leakage of 6×10^{-5} Ci/cube would be expected under steady state conditions.

The choice of ballast would have a large influence on the sorption and the mass transfer rate of cesium in concrete (an increase in retention, i e water velocity/nuclide velocity, by at least one order of magnitude seems feasible).

The addition of suitable "getters" with high sorption of cesium, iodide or any other radionuclide might improve the already good properties of intact concrete as an encapsulation material for low and medium level radioactive waste further more.

Thus an intact concrete encapsulation or overpack in a waste repository constitutes an effective barrier in preventing the release of ^{137}Cs into the groundwater.

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