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The diffusion of ions through water-saturated cement

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The interdiffusion of I^- and Cl^- ions and the tracer diffusion of Cs^+ ions in water-saturated Ordinary Portland Cement have been measured at 30° C as a function of water/cement ratio at fabrication. The diffusion was strongly influenced by the water/cement ratio in an approximately exponential manner and the Cs^+ ions were significantly less mobile than the other ions. Diffusion measurements and electrical conductivity measurements have also been made as a function of temperature and reveal that significant irreversible changes in pore structure were induced on heating. The implications of the observations for the diffusion mechanism and the probable pore structure of the cement paste are discussed.

Nomenclature

Symbol	*Quantity*	*Units*
c_1, c_s	Concentration in liquid, or solid	atom m^{-3}
$\langle c \rangle$	Average concentration in the porous medium	atom m^{-3}
D_a	Apparent diffusion coefficient in porous medium	$m^2\ sec^{-1}$
D_f	Diffusion coefficient in free liquid	$m^2\ sec^{-1}$
D_i	Intrinsic diffusion coefficient in porous medium	$m^2\ sec^{-1}$
D_p	Diffusion coefficient in pore liquid	$m^2\ sec^{-1}$
e	Charge on the electron	C
J_x	Flux of diffusant along direction x per unit area of liquid	atom $m^{-2}\ sec^{-1}$
$\langle J_x \rangle$	Flux of diffusant per unit area of porous medium	atom $m^{-2}\ sec^{-1}$
k	Boltzmann constant	$J\ K^{-1}$
K_d	Gravimetric distribution coefficient between solid and liquid	$m^3\ kg^{-1}$
Q	Diffusibility of porous medium	–
t	Time	sec
T	Absolute temperature	K
x	Position	m
z	Valency on an ion	–
α	Capacity factor	–
γ	Volumetric distribution coefficient between solid and liquid	–
δ	Constrictivity of pore structure	–
ϵ	Volume fraction of porosity	–
ρ_a	Apparent density of porous medium	$kg\ m^{-3}$
λ^0	Equivalent ionic conductivity at infinite dilution	$\Omega^{-1}\ m^2\ equ^{-1}$
σ	Electrical conductivity	$\Omega^{-1}\ m^{-1}$
σ_f	Electrical conductivity of free electrolyte	$\Omega^{-1}\ m^{-1}$
σ_s	Electrical conductivity or porous medium saturated with electrolyte	$\Omega^{-1}\ m^{-1}$
τ	Tortuosity of pore structure	–

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1. Introduction

Materials based on Ordinary Portland Cement (OPC) are now being seriously considered in the nuclear industry for the immobilization of intermediate-level radioactive waste. Cementitious materials are also likely to be further used in the technology of radioactive waste disposal for the construction of trenches for low-level waste disposal and for backfilling and sealing intermediate-level waste repositories. Consequently, to understand and predict the migration of radionuclides and other species through the wasteform (leaching) and the backfill it is necessary to have some knowledge of the diffusion of aqueous ions through these porous materials when they are saturated with water. Such data are also required for predicting the transport of aggressive ions to metals encapsulated in cementitious material, e.g. Cl^- ions initiating the corrosion of steel reinforcing bars in concrete.

It is useful at this stage to review the description of diffusion through a water-saturated porous medium so as to clearly define the parameters which can be used to characterize the transport. In the description which follows it is assumed that diffusion only takes place in the aqueous phase and that any ions adsorbed on to (or absorbed into) the solid phases and can only move by desorption into the liquid with which they are in equilibrium. For such a system it is possible to define various different diffusion coefficients and care must be taken when quoting "the diffusion coefficient" to indicate which one is being considered. In the free liquid phase there is no ambiguity and the diffusion coefficient, D_f, is defined in the usual way by

$$J_x = -D_f \frac{dc_l}{dx} \tag{1}$$

where c_l is the concentration in the liquid. When the liquid is constrained by the pore structure of the porous medium we can define a similar diffusion coefficient, D_p, for diffusion within the pore liquid:

$$J_x = -D_p \frac{dc_l}{dx} \tag{2}$$

in which J_x is the flux per unit cross-sectional area of the liquid (i.e. the pores) rather than per unit area of the porous medium. D_p is less than D_f for two reasons. The first is that the diffusion paths, being constrained by the pore structure, are tortuous compared to diffusion in the free liquid and the path direction is not parallel to the concentration gradient. Secondly, the diffusion paths are unlikely to be of uniform cross-section and may become very constricted at certain points. These considerations have led to the introduction of a constrictivity, δ, and tortuosity, τ, to describe the porous medium (see, for example, [1]) such that

$$D_p = D_f \frac{\delta}{\tau^2} \tag{3}$$

Experimentally, it is easier to work in terms of the average flux per unit area of the medium (rather than the liquid) leading to another diffusion coefficient, D_i, sometimes called the intrinsic diffusion coefficient:

$$\langle J_x \rangle = -D_i \frac{dc_l}{dx} \tag{4}$$

and

$$D_i = D_f \frac{\epsilon\delta}{\tau^2} \tag{5}$$

where ϵ is the volume fraction of porosity.

The quantity $\epsilon\delta/\tau^2$ is known as the diffusibility of the medium (Q) and is a particularly useful parameter to measure as characterizing the transport properties of the medium. Whilst ϵ and τ are properties of the porous medium alone, δ depends both on the porous medium and the diffusion process.

If one chooses to work in terms of average concentration gradients in the medium (rather than in the liquid) one can define an apparent diffusion coefficient, D_a, by the equation

$$\langle J_x \rangle = -D_a \frac{d\langle c \rangle}{dx} \tag{6}$$

$\langle c \rangle$ is an average over the solid and liquid phases:

$$\langle c \rangle = \epsilon c_l + (1-\epsilon)c_s \tag{7}$$

and therefore D_a is influenced by adsorption phenomena. If γ is the volumetric distribution coefficient of the species between the solid and the liquid ($= c_s/c_l$) then

$$D_a = D_f \frac{\delta}{\tau^2}\frac{\epsilon}{\alpha} \tag{8}$$

where

$$\alpha = \epsilon + (1-\epsilon)\gamma \tag{9}$$

Thus when there is no adsorption ($\gamma = 0$) $D_a = D_p$, but when there is significant adsorption D_a is less than D_p. The parameter α can be regarded as a measure of the "capacity" of the medium for a particular diffusant. In batch adsorption experiments it is usual to measure a gravimetric distribution coefficient, K_d. This is the number of adsorbed ions per unit mass of the medium, divided by the number of ions per unit volume of liquid. Thus

$$K_d = \frac{\gamma(1-\epsilon)}{\rho_a} \qquad (10)$$

and

$$\alpha = \epsilon + K_d \rho_a \qquad (11)$$

where ρ_a is the apparent density of the porous medium.

There have been only a few studies of the diffusion of ions through water-saturated cement reported in the literature. Page *et al.* [2] measured D_i for NaCl diffusion through cements of various compositions. They found that D_i in OPC samples was strongly dependent on the water/cement ratio of the original paste mix. D_i in specimens with a water/cement ratio of 0.6 was approximately five times greater than in those with a water/cement ratio of 0.4. They also measured D_i as a function of temperature in the range 7 to 45° C and found it to have an apparent activation energy of 0.41 eV per ion (9.4 kcal mol^{-1}) which is considerably greater than the 0.15 eV per ion (3.5 kcal mol^{-1}) normally associated with diffusion in free water. The diffusion coefficient was sensitive to the conditions under which the cement paste was cured; D_i for specimens cured in saturated air being approximately double that for specimens cured in saturated $Ca(OH)_2$ solution. Their results (for a water/cement ratio of 0.4) are in good agreement with the earlier work of Collepardi *et al.* [3]. Goto and Roy [4] carried out similar experiments, also with NaCl as diffusant, in cements comparable with OPC. In contrast to Short and Page, they report observing no "pronounced" effects of water/cement ratio (in the range 0.35 to 0.45) or curing conditions on D_i. Furthermore they found that the Cl^- ion concentration in the low concentration side of their diffusion cell increased at a faster rate than did the Na^+ ion concentration. This not only indicates that Cl^- has a greater diffusion coefficient than Na^+, but also that other species must be diffusing during the experiment in order to maintain electrical neutrality (e.g. Ca^{2+} and OH^- ions). Thus, the interpretation of these experiments is uncertain. In common with Page *et al.* they also observed a relatively high activation energy in the range 0.5 to 0.9 eV per atom (12 to 20 kcal mol^{-1}).

The results of these two studies in cements of different water/cement ratio at 27° C are shown in Fig. 1 from which it can be seen that the uncertainty in D_i from the measurements of Goto and Roy is extremely large. Both these studies are also dubious because they employed diffusion cells with a concentrated NaCl solution on one side (~ 1 M) and deionized water on the other. Under such conditions there may have been an osmotic flow of liquid through the cement from the low concentration to the high concentration side of the cell.

The objectives of the experiments described here were to carry out diffusion measurements over a wider range of water/cement ratios, to resolve some of the discrepancies and scatter in the earlier data and to modify the techniques so as to remove some of the uncertainties in interpretation of the earlier measurements.

2. Experimental details

2.1. Specimen preparation

The cement pastes were prepared by mixing batches of 500 g OPC and the required quantity of water in a mechanical mixer for 10 min. The slurry was cast into rubber moulds 32 mm diameter and vibro-compacted (at 122 Hz and an acceleration of 10 to 30 *g*) for 10 min. The cement pastes were then allowed to cure for 28 days in 100% r.h. at 20° C (they were demoulded after 2 days curing).

Disc-shaped diffusion specimens approximately 3 mm thick and 32 mm diameter were cut from the cast cylinders. The specimen surfaces were ground on 600 grit SiC paper and then ultrasonically cleaned to remove debris before sealing into the diffusion cell. Care was taken to select specimens which were free of defects apparent on either surface.

2.2. Diffusion measurements

The basic arrangement which was used to measure D_i was similar to that employed by Goto and Roy [4] and Page *et al.* [2] in the earlier studies. The cement sample formed a partition between two sides of a diffusion cell as shown in Fig. 2. The cell was constructed of perspex and the sample was sealed into position using a proprietary silicone-based sealant. The quality of the seal was checked in a dummy experiment, using an impermeable glass disc in place of the cement sample, and found to be satisfactory.

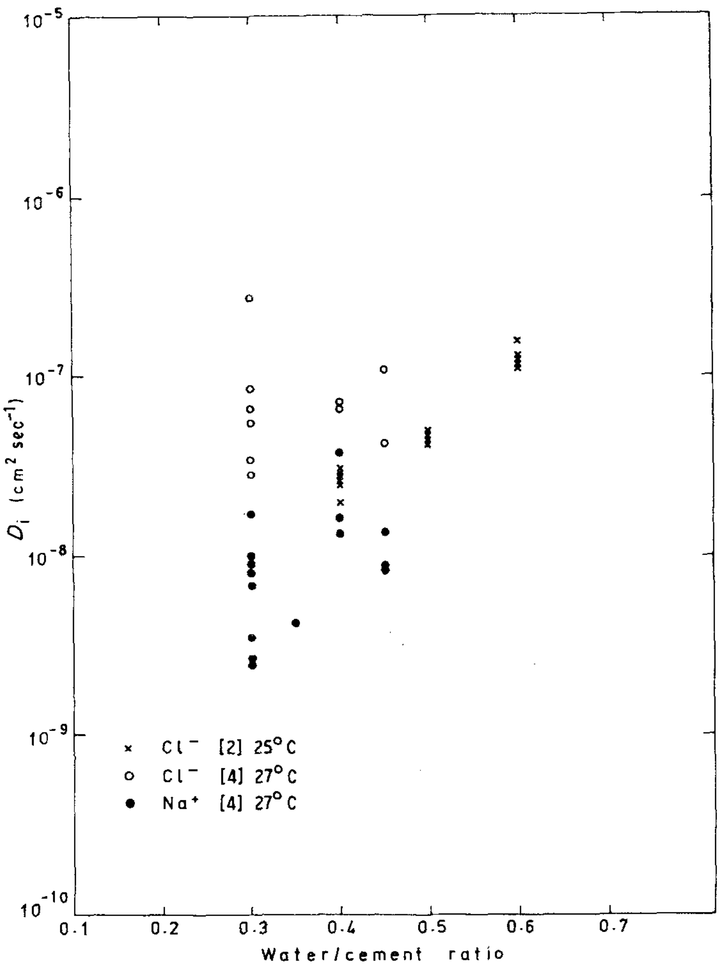

Figure 1 Reported data [2, 4] for the intrinsic diffusion coefficient, D_i, for Na^+ and Cl^- ions in water-saturated cement pastes as a function of the water/cement ratio at fabrication.

The diffusion experiment consisted of measuring the concentration of diffusant in the low concentration side of the cell (c_2) as a function of time. The boundary conditions were that at $t = 0$, $c_2 = 0$ and the concentration in the sample was also zero. In the high concentration side the concentration (c_1) was maintained constant for all t. The results of such an experiment should ideally be of the form shown schematically in Fig. 2 [5]. At short times there is a transient behaviour during which porosity is filled with diffusant, the concentrations in the solid and the liquid come into equilibrium (by adsorption) and a linear concentration gradient becomes established through the

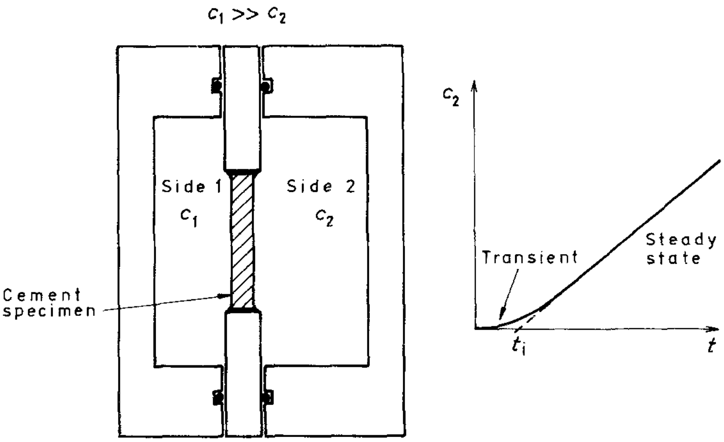

Figure 2 Schematic diagram of the diffusion cell and idealized diffusion kinetics.

sample. Once this is established, diffusion is in a steady state and c_2 increases linearly with time. The diffusion coefficient D_i can be obtained from the steady state region since

$$D_i = \frac{lV}{Ac_1}\frac{dc_2}{dt} \tag{12}$$

where V is the volume of the low concentration side of the cell and the sample has thickness l and cross-sectional area A. The intercept on the time axis (t_i) is related to the magnitude of the capacity factor α by

$$\alpha = \frac{6D_i t_i}{l^2} \tag{13}$$

Thus any adsorption only influences the time to reach a steady state and not the steady state transport itself. α was also obtained by elution of the diffusant from the sample into a known volume of liquid on completion of the diffusion experiment.

Two types of diffusion experiment were carried out. In the first type interdiffusion of KI and KCl was measured. The sample was allowed to equilibrate in 1 M KCl solution for several days before removing the KCl from side 1 and replacing it with 1 M KI at $t = 0$. 1 M solutions of KCl and KI have approximately the same osmotic coefficients at 25° C ([6], p. 484) and therefore there should be no osmotically driven flow between the two sides of the diffusion cell. Since the concentration of K^+ ions is uniform, these experiments measure the interdiffusion of Cl^- and I^- through the porous cement samples. The diffusion was monitored by measuring the I^- concentration in side 2 as a function of time using an iodide specific ion electrode (Orion Research Inc., Cambridge, USA).

In the second type of diffusion experiment the tracer diffusion coefficient of Cs^+ ions was measured using the ^{137}Cs radioisotope. In these experiments the whole of the diffusion cell was filled with 0.1 M CsCl solution saturated with $Ca(OH)_2$ (to be close in composition to the water in the cement pores) and allowed to equilibrate for 1 week. Previous experiments had shown that at this concentration [7] adsorption on to the cement was negligible. At $t = 0$ ^{137}Cs tracer was added to side 1 of the diffusion cell to give an activity of approximately 1 μCi ml^{-1} and the activity of ^{137}Cs in side 2 was monitored as a function of time by counting 5 ml aliquots and then returning them. In such experiments there exists only a concentration gradient of tracer ions and there are no gradients in chemical activity of any species.

In all experiments the temperature was controlled using a thermostatic water bath.

2.3. Electrical conductivity measurements

In studies of the transport properties of porous rocks, measurements of the electrical conductivity of specimens saturated with an aqueous electrolyte have proved useful as a rapid substitute for diffusion or permeability measurements [8]. Provided that the solid phase is effectively an insulator, diffusion and ionic conductivity are controlled by the same processes and are connected by the Einstein relation:

$$\sigma = \frac{e^2}{kT}\sum_j c_j |z_j| D_j \tag{14}$$

In this expression c_j is the number of ions per unit volume, z_j the valency and D_j the diffusion coefficient of ions of type j. It follows that the ratio of the ionic conductivity of a sample saturated with electrolyte, σ_s, to that of the free electrolyte, σ_f, is the diffusibility of the porous medium, i.e.

$$\frac{\sigma_s}{\sigma_f} = \frac{\epsilon\delta}{\tau^2} = Q \tag{15}$$

which may be compared with Equation 5.

The ionic conductivity, σ_s, was measured in a cell similar to the diffusion cell, but equipped with Ag/AgCl wire electrodes in the form of a spiral whose overall diameter was slightly larger than that of the cement sample. The electrolyte was 3 M NaCl and the resistance was measured using a.c. impedance techniques to eliminate the polarization phenomena at the electrodes [9].

3. Results

Fig. 3 shows a typical plot for I^- ions diffusing through a cement sample. The steady state region is clearly identifiable and the intercept on the time axis is quite small. In general the intercept was so small that it was subject to relatively large uncertainty. A similar plot for ^{137}Cs tracer diffusion in a specimen of lower water/cement ratio is shown in Fig. 4. Again, the intercept on the time axis is small and the somewhat greater scatter in the ^{137}Cs activity measurements than in the I^- concentration measurements leads to an even greater uncertainty in the intercept on the time axis. It should also be noted that experiments using specimens of the low water/cement ratio, such as that shown in Fig. 4, require long times for completion (several months).

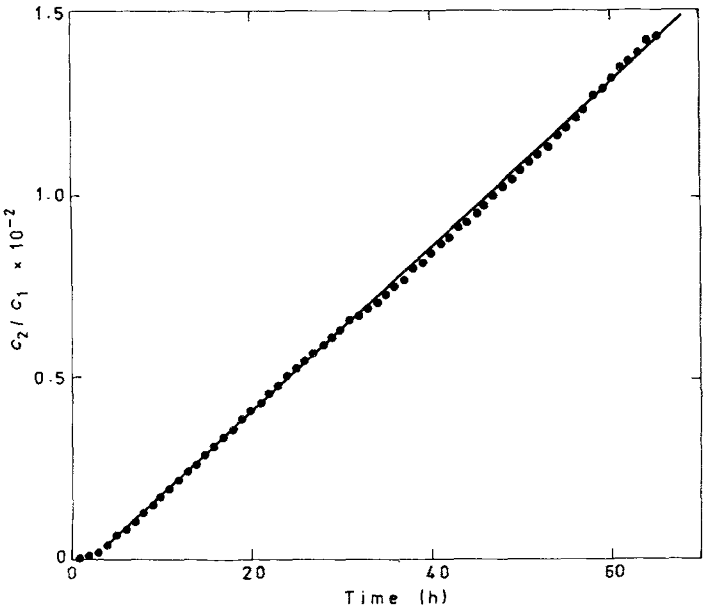

Figure 3 An example of the kinetics of diffusion of I^- ions at 30° C through a cement specimen having a water/cement ratio = 0.6, and l = 2.28 mm.

The measurements of D_i at 30° C for I^- and Cs^+ diffusion are shown in Fig. 5 as a function of water/cement ratio. The solid lines are intended to link measurements of the same diffusing species and do not imply any theoretical basis for expecting an exponential dependence of D_i on water/cement ratio. Also shown in Fig. 5 for comparison are the ranges of D_i which have been reported for other materials which may be present with cement in the neighbourhood of a nuclear waste repository.

The effect of temperature on D_i for I^- diffusion through a single cement specimen (water/cement ratio 0.4) is shown in Fig. 6. D_i was measured in the same specimen as a function of temperature at points around a temperature cycle from 20° C up to 60° C, down to 10° C and then back to 20° C. The results clearly demonstrate that these temperature changes have an irreversible effect on the structure of the cement in such a way as to increase the diffusion coefficient. Also shown in Fig. 6 are the diffusion data of Page *et al.*, which are in good agreement with the present data for increasing

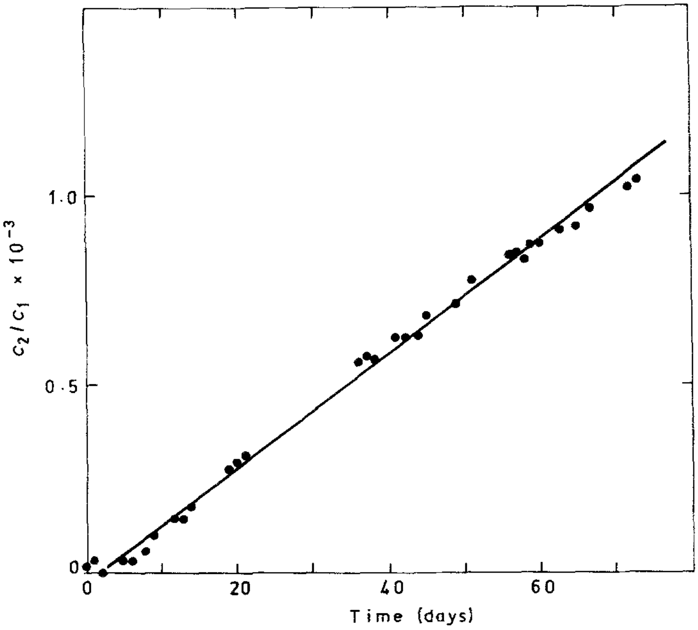

Figure 4 An example of the kinetics of diffusion of ^{137}Cs tracer ions at 30° C through a cement specimen having a water/cement ratio = 0.3, and l = 2.55 mm.

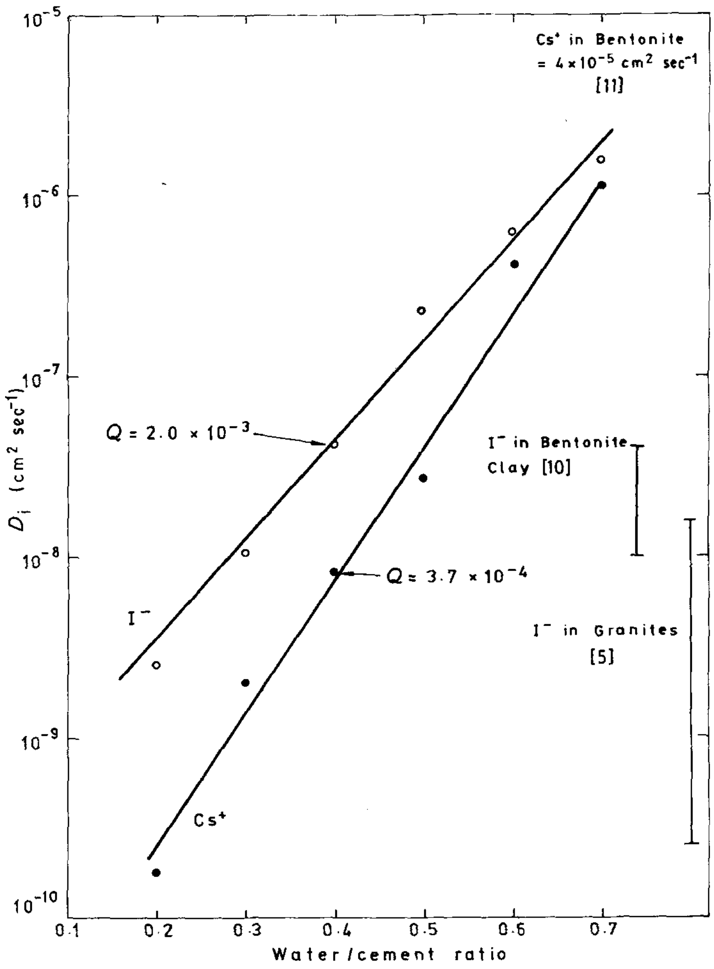

Figure 5 The intrinsic diffusion coefficients for I^- and $^{137}Cs^+$ ions measured at 30° C as a function of water/cement ratio. Values of diffusibility, Q, at a water/cement ratio of 0.4 are indicated and the ranges of D_i in some other materials of relevance to nuclear waste disposal are also indicated. Data from [5, 10, 11].

temperature, and the equivalent conductivity of the I^- ion at infinite dilution, λ^0, ([6], p. 465) which is indicative of the expected temperature dependence of diffusion in the free liquid.

The ionic conductivity of a similar specimen (also having a water/cement ratio of 0.4) saturated with 3 M NaCl is shown in Fig. 7 as the specimen was taken around two temperature cycles separated by a period of 1 month during which the specimen remained immersed in the electrolyte. These data confirm that irreversible changes are induced by the thermal cycles.

The measurements of α both from the diffusion experiments, α_d, and subsequent elution, α_e, are shown for both I^- and $^{137}Cs^+$ as a function of water/cement ratio at 30° C in Fig. 8. The wide scatter in the data is readily apparent. Measurements of porosity, ϵ, by mercury intrusion porosimetry [12] are also shown in Fig. 8. α should be equal to ϵ if the diffusant is not adsorbed on to the solid (Equations 9 and 11).

4. Discussion

The data in Fig. 5 for both I^- and $^{137}Cs^+$ diffusion clearly confirm that diffusion in water-saturated cement paste is a strong function (approximately exponential) of the water/cement ratio at fabrication. This resolves the discrepancy in the previously published data and is in agreement with the observations of Page *et al.* [12]. The "centre of gravity" of the scattered earlier results (Fig. 1) is $D_i \sim 4 \times 10^{-8}\ \mathrm{cm^2\ sec^{-1}}$ $(4 \times 10^{-12}\ \mathrm{m^2\ sec^{-1}})$ at a water/cement ratio of 0.4 which is in good agreement with the I^- diffusion measurements of the present study (Fig. 5). As noted earlier, these measurements actually measure the interdiffusion of Cl^- and I^- ions and it is useful to compare D_i with the expected interdiffusion in free water to obtain the diffusibility, Q. The limiting equivalent conductances (λ^0) at 25° C for K^+, Cl^- and I^- (which are proportional to their diffusion coefficients) are 73.5, 76.5 and 76.8 $\mathrm{cm^2\ \Omega^{-1}\ equ^{-1}}$. These are so similar that the interdiffusion coef-

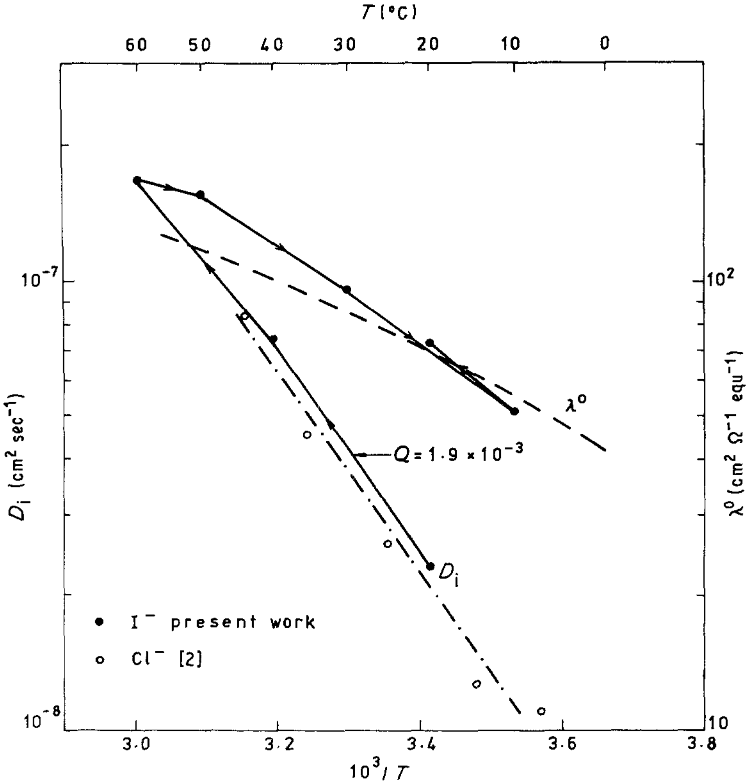

Figure 6 The effect of temperature on the diffusion of I^- ions through a single specimen of water/cement ratio = 0.4. The specimen was taken around the thermal cycle in the direction of the arrows and the diffusibility at 30° C is indicated. The temperature dependence of the limiting conductivity at infinite dilution in free water (λ^0) is also shown.

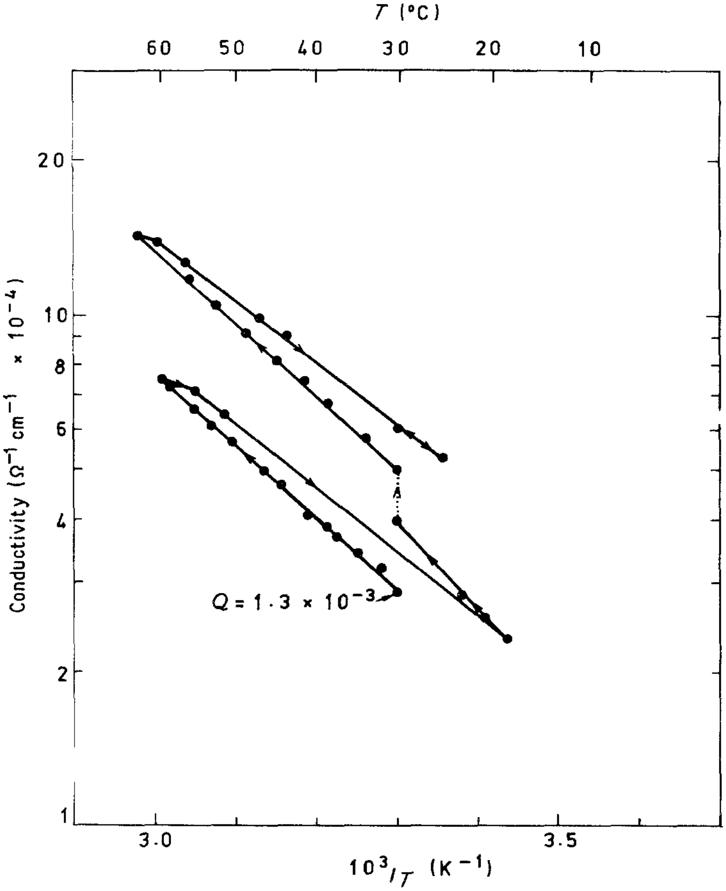

Figure 7 The ionic conductivity of a specimen of water/cement ratio 0.4 saturated with 3 M NaCl measured as a function of temperature around two thermal cycles separated by 1 month. The conductivity of the free electrolyte was 0.22 Ω^{-1} cm^{-1} and the diffusibility at 30° C is indicated.

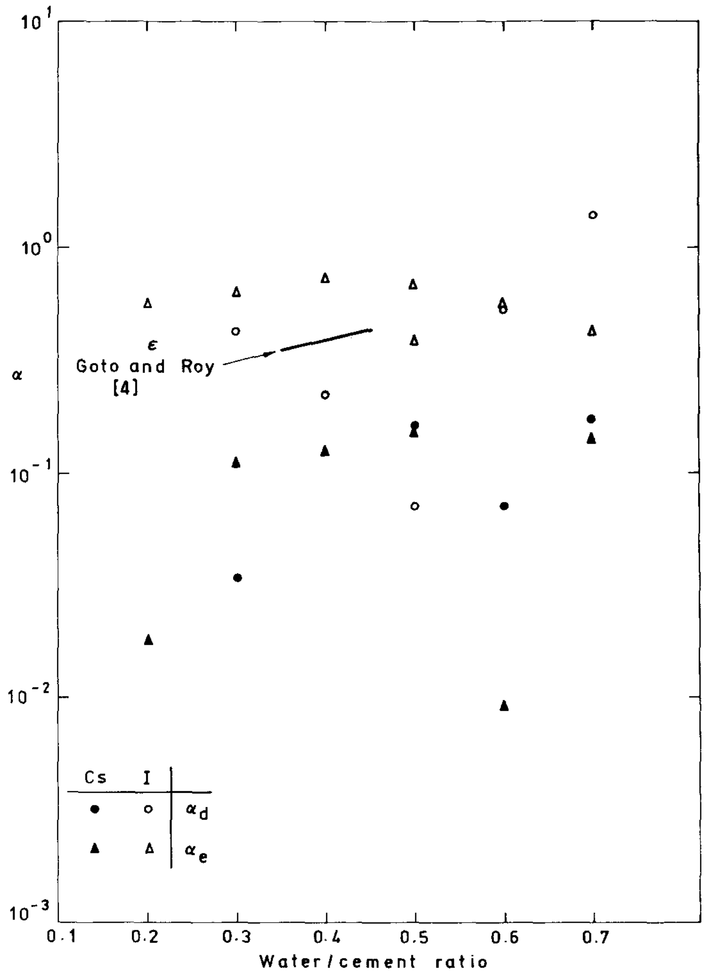

Figure 8 The "capacity factor", α, deduced from the diffusion kinetics (α_d) and from elution after the diffusion experiment (α_e) as a function of water/cement ratio. Published values of porosity (ϵ) measured by mercury intrusion porosimetry are also shown [12].

ficient in free water will be approximately equal to the diffusion coefficient of the electrolytes. This is 2.0×10^{-5} cm^2 sec^{-1} at 25° C ([6], p. 515) from which we can estimate D_f to be 2.2×10^{-5} cm^2 sec^{-1} at 30° C. Thus the diffusibility, Q, for the I$^-$ diffusion data decreases from approximately 0.1, at a water/cement ratio of 0.7, to 10^{-4} at a water/cement ratio of 0.2. The diffusibility at a water/cement ratio of 0.4 (for later comparison with the conductivity measurements) is 2.0×10^{-3}. λ^0 for Cs$^+$ is 77.3 cm^2 Ω^{-1} equ^{-1} (i.e. very similar to the values for the other ions) and its free water diffusion coefficient, even at the lower concentration of 0.1 M, is also estimated to be 2.2×10^{-5} cm^2 sec^{-1} at 30° C. Thus the lower values of D_i for ^{137}Cs$^+$, particularly at the lower water/cement ratios, indicate a different diffusion behaviour for Cs$^+$ and I$^-$ ions within the porous cement structure. This means that the diffusion process cannot be envisaged as being the same diffusion mechanism as in the free liquid simply constrained by the pore structure since the diffusibility should then be the same for all ions.

The experiments on both electrical conductivity and diffusion as functions of temperature demonstrate that the apparent temperature dependence has at least two contributions. One comes from the temperature dependence of the diffusion mechanism and the other from temperature-induced changes in the pore structure. The apparent activation energy for I$^-$ diffusion, derived from the slope of an Arrhenius plot, for the part of the cycle during which the temperature is increasing (Fig. 6) is 0.48 eV per ion (11 kcal mol^{-1}) and is in reasonable agreement with the previously published values. However, on the part of the cycle in which the temperature is decreasing the apparent energy is only 0.2 eV per ion (4.6 kcal mol^{-1}). This is closer to the apparent activation energy of λ^0 (also shown in Fig. 6) for the free aqueous I$^-$ ion at infinite dilution which is 0.14 eV per ion (3.2 kcal mol^{-1}) ([6], p. 465). It can, therefore, be concluded that the previously reported high activation energies are mainly a result of the pore structure becoming more "open" at higher temperatures, despite the probability that at the higher temperatures there would be further hydration and a decrease in the volume fraction of porosity. Measurements of the water permeability of cement pastes [12] also show that there is no simple correlation between porosity and transport properties. They found that samples cured at 60° C had lower porosity, but greater permeability, than those cured at 27° C.

The value of diffusibility, Q, at 30° C and a water/cement ratio of 0.4 deduced from the electrical conductivity experiments is 1.3×10^{-3} (Fig. 7). This is in reasonable agreement with the corresponding value of I^- diffusion (2.0×10^{-3}) considering the typical scatter in Fig. 5 which is mainly the result of sample to sample variability. The apparent activation energies from the conductivity experiments are 0.28 eV per ion, when the temperature is increasing, and 0.24 eV per ion when it is decreasing. The former is considerably lower than the corresponding value obtained from I^- diffusion. The most likely reason for this is that the entire temperature cycle was completed in 10 h in the conductivity experiment, whereas in the diffusion experiments each data point required at least 1 day, thereby providing more time for reactions to take place in the cement.

It is not possible to explain the observed values of diffusibility and the dependence on water/cement ratio in terms of the behaviour found in other porous media. For a wide range of porous rocks it has been found empirically [8] that diffusibility and porosity are related by $Q \simeq \epsilon^2$. On this basis one might expect the diffusibility (at a water/cement ratio of 0.4) to be 0.14 which is 100 times greater than the measured value. Similarly, both theoretical and experimental determinations of δ/τ^2 for the packing of solid spheres are ~ 0.5 [1] and hence Q would be expected to be ~ 0.2 for a medium of porosity ~ 0.4. The much lower values of Q measured in the cement pastes indicate that their pore structures must be much more complex. Since the porosity is quite large it is difficult to envisage that the tortuosity of diffusion paths could be responsible for the small values of Q. It seems more likely that it is the constrictivity, δ, of the pore system which is the crucial factor and that the porosity observed microscopically in cement pastes is best regarded as relatively large caverns which are interconnected by pores of very small diameter. The effect of temperature can be explained by postulating that these pores, which are probably in the hydrated gel structure of the cement, coarsen as the temperature increases. Given the uncertainties introduced by these changes in pore structure in interpreting the effect of temperature on diffusion, it appears that apparent activation energies on cooling may be sufficiently close to the value in free water for the porous medium description of diffusion to be valid for I^-, Cl^- and Na^+ ions. However, the significantly lower diffusibility for Cs^+ diffusion indicates that this interpretation is oversimplistic at the lower/cement ratios and that the fine porosity which interconnects the coarse porosity must be on such a scale that the bulk liquid diffusion process is significantly perturbed. Furthermore, the generally lower values of α for Cs^+ than for I^- (Fig. 8) could result from some parts of the pore structure accessible to I^- not being accessible to Cs^+ ions. However, the reasons for the different behaviour of the different ions are not clear and further experiments of the simultaneous tracer diffusion of Cs^+ and I^- ions would be required to confirm the difference.

5. Conclusions

The diffusion of ions through water-saturated cement pastes is a strong function of the water/cement ratio at fabrication. The relationship is approximately exponential and D_i changes by 10^3 for I^- ions and 10^4 for Cs^+ ions as the water/cement ratio increases from 0.2 to 0.7.

The diffusibility for Cs^+ ions is significantly lower than for I^-, Cl^- and Na^+ ions. (This is the opposite of the behaviour of these ions in water-saturated clays shown in Fig. 5.)

The apparent activation energies for D_i are significantly affected by irreversible thermally induced changes in the pore structure, particularly during the heating part of a thermal cycle. Consequently, the apparent activation energy is not that of the diffusion mechanism.

Measurements of electrical conductivity of specimens saturated with a strong electrolyte give diffusibilities in reasonable agreement with diffusion measurements and are useful for assessing diffusion properties either quickly, or in large specimens.

The model of the pore structure which is in best accord with the diffusion behaviour is one in which relatively large pores are interconnected by much finer ones. Whilst most of the observations can be explained in terms of bulk liquid diffusion constrained by the porous medium, the significantly different behaviour of Cs^+ ions indicates that this explanation is not complete, probably because the fine connecting pores are very small (~ 1 nm).

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