MASS TRANSFER IN WATER-SATURATED CONCRETES

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ABSTRACT

Cements and concretes are often considered as components of barriers for the containment of radioactive waste. The performance of such materials as mainly physical barriers to the transport of dissolved radionuclides depends on the mass transfer characteristics of the material. In particular the diffusion and sorption behaviour of the radionuclides and the water permeability are important. These parameters also influence how the chemistry of the concrete is imposed on the repository. In addition, the transport of gas through concrete controls the way in which gases escape from the repository.

Diffusion and gas transport have been measured in a variety of cementitious materials, covering both structural concretes and cementitious backfills; all possible repository construction materials. Measurements have been made using aqueous iodide, strontium and caesium ions and tritiated water as diffusants. The results show that the diffusion of tritiated water is more rapid than that of other species, whilst the transport of strontium and caesium is hindered by sorption; particularly in materials containing blast furnace slag. The transport of gas in these materials has been found to be very sensitive to the degree of water saturation and is extremely low in fully saturated structural concretes. Cementitious backfills have, nevertheless, been identified that have appreciable gas transport even when almost water saturated.

The consequences of the results for the performance of cementitious barriers are discussed.

INTRODUCTION

In the UK it is intended that a radioactive waste repository for intermediate and low level waste will be established at some depth below ground and will be saturated by groundwater soon after closure. Thus, the transport of radionuclide species will occur by the movement of dissolved material in the aqueous phase. The time-scale for the physical containment of a radionuclide species by a radioactive waste repository is determined by the rate at which the species can traverse the barrier presented by the waste containers (steel) and the structure of the repository (reinforced concrete walls and floors and a cementitious backfill). In the long term, the near-field barriers are primarily concerned with the retention of radionuclides by chemical means; that is, the reduction of the effective solubility of a species by maintaining a high pH environment and strong sorption within the repository [1]. However, during the immediate post closure period, the containment of some relatively soluble and short-lived isotopes, such as strontium and caesium, will benefit from the physical barriers presented by the steel waste containers and the concrete structure of the repository. The long term chemical containment will also be influenced by the rates and nature of the transport of the dissolved species into the concrete components that provide the sorption sites. Hence, the physical properties of the cementitious materials will have an impact on radionuclide containment over all time frames.

In addition, gases will be generated within a radioactive waste repository. An increase in the local gas pressure has the potential to cause unexpected water flows and, ultimately, may affect the integrity of the repository structure. The structure will exhibit some degree of gas permeability and the magnitude of the pressure caused by the build-up of such gases will depend on the relative rates of gas generation and release from the repository. It is essential, therefore, to understand the migration of gases in order to predict these effects. The bulk of the gas produced will be hydrogen, from the anaerobic corrosion of steels, but a contribution from methane produced by the degradation of organic components in the waste may also be significant. The migration of gas within the pore structure of the concrete will be influenced by the presence of water. If sufficient gas-filled pore space is available the gas can migrate by bulk flow, but if water blocks all through-pathways, the migration must proceed via solution and diffusion in the pore water. Hence, the migration mechanism is expected to depend on the degree of water

saturation of the concrete.

    The work reported here is concerned with materials intended for potential use either as

Table 1   Constitution of concretes used in this study (kg m^{-3})

	Cementitious	Water	Aggregate
PFA concrete	400 OPC/PFA=3	190	1815
SRPC concrete	401	185	1850
BFS concrete	414 OPC/BFS=0.25	186	1805
SRPC mortar	500	280	1500
BFS mortar	500 OPC/BFS=0.25	280	1500
BFS grout	1350 OPC/BFS=0.11	540	-
Lime grout	770 OPC/Lime=0.5	690	-

structural concretes or as backfill to fill between or within waste packages. The structural concretes studied were based on sulphate resistant Portland cement (SRPC), a mixture of blast furnace slag and ordinary Portland cement (BFS/OPC) and a mixture of pulverised fuel ash and OPC (PFA/OPC). Several potential backfill grouts were also studied. These were based on the SRPC and BFS/OPC concretes, but containing only a fine aggregate (referred to as mortar), and on mixtures of 2:1 lime and OPC (referred to as lime grout) and 9:1 BFS and OPC (referred to as 9:1 BFS/OPC grout), both containing no aggregate [2].The constitution of the concretes is summarised in Table 1.

    This paper briefly describes the experimental techniques applied to the measurement of the diffusion parameters for various dissolved species, the water permeability and the transport of gases, in particular helium and argon, in the experimental materials. Some of the implications of the magnitude of these parameters for the behaviour of a radioactive waste repository are discussed.

EXPERIMENTAL METHODS

Diffusion of dissolved species

    The diffusion parameters were measured by monitoring the transport of diffusant through a membrane of water-saturated concrete. The concentration gradient eventually becomes constant as the system reaches a steady state in this method. The diffusion parameters are determined from the flux of the diffusant in the steady state and the time to reach the steady state[2,4]. The diffusants employed were iodide, caesium and strontium ions and tritiated water (HTO). The diffusion of a dissolved species under a concentration gradient is governed by Fick's first and second laws of diffusion [3]. Applying these laws to the experiments, the data were analysed to give an intrinsic diffusion coefficient, D_i, and a capacity factor, α (related to the degree of sorption) as follows [2-4];

$$\langle J \rangle = -D_i \frac{dc}{dx} \qquad \text{.....(1)}$$

$$\alpha = \varepsilon + \rho K_D \qquad \text{.....(2)}$$

where $\langle J \rangle$ is the average flux per unit area of the porous medium, c the diffusant concentration in the aqueous phase, x the thickness of the membrane, ε the fractional porosity, ρ the density of the porous medium and K_D the gravimetric distribution coefficient for the sorption process.

The through diffusion technique does not produce results in an acceptable elapsed time for species with ratios of D_i/α less than about 2×10^{-12} m^{2}s^{-1} [2,4]. The diffusion of such species was investigated using a penetration profiling method [5,6]. A single face of a cylindrical specimen of each of the experimental materials was exposed to radiotracer solutions for periods of six, twelve and eighteen months and the concentration profiles reconstructed by sectioning the specimens parallel to the exposed face and analysing the resulting slices of material. The depth profiles were analysed using Fick's second law, for diffusion under a varying concentration gradient. The profiles were fitted to an equation of the following form [3];

$$c = c_0 \, \text{erfc} \frac{x}{\sqrt{4Dt}} \qquad \text{.....(3)}$$

where D is an effective diffusion coefficient, equal to D_i/α, and c_0 is the concentration of the diffusant at the surface of the specimen. The parameter α in this method is given by c_0 divided by the concentration of diffusant in the reservoir.

Gas transport

The parameters describing gas transport were also measured in a membrane configuration by monitoring the decay of the pressure difference between two compartments separated by a membrane of concrete. Assuming the validity of Darcy's equation the pressure decay can be analysed to give an effective permeability coefficient for the transport of gas.

The apparatus used for the measurement of gas permeability is illustrated schematically in Figure 1. The concrete specimen was sealed into a perspex holder using a cold-setting urethane rubber. Control experiments have shown that this material provides a gas-tight seal.

The permeabilities of the cementitious materials to various gases were measured at different degrees of saturation by water using a pressure gradient of 10 MPa m^{-1}. The degree of water saturation in the materials was controlled by the relative humidity of the gas in the apparatus. The relative humidity was established by the addition of small quantities of solutions of known vapour pressure to the gas reservoirs. In these experiments, three levels of saturation were studied; zero (dry), 70% saturated (utilising an NaCl solution) and fully water saturated.

Water permeability

The water permeability experiments monitored the flow of water through specimens of the materials under a pressure gradient of approximately 4 MPa m^{-1}, recording the measured change in the volume of water in a capillary tube [2]. The flow rates were recorded when the flow of water into and out of the specimens had equalised. The resulting volumetric flow rate was converted to a permeabilty coefficient using the D'Arcy equation for the flow of an incompressible fluid.

RESULTS

Diffusion of dissolved species

An example of typical results from a through diffusion experiment is presented in Figure 2. The intrinsic diffusion coefficient is obtained from the linear region of the graph where the concentration gradient in the concrete is constant. The capacity factor is obtained from the
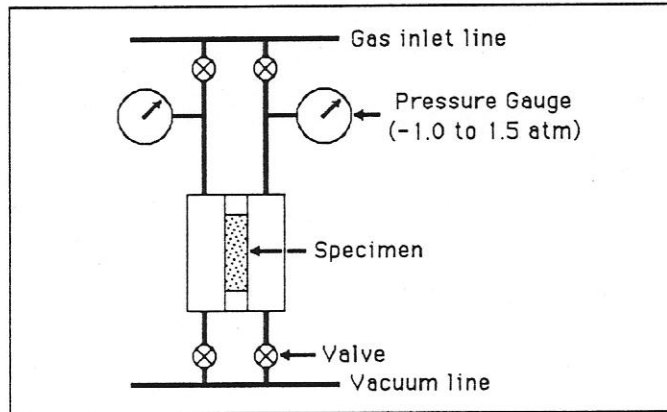
Figure 1   Schematic diagram of the apparatus used for measurement of gas permeability.
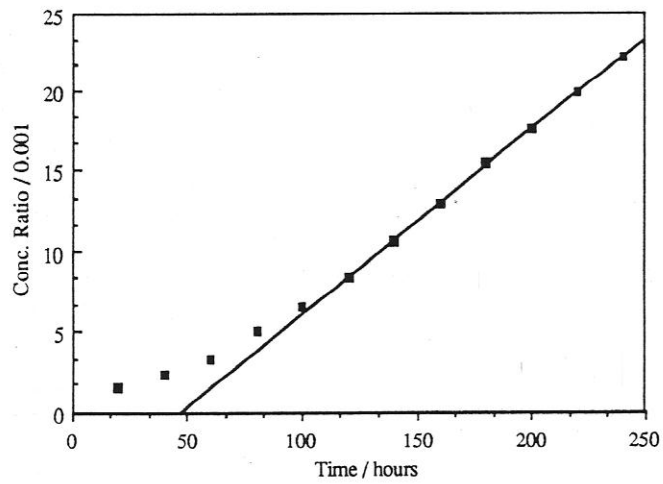

Figure 2   Typical experimental results from a through diffusion experiment. In this example the diffusant is iodide and the concrete is an SRPC mortar. The concentration ratio refers to the two sides of the membrane.

intercept on the time axis.

The parameters for strontium and caesium were measured by penetration profiling in the SRPC- and BFS/OPC-based concretes and mortars (six month data is quoted) and by through diffusion in the lime grout. The measured values are summarised in the Table 2.

No results were obtained for iodide diffusion in the BFS/OPC-concrete in an elapsed time of at least a year. To be consistent with this observation, the value of the ratio D_i/α must be less than about 2×10^{-12} m^{2}s^{-1}. The sample to sample variability in the measurements was typically less than a factor of two.

Gas transport

Figure 3 shows typical results from the gas transport measurements [7,8]. The variation in pressure in the two reservoirs of the gas permeability apparatus is presented as a function of time during an experiment to measure argon flow through the lime grout in the "100% relative humidity" condition. The timescale for this material is much shorter than that for the 9:1 BFS/OPC grout and the PFA/OPC-concrete, where several weeks was required to reach equilibrium. The measured permeability coefficient for the results illustrated is 6.3×10^{-17} m^2.

Table 3 gives the measured gas permeability coefficients for the PFA/OPC structural concrete, the 9:1 BFS/OPC grout and the lime grout at an average pressure of 100 kPa with the three different degrees of water saturation. Also given in Table 3 are the percentage changes in weight of the samples in going from their curing conditions (immersed in water) to the test conditions. For the dry test conditions the large negative wieght change is proportional to the porosity of the concrete. All permeability coefficients are expressed as $k / $m^2.

Water permeability

The water permeabilities of the SRPC-, BFS/OPC- and PFA/OPC-based materials were all extremely low. The observed water flow-rates were exceeded by the rate of water absorption caused by continuing hydration during the period of the experiments; approximately six months. In the case of the SRPC fine aggregate concrete a single measurement was made, indicating a permeability coefficient of about 10^{-20} m^2. The lime grout material was designed to give a high permeability coefficient and the measured values of 4.1 and 3.7×10^{-16} m^2 confirmed that this had been achieved.

DISCUSSION

The experimental data all indicate that the mass transport properties of a cementitious material are very dependent on its composition. In particular, the denser structural materials have permeabilities and diffusion coefficients lower by orders of magnitude than does the lime grout. The second backfilling grout design, the 9:1 BFS/OPC grout, has properties which are intermediate between those of the lime grout and the PFA/OPC structural concrete.

The hydrostatic water pressure difference across a repository is expected to be very low and, combined with the very low permeabilities exhibited by the possible structural concretes, this will lead to essentially zero water flow rates through the structural materials. The flow of water on the repository scale will thus be determined by the distribution of relatively permeable defects, such as cracks and joints. Under these conditions the principal mechanism of radionuclide transport through structural concretes will be by the diffusion of dissolved species. The typical time required for a particular species to traverse an intact barrier can be represented by the intercept time in the through diffusion configuration (Figure 2). This quantity is given by [3];

$$t = 0.167 \, l^2 \, \alpha / D_i \qquad\qquad (4)$$

where t is the breakthrough time and l is the barrier width. For a 300 mm barrier, equation 4 gives times of 1.5 years for the lime grout and over 1000 years for the SRPC- and BFS/OPC-based structural concretes using the data for caesium diffusion. This value is indicative of the relative properties of the materials and does not represent a predicted

Table 2   Summary of experimental parameters for diffusion through concretes.
(All intrinsic diffusion coefficients are given as $D_i/10^{-12}$ m^2s^{-1}.)

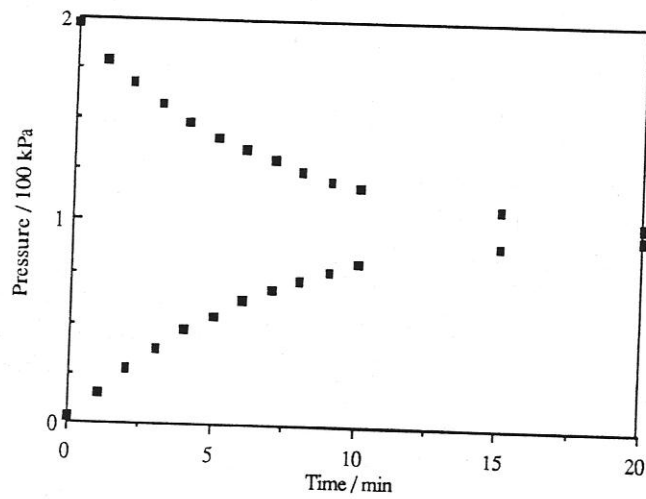|	Iodide		HTO		Strontium		Caesium	
	D_i	α	D_i	α	D_i	α	D_i	α
SRPC-mortar	9.6	0.2	12.0	0.16	0.6	0.67	3.52	4.4
SRPC-conc.	2.2	0.12	3.3	0.16	0.41	0.63	1.86	5.3
BFS/OPC-mort.	0.02	0.2	0.56	0.16	0.004	0.02	0.07	0.56
BFS/OPC-conc.	–	–	0.77	0.16	0.032	0.14	0.13	0.44
Lime grout	110	0.09	263	0.28	39	0.32	184	0.18

Figure 3   Pressure relaxation curves for the transport of Ar gas through a specimen of the lime grout equilibrated at 100% relative humidity. The two curves are for the two sides of the membrane, initially at different pressures.

Table 3   Apparent gas permeabilities (m^2) for concretes in different humidity conditions

	Dried material (rh.=0)					
	-wt.	H$_2$	He	CH$_4$	Ar	CO$_2$
PFA/OPC-conc.	6.0	4×10^{-17}	7×10^{-17}	3×10^{-17}	3×10^{-17}	2×10^{-17}
9:1 BFS/OPC	23.5	-	2×10^{-16}	-	3×10^{-16}	-
Lime grout	45.5	-	2×10^{-14}	-	10^{-14}	-

	Relative Humidity = 75%					
	-wt.	H$_2$	He	CH$_4$	Ar	CO$_2$
PFA/OPC-conc.	0.3	4×10^{-19}	4×10^{-19}	2×10^{-19}	1×10^{-19}	6×10^{-20}
9:1 BFS/OPC	0.12	-	-	-	3×10^{-18}	-
Lime grout	30.4	-	-	-	-	-

	Relative Humidity = 100%					
	-wt.	H$_2$	He	CH$_4$	Ar	CO$_2$
PFA/OPC-conc.	0.06	-	6×10^{-20}	-	10^{-21}	-
9:1 BFS/OPC	-0.09	-	3×10^{-19}	-	10^{-21}	-
Lime grout	20.2	-	10^{-16}	-	5×10^{-17}	-

containment time. The sorption may be enhanced at lower concentration levels than those used in the experiments, due to a non-linear sorption isotherm. This has been observed for caesium in batch sorption experiments [2] and is shown by the relatively large capacity factor for caesium measured in the penetration profile experiments in the SRPC-based structural materials. The caesium concentration in the penetration profile experiments was about 10^{-9} M, compared to 10^{-4} M in the through diffusion measurements. Conversely, sorption is likely to be considerably weakened in conditions of high ambient ionic strength.

The lime grout has an extremely high fractional porosity, of the order of 60% [8], and hence has a large surface area available for sorption of species from solution. In contrast, the fractional porosity of the PFA/OPC-concrete is only about 10% [8]. The high porosity of the grout should ensure that the water within a repository will remain conditioned to a high pH for a long period. The high pH is mainly responsible for the long term chemical containment of radionuclides, ensuring that the solubility of the radionuclide species is low.

It is expected that a waste repository in the UK will be saturated by water relatively rapidly after closure. Hence, the behaviour of gases within a water-saturated material is of importance. If the transport of gas is too slow pressurisation could cause mechanical damage and thereby provide rapid transport pathways for water flow driven by the gas. The data given above show that the gas permeabilities decrease by factors of several hundred when concretes go from the dry to a wet condition. For the PFA/OPC-concrete, the permeability in the "100% relative humidity" case is of the order of 10^{-21} m^2 and it is likely that gas transport is proceeding by solution and diffusion in the pore-water. In contrast, the lime grout retains substantial permeability even at "100% relative humidity" and should allow gas pressure to be relieved relatively easily and uniformly. The weight loss data show that the lime grout conditioned at "100% relative humidity" contains less water than prior to conditioning. Work is currently in progress to establish the implications of this effect under repository conditions.

CONCLUSIONS

The diffusion parameters and water and gas permeabilities under water-saturated conditions have been measured for a variety of potential radioactive waste repository construction materials based on hydraulic cements. It is apparent that all properties are strongly dependent on the composition of the materials. The diffusion coefficients for dissolved species vary over three orders of magnitude between structural concretes and high-porosity backfill grout. The diffusion of radionuclides species such as strontium and caesium is slow compared to the other species studied due to enhanced sorption. The use of BFS as a cement modifier gives material with the lowest diffusion coefficients.

Gas permeability is shown to be very sensitive to the degree of water saturation of the material. The permeability coefficients for saturated materials are about three orders of magnitude lower for fully saturated materials than for dried. The transport of gas in the structural concretes appears to proceed by solution-diffusion. The dissipation of gas generated within a repository depends on the permeability of the construction material. High permeability materials, such as the lime grout studied here, may be required to prevent the formation of rapid flow pathways through cracks in the structure caused by the gas pressure.

ACKNOWLEDGEMENTS

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