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Diffusion Measurements in Cement Paste by Water Replacement Using Propan-2-ol

by R.F. Feldman

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RÉSUMÉ

On a mesuré les changements de longueur et de poids de pâtes de ciment Portland préparées dans des rapports eau-ciment de 0,3 à 0,1 et immergées dans du propanol-2 et du méthanol. On a déterminé la diffusivité et le taux de diffusion, qui ont été comparés aux paramètres de structure des pores mesurés par intrusion de mercure. Les mesures de longueur indiquent que le méthanol réagit avec le ciment hydraté et ne convient donc pas pour mesurer la diffusivité. Par contre, le propanol-2 est relativement inerte et produit des valeurs de diffusivité similaires à celles obtenues pour les ions chlorure dans des matériaux similaires.

DIFFUSION MEASUREMENTS IN CEMENT PASTE BY WATER REPLACEMENT
USING PROPAN-2-OL

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ABSTRACT

Length and weight changes were measured when saturated portland cement pastes prepared at water-cement ratios of 0.3 to 1.0 were immersed in both propan-2-ol and methanol. Diffusivities and diffusion rates were determined, and were correlated with pore structure parameters, measured by mercury intrusion. Length measurements indicate that methanol interacts with the hydrated cement and is thereby unsuitable for measuring diffusivities. Propan-2-ol on the other hand is relatively inert and produces diffusivity values similar to those obtained for chloride ions in similar materials.

Most physical and engineering properties including durability of hardened cement pastes and concretes are related to their microstructure (1-5). The physical property most directly related to durability and microstructure is permeability. Permeation may occur in the liquid state, which may involve various ions, or in the gaseous state. In many instances the transport mechanism involves diffusion, eg. penetration of chloride ions, and is related to pore structure parameters, as is permeability (6).

Specifications for concrete have mostly been based on 28-day strengths but it is clear where durable high-quality concrete is the major concern, permeability or diffusivity becomes very important.

Several techniques for measuring permeability or diffusivity have been used (6). However, some of these techniques may involve a particular form of drying that may unduly damage or alter the structure of the pores, even to the point of causing cracking (4). In addition, the specific technique may not be relevant to the particular form of material attack that the concrete may be subjected to.

Parrott (7) showed that several organic solvents could replace a large portion of the water in cement paste and suggested that the process of exchange of water from the saturated specimen was a simple physical process of counter diffusion. He used methanol to determine a value $\epsilon_{1/2}$

the time taken to exchange methanol with half the water present in the paste, and used this parameter as a measure of the diffusivity of the specimen.

Other workers (8) measured the replacement of water by methanol from concrete and mortar. These authors considered their results encouraging with regard to the development of a test which can indicate the potential durability of a specimen. However, several workers (9-11) have suggested that methanol reacts with both Ca(OH)_2 and CSH in hydrated paste to form calcium methoxide or a methylated complex. Thus measurements using methanol may not yield realistic values. Propan-2-ol does not react with hydrated paste and thus the use of propan-2-ol as a solvent for drying should be more appropriate. This paper investigates the use of propan-2-ol as a solvent to measure the intrinsic diffusion coefficients of cement pastes by counter-diffusion.

Experimental

Materials

Normal Type I portland cement was used. Pastes were prepared at water/cement ratios of 0.3, 0.40, 0.5, 0.60, 0.80 and 1.0. All samples were cured in saturated Ca(OH)_2 solution for more than 10 years except the sample prepared at a water-cement ratio of 0.5, which was cured for only 1.4 years.

Reagent grade anhydrous methanol and propan-2-ol were used in this work.

Properties

Pore size distribution (Hg porosimetry to a pressure of 414 MPa) was determined on all paste preparations. Specimens were dried by soaking pieces of paste 1.14 mm thick in anhydrous propan-2-ol for 10 days. Samples were then maintained in vacuum for approximately 17 h and then heated for 24 h at 38°C while being maintained in vacuum.

Evaporable and non-evaporable water contents were measured by determining the loss in weight between the saturated condition and 100°C, and between 100°C and 1000°C using a Thermogravimetric Module of the DuPont 1090 system.

Length change was measured using a modified Tuckerman optical strain gauge. Specimens of each paste were sliced from their discs (which had been cut from cylinders by a diamond saw) and were rectangular, approximately 30 x 10 mm and usually 1.14 mm thick. The effect of thickness on length change was also investigated by using additional specimens 2.33 and 3.45 mm thick.

Diffusion Measurements

Slices of paste cut from saturated cylinders 30 mm in diameter were used to measure the rate of diffusion of propan-2-ol (or methanol) into the pores. The slices were in the form of discs generally 1.14 mm thick. The discs were wiped free of excess water just before weighing and were then immersed in anhydrous alcohol. The volume of the alcohol in the containment vessel (a dessiccator) was large (1.5 litres) compared to the size of the specimen (25 g). Specimen weight was recorded after surface drying and weighing every few minutes and the alcohol was renewed after 1, 2, 4, 8 and 24 h, and then every 24 h and less frequently after 7 days. Some measurements were taken after 65 days of immersion. Similar changes in the intake of alcohol were made during measurement of length change.

Results

(i) Length Change

The rates of change of length of water-saturated paste specimens (when immersed in propan-2-ol) are presented in Figure 1. These specimens were prepared at W/C ratio of 0.8, and were 1.14, 2.33 and 3.45 mm thick. The length response is a shrinkage and it may be observed that the rate of shrinkage is greatest for the thinnest sample at the earliest periods probably because it is subjected to lesser restraining influence than the thicker specimens. The thicker specimens after 500 h of immersion show less length change than the sample of 1.14 mm thickness after only 60 h immersion.

FIG. 1
Length change versus time on immersion of water saturated paste specimens in propan-2-ol.

The 1.14 mm thick specimen was removed from the propan-1-ol after 140 h immersion and placed in methanol. The length change response was a relatively rapid expansion, approximately 0.11 per cent in 10 h, compared to a shrinkage of 0.057 per cent in the same time, when the water saturated sample was immersed in propan-2-ol. After 360 h of immersion the sample had not re-attained the length when in the water-saturated state, and had expanded to a total of approximately 0.14 per cent.

Samples prepared at water-cement ratios of 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0 and immersed in propan-1-ol, showed shrinkages of 0.21, 0.137, 0.173, 0.12, 0.14 and 0.16 per cent respectively when steady state was attained after periods of immersion in propan-2-ol varying from 6 to 10 days.

Length change as a function of time^{1/2} of the water-saturated paste prepared at water-cement ratio of 0.8 (1.14 mm thick) on immersion in methanol is presented in Figure 2. Length change is plotted as a function of the square root of immersion time, and the results of propan-2-ol immersion are also included for comparison. The response to methanol immersion is an expansion which exceeds 0.10% after 32.5 h and appears to be continuing while the response to propan-2-ol immersion is a shrinkage which appears to terminate after 100 h.

(ii) Weight change on immersion in methanol or propan-2-ol.

The water-saturated specimen of paste loses weight when immersed in water-free methanol or propan-2-ol. This is due to the displacement of the denser water by the alcohol. A knowledge of the densities of the fluids allows a calculation of the quantity of alcohol (W_t) diffusing through the pores into the specimen. The result for the 1.14 mm thick paste, prepared at a water-cement ratio of 0.8 is presented in Figure 3. These are plotted as W_t/W_∞ versus square root of time, where W_∞ is the value attained at approximately equilibrium conditions, after 240 h. The curves are approximately linear up to 2.25 h for methanol and 6.25 h for propan-2-ol, and indicated that the initial processes of water replacement by the alcohols are diffusion controlled.

FIG. 2
Length change versus $(\text{time})^{1/2}$ on immersion of water saturated paste specimens in methanol and propan-2-ol respectively.

Fig. 3
Relative rate of diffusion (W_t/W_∞) of propan-2-ol and methanol into water-saturated paste.

A comparison of Figures 2 and 3 shows that when 90 per cent of the methanol has entered the specimen, only 0.03 per cent expansion or less than 30 per cent of the ultimate expansion has taken place. On the other hand at the same level of entry of propan-2-ol a shrinkage of 0.095 per cent or 68 per cent of the ultimate shrinkage has taken place.

(iii) Rate of diffusion of propan-2-ol on immersion as a function of water-cement ratio.

Water saturated paste specimens, 1.14 mm thick were used at water-cement ratios of 0.30, 0.4, 0.5, 0.6, 0.8 and 1.0 to measure rates of diffusion of propan-2-ol into the specimens. Results in units of weight of propan-2-ol entering the pores per unit volume of sample as a function of square root time are presented in Figure 4. Results are given for the

FIG. 4
Diffusion of propan-2-ol (g/m^3) into water-saturated pastes versus $(\text{time})^{\frac{1}{2}}$ as a function of water-cement ratio.

FIG. 5
Rate of diffusion of propan-2-ol into water-saturated pastes as a function of water-cement ratio.

different water-cement ratios at a constant thickness, and are linear up to between 65 and 85 per cent of the total diffusion. The slopes of the linear portions were established within less than one hour. The results for the sample prepared at water-cement ratio of 0.5 are not included in this figure since they partially cross over the other curves as can be inferred from Figure 5. In Figure 5, the rate of diffusion is plotted in units of grams of alcohol per cubic metre of sample per hour², versus water-cement ratio. This value decreases with water-cement ratio except for the value of the specimen prepared at water-cement ratio of 0.4 which is greater than the value for the specimen prepared at water-cement ratio of 0.5 and which in turn is about equal to the value of 0.3. However at each water-cement ratio, there is some spread in the results. These features in the results are probably due to difficulty in compaction during sample preparation at water-cement ratios of 0.4 and 0.3. Similar results were observed in plots of diffusivity (m^2/s) and $\epsilon\tau_{1/2}$ (h) versus water-cement ratio. $\epsilon\tau_{1/2}$ is the parameter used by some other workers and represents the time taken for half of the total methanol to diffuse into the specimen. Values of diffusivity were calculated from a form of Fick's Law: (6)

$$W_t/W_\infty = 1.127 \sqrt{\frac{D t}{L^2}}$$

where D is the diffusivity, m^2/s , ' t ' the time, s and L (m) is half the thickness of the specimen. Values of the various diffusion parameters, correlation coefficients for the W_t/W_∞ vs $\sqrt{t}$ plots, and values for the evaporable, non-evaporable water content and porosity at each water-cement ratio, are presented in Table I.

iv) Relationship between length and weight changes due to immersion in alcohol.

The plot of the length change versus weight change due to immersion of the paste prepared at water/cement ratio of 0.8 in the alcohols is presented in Figure 6. The fact that methanol causes an expansion and propan-2-ol, a shrinkage is immediately clear. However, in addition the initial length per unit weight change response to methanol immersion is much lower than for propan-2-ol; up to 6 per cent weight change, the length

FIG. 6
Length versus weight changes due to immersion of water-saturated paste (water/cement = 0.8) in alcohols.

change for propan-2-ol is twice as great and at 8 percent it is four times. However, in the final 0.15 per cent weight change in methanol immersion there is an expansion of 0.04 per cent, a large increase in slope and resulting in a total expansion of 0.10 per cent. This compares to a total shrinkage of 0.14 per cent for propan-2-ol immersion. The final length change to weight change ratio $(\Delta l/l)/(\Delta W/W)$ is unexpectedly high for methanol, 0.27, eliminating possibilities that adsorptive forces can explain the expansion due to methanol immersion (12).

The effect of water-cement ratio on the length-weight change relationship due to propan-2-ol immersion is presented in Figure 7. For specimens prepared at water-cement ratios of 1.0 and 0.8, when 80 per cent of the weight change has occurred only 25 per cent of the length change was recorded. At water-cement ratio of 0.3, however 88 per cent of the length change has occurred at the above level of weight change. Intermediate trends were observed for water-cement ratios between 0.8 and 0.3.

FIG. 7
Length versus weight changes due to immersion in propan-2-ol of water-saturated pastes prepared at different water-cement ratios.

The model of a coarse pore structure at higher water-cement ratios having access to a finer pore structure adequately explains these results. The coarse pore structure is eliminated at low water-cement ratios and most of the length change occurs when the propan-2-ol directly enters the finer pores. Most of the surface area of the hydrated paste is associated with the finer pores. High surface area materials are associated with a significant amount of surface energy. When a foreign material is adsorbed on the surface, an interaction occurs, the extent depending on the nature of the adsorbent, (the hydrated cement) and adsorbate (the alcohol and the water). Normally the interaction results in a decrease in surface energy and an expansion; however in this case water is being removed from the surface and replaced by propan-2-ol which interacts to a lesser degree than water. The net result of the replacement of several molecular layers of water close to the surface of the hydrated cement by molecular layers of propan-2-ol should thus be a shrinkage.

FIG. 8
Pore size distribution of pastes prepared at different water-cement ratios and dried by propan-2-ol treatment.

(v) Pore size distribution.

The pore size distributions for the six specimens prepared at the different water-cement ratios are presented in Figure 8. At higher pressures, ca. 414 MPa the total volume of mercury intruded decreases with water-cement ratio. However the volume of mercury intruded in pores $> 0.088 \mu\text{m}$ diameter ($880 \text{ \AA}$), is relatively low for all water-cement ratios except 0.8 and 1.0. Both durability and permeability have been shown to be more strongly related to pores of this size range than the total porosity (1, 3, 6). The values are tabulated in Table I. The plot in Figure 9 for diffusivity versus porosity $> 880 \text{ \AA}$ illustrates the similarity between specimens prepared at water-cement ratios of 0.3, 0.4, 0.5 and 0.6. The spread between points within a specimen type prepared at one water-cement ratio is greater than the difference between values for specimens prepared

FIG. 9
Diffusivity of propan-2-ol in pastes as a function of porosity $> 880 \text{ \AA}$ diameter.

at several water-cement ratios. There may be several reasons for this, one being that there is a large variation in pore structure within one water-cement ratio formed during preparation, and that the pore structure measured does not necessarily represent the average value for the specific sample for which the diffusivity was measured. Another reason is that the determination of W_{∞} , which takes longer periods of time to measure, might cause error in the calculation of the diffusivity due to the inclusion or exclusion of dead-end or almost isolated pores. A plot of diffusion rate (W_t per unit volume of sample per $h^{\frac{1}{2}}$ determined at constant sample thickness) versus porosity is presented in Figure 10. This diffusion parameter, diffusion rate, is now free of the influence of W_{∞} . As can be seen in Figure 5 this parameter decreases continuously with water-cement ratio if the value at 0.5 is not considered. Although there is an increased difference between results for samples prepared at water-cement ratios of 0.6 to 0.3 on the one hand and 0.8 to 1.0 on the other in the plot in Figure 10, there is no clear differentiation between the lower water-cement ratio preparations with regard to porosity.

FIG. 10
Diffusion rate of propan-2-ol in pastes as
a function of porosity > 800 Å diameter.

Discussion

Previous workers (9-11) have discussed the possibility that methanol reacts with components of hydrated portland cement. Length change measurements carried out in this work confirm these findings. Displacement of water adsorbed on porous silica glass by methanol produces little or no length change, showing that the interaction of both water and methanol with porous silica glass is similar. The total length change measured when the glass dried to zero per cent relative humidity is saturated with water is 0.30 per cent (13). Thus in comparison the expansion of approximately 0.10 per cent observed when water-saturated hydrated portland cement paste is immersed in methanol is relatively large. Other evidence including a detection of a considerable decline of Young's modulus following immersion in methanol, a large shrinkage on desorption of methanol immersed specimens (14) and increases in surface area due to various treatments with methanol (15) suggest that methanol penetrates the layered structure of the calcium silicates and increases the separation of the sheets.

The values for the diffusion coefficient tabulated in Table I vary between approximately 5×10^{-12} to 2×10^{-11} m²/s. This is in the same range as values obtained by other workers for ions such as Na⁺, Cl⁻, I⁻, Cs diffusing through water-saturated ordinary portland cement (6). The coefficients were determined by both transient and steady state methods. Page et al (16) reported a value of 4.5×10^{-12} m²/s for the effective diffusivity of chloride ions through ordinary portland cement paste prepared at water-cement ratio of 0.5. This is remarkably similar to the value obtained here for the diffusion of propan-2-ol in paste prepared at the same water-cement ratio.

This technique shows promise as a rapid method of testing for the quality of concrete. It appears possible to evaluate thin concrete sections in such areas as cover over reinforcing steel. This method, requiring only simple equipment, is being developed for investigations of mortars and concrete.

Conclusions

1. Methanol interacts with hydrated portland cement by penetration of the layered silicate structure. It is thus unsuitable for use when diffusion coefficients are to be measured.
2. Counter-diffusion of propan-2-ol into water-saturated hydrated portland cement yields diffusion coefficients similar to those obtained for chloride ion diffusion into similar materials.
3. Propan-2-ol is an acceptable fluid for diffusion coefficient measurements of hydrated portland cement since no interactions seem to occur.
4. Propan-2-ol can be used to assess the quality and durability of concrete.

TABLE I. Diffusivity and Related Parameters for Pastes of Different Water-Cement Ratios

W/C	$D \times 10^2$ m ² /s	Corr. Coeff.	$\epsilon_{\frac{1}{2}}$ h	Diffusion Rate, g/m h	Evap. Water, % d-dry	Non-Evap. Water, % Ignited	Porosity, Vol % > 0.088 μ m
0.3	0.753	0.9847	2.62	937.2	13.0	16.2	1.16
0.3	0.535	0.9820	3.24	862.4	13.0	16.2	
0.3	0.895	0.9826	2.25	1179.7	13.0	16.2	
0.4	1.025	0.9902	1.90	1307.7	19.4	18.7	0.24
0.4	0.880	0.9600	2.07	1494.6	19.4	18.7	
0.4	0.672	0.9300	1.77	1257.0	19.4	18.7	
0.5	0.467	0.9830	3.57	---	26.6	21.57	0.74
0.5	0.366	0.9704	4.00	883.6	26.6	21.57	
0.5	0.440	0.9965	4.00	948.9	26.6	21.57	
0.6	0.872	0.9986	2.25	1597.1	28.0	24.32	0.93
0.8	1.059	0.9671	---	---	36.0	22.5	12.67
0.8	1.382	0.9964	1.30	2323.0	36.0	22.5	
1.0	2.289	0.9991	0.90	2910.0	42.2	27.7	21.29

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