Water diffusion and microstructure of hydrated cement pastes

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Water migration in Portland cement paste follows closely the theoretical diffusion equation. The diffusion coefficient decreases with increasing curing time of the paste specimen at first, but after 14 days the value becomes nearly constant. The temperature dependence of the diffusion coefficient indicates that diffusion involves an activation process, but the characteristic energy depends on the temperature range. The behaviour of aluminous cement is similar, but the value of the diffusion coefficient and its temperature dependence are about double those for Portland cement. Stereoscan electron micrographs of aluminous cement show a temperature sensitive microstructure and this probably causes the change in the diffusion activation energy. No comparable clear change can be seen in Portland cement structure.

INTRODUCTION

The water content of concrete influences a range of physical properties, for example, the crushing strength, creep, shrinkage and thermal conductivity. Hence, the study of water migration in concrete on drying is important, and this is particularly so in relation to prestressed concrete pressure vessels for nuclear reactors. These structures have sections up to 6 m thick and water movements may be expected to continue over many years. Furthermore a thermal gradient exists in the inner layer of the vessels and this will accentuate the process of water migration.

The first systematic work on the drying mechanism of solids was reported by Sherwood [1] who distinguished three regions of behaviour. A very wet solid evaporates at a constant rate substantially similar to that from a free water surface under identical drying conditions, then the drying rate falls steadily as an increasing proportion of the surface dries out. During a second falling rate region, water loss is controlled by the rate of diffusion of water vapour inside the solid. In this case the solid surface is dry and the rate of evaporation is independent of the movement of the adjacent air so long as the partial pressure of water in air is less than that at the concrete surface. The drying of concrete is mostly controlled in this way [2, 3], but the surface drying mechanisms can also be significant [3].

To examine the range of diffusion controlled drying and to attempt to relate the phenomena to the microstructure of the concrete we have made measurements of the diffusion rates of water in hydrated ordinary Portland cement (OPC) at different temperatures after varying curing times. Some measurements were also made with concrete specimens made with crushed limestone and with sulphacrete cement pastes as well as with OPC and pulverised fuel ash (p.f. ash) mixes. Sulphacrete or p.f. ash as a partial replacement of OPC, are used in the construction of concrete pressure vessels in order to reduce the temperature peak caused by the rapid hydration of OPC. In addition to the two types of calcium silicate cements, specimens for diffusion experiments were also made from calcium aluminate cement (aluminous cement).
EXPERIMENTAL

Water diffusion rates were measured by following the weight loss of a spherical sample in a stream of dry nitrogen using a thermobalance. Spherical form was chosen for geometric symmetry and small samples were used, 15 to 20 mm in diameter. This made it possible to take the sample to equilibrium dryness in the comparatively short time of ten days.

Samples were cast in borosilicate glass bulbs with small necks, and were compacted by vibrating in a laboratory shaker for two minutes to remove air bubbles. After one day the thin glass bulb was broken off, the casting runner trimmed away and the sample stored in a moist CO₂-free atmosphere over lime water.

This technique ensured the uniformity of samples, but vibrating in the closed vessel limited the choice of the amount of water which could be used in the mixes with segregation. In the neat cement paste the water to cement ratio was 0.28 (w/cm), in the OPC/ash mix it was 0.4, and in the concrete specimens the ratio was 0.5. The small size of concrete samples meant that the amount and size of the aggregate had to be reduced in proportion. A sample of limestone aggregate was crushed and a sample reconstructed from different size fractions according to a formula used by Imlach [4].

For the diffusion experiments the Stanton thermobalance was modified by incorporating a Eurotherm temperature controller and this permitted a temperature control within ± 0.5 °K. The furnace was purged with dry nitrogen and it was preheated to the required temperature. Immediately before the run the sample was weighed and its diameter measured with a micrometer. The sample was supported on three platinum pins welded to a platinum plate. This arrangement gave a free access of the purging gas.

RESULTS

**Diffusion Equations for a Sphere**

The spherical sample of cement paste starts with a uniformly saturated water concentration and in a flowing stream of dry nitrogen it loses water. The rate of loss is controlled either by diffusion of water inside the matrix, or by the rate of transport of water vapour away from the outer surface. For the former case, Crank [5] found two equivalent solutions of Fick’s Law relating the diffusion coefficient to the weight loss against time curve:

\[
\frac{W - W_\infty}{W_0 - W_\infty} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -D n^2 \pi^2 t/a^2 \right),
\]

or

\[
\frac{W - W_\infty}{W_0 - W_\infty} = 1 + 3 \frac{Dt}{a^2} - 6 \left( \frac{Dt}{a^2} \right)^{3/2} \left\{ \pi^{-1/4} + 2 \sum_{n=1}^{\infty} \text{ierfc} \left( \frac{na}{\sqrt{D}t} \right) \right\}
\]

where \(a\) is the radius of the sphere, \(D\) is the diffusion coefficient, \(n\) is an integer, \(t\) is time, \(W\) is the weight of the sample at time \(t\), \(W_0\) is the initial weight and \(W_\infty\) is the final equilibrium weight. \(\text{ierfc} \) is the integral of the complementary error function,

\[
\text{ierfc} \ z = \frac{2}{\sqrt{\pi}} \int_{z}^{\infty} \exp \left( -t^2 \right) dt.
\]

Equations (1) and (2) derive from different methods of solving the differential diffusion equation and, although they appear dissimilar, they yield identical numerical results. In application, the equations are complementary since equation (1) is easily solved for long times when the summation converges rapidly, whereas equation (2) simplifies for short and medium times when the term in \(\text{ierfc} \) may be neglected.

**Statistical Treatment of Diffusion Data**

When the weight loss data extended over a sufficiently wide range, a statistical procedure was followed, using a computer program. To allow for the uncertain time origin of the experiment, equation (1) is rewritten

\[
\frac{W - W_\infty}{W_0 - W_\infty} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left\{ -D n^2 \pi^2 (t - t_0)/a^2 \right\}
\]

Fig. 1. — Rates of water diffusion - 7.57 mm rad. cement paste sphere at 303 °K.

(a) Comparison of internal and external diffusion for short times
(b) Diffusion rates after two days.