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Novel Methods of Processing Cement Gel to Examine and Control Microstructure and Properties [and Discussion]

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Novel methods of processing cement gel to examine and control microstructure and properties

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The microstructure of the gel produced by hydrating cement is sensitive to the manner in which the original pore water is removed. Exchange of the pore water with a miscible, low surface-tension fluid by a process of counter-diffusion is examined. Diffusion rates in the hydrated cement can be assessed from the kinetics of the exchange process. Evaporation of the low surface-tension fluid from the pores caused less alteration to the microstructure than direct removal of the original pore water.

The sensitivity of the microstructure of hydrated cement to normal environmental drying is industrially significant because it is associated with increases in diffusion rates that could affect the durability of concrete. Drying lowered the correlation between diffusion rate and compressive strength. Possible methods of processing the cement gel to make it more resistant to the disruptive effects of drying are discussed.

INTRODUCTION

The particular method of processing cement gel that will be a major theme in this paper is the exchange of the original pore water with a miscible fluid by a process of counter-diffusion. Various observations that have emerged during the study of this fluid exchange process will be discussed and particular emphasis will be placed upon the importance of drying history. The rate of fluid exchange gives an indication of the diffusivity of hydrated cement and the use of a low surface-tension fluid minimizes capillary tension stresses during subsequent drying. This latter point is significant when preparing samples for pore structure analysis. Fluid exchange can be used to introduce probe molecules into the pores of the hydrated cement so that they fully replace the original pore water.

The effects of drying are industrially important as well as being significant when preparing samples for porosity tests. Even very moderate drying can increase diffusion rates irrecoverably by a factor of two or three. Such changes in diffusion characteristics are readily detected by measurement of the kinetics of fluid exchange. The surface layer of concrete that is responsible for protecting the reinforcing steel in most concrete structures is subjected to environmental drying and its diffusion characteristics will therefore be modified. Furthermore the changes in microstructure induced by drying are associated with the development of irrecoverable shrinkage in the hydrated cement. This may cause stresses to develop in structural concrete, which could be of significance in design calculations.

The small increase in compressive strength that accompanies drying is largely reversible with rewetting. Since the changes in diffusion rate are not recoverable with rewetting, normal environmental exposure will lower the correlation between compressive strength and diffusion characteristics. This calls into question the prevalent view that the durability of concrete is directly related to its compressive strength.

Another aspect of the processing of cement gel is embodied in the problem as to how cement gel can be processed to make it more resistant to the effects of drying. Variables that can be manipulated on an industrial level will be considered and will include cement gel composition, the use of reactive siliceous materials, admixtures, water/cement (w/c) ratio, age and heat treatment.

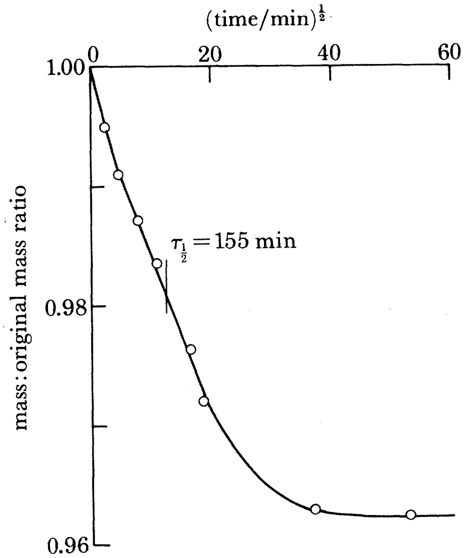

Figure 1. Solvent exchange for porous glass where original pore water is exchanged for propan-1-ol.

Table 1. Porosity† estimates for a tricalcium silicate cement hydrated for 9 days

sample	fluid	porosity	fluid	porosity	fluid	porosity	fluid	porosity
1	water	0.493	methanol	0.471	*n*-pentane	0.433	benzene	0.449
2	water	0.515	ethanol	0.494	*n*-pentane	0.468	benzene	0.472
3	water	0.502	propan-1-ol	0.487	*n*-pentane	0.446	benzene	0.460
4	water	0.497	propan-2-ol	0.486	*n*-pentane	0.457	benzene	0.463

† Fraction of total volume.

Fluid exchange

Fluid exchange typically involves the immersion of a water-saturated sample of porous material in a water-miscible fluid such as methanol or propanol and measuring the weight change of the sample as a function of time. Normally, 3 mm thick slabs of mass *ca.* 1 g were immersed in 150 ml of exchange fluid. Dependant upon sample pore structure, mass equilibrium was reached after periods ranging from a few hours to a few weeks. Figure 1 illustrates a solvent exchange curve for propan-1-ol diffusing into a porous glass that has 4 nm diameter pores and about 30 % porosity. Secondary and tertiary exchanges were feasible with fluids that did not need to be miscible with water. The counter-diffusion process generally followed a standard three-dimensional diffusion equation, the diffusion rate being linearly related to the viscosity of the penetrating fluid (Parrott 1982).

Table 1 illustrates the porosity data obtained from a tricalcium silicate cement. The porosity estimates were based on the various fluid-saturated weights, subtraction of a final dry mass and division by the measured density of the exchange fluid (Parrott 1982). The variations between samples for a single fluid suggest that porosity differences of about 0.02 can be reliably detected. The estimates of porosity based on water penetration are slightly higher than those determined with organic fluids. However, it is important to note that pore water replacement levels for fluid exchange are much higher than those obtained after direct drying and adsorption (Mikhail 1966).

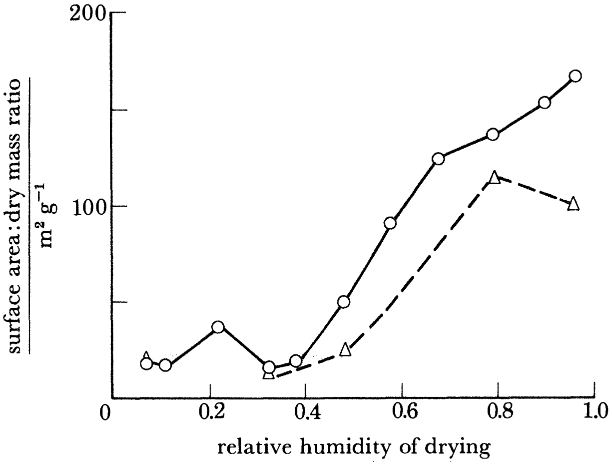

Figure 2. Effect of previous drying for 78 days at different relative humidities upon the nitrogen surface area of solvent exchanged and dried tricalcium silicate hydrate. *Key*: ○, w/c ratio 0.6; △, w/c ratio 0.4.

Evidence that solvent exchange followed by evaporation of the solvent produces less pore structure alteration, than does direct drying of pore water, is available from tests on several materials. Swanson (1979) demonstrated that the surface area measured by nitrogen adsorption on samples of wood pulp increased from 0.6 to 140 $m^2\ g^{-1}$ with a reduction in the surface tension of the exchange fluid from 0.72 to 0.15 $mN\ cm^{-1}$. Iler (1979) has reviewed comparable studies on the drying of silica gels from low surface tension fluids and concluded that solvent replacement was an effective way of minimizing pore shrinkage and loss of surface area. The effect of previous drying upon the surface area of two hydrated tricalcium silicate cements is illustrated in figure 2 (Parrott *et al.* 1980). The surface area was measured by nitrogen adsorption after fluid exchange and drying. The results indicate that calcium silicate hydrate, the main cementing component in hydrated Portland cement, is very sensitive to the capillary tension stresses developed during conditioning at the different relative humidities. Data comparable to those shown in figure 2 have been obtained for Portland cement by using nitrogen adsorption (Hunt *et al.* 1960; Litvan 1976), low angle X-ray scattering (Winslow 1973) and calorimetry (Sellevold & Bager 1980). Sellevold & Bager used low temperature, scanning calorimetry to measure the freezing point of pore water; the depression of freezing point is an indication of pore radius. Sellevold & Bager's results in figure 3 show trends similar to those in figure 2.

Additional evidence that solvent exchange followed by drying minimizes the stresses that act upon the cement hydrates can be derived from measurements of dimensional changes. The exchange of pore water for methanol in hydrated tricalcium silicate cements and secondary exchange of the methanol for *n*-pentane did not cause any significant dimensional change (i.e. strain changes were less than 3×10^{-5}, Parrott & Young (1982)). Furthermore, irrecoverable shrinkage strains due to methanol desorption and adsorption were about 40×10^{-5} compared with 450×10^{-5} for desorption and adsorption of water (Parrott 1981).

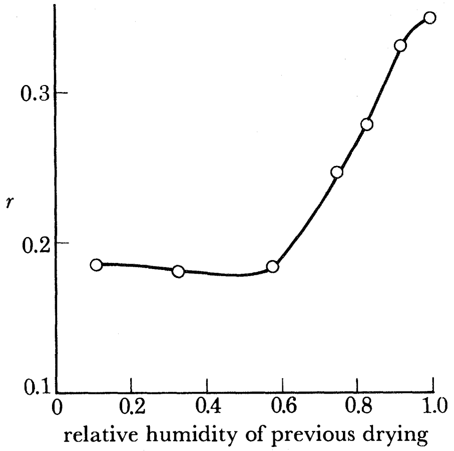

FIGURE 3. Effect of previous drying for several months upon the volume of small pores in a mature Portland cement paste (w/c ratio = 0.6 by mass) as defined by the mass ratio, r, of pore water not frozen at -10 °C to dry mass (Sellevold & Bager 1980).

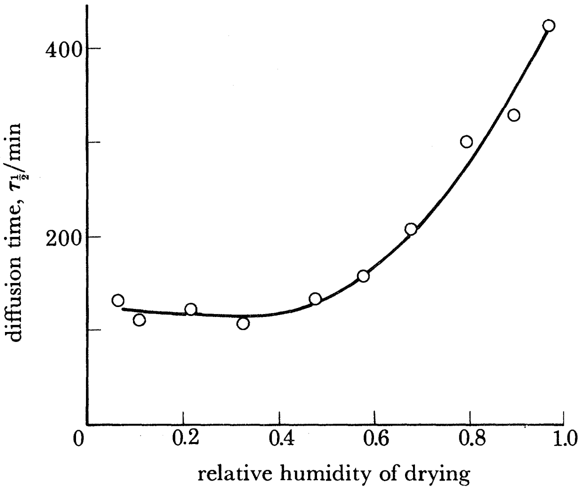

FIGURE 4. Effect of previous drying for 78 days at different humidities followed by resaturation upon the rate of exchange of pore water with methanol (water/tricalcium silicate ratio 0.6 by mass).

SIGNIFICANCE OF CHANGES IN MICROSTRUCTURE DUE TO DRYING

The effect of drying followed by resaturation upon the diffusion rate in a hydrated tricalcium silicate cement is illustrated in figure 4, where the time for half of the pore water to be exchanged with methanol, $\tau_{\frac{1}{2}}$, is plotted against the relative humidity during previous drying. The diffusion rate was increased by a factor in excess of three by prolonged drying at relative humidities less than 60% (Parrott 1981). Subsequent methanol adsorption measurements on the diffusion test samples showed that the minimum in $\tau_{\frac{1}{2}}$ corresponded to a maximum in the volume of pores larger than 5 nm and a minimum in the volume of smaller pores. Drying caused a coarsening of the structure without any great change in total porosity. This is in general agreement with the views of Sellevold & Bager (1980). Related studies by Powers *et al.* (1954) demonstrated that prolonged drying of a well hydrated Portland cement to 79% relative humidity caused a

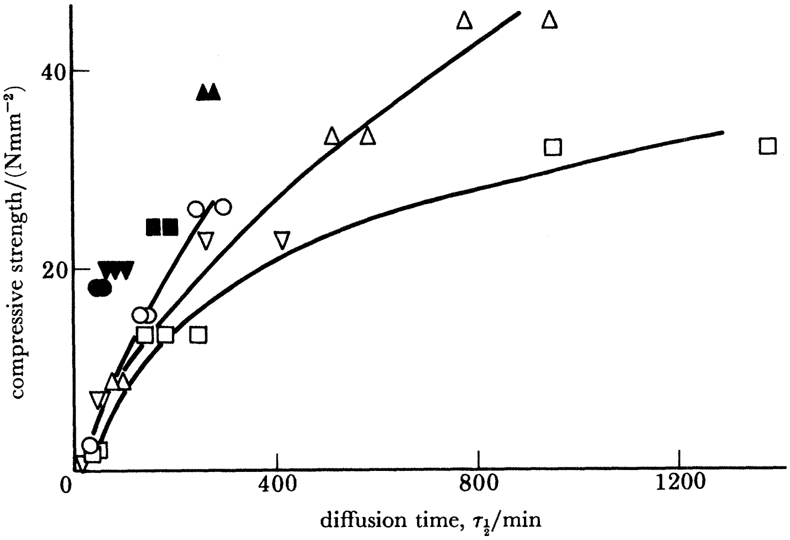

FIGURE 5. Diffusion time, $\tau_{\frac{1}{2}}$, against compressive strength for a variety of hydrated cements (w/c ratio 0.59 by mass). Cement: ○, ●, tricalcium silicate; □, ■. 0.75 tricalcium silicate with 0.25 dicalcium silicate; ▽, ▼, 0.50 tricalcium silicate with 0.50 dicalcium silicate; △, ▲, ordinary Portland cement. Open symbols, samples were not dried; filled symbols, samples were dried and resaturated.

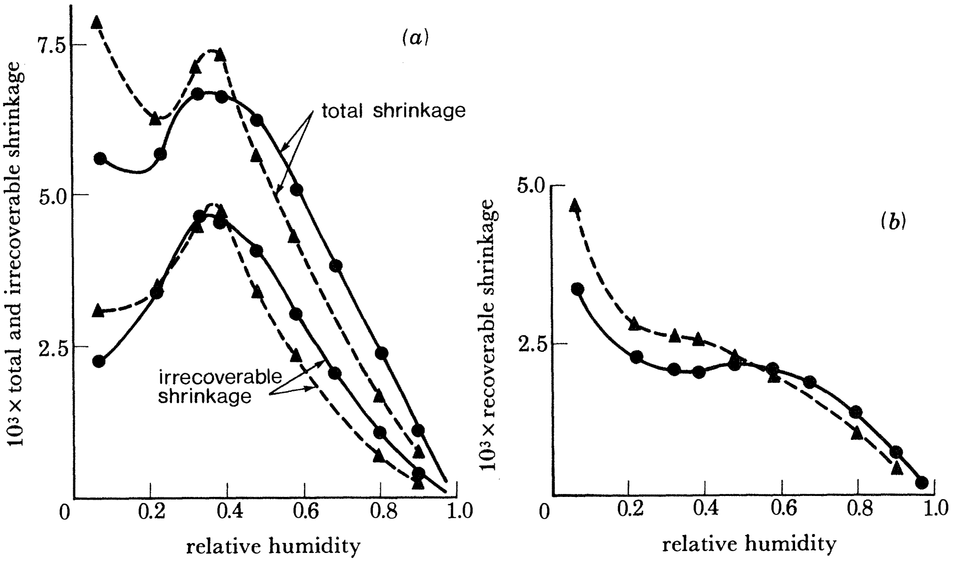

FIGURE 6. Shrinkage of hydrated tricalcium silicate (alite) cement against relative humidity of drying. Dried for 78 days, resaturated for 21 days. *Key*: ●, water/alite ratio 0.6; ▲, water/alite ratio 0.4.

70-fold increase in permeability to water. Both Powers and Sellevold commented that the primary effect of drying was to increase the continuity of the larger pores.

Drying can cause an increase in the compressive strength of hydrated Portland cement (Parrott 1973) but this effect seems to be largely recoverable upon resaturation (Parrott 1977). The effect of drying upon diffusion rate that was mentioned previously was irrecoverable and it follows that correlation between diffusion rates and compressive strength will be reduced by including the effects of drying. This is illustrated in figure 5 where the diffusion time, $\tau_{\frac{1}{2}}$, as measured by methanol exchange, is plotted against compressive strength for a variety of cements.

Consideration of the data from dried and resaturated samples shows that scatter increased to such an extent that compressive strength cannot provide a reasonable indication of diffusion characteristics. Thus the engineering tradition of equating the quality and durability of concrete to a standard measure of compressive strength requires close examination and some revision.

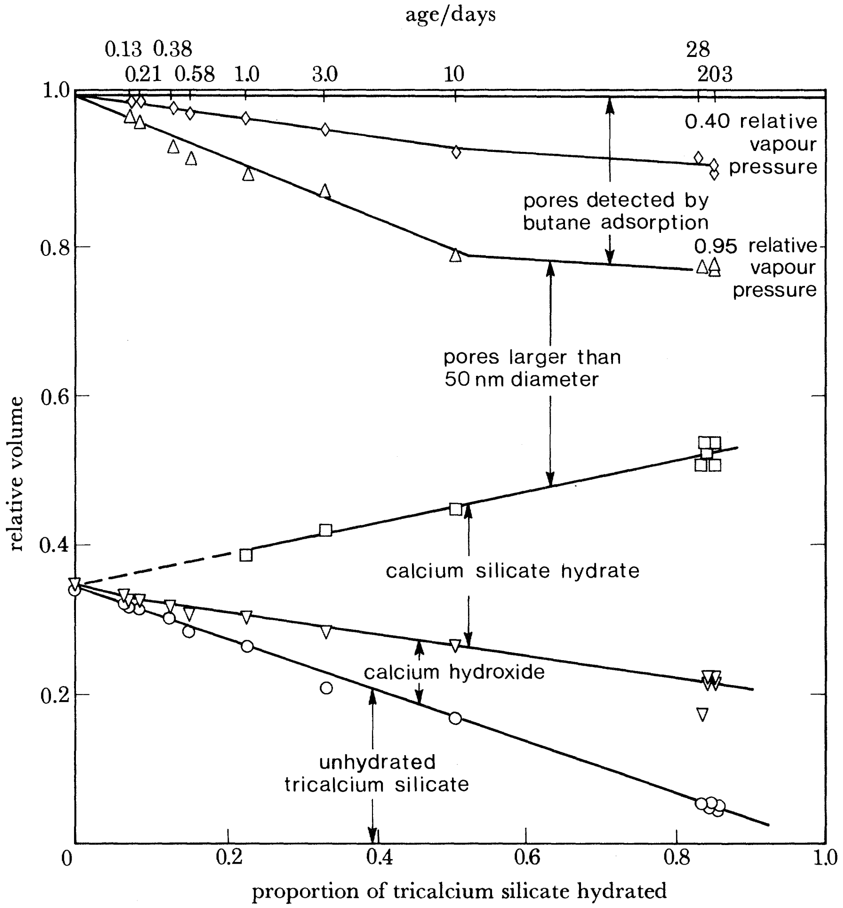

Figure 7. Phases present in a simple tricalcium silicate cement as a function of hydration (w/c ratio 0.59 by mass).

Shrinkage of hydrated cement is a direct consequence of drying and, as illustrated in figure 6, it is only partly recoverable with resaturation (Parrott & Young 1982). The pattern of irrecoverable shrinkage against relative humidity of previous drying has obvious parallels with the diffusion results shown in figure 4 and indeed the explanations are similar. Experiments involving methanol exchange followed by drying and methanol adsorption indicated that irrecoverable shrinkage is a direct reflexion of the internal stresses that cause a reduction in volume of the smaller pores and a corresponding increase in the volume of larger pores. The shrinkage results suggested that the stresses originated from capillary tension forces (Parrott & Young 1982).

Processing cement gel to resist the effects of drying

The earlier sections of this paper have shown how the coarsening of porosity in hydrated cement that results from drying can be controlled in the laboratory by the use of fluid exchange followed by fluid evaporation. This approach can be used in the industrial production of silica gels (Iler 1979) but it leaves the gel susceptible to capillary tension stresses if it is subsequently exposed to water vapour (Johnson & Ries 1950). Clearly a different approach is needed for industrial production of cement-based products that remain impermeable and have good dimensional stability under fluctuating water vapour pressures.

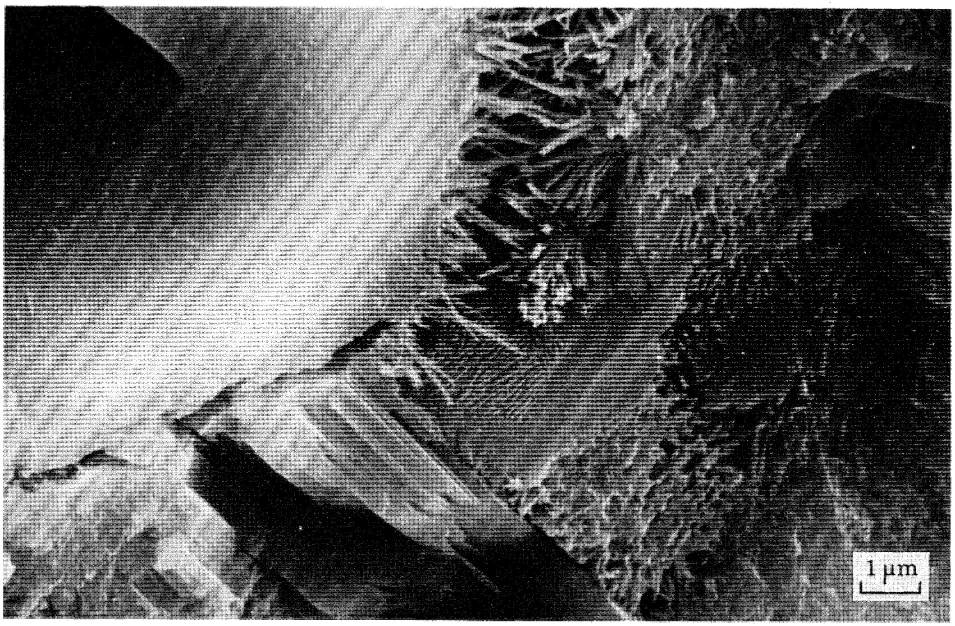

Figure 8. Scanning electron micrograph of fracture surface in a hydrated tricalcium silicate cement hydrated for 200 days (w/c ratio 0.59 by mass).

It is helpful, when considering how cement gel can be processed to resist the effects of drying, to review the phase volume composition of a simple hydrated tricalcium silicate cement. The phase volume diagram shown in figure 7 was based upon adsorption studies to provide porosity data, and thermogravimetric analysis to give volumes of calcium hydroxide and unhydrated alite (an impure form of tricalcium silicate cement). The spacial relations of these phases can be assessed in a qualitative manner by electron microscopy. The calcium silicate hydrates seem to coat the hydrating alite grain and the outer region is composed of radially oriented acicular growths. This is illustrated in figure 8, where the more compact, featureless inner hydrate can be seen adjacent to the angular particle of unhydrated alite. The calcium hydroxide is able to grow as fairly large crystals several micrometres in size. It is evident from scanning transmission electron microscopy that the acicular growths from adjacent cement grains intergrow and provide some skeletal continuity (Jennings *et al.* 1981).

The effect of ageing is, given sufficient water, to increase cement hydration and reduce the volume of the pores originally filled by the mixing water with a porous calcium silicate hydrate gel and calcium hydroxide, as illustrated in figure 7. While this reduces diffusion rates and increases strength, hydration will not greatly reduce the sensitivity of the porous cement gel to shrinkage during subsequent drying. Since drying does not greatly alter the total volume of the hydrated cement, nor does it significantly reduce the volume of the solid phases, the shrinkage of the porous gel increases the volume of the larger pores and thus increases the rate of diffusion. Reductions in w/c ratio normally reduce the volume of larger pores without greatly affecting the other phases, and the material remains susceptible to the effects of drying. This view is supported by comparison of the changes in diffusion times, $\tau_{\frac{1}{2}}$, resulting from drying for two hydrated tricalcium silicate cements of 0.6 and 0.4 w/c ratio, table 2.

TABLE 2. EFFECT OF DRYING FOR 78 DAYS UPON DIFFUSION RATES IN TWO HYDRATED CALCIUM SILICATE CEMENTS (PARROTT 1981)

	diffusion time, $\tau_{\frac{1}{2}}$/min		
w/c ratio	not dried	dried 80 % r.h.	dried 40 % r.h.
0.4	1850 (1.00)	1100 (0.59)	250 (0.14)
0.6	400 (1.00)	180 (0.45)	75 (0.19)

The changes relative to the undried samples show that lowering the w/c ratio did not significantly reduce sensitivity to drying.

Tricalcium silicate and dicalcium silicate are major constitutents of Portland cements and they hydrate to form similar calcium silicate hydrates with different quantities of calcium hydroxide (Kantro *et al.* 1966). Since the morphology of calcium silicate hydrate differs from that of calcium hydroxide (Diamond 1976 and figure 8) the relative quantities of tricalcium silicate and dicalcium silicate in a cement could, in theory, affect diffusivity. Diffusion measurements in which pore water was exchanged for methanol were obtained for cements blended from tricalcium silicate and dicalcium silicate. The results are plotted in figure 5 against compressive strength and it can be observed that for a given strength a wide range of $\tau_{\frac{1}{2}}$ values were obtained with non-dried samples. An intermediate proportion of dicalcium silicate (25 % of the total weight of cement) gave the longest diffusion times, suggesting that the quantity of calcium hydroxide was not a dominant factor. A more fundamental view of the diffusion results is illustrated in figure 9 where $\tau_{\frac{1}{2}}$ is plotted against the volume of pores larger than 4 nm diameter. Scatter is smaller than that in figure 5 and the dried and non-dried samples conform to a similar relation. Figure 9 suggests that diffusion is dominated by the larger pores and the relative quantities of tricalcium silicate and dicalcium silicate have only an indirect effect on diffusion via control of the rate of hydration and pore filling. The increase in tricalcium silicate: dicalcium silicate ratio from 1:1 to 3:1 corresponds roughly to the change in the relative proportions of these minerals in ordinary Portland cement over the last sixty years (Corish & Jackson 1982). Figures 5 and 9 suggest that this change is beneficial for non-dried cements but a cautionary note should be added that if the moist conditions encourage dissolution of the calcium hydroxide the benefit might be lost. In drying conditions any effect of tricalcium silicate to dicalcium silicate ratio in the cement upon diffusion characteristics would be masked by the change in pore structure associated with drying (figure 5).

Preliminary studies with cements containing calcium aluminates suggest that the porosity–diffusion relation shown in figure 9 is not unique and at early ages it is possible to obtain longer diffusion times for a given volume of large pores. The reasons for this are currently under investigation.

Materials that contain reactive silica such as pulverized fuel ash and silica fume can be blended with Portland cement so that their reaction with the calcium hydroxide from the cement reaction yields additional calcium silicate hydrates. Silica fume reacts with calcium hydroxide to yield a calcium silicate hydrate that is not significantly greater in volume than the reactants (Sellevold *et al.* 1981). However, the calcium silicate hydrate forms as a porous gel and the gel pores contribute to the filling of the larger pores. Thus the addition of silica fume to a Portland cement reduced the volume of larger pores and reduced diffusion rates without any reduction in total porosity. Nevertheless the porous gel was still sensitive to drying, with corresponding increases in the volume of larger pores.

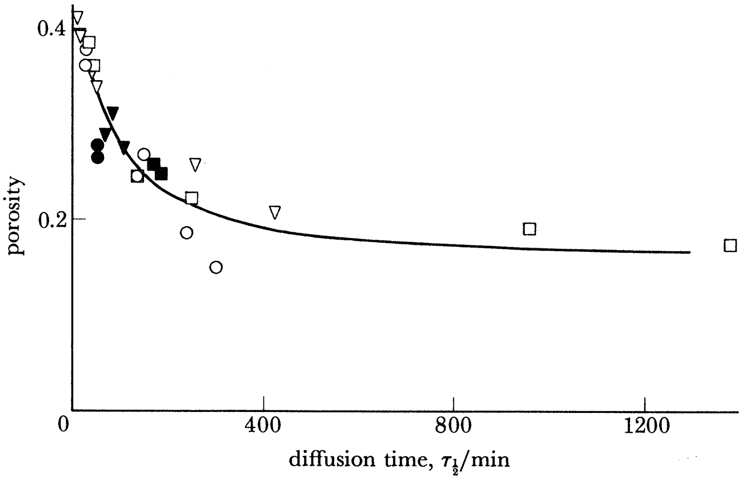

FIGURE 9. Diffusion time, $\tau_{\frac{1}{2}}$ against volume of pores larger than 4 nm diameter (w/c ratio 0.59 by mass). Cement: ○, ●, tricalcium silicate; □, ■, 0.75 tricalcium silicate with 0.25 dicalcium silicate; ▼, ▽, 0.50 tricalcium silicate with 0.50 dicalcium silicate. Open symbols, samples were not dried; filled symbols, samples were dried and resaturated.

Sereda *et al.* (1980) have reviewed the effect of admixtures upon the microstructure of hydrated cement. There was no evidence to suggest that any commonly used admixtures can limit the increases in diffusion rate that result from first-time drying. Where admixtures affected cement hydrate morphology and pore structure they seemed to leave the hydrated cement more susceptible to the disruptive effects of drying. This was deduced from the development of irrecoverable shrinkage (Feldman & Swenson 1975).

Heat treatment of saturated hydrated cement has been used to stabilize it against changes due to subsequent drying, but unfortunately heating leads to a coarsening of the pore structure similar to that induced by drying (Sellevold & Bager 1980). This coarsening of the pore structure was also observed in a study of the effects of heating upon creep and shrinkage in hydrated Portland cement (Parrott 1977). Thus it seems unlikely that heat treatment will yield a hydrated cement with reduced diffusion rates.

The effects of drying upon the pore structure and diffusion properties of hydrated cement are substantial and are of industrial importance, particularly with regard to the durability of concrete. At present there appears to be no obvious way of making hydrated cement resistant to the disruptive effects of drying and further work on this topic seems desirable.

CONCLUSIONS

Hydrated cement can be processed by using fluid exchange techniques in which pore water is exchanged for another miscible fluid by a process of counter-diffusion. The kinetics of the exchange process are indicative of the diffusion properties of the hydrated cement. If the exchange fluid has a low surface tension then capillary tension stresses during subsequent drying are reduced. Correspondingly, shrinkage and pore structure changes are reduced and later pore structure analysis is thereby facilitated.

Under practical conditions the drying of hydrated cement does not involve fluid exchange and substantial coarsening of the pore structure occurs. This coarsening leads to faster diffusion rates and is therefore industrially important particularly with regard to the durability of concrete. Drying lowered the degree of correlation between compressive strength and diffusion rate, indicating that compressive strength is not a reliable measure of durability.

Further work is needed to produce a hydrated cement that is resistant to the disruptive effects of drying.

The author wishes to thank Miss K. Scrivener of the Department of Metallurgy and Materials Science, Imperial College, London for providing the micrograph in figure 8.

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Discussion

K. S. W. Sing (*Department of Chemistry, Brunel University, Uxbridge, U.K.*). I wish to make two comments concerning the interesting results presented by Dr Parrott.

(1) The solvent exchange technique is similar to the procedure introduced many years ago by Kistler to prevent the collapse of pore structure that normally takes place during the drying of an aerogel (i.e. conversion to the more compact xerogel). Various additives have been used to modify the surface structure of alumina and silica to render the surface more hydrophobic and it is possible that this type of approach could be used as a means of stabilizing the pore structure of the cement hydrogel.

(2) It should be noted that the pore structure of the cement gel is not rigid even when the continuous aqueous phase has been removed. Special care is required therefore in the interpretation of adsorption and other data in the assessment of pore size distribution.

L. J. Parrott. With regard to Professor Sing's first point I would like to thank him for his suggestion and I will examine the use of additives that create a hydrophobic surface for stabilizing the pore structure of cement gel.

I fully agree with the second point in which Professor Sing states that the gel may not be stable even when the pore water has been removed. Fortunately this did not seem to be a major problem in the present work. As I mentioned in my paper, results from adsorption experiments showed the same trends as results from the low temperature calorimetry where drying of the cement was not necessary.

A. A. Rahman (*Aberdeen University, U.K.*). Results presented by Dr Parrott on the changes of surface area, amounts of water not frozen at –10 °C and diffusion rates with relative humidity showed interesting features. There was a maximum for surface areas (nitrogen) at around 0.2 r.h., while the trends (slopes of the lines) for unfrozen water and diffusion rates changed at about 0.5 r.h. Is there an explanation for these? Could these be explained in terms of removal of water or other adsorbed molecules?

The surface areas reported would be affected by the nature of interaction between the gel surface and the adsorptive, particularly the specificity component of the interaction. The displacement of one fluid by another may leave a residual adsorbed layer of the initial (liquid) molecules. Is there any evidence for the specificity of interaction with the gel system and the several molecular probes Dr Parrott used? Further, how has the complete removal of the adsorptive layer been ascertained? Is it likely that the surface areas reported would represent values for a gel-adsorptive surface rather than a true gel surface?

L. J. Parrott. Nitrogen surface areas, water not frozen at –10 °C, diffusion times and published methanol adsorption results (Parrott 1981) all show a major decline with drying in the relative humidity range from saturation down to 0.5. The most obvious explanation for this behaviour is that surface tension forces cause compaction of the porous cement gel and thereby alter the pore size distribution.

In reply to Dr Rahman's second point there was remarkably little evidence of an interaction between the cement gel and probe molecules. This seemed to be related to the method of introducing the probe molecule; normal drying compaction of the porous gel can produce molecular sieve effects that might be regarded as an interaction between gel and probe molecule but with fluid exchange the gel remains dispersed and non-polar fluids with relatively large molecular radii can replace a comparable volume of pore water (see table 1).

D. Pearson (*A.E.R.E. Harwell, U.K.*). Recent work using small angle neutron scattering has indicated results that are in close agreement with those presented by Dr Parrott. From looking at pore size distributions below about 25 nm, it appears that drying at either 105 °C or 11% r.h. does have a significant effect on pore structure. Changes in water/cement ratio or additions of silica fume, on the other hand, appear to have little effect on gel porosity.

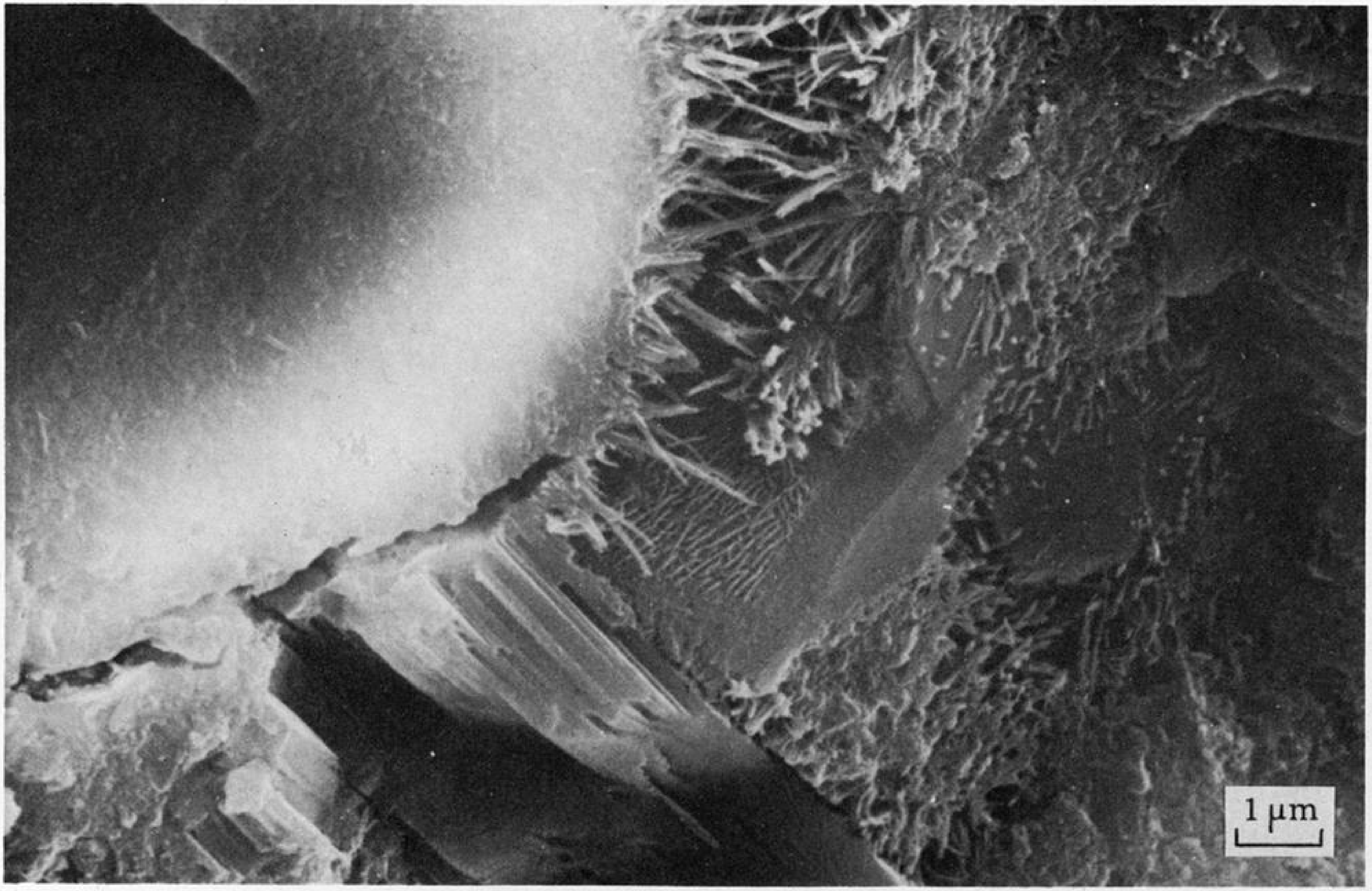

Figure 8. Scanning electron micrograph of fracture surface in a hydrated tricalcium silicate cement hydrated for 200 days (w/c ratio 0.59 by mass).