

Influence of curing at different relative humidities upon compound reactions and porosity in Portland cement paste

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The reduction in relative humidity within drying concrete depends mainly on the depth from the exposed surface, exposure duration, temperature and environmental humidity; this limits hydration and coarsens pore structure, thus impairing durability. OPC paste, of 0.59 water/cement ratio, was cured for 2 days and then exposed to controlled relative humidity environments. After 14 and 90 days exposure, hydration of the individual compounds was measured using quantitative X-ray diffraction and thermogravimetry. Methanol adsorption was used to monitor porosity and gel formation. Even a small drop in relative humidity below 95% r.h. significantly limited cement hydration. Gel porosity increased with amount of hydration and, for a given level of hydration, decreased with drying. Curing below 80% r.h. produced a coarsened pore structure with a large-diameter porosity three times greater than that obtained with saturated curing.

1. INTRODUCTION

Moisture gradients created by exposing concrete to a drying atmosphere can cause gradients of hydration and porosity. The extent and severity of these gradients will depend on a number of factors such as the ambient relative humidity, the temperature, the wind speed, the age at exposure, the depth from the exposed surface and the duration of the exposure. If the relative humidity of the surrounding air is low enough, the hydration of the cement at the exposed surface of an element will cease [1]. In the interior of the concrete, the cement will continue to hydrate while adequate pore water is available. The pore water will be partly consumed in the hydration process and some will be lost through the drying surface.

It has been suggested by Powers [2] that the hydration of cement virtually ceases when the relative water vapour pressure in the capillaries drops below about 0.8. Spears [3] maintains that continued curing below 80% relative humidity (r.h.) does not lead to the increase in cement hydration that is necessary for further improvement of concrete quality. In practice, site concrete is subjected to daily humidity cycles superimposed upon seasonal variations, and active curing may stop before the cement has fully hydrated. Data in the literature concerning the effect of relative humidity of curing on the hydration and microstructural properties of either a cement or its individual compounds are scarce [4]. This report examines compound hydration and porosity development in Portland cement paste as a function of relative humidity whilst curing in the absence of carbon dioxide. The study is intended to

provide a better understanding of the properties of concrete subjected to practical curing regimes and to aid prediction of these properties.

2. EXPERIMENTAL DETAILS

A slab of ordinary Portland cement (OPC) paste was cast with a water/cement (w/c) ratio of 0.59 and the sealed mould was rotated during setting to avoid sedimentation. Details of the OPC are given in Table 1. The slab was demoulded after one day and stored for a

Table 1 OPC Composition and related properties

| Oxide | Content (wt %) | Compound | Content (wt%)† |
|--------------------------------|----------------|---|----------------|
| SiO ₂ | 20.32 | Alite | 68.0 |
| Fe ₂ O ₃ | 2.36 | Belite | 13.5 |
| Al ₂ O ₃ | 5.47 | C ₃ A* | 5.5 |
| CaO | 64.00 | C ₄ AF* | 7.0 |
| MgO | 2.30 | Gypsum | 4.5 |
| SO ₃ | 2.80 | Density (kg m ⁻³) | 3160 |
| Others | 1.59 | Specific surface (m ² kg ⁻¹) | 320 |
| Loss on ignition | 1.06 | | |

*C = CaO, A = Al₂O₃, F = Fe₂O₃.

†By X-ray analysis.

further day at 100% r.h. The slab was then cut with a water-lubricated diamond saw to produce 61 slices measuring 3 mm × 20 mm × 28 mm. Five slices were tested at an age of 2 days, three by methanol adsorption and one each by thermogravimetric analysis (TG) and quantitative X-ray diffraction (QXRD). The remaining slices were conditioned at selected relative humidities (33, 49, 69, 81, 91, 97, 100%) in desiccators containing appropriate saturated salt solutions. The initial saturated curing period of 2 days was selected. This produced an initial degree of cement hydration around 50%, thus ensuring that there would be subsequent changes in hydration which could be readily measured. The temperature was controlled at 20°C during the periods of curing and conditioning.

At ages of 14 and 90 days, four slices were removed from each desiccator. Of these two were dried over silica gel (one for TG measurements and the other for QXRD) and the remaining two were immersed in methanol prior to adsorption measurements. The hydrated fractions of alite, belite, tricalcium aluminate and ferrite phase were measured by QXRD using an automatic powder diffractometer with CuK α radiation [5,6]. The degree of cement hydration was calculated from these measurements using weighting factors based upon the compound composition of the unhydrated cement. Thermogravimetric analysis was carried out in dry nitrogen on 20 mg samples heated to 750°C at 2°C min⁻¹ [7]. Four weight-loss parameters were obtained from the thermogravimetric curve: 100 to 200°C, 200 to 425°C, 100 to 750°C and the stepwise loss associated with the calcium hydroxide dehydration at 425°C. The weight loss between 100 and 750°C was used to calculate the degree of hydration by assuming a value of 0.272 g per gram of ignited cement (extrapolated from QXRD data) for complete hydration.

Slices for adsorption measurements were removed from the methanol after 3 weeks of immersion, by which time any pore water and air had been exchanged with methanol. Methanol was then removed by drying over silica gel at 20°C. This procedure minimized changes in pore structure after conditioning of the slices [8,9]. The gravimetric technique used for methanol adsorption has been described previously [9]. In principle the weight of methanol vapour adsorbed on a slice is compared with that adsorbed by a well-characterized granulated porous silica glass (BDH Chemicals, CPG-10-350) stored in the same evacuated adsorption vessel. Stepwise adsorption is achieved by adding small quantities of methanol to the adsorption vessel; the methanol evaporates and is adsorbed partly by the slices and partly by the porous glass granules. Filling of the 37 nm diameter pores in the silica glass is readily detected by a substantial increase in weight and it is assumed that pores of the same size in the paste slices are also filled at this stage. Previous adsorption studies with another well-characterized porous glass enabled the stage where 4 nm pores were filled to be identified. Subsequently the slices and granules are dried first at 20°C over silica gel and then for 24 h at 105°C to obtain

the dry weight. The dried slices were heated at 900°C for 2 h to obtain the loss on ignition.

Three parameters were obtained directly from the curves of methanol adsorbed on the slices against that on the porous glass granules; initial adsorption, gel porosity and small porosity. Initial adsorption is the methanol uptake of a slice when the uptake of the silica glass is 0.02 g per gram of dry glass, and it is an indicator of the amount of hydrate surface. If the surface-to-volume ratio of the hydrate remains constant then the initial adsorption is a measure of hydrate volume [1]. Gel porosity is defined here as the relative volume of pores less than 4 nm in width, although it is realised that some pores in the gel phase are larger than this. Small porosity is the relative volume of pores less than 37 nm width and this includes gel porosity.

Total porosity was obtained from the sample volume, the dry weight and saturated weight measured after the methanol immersion. Large porosity is the relative volume of pores wider than 37 nm and is the difference between total porosity and small porosity.

3. RESULTS AND DISCUSSION

3.1 Hydration of individual compounds in OPC

The relationship between the relative humidity maintained during curing beyond 2 days and the fractions of alite and belite reacted at 14 and 90 days are shown in Fig. 1. Alite reaction at 14 days does not increase greatly with increasing relative humidity because a substantial proportion had already reacted during the initial 2-day curing period (the rate of compound reaction diminishes at higher degrees of reaction [4]). The increase in fraction of alite reacted with increasing relative humidity is more noticeable after 90 days. The increase from 14 to 90 days is only statistically significant above 80% relative humidity. Belite reaction increases rapidly with an increase in relative humidity above 80% at 14 days and above 70% at 90 days, and is clearly very sensitive to the curing conditions; this

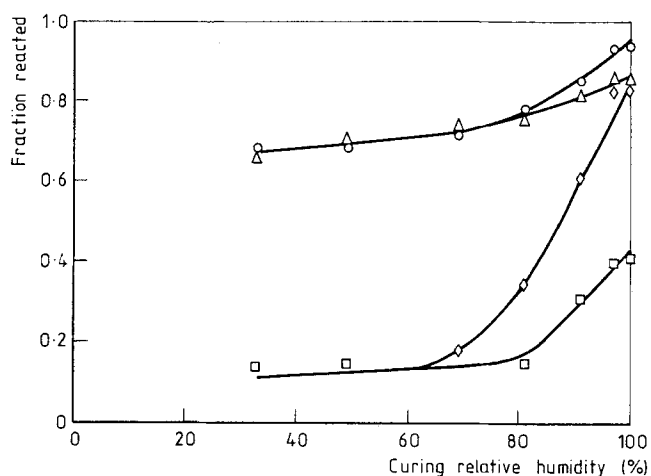


Fig. 1 Alite and belite hydration against curing relative humidity: (Δ) alite, 14 days; (○) alite, 90 days; (□) belite, 14 days; (◇) belite, 90 days.

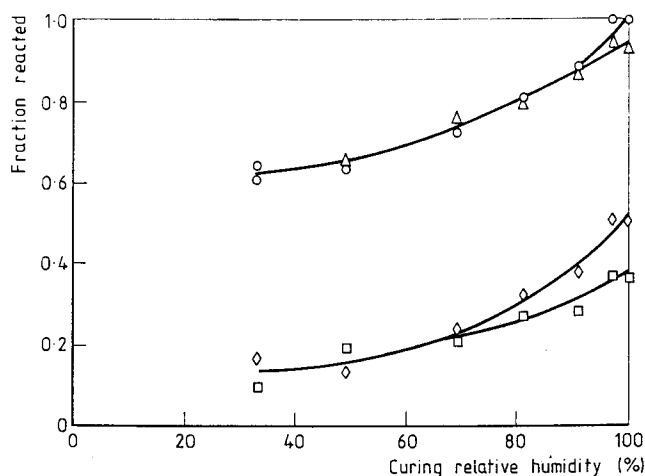


Fig. 2 C_3A and C_4AF hydration against curing relative humidity: (Δ) C_3A , 14 days; (\circ) C_3A , 90 days; (\square) C_4AF , 14 days; (\diamond) C_4AF , 90 days.

sensitivity arises from the small amount of belite reacted at 2 days and the correspondingly high potential for subsequent reaction [4]. The limited extent of belite hydration in Fig. 1 suggests that under poor curing conditions (e.g. early-age drying at low relative humidities) it would be beneficial to use a low-belite cement. In this regard the reported lower belite contents of modern cements [10] appear beneficial.

The hydrated fractions of the aluminate and ferrite phases are plotted as a function of the relative humidity during curing in Fig. 2. These phases show a gradual increase in hydration with an increase in humidity in contrast to the curves for alite and belite in Fig. 1. The amount of C_3A reacted between 14 and 90 days is extremely small because much of it has been consumed at the earlier age. However, the amount of ferrite

phase reacted between 14 and 90 days is statistically more significant, particularly above 70% r.h. Overall the dependence of compound hydration upon relative humidity described above is comparable and consistent with that of OPC hydration published elsewhere [11]. These results suggest that the water available at low humidities (mainly adsorbed in small pores) does not contribute greatly to the process of hydration.

3.2 OPC hydration and its products

Three different techniques (QXRD, TG and loss on ignition) were used to estimate the degree of hydration. The measurements, although differing in absolute values, all exhibit a similar dependence upon relative humidity of curing (Table 2). From 33 to 69% r.h. the degree of hydration measured by each technique shows only a small increase above the 2-day value. Above 81% r.h., on the other hand, there are substantial increases in the degree of hydration. Comparison between the 14- and 90-day results emphasizes that the benefit of increased hydration can only be achieved if cement-based materials are cured at high humidities.

The TG and QXRD measurements shown in Fig. 3 indicate that above 70% r.h. the formation of calcium hydroxide increases with curing humidity. At levels of humidity between 33 and 70%, the amount of calcium hydroxide is fairly constant irrespective of the hydration age and reflects the patterns of hydration described above. As might be expected, the calcium hydroxide data shown in Fig. 3 resemble closely the alite data in Fig. 1 since calcium hydroxide is predominantly produced by the alite hydration. The TG and QXRD methods of calcium hydroxide measurement produce curves of very similar shapes (see Fig. 3) but the TG values are slightly higher. This is illustrated in

Table 2 Degree of hydration and total porosity at various humidities and ages

| Age (days) | Curing r.h. at 20°C | Degree of hydration | | | Total porosity |
|------------|---------------------|---------------------|-------|-------|----------------|
| | | QXRD | LOI* | TG† | |
| 2 | 100 | 0.474 | 0.594 | 0.457 | 0.518 |
| 14 | 33 | 0.538 | 0.521 | 0.554 | 0.516 |
| | 49 | 0.581 | 0.482 | 0.488 | 0.528 |
| | 69 | 0.621 | 0.541 | 0.513 | 0.512 |
| | 81 | 0.635 | 0.554 | 0.663 | 0.523 |
| | 91 | 0.705 | 0.614 | 0.703 | 0.513 |
| | 97 | 0.764 | 0.665 | 0.703 | 0.502 |
| 90 | 100 | 0.762 | 0.666 | 0.745 | 0.513 |
| | 33 | 0.553 | 0.577 | 0.467 | 0.503 |
| | 49 | 0.560 | 0.669 | 0.602 | 0.502 |
| | 69 | 0.605 | 0.624 | 0.649 | 0.506 |
| | 81 | 0.687 | 0.691 | 0.652 | 0.503 |
| | 91 | 0.788 | 0.834 | 0.819 | 0.475 |
| | 97 | 0.892 | 0.899 | — | 0.463 |
| | 100 | 0.900 | 0.899 | 0.899 | 0.472 |

* Loss on ignition. From loss between 105 and 900°C (g per gram ignited)

† From thermogravimetric loss between 100 and 750°C (g per gram ignited).

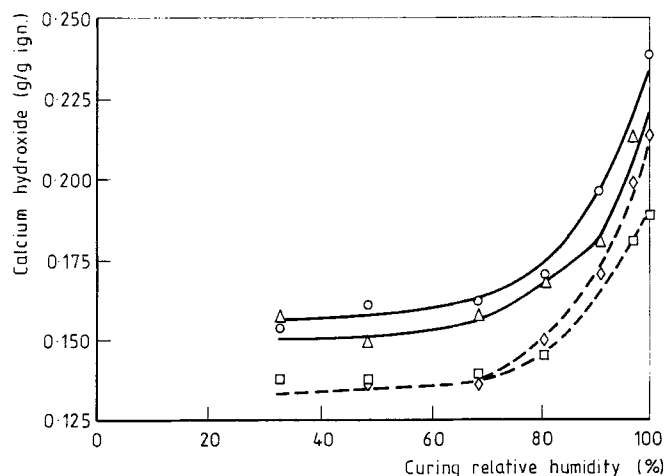


Fig. 3 Calcium hydroxide against curing relative humidity: TG at (Δ) 14 days, (\circ) 90 days and QXRD at (\square) 14 days, (\diamond) 90 days.

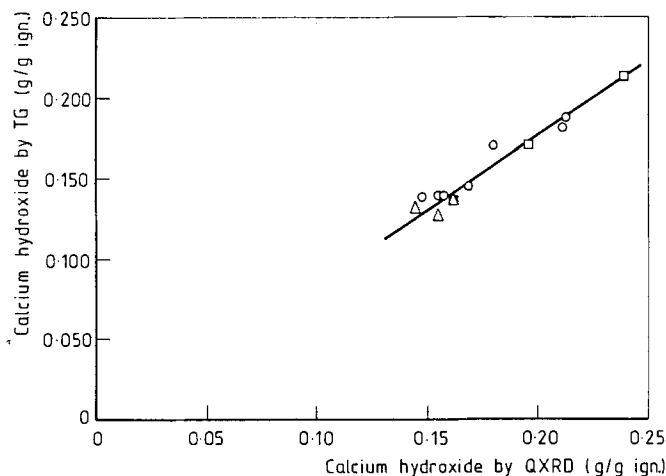


Fig. 4 Comparison of calcium hydroxide measurements by QXRD and TG: (Δ) 2 days, (\circ) 14 days, (\square) 90 days.

Fig. 4, where calcium hydroxide contents determined by both methods are plotted against each other. A similar relationship was also found to exist [5] for the measurement of calcium hydroxide in hydrated OPC, with or without pulverized fuel ash (PFA).

The results in Fig. 5 show a straight-line correlation between thermogravimetric loss from 100 to 200°C and loss between 200 and 425°C. This suggests that the nature of the hydrates, other than calcium hydroxide, as indicated by their bound water distribution, is not significantly affected by either the relative humidity or by the duration of curing.

One further way to monitor hydration is by measurement of initial adsorption; this is examined as a function of the relative humidity during curing in Section 3.3.2 below.

3.3 Porosity

3.3.1 Total porosity

Total porosity data at 2, 14 and 90 days are shown in Table 2. At 14 days, any trends in total porosity with

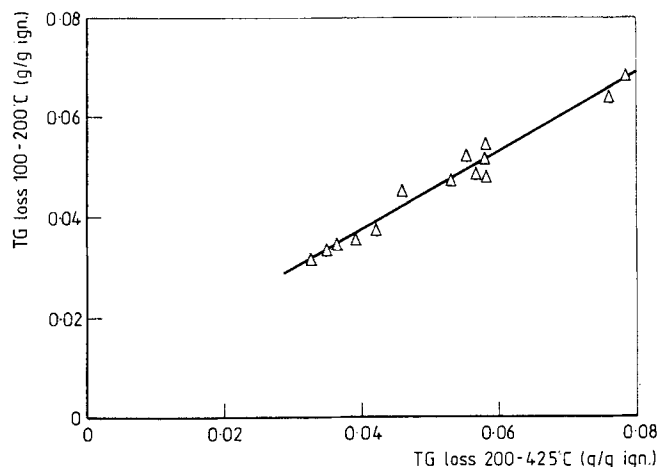


Fig. 5 TG losses from 100 to 200°C against losses from 200 to 425°C.

relative humidity are obscured by experimental scatter. The 90-day results, however, clearly reflect the relationship between hydration and relative humidity discussed earlier; the variation in total porosity is negligible below 81% r.h. and above this value there is a noticeable reduction in porosity due to increased degree of hydration.

3.3.2 Initial adsorption

It can be seen in Fig. 6 that the initial adsorption increased with an increase in the relative humidity of curing. This reflects an increased amount of gel formation. It is interesting to note, however, that the 14- and 90-day curves of initial adsorption cross over at around 60% relative humidity (this figure was checked statistically). Below 60% r.h. the initial adsorption at 90 days is lower than at 14 days; this is believed to be due to a partial collapse in the small pores that is induced by the surface tension forces that arise during drying [1,8,9]. This seems to reduce the accessibility of the hydrate

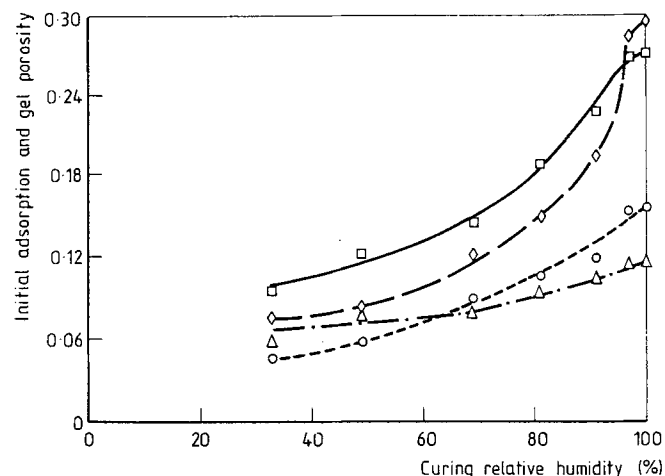


Fig. 6 Gel porosity (pore width < 4 nm) and initial methanol adsorption against curing relative humidity. Gel porosity at (\square) 14 days, (\diamond) 90 days; initial adsorption at (Δ) 14 days, (\circ) 90 days.

surfaces to methanol and suggests that the initial adsorption of methanol is not a direct indicator of gel formation below 60% r.h.

3.3.3 Gel porosity

The volume of pores below 4 nm in width, a portion of gel porosity, increased with the amount of gel formed but is reduced by drying [1,8,9,12]. Gel porosity is plotted against relative humidity in Fig. 6. From the hydration results described in Section 3.2, it might be expected that the gel porosity would be higher at 90 days than at 14 days, particularly above 70% r.h. The results in Fig. 6, however, show that the gel porosity is higher only above the humidity level of 95%, but because of the scatter in the results the significance of the crossover characterization can only be described as weak. Even so this behaviour might be explained by the pore collapse mechanism described above. Similar behaviour was noticed with the gel product in hydrated alite paste [13].

3.3.4 Small porosity

Normally the small porosity increases with hydration and thus is greater when curing at higher relative humidities as shown in Fig. 7. The curves in Figs 1, 3 and 7 are similar in shape but it should be noted that in Fig. 7 at 90 days the small porosity is lower than at 14 days over the complete range of humidities examined. The difference in small porosity between the two ages is virtually constant up to 91% r.h. It is thought to be caused by a time-dependent partial collapse of the small pores under stresses due to drying [1]. Under saturated conditions the slight reduction in small porosity with age is contrary to the normal trend. Possibly this may be due to infilling of the small pores when space for growth of the porous gel is restricted.

The adsorption results discussed above can be summarized as follows: initial adsorption, gel porosity and small porosity increase with increasing cement hydration but exhibit time-dependent reductions as a result of drying stresses.

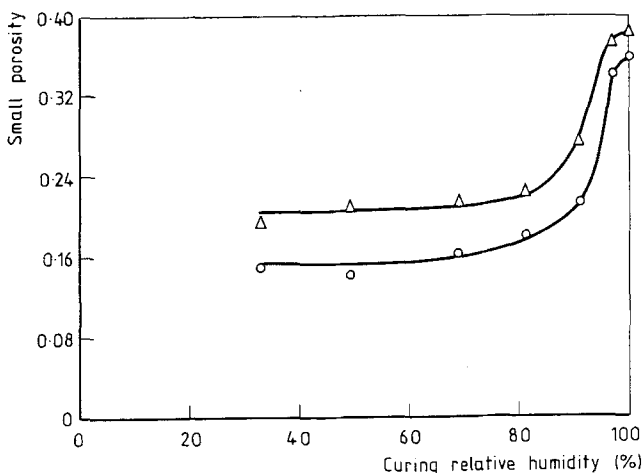


Fig. 7 Small porosity (pore width < 37 nm) against curing relative humidity: (Δ) 14 days, (\circ) 90 days.

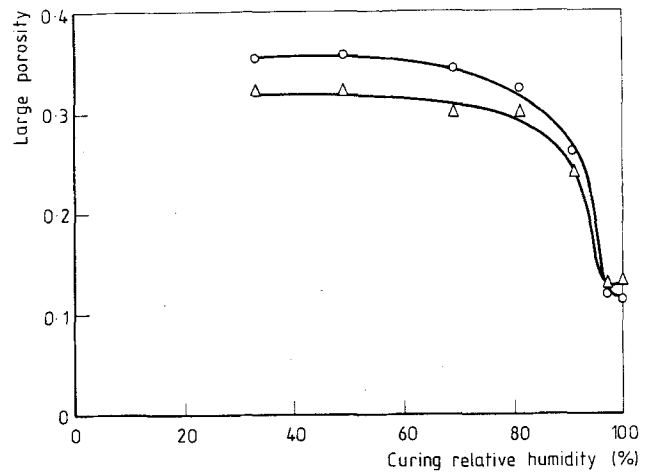


Fig. 8 Large porosity (pore width > 37 nm) against curing relative humidity: (Δ) 14 days, (\circ) 90 days.

3.3.5 Large porosity

Large porosity is plotted against the relative humidity whilst curing in Fig 8. It can be seen that the large porosity reduces only with curing at relative humidities above 81%. The volumes of large pores obtained with curing below 81% r.h. were about three times higher than those obtained at or near saturated curing conditions. This difference is thought to be due to a combination of hydration differences and a coarsening of the pore structure with drying [1,9,14]. A reduction in large porosity with age is observed only at humidities higher than 95%.

The high value of large porosity observed with curing at low relative humidities would be associated with significantly increased rates of diffusion [9,14] and could thereby adversely affect durability.

4. CONCLUDING REMARKS

The relative humidity of curing has a major effect on the rate of hydration of the four main phases of OPC; each phase reacts more slowly as the humidity of the curing environment drops. This is particularly evident in the range 97 to 70% r.h. and is consistent with other data on OPC [11]. The present experimental results are in broad agreement with an earlier study [2] suggesting that hydration is significantly restricted when the vapour pressure in the capillary pores falls below 80% of saturation. All of the results indicate that the amount of water in the capillary structure of the paste is important for hydration to proceed. The measurements of calcium hydroxide and initial methanol adsorption confirmed the dependence of hydration on the relative humidity.

The present investigation has shown that the initial adsorption could be regarded as an indicator of hydration only at curing humidities above 60% r.h. (statistically 60.7% r.h. with 95% confidence limits of $\pm 5.7\%$ r.h.). At these humidities it can provide a measure of gel surface area. The relative volumes of pores smaller than 4 nm and smaller than 37 nm

decrease with a reduction in the relative humidity due to the effects of drying and reduced hydration. The reduction in the volume of small pores due to drying was accompanied by a corresponding increase in the volume of large pores. The high porosity values observed at relative humidities below 80% for pores wider than 37 nm are thought to be of practical significance, since they could adversely affect the durability of *in situ* concrete. This effect would be greatest in the surface regions where the concrete is expected to provide protective cover to any steel reinforcement and the underlying concrete. Such ideas are consistent with a previous investigation of the microstructure and diffusion property gradients observed in drying cement paste [1].

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