Reply to 'Comments "On the factors affecting strength of Portland cement"'

We thank Alford *et al.* for their interesting comments on our recent paper [1]. These comments are most instructive, in that they highlight some important misunderstandings of the model of Portland cement paste, proposed earlier [2], for which direct microstructural evidence was obtained [3], upon which our work was based. In view of this, we will provide a summary of the evidence for the model, although it is important first to examine the comments made as set out by Alford *et al.*

Their quotation of our first conclusion should be read in its context, namely the Introduction and other conclusions. In this context, it can be seen that the 15% increase in flexural strength found upon removal of air voids [1] is not significant when compared to the 500% increase claimed originally for the polymer modified "MDF" cement [4].

Alford *et al.* quote the work of various authors, indicating that air voids can, in some circumstances, be considered simply as an addition to the total porosity remaining in originally water-filled spaces. In support of this they quote the results of Wright [5], a study of the effect of air entrainment on the compressive strength of concrete. Two points should be made about this figure (Fig. 1 of Alford *et al.*).

1. The air content is expressed as a percentage of the volume of *concrete*, and not of the cement paste fraction of the concrete. If allowance is made for the paste (i.e. cement + water) only taking up about 22% of the volume of the concrete mixes used, the abscissa of this figure should be multiplied by about 5. It is then clear that the (porosity) effect of a few per cent of air is even less (a few per cent) than predicted by the Dugdale model [1]. In connection with this, it is relevant to note that such work as quoted above has been carried out on concrete mixes of water/cement ratios of 0.45 or more [5, 6]; far from being designed to "give the impression that air is not significant", as suggested by Alford *et al.*, our use of a w/c ratio of 0.3 should emphasize this effect.

2. Wright [5] said of the original of this figure, which also compared the effects of deliberately and accidentally entrained air " . . .this shows that the effect on strength is materially the same whether the air is entrained intentionally in the form of numerous minute bubbles, or occurs unintentionally in the form of comparatively large irregular voids". This is not in agreement with either the Dugdale or Griffith approach, and indicates that results obtained on concrete, which contains a large quantity of aggregate, are not relevant to the present discussion.

The above points also centre around strength in compression, which is a complex stress system, and may not be appropriate to tensile failure mechanisms.

The next point involves the pressure compaction of cement to produce higher flexural strength. It is important here to differentiate between attempts to remove large volumes of air in order to increase the packing density of the cement [7, 8], in which case the w/c ratio is kept very low to prevent the build-up of undue hydrostatic pressure, and attempts to remove small volumes of air from pastes of plastic or fluid consistency to eliminate gross flaws [1]. In the latter case, pressure compaction would not lead to significant decrease in porosity because the small volume of air would remain entrapped by surface tension.

Kendall *et al.* [9] have also illustrated the difficulty in compacting plain cement crumbs due to the friction between the particles; application of a pressure of 10 MPa only reduced air content of a w/c 0.19 crumb by about half [9].

The illustration of the effect of air content on flexural strength underlines another problem in the testing of Portland cement pastes, that of drying cracking. This has been well documented [10, 11] and all our work was carried out under water to avoid this problem. Drying of plain cement pastes produces large tensile shrinking stresses on the surface of the specimens, leading to surface cracking. This appears to be the reason for the very low flexural strength (10 MPa) quoted by Alford *et al.* even when all air had been excluded from a mix of w/c 0.14.

The different effects of drying upon plain and polymer-containing mixes were noted in our paper [1] and are considered in more detail elsewhere [12].

Fig. 2 of Alford's Comments shows considerable scatter, and it is not immediately obvious that the effect of the air bubbles is anything more than a reduction in the cross-sectional area of the specimens. It is known that "assiduous vibration" leads to segregation of cement pastes [6] and hence an unexpectedly high increase in packing density, perhaps leading to the one high strength of 35 MPa in the figure. The results of other workers [13–15]

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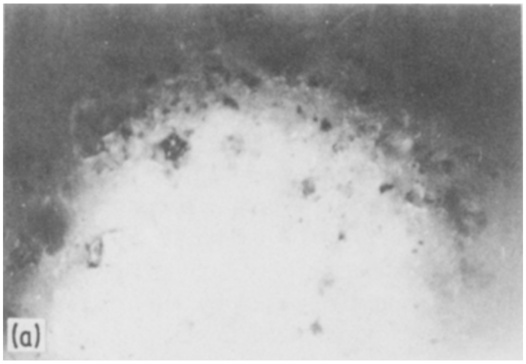

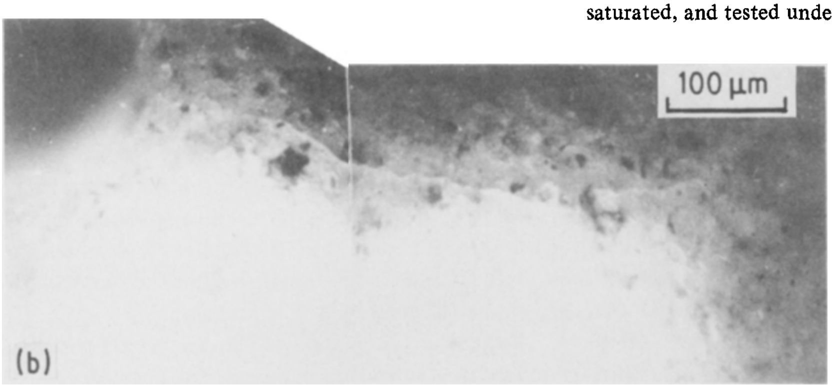

Figure 1 Subcritical crack growth in a notched three-point bend specimen viewed under diffuse optical illumination [3], (a) prior to loading, (b) at 95% of the final fracture loading. The tip of the notch is in the top left-hand corner, tensile stress direction is approximately vertical. Specimen saturated, and tested under water.

refer to concretes in which the paste fraction has been strengthened by incorporation of finely divided (0.1 μm) silica, and should not be confused with normal cement pastes. Some plain mixtures of cement and water can indeed exhibit high strengths; it is likely that the pressed cements of Roy and Gouda [8] were free from "macro defects" and showed tensile (splitting) strengths in excess of 60 MPa. This is because the porosity had been considerably reduced.

We should point out here that there appears to be some misunderstanding of the term "intrinsic strength". The term does not refer to a ceiling value above which no cement preparation can rise, and confusion perhaps arose because Higgins and Bailey [2] only used one w/c ratio (0.3). We would expect w/c ratio to affect the intrinsic strength; a lower w/c ratio will lead to a higher intrinsic strength. In that w/c ratio of a mature paste is reflected in the overall porosity, it can be seen that a relationship may exist between intrinsic strength and intrinsic porosity [17].

Porosity in some systems, such as brittle ceramics, results from imperfect compaction because the ceramic must be made on a commercial scale [16]. However, in the case of hydraulic cements, where a large volume of liquid (water) is added to the powder, it is the volume ratio of solid to liquid which governs the packing density, and hence the initial porosity, from which the final *intrinsic* porosity, after hydration, derives.

Reiteration of the findings of Higgins and Bailey [2, 3] may serve to clear this confusion. Under very careful optical microscope examination, using a special diffuse illumination technique [3], it was found that a stable crack could form prior to failure, even in an unstable notched flexural specimen, at close to the failure load, and develop for up to about 1 mm in length prior to final collapse Fig. 1. This suggested that some yield phenomenon was present, and prompted the use of the Dugdale process zone model to explain the mechanical properties observed [2]. Further confirmation of this model was obtained when it was found that the value calculated for the critical crack opening displacement (COD) of 1 μm [2] agreed closely with those observed by optical microscopy, and was of the same size as the calcium silicate hydrate fibrils. From the relationship between process zone length and COD [18], the process zone is calculated to be about 1.7 mm, close to the stable crack length, noted above, of 1 mm. It was postulated that the yield was produced by the pulling apart of the fibrils, effectively "tying" the crack until they finally parted at a COD equal to their length.

Clearly even the Dugdale model provides a simplified description of the failure process, since it is well established that the structure is heterogeneous and there must be differences in the force–displacement relationships across the tied crack [12].

It is clear from the above that the intrinsic strength, far from being the "additional arbitrary constant" suggested by Alford *et al.*, was calculated from an extensive study of the fracture mechanics of the cement paste used [2].

Davidge [19] has independently suggested that an analysis more detailed than the Griffith equation is needed in the case of cement paste, particularly where subcritical crack growth is known to occur.

The most important difference between the Griffith and Dugdale approaches is very clearly illustrated by Fig. 3 of Alford *et al.* As we pointed out [1], there is little difference for a flaw size of 1 mm, but our paper was concerned with the air bubbles in an already well-compacted paste [2], in the region 0.1 to 1 mm, and the figure clearly shows that it is here where the significant differences between the two theories lie.

The remainder of the comments suggest ways in which flaws other than air bubbles might be produced. Such potential flaws will reduce strength according to the Dugdale equation. Indeed we have suggested [12] that large, stiff particles such as calcium hydroxide crystals may account for the small size effect observed in unnotched flexural specimens [1]. Furthermore, we pointed out that defects caused by inhomogeneous wetting or water distribution can be minimized by careful mixing and use of admixtures; even if large water-filled areas remained, these should be visible on polished sections of the hardened paste, and we clearly showed that this was not so.

In conclusion, we would say that:

1. the unmodified Griffith equation is an inadequate description of the fracture of Portland cement paste. What is required is not so much an economical analysis, as one which best describes and predicts the mechanical properties and "stimulates improved understanding" [19]. The Dugdale approach accounts quite accurately for the experimental observations;
2. further work must be concentrated on obtaining an understanding of the way in which strength and fracture mechanics relate to the intrinsic porosity;
3. our experimental evidence indicates that strength is controlled by the fibrillar or layer-like microstructure of the material, which leads to yielding phenomena, and hence a microstructurally controlled (intrinsic) strength level, dependent in particular upon w/c ratio;
4. there is no error in our paper.

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