MATTERS ARISING

Flexural strength of cements

BIRCHALL *ET AL.*[1] are to be congratulated on the improvements made in the flexural strength of cement, however, we question their scientific explanation which is given in terms of the removal of large size pores $\gtrsim 100\ \mu\text{m}$; it is postulated that these pores are simple strength controlling Griffith flaws. We have shown[2] that although notched specimens of ordinary cement paste tested in flexure seem to behave according to simple Griffith theory for specimens having a fixed beam depth, nevertheless, when the beam depth is altered different values are obtained for the fracture energy, R. In fact the apparent value of R increases with increasing specimen depth and R is not therefore behaving as a material constant, and a simple application of the Griffith equation is not acceptable. It is apparent from their conclusions that Birchall *et al.* have carried out measurements on beams of fixed overall depth. Note that in our experiments, specimens of differing size were cut from the same cured samples of cement and therefore the variation in R values could not result from changes in specimen microstructure from one sample to another. By extrapolation we deduced the behaviour of apparently sharp flaws in large cement samples and showed that the material can be regarded as intrinsically weak, for example, for a w/c ratio of 0.3 having an intrinsic strength of ~15 MPa, and that sharp flaws have an effective radius of curvature of ~0.5 cm; therefore flaws $\lesssim 0.5$ cm in size will have a comparatively small effect on strength.

To improve strength it is necessary to increase the intrinsic strength by increasing the total number of effective chemical bonds per unit area of the material for example by reducing the total amount of unfilled space in the material, that is increase density. Birchall *et al.* quote a value for elastic modulus of 40 GPa for improved (MDF) cement—about twice that of OPC which suggests that its basic structural properties have been changed. We conclude therefore that it is a little misleading to attribute the strength increase solely to the elimination of large flaws and that the high strength has been achieved by a reduction in w/c ratio, good packing, compaction and drying out, all of which are expected to increase strength. The resulting MDF cement, although intrinsically stronger, is sensitive to flaws and will need to be free of macroscopic flaws to achieve the higher strengths; for example a 1-mm flaw will reduce the strength of MDF cement by a factor of 3, whereas a similar size flaw in ordinary Portland cement $w/c = 0.3$ will only reduce the strength by a factor of 1.6. Therefore, flaws must be eliminated during processing. However, as discussed above, simply eliminating flaws from an ordinary cement paste would not result in strengths as high as those quoted for the MDF cement.

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2. Higgins, D. D. & Bailey, J. E. *J. mater. Sci.* **11**, 1995–2003 (1976).

BIRCHALL *ET AL.*[1] have shown that the flexural strength of a Portland cement paste can be increased to ~65 MPa. They termed the modified paste as "macro-defect-free" (MDF) paste and attributed the improvement to the removal of macro-defects. However, this interpretation may be queried.

Birchall *et al.* have observed that the flexural strength data of both the MDF paste and the ordinary Portland cement paste could be fitted to the Griffith equation.

$$\sigma = (ER/\Pi C)^{1/2}$$

where "tensile cracking stress (σ) is related to an effective critical crack length (C) which may be a pore; Young's modulus (E) and fracture surface energy (R) being taken as material constants". They found that E and R are 20 GPa and 19 J m^{-2} for an ordinary Portland cement paste and 40 GPa and 30 J m^{-2} for the MDF paste even though both the pastes have very similar porosities.

It appears that both the material constants E and R are so dependent on the pore size distributions that their product could be altered by a factor of 3. In that case one may wonder how the Griffith equation could be applied to these pastes. This uncertainty has been further emphasised in their Fig. 3 which shows that the MDF paste has higher strengths than the ordinary Portland cement paste even when both pastes have similar sized critical flaws. More probably Birchall *et al.* have altered the nature of the paste altogether by using rheological aids such as plasticizers and superplasticizers, which are generally organic products of some chain lengths; some even contain organic polymers. The addition of polymers to a cement paste increases its flexural strength as well as its flexural/compressive strength ratio from ~0.1 for a brittle failure to a higher value characteristic of a plastic failure. Note that the MDF paste has also a flexural/compressive strength ratio of 0.3 (65/200).

It will not be very difficult to ascertain experimentally if the nature of the paste has been modified in which case the observed improvement may have little to do with the removal of macro-defects.

Note added in proof: The patent application by Birchall *et al.*[2] shows that polymers have been used by them.

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2. Birchall, J. D., Howard, A. J. & Kendall, K. *European Patent Application* No. 80301909.

BIRCHALL *ET AL.* REPLY—Bailey, Higgins and Chatterji have raised interesting questions, some perhaps prompted by the lack of detail in our short paper[1]. We are aware of the detailed arguments relating to the fracture behaviour of cement paste and of the careful work by Bailey and Higgins on this. Our proposition is that, bearing in mind the heterogeneous and inconstant nature of cement paste, the Griffith criterion is an adequate explanation of the failure behaviour of the material. It has the advantage of predicting what steps should be taken to improve the material—the removal of macroscopic flaws—and our paper shows that this is demonstrably effective.

As Bailey and Higgins correctly point out, fracture tests on ordinary cement paste give a spread of values of R, the fracture energy, a parameter which appears to change significantly with test geometry and crack speed among other variables. We believe that these variations in R make it impossible by conventional experiments to distinguish the Griffith theory from more complex theories of fracture. The experimental scatter is too great. Essentially, what we have done is to extend the study into an unexplored range of flaw size, down to $10\ \mu\text{m}$, when the overall behaviour is seen to fit the Griffith theory satisfactorily.

It is suggested that the high value of elastic modulus (40 GPa) quoted in our paper for MDF cement indicates a higher number of bonds per unit area or a higher bond strength and a microstructure fundamentally different from that of normal paste. It is indeed implicit in our understanding of the mechanism of hydration and setting[2], that hydrate morphology will vary with the volume of space to be filled and hence with packing, and so on. However, a major point in our paper is that whereas elastic modulus is dominantly related to total porosity volume, the flexural strength is

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