Discussion

Comments on "The factors affecting strength of Portland cement"

The principal conclusion of a recent paper in this journal by Eden and Bailey [1] was that "removal of air bubble defects from conventionally prepared and compacted cement pastes does not result in significantly improved mechanical properties". This conclusion is false and must not be allowed to pass unchallenged.

Since 1897 [2], it has been known that the removal of air bubbles from cement mixes produces a substantial improvement in mechanical strength. So well established is this fact that it has been embodied in the standards for defining the mixing of cement slurries, "... ensure the removal of large entrapped air bubbles ..." [3]. Indeed, when air is deliberately entrained into cement mixes to produce lightweight, insulating or freeze–thaw resistant materials, the mechanical properties are known to deteriorate rapidly [4]. The whole purpose of densifying cement mixes by conventional compaction (i.e. by vibration, by mixing with additives, or by mechanical compression) is to increase strength by removing air and by eliminating packing defects (water inhomogeneities).

This note outlines evidence for the significant effect of air bubbles and other defects on the strength of Portland cement.

Feret [2] demonstrated that the compressive strength, σ_c, of cement products depended on the volume of air, V_a, in the mix according to the equation

$$\sigma_c \propto [V_c/(V_c + V_a + V_w)]^2, \qquad (1)$$

where V_c was the volume of cement and V_w the volume of water. Clearly, this equation shows the effect of air to be as significant as the effect of water. Thus, it is always possible to increase the volume of water in the mix to dominate the air and give the impression that air is not significant. Eden and Bailey appear to have fallen into this trap. Yet, from Equation 1, the air is significant to cement strength and becomes increasingly significant as the water volume is diminished.

Many results showing the dependence of compressive strength on air volume for cement products have been published [4–6]. Some are given in Fig. 1.

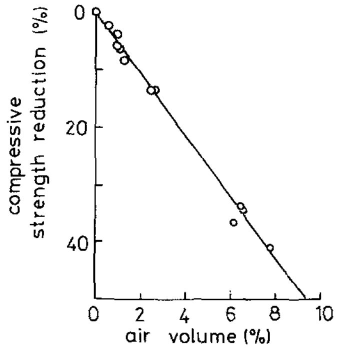

Figure 1 Effect of air bubbles on the compressive strength of concrete [6].

The fall in strength with air content is highly significant.

In order to demonstrate the same effect in bending failure, Portland cement pastes were compacted by mechanical pressure to make beams 100 mm long by 25 mm wide by 4 mm deep. Several previous investigators have noted the considerable improvement in mechanical properties of cement following mechanical compaction to remove air [7–9]. The experiment was designed to prevent water being squeezed out at the same time as the air. An ordinary Portland cement paste (water/cement ratio 0.14) was mixed to a damp crumble and pressed in a mould. One series of samples was pressed at a low pressure of 1 MPa which left a 30% volume of air in the cement compacts. The other series of specimens were pressed at a higher pressure of 10 MPa, just sufficient to remove all the air from the samples. After curing at 100% humidity for 1 day the samples were immersed in water for 1 week, dried and bend tested, giving the strengths shown in Table I. The effect of air was significant to the 99.9% confidence level by the t-test.

TABLE I The effect of air content in the mix on the bending strength of mechanically compressed cement paste (Portland cement, w/c = 0.14)

Air content (vol %)	Bend strength (MPa)
0	10.16 ± 0.97
30	6.39 ± 0.84

0022–2461/85 $03.00 + .12

There is little doubt that when large artificial air bubbles are introduced into a cement paste by cutting with a diamond saw, the bending strength of the material falls [10] in reasonable accord with the Griffith [11] equation of brittle fracture, the strength, σ_b, decreasing with the length, c, of the cavity according to the relation

$$\sigma_b = \left(\frac{ER}{\pi c}\right)^{1/2}. \tag{2}$$

Higgins and Bailey [12] presented results which were consistent with this view, and other studies [13, 14] have amply confirmed it. In other words, Feret's law is not the whole story. Not only does the volume of air in the mix have an influence; the size of the largest bubbles is also crucial.

To demonstrate this effect, Portland cement mixes (Snowcrete, Blue Circle) with 0.25 water/cement ratio and 1% sulphonated naphthalene condensate (Mighty 150) were vibrated to various extents before casting between polyester films. The bending strength of these compositions depended markedly on the length of the largest bubbles seen on the stressed surface of the samples (Fig. 2). Whereas stirred mixes gave bending strengths around 12 MPa, strengths exceeding 30 MPa could be attained by assiduous vibration. Such strengths were far greater than those achieved by Eden and Bailey [1], and have been noted by numbers of other workers [15–17]. We carried out additional experiments on MDF cements which contain no polymer, and have found bending strengths of 40 MPa, suggesting that removal of defects is, in itself, sufficient to raise the strength of cement pastes to high levels, much higher than the "intrinsic strength" of cement defined by Higgins and Bailey.

If the "intrinsic strength" of cement can be exceeded simply by removing defects from the material then it is a concept of dubious merit. Indeed, there appears to be little evidence to distinguish the Dugdale model used by Higgins and Bailey from the simpler Griffith theory. Fig. 3 compares the Griffith and Dugdale predictions for strength of cement and shows the typical scatter in the bending strength results. Note that the value of K_{IC} used to plot the Griffith curve was 0.6 MPa m$^{1/2}$. This is the maximum value *measured* by Higgins and Bailey, not a predicted value. The difference between the two theories is small in relation to the errors in the data. Therefore, there seems to be little point in discarding the simple Griffith argument for the more complex Dugdale model which requires an additional arbitrary constant, the "instrinsic strength", varying with compaction of the material. As Eden and Bailey point out, the advantage of the Griffith approach is its freedom "from any of the empirical constants or correction factors which have continually appeared in attempts to describe mechanical behaviour".

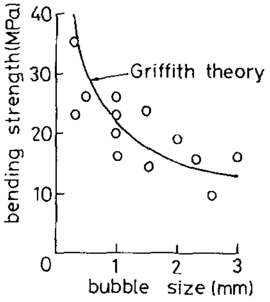

Figure 2 Influence of superplasticizer and vibration on the removal of large air bubbles, and the corresponding increase in bending strength.

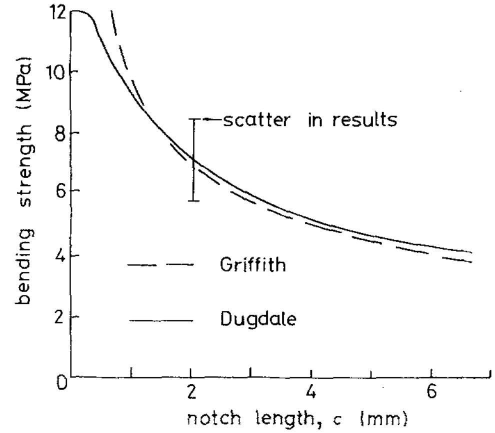

Figure 3 Similarity of the Griffith and Dugdale models describing the bending strength of notched cement paste.

It is evident from Equation 1 that air bubbles are not the only problem; the water in the mix also plays a large part in determining the strength of hydraulic cements. The volume of water is important from Feret's law. In addition, the homogeneity of the water distribution is influential because regions of the mix containing water but no cement grains appear as low-density areas or even as holes (packing defects) in the final product.

In general, strength results for cement products are consistent with the concept of a hierarchy of flaws. If air bubbles form the critical flaws then they will cause failure. Remove the air, and the packing defects become critical instead. However, this does not mean that any remaining air is insignificant, because removal of packing defects may make the air bubbles critical once again.

When all efforts were made to remove air bubbles and packing defects, it was found that there were no observable cavities exceeding 15 μm in the hardened material [10]. But the bending strength indicated a flaw size near 100 μm. Eden and Bailey state that there is yet "no microstructural explanation of this apparently constant flaw size". This is untrue. Birchall and co-workers [10, 14] noted that the residual cement grains were about 100 μm in length and that "grain interfaces dominated at this juncture". Similarly, Alford and Double [18] state that "below a certain pore size, other inhomogeneities (such as cleavage cracks within the cement particles themselves, or discontinuities at the cement particle/hydrate matrix) are acting as strength limiting flaws" or in Alford [19] "gel/clinker interfaces or gel/portlandite interfaces may play a dominant role in determining strength". It has been established that large grains of different elastic modulus to the matrix can cause local stress concentrations and may, therefore, act as flaws in cement or glass systems [20, 21]. In this connection, we have shown [14] that the addition of large, high-modulus grains to MDF cements reduced the bending strength systematically, and that sieving out the larger grains (above 45 μm) from a cement mix increased the bending strength by 30%.

1. The volume of air bubbles in a cement mix significantly reduces strength in accord with Feret's law.

2. The size of the largest air bubbles in a cement sample significantly affects strength in accord with Griffith's equation. The Dugdale model does not describe the results as economically as the Griffith equation.

3. Other defects are at least as important as air bubbles in dictating the strength of cement. Packing defects and large grains have been identified as significant sources of weakness. It is wrong to say that air bubbles are not significant merely because packing defects happen to be larger in a given experiment. This is the error in the paper by Eden and Bailey.

References

1. N. B. EDEN and J. E. BAILEY, *J. Mater. Sci.* **19** (1984) 150.
2. R. FERET, *Bull. Soc. Encour. Ind. Nat. Paris* **II** (1897) 1604.
3. ASTM Annual Standards Part 14.C31 (ASTM, Philadelphia, 1977) p. 11.
4. A. SHORT and W. KINNIBURGH, "Lightweight Concrete" (Applied Science, London, 1978).
5. A. M. NEVILLE, "Properties of Concrete" (Pitman, London 1977) p. 424.
6. P. J. F. WRIGHT, *Proc. Inst. Civ. Eng. Part I* **2** (1953) 337.
7. R. L'HERMITE and M. VALENTA, *Anals. Int. Tech. Batim,* **6** (1937) 23.
8. C. D. LAWERENCE, *Res. Notes, Cem. Concr. Assoc.* No. 19 (1969) 1.
9. D. M. ROY and G. R. GOUDA, *Cem. Concr. Res.* **5** (1975) 153.
10. J. D. BIRCHALL, A. J. HOWARD and K. KENDALL *Nature* **289** (1981) 388.
11. A. A. GRIFFITH, *Phil. Trans. Roy. Soc. Lond.* **A221** (1920) 163.
12. D. D. HIGGINS and J. E. BAILEY, *J. Mater. Sci.* **11** (1976) 1995.
13. J. D. BIRCHALL, A. J. HOWARD and K. KENDALL, *Proc. Brit. Ceram. Soc.* **32** (1982) 25.
14. K. KENDALL, A. J. HOWARD and J. D. BIRCHALL, "Technology in the 1990s Developments in Hydraulic Cements" (Royal Society, London 1983) p. 139.
15. L. HJORTH, *Phil. Trans. Roy. Soc. Lond.* **A310** (1983) 167.
16. H. H. BACHE, 2nd International Conference Superplasticizers in Concrete, June (1981) Ottawa (Department of Energy, Ottawa, 1981).
17. L. HJORTH, Nordic Concrete Research Publication No. 1 (Nordic Concrete Foundation, Oslo 1982) p. 901.
18. N. McN. ALFORD and D. D. DOUBLE, "Adsorption at the gas–solid and liquid–liquid interface" edited by J. Rouquerol and K. S. W. Sing (Elsevier, Amsterdam, 1982) p. 259.
19. N. McN. ALFORD, *Cem. Concr. Res.* **11** (1981) 605.
20. J. N. GOODIER, *J. Appl. Mech.* **1** (1933) 39.
21. A. K. KHAUND and P. S. NICHOLSON, *J. Mater. Sci.* **15** (1980) 177.

Received 27 February
and accepted 10 April 1984

N. McN. ALFORD
J. D. BIRCHALL
A. J. HOWARD
K. KENDALL
ICI New Science Group,
The Heath,
Runcorn,
Cheshire,
UK