The Relation between Porosity, Microstructure and Strength, and the Approach to Advanced Cement-Based Materials [and Discussion]

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The relation between porosity, microstructure and strength, and the approach to advanced cement-based materials

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[Plate 1]

A theory is formulated to connect the strength of cement paste with its porosity. The theory shows that bending strength is largely dictated by the length of the largest pores, as in the Griffith (1920) model, but there is also an influence of the volume of porosity, which affects toughness through changing elastic modulus and fracture energy. Verification of this theory was achieved by observing the large pores in cement, and then relating bending strength to the measured defect length, modulus and fracture energy. The argument was proved by developing processes to remove the large pores from cement pastes, thereby raising the bending strength to 70 MPa. Further removal of colloidal pores gave a bending strength of 150 MPa and compression strength up to 300 MPa with improved toughness. Re-introduction of controlled pores into these macro-defect-free (MDF) cements allowed Feret's law (1897) to be explained.

1. Introduction

The purpose of this paper is to define, both theoretically and experimentally, the connection between the strength and porosity of hardened hydraulic cement pastes. Although this connection has been suggested many times previously, two outstanding problems have remained. First, there is the difficulty that ordinary cements are remarkably porous, an embarrassment that has traditionally been alleviated by polymer impregnation, by water reduction, or by high pressure compaction. Second, there is the lack of a theory relating cement strength to porosity; mathematical descriptions of cement strength have been empirically based.

Here we present a fundamental explanation of the relation between cement strength and porosity, starting from the Griffith (1920) model of brittle fracture, and postulating that cements contain two types of pore; colloidal pores, submicrometre in size, and 'crack-like' pores some millimetres in length. It is shown that the colloidal pores influence the elastic modulus and fracture energy of the cement, whereas the 'crack-like' pores initiate fracture and thus determine failure.

The experimental advance was in devising new processes for controlling the porosity of cement products. Addition of water-soluble polymer to the wet cement composition improved the plasticity of the slurry, allowing the material to be mixed in a novel way, which removed large pores. A further cold sintering step also permitted the colloidal porosity to be reduced. By studying these new cement products of controlled porosity, the theory connecting cement strength and porosity has been verified. The benefits of this approach were twofold. In the first place, Feret's (1897) original law of cement strength was explained and extended. Second, it has been demonstrated that strong hydraulic cements can be made by practical methods, thereby allowing them to compete with metals, plastics and ceramics in some applications.

2. The problem of weak cement products

Considering its ubiquity as an engineering material, conventional hardened cement is extremely weak. This weakness may be illustrated by contrasting the strength properties of hardened Portland cement paste with those of polymethylmethacrylate, sintered alumina, and steel (table 1). In fact, cement compares in strength to dry spaghetti. Sheets 100 mm square and 3 mm thick can be readily broken by bending between the fingers or by dropping from a few centimetres onto a hard surface.

TABLE 1. STRENGTH PROPERTIES OF HARDENED PORTLAND CEMENT PASTE COMPARED WITH
POLYMETHYLMETHACRYLATE (PMMA), SINTERED ALUMINA, AND STEEL

	cement	PMMA	alumina	steel
compressive strength/MPa	40	100	3000	500
flexural strength/MPa	7	130	500	700
fracture energy/($J\,m^{-2}$)	15	1000	30	10^5

That this weakness is associated with porosity may be proved by polymer impregnation of the cement. Organic monomer is soaked into a dry hardened cement and then polymerized (Swamy 1979). This leads to a doubling of modulus and quadrupling of tensile and compressive strengths, albeit from low values of 3 and 30 MPa respectively. The problem with this approach is the large volume, around 25 %, of organic material needed to fill the pores.

A more economical way of reducing cement porosity is to use less water in the mix. This can be achieved chemically by adding 1 % (by mass of cement) of surfactants such as sulphonated naphthalene or melamine formaldehyde condensates, which disperse the cement grains and allow the water content to be reduced from 0.39 to 0.26 w/c at equivalent rheology, to increase compressive strength from 41 to 74 MPa (Hattori 1978). Vibration has a similar effect on the dispersion of cement grains and allows comparable water reductions and strength improvements.

Alternatively, water can be squeezed out of the mix by applying pressure to the cement grains, pushing them closer together. For example, pressing cement paste in a hydraulic press at 10 MPa raises the bending strength from 10 to 20 MPa. Compaction at several hundred MPa can reduce porosity to 2 volume %, raising the bending strength to 60 MPa and compressive strength to 655 MPa (L'Hermite & Valenta 1937; Lawrence 1969; Roy & Gouda 1975). The difficulty with such brute methods is that only small articles of simple shape can be produced.

Having reviewed these experimental problems of porosity and strength, it is now necessary to study the theory.

3. The theoretical problem

The idea that porosity should determine strength is an old one; Lucretius wrote in the first century B.C. 'The more vacuum a thing contains within it, the more readily it yields...'. Early empirical studies of cement supported this view by correlating compressive weakness with the amount of water in the wet cement mix, as in Feret's law (1897). Feret connected compressive strength σ_c with the volume V_c of cement, V_w of water and V_a of air by the equation

$$\sigma_c = A[V_c/(V_c + V_w + V_a)]^2, \tag{1}$$

where A was a constant. This equation embodied the hydraulic paradox that water was essential to fluidize the cement and to provide hydrate reaction products, yet the more water was added,

the weaker was the final hardened material. The strongest cements should be made with no water! (Abrams 1918).

Powers (1960) and Schiller (1958) explained this paradox by recognizing that the quantity of water in the mix controlled the volume porosity of the hard product. Since $1\,cm^3$ of Portland cement, on full hydration, converted to $2.2\,cm^3$ of hydrate, itself $28\,\%$ porous, it was clear that $1\,cm^3$ of water led to $0.513\,cm^3$ of porosity volume.
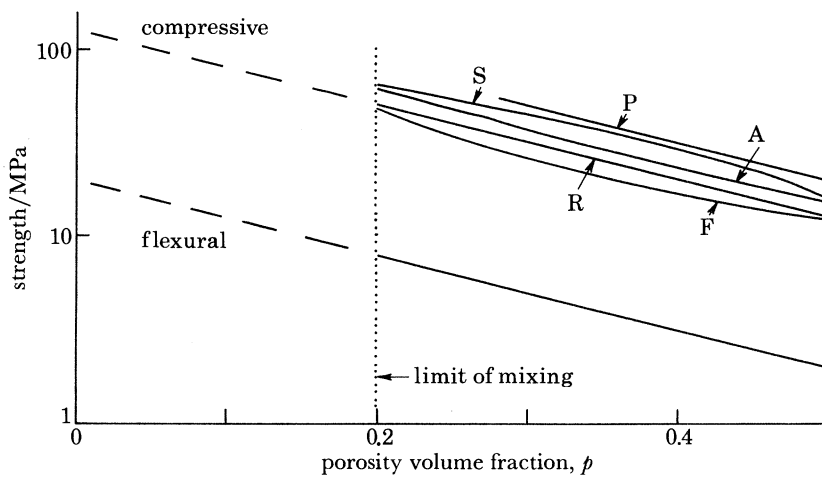

FIGURE 1. Empirical laws relating strength of cements to their volume porosity. (The compressive strength curves have been displaced vertically for clarity.) References: S, Schiller (1958); P, Powers (1960); A, Abrams (1918); R, Ryshkewitch (1953); F, Feret (1897).

Following this argument, it was the volume fraction of porosity p that caused strength to fall, and the several mathematical descriptions of cement strength could be plotted on a single graph (figure 1), which was a close approximation to Ryshkewitch's (1953) equation for the compressive strength of ceramics

$$\sigma_c = \sigma_0 \exp(-bp), \qquad (2)$$

where σ_0 was the strength at zero porosity and b was a constant. Bending strength also followed this curve but was less than compressive strength by a factor of about seven.

In practice, porosities less than 0.2 are not attainable by merely mixing at such a low w/c ratio, but the curves may be extrapolated to zero porosity to estimate the intrinsic strength of cement. The conclusion is that ordinary cements are intrinsically weak with a maximum compressive strength of about $130\,MPa$ and flexural strength of around $20\,MPa$.

The above logic, relating strength to *volume* porosity is well accepted in the literature, but does not fit experimental observations. Cements made by different processes can exhibit strengths that do not lie on the curves of figure 1. For example, cement that was frozen immediately after mixing, then thawed and hardened, gave a porosity volume increase of $3\,\%$, but a strength decrease of $60\,\%$. Birchall *et al.* (1981 *a*) showed that cement compositions could display the same volume of porosity but flexural strengths that varied by a factor of six.

The reason for this is that there is a particular kind of pore that has an enormous weakening effect. As Vitruvius observed 'Cracks make...bricks weak'. These crack-like pores need contribute very little to the total volume of pores. It is their length that is the important parameter, as Griffith (1920) demonstrated from the first law of thermodynamics. Tensile, or bending

strength of brittle materials of Young modulus E and fracture energy R depend on the length c of a crack-like pore according to the equation

$$\sigma = (ER/\pi c)^{\frac{1}{2}}. \tag{3}$$

Application of equation (3) to cement products has been controversial. Kaplan (1961) concluded that it described the flexural fracture of notched concrete beams, but this was denied by Wright & Byrne (1964), who found that concrete was insensitive to notches. Other authors had difficulties with test methods (Kesler *et al.* 1972; Swartz *et al.* 1978) and some found that resistance to cracking varied with crack length and specimen size (Higgins & Bailey 1976; Brown 1972; Hillemeier & Hilsdorf 1977). Mindess (1981) has reviewed this issue.

For hardened cement pastes, Birchall *et al.* (1982 a) showed that the Griffith theory did describe flexural strength of notched beams, but only for notches exceeding the natural flaw size, around 1 mm, in the material. Moreover, they pointed out that the key question was how to reconcile equation (2), which predicts a *volume* porosity dependence of strength and intrinsic weakness, with equation 3, which gives a pore *length* dependence and an apparently limitless rise in strength as pore length is reduced. This question was resolved by formulating a theory that explained both the pore volume and the pore size effects.

4. THEORY OF STRENGTH AND POROSITY

The theory was based on the observation of two kinds of pore in hardened cement paste (figure 2, plate 1). There were colloidal pores trapped between the hydrate particles, at 2 nm in size too small to initiate cracking, but of sufficient volume to reduce the elastic modulus and fracture energy of the cement. Then there were crack-like pores some millimetres in length, long enough to initiate cracks at low stress levels, but contributing only about 10 % to the total volume fraction of porosity. Having recognized these two distinct types of pore, it was possible to imagine an ideal porous solid with two *independent* populations of pore; one population with volume p but no length; the other with length $2c$ but no volume (figure 3 a).

A model of such a perfect material was porous silica glass (provided by Dr C. Howard, Pilkington Brothers) containing 48 % by volume of pores 10 nm in size, but no long cracks. Such a material was found to be strong, with a flexural strength of 60 MPa, proving that a large *volume* of pores does not necessarily cause low strength. However, its Young modulus E and fracture energy R were found to be reduced by the volume of pores, as shown by the results of figure 3 b. When a crack-like pore of length 1 mm was cut into the porous glass with a saw, the bending strength fell dramatically to 5 MPa, reminiscent of cement strength, and the results were found to follow the Griffith (1920) curve (figure 3 c). If the porosity volume of the porous silica was reduced by sintering, then the flexural strength again followed the Griffith relation when notched, but the curve was shifted to a higher level, because of the increased modulus and fracture energy.

To describe this behaviour mathematically, the Griffith energy balance approach was applied to the material (figure 3 a) with the microporous glass treated as a continuum of the Young modulus (Hansen 1965; Helmuth & Turk 1966)

$$E = E_0(1-p)^3 \tag{4}$$

and fracture energy (Rice *et al.* 1978)
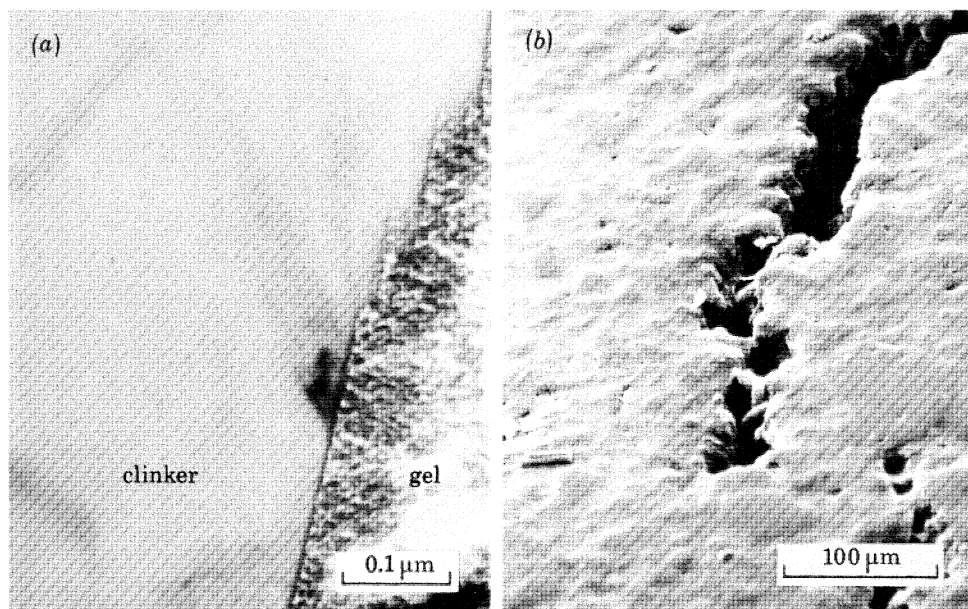
$$R = R_0 \exp(-kp), \tag{5}$$

FIGURE 2. (*a*) Porous colloidal hydrate gel formed on an ion-thinned tricalcium silicate crystal (courtesy of Dr G. W. Groves). (*b*) Crack-like pore in polished cement paste; the cement grain residues can be seen protruding from the gel matrix.
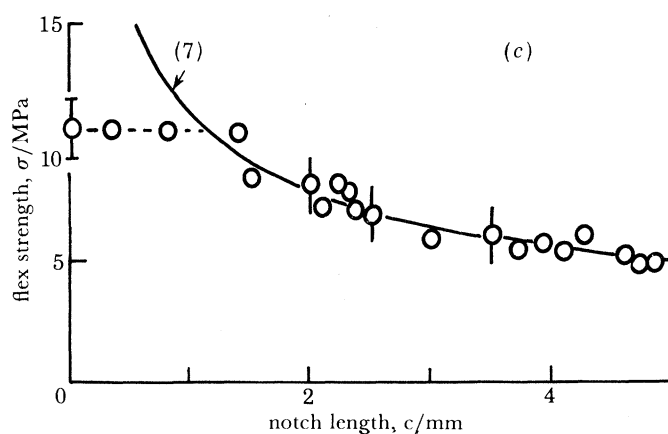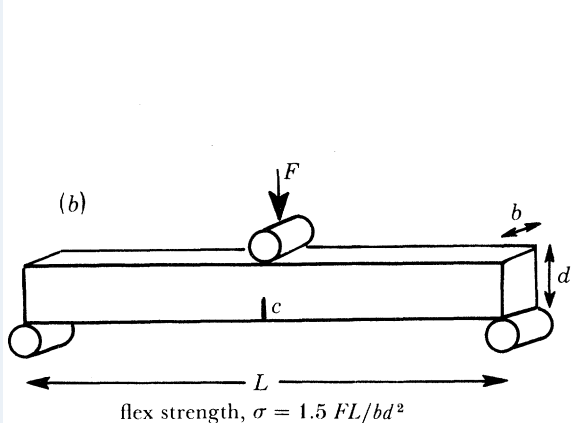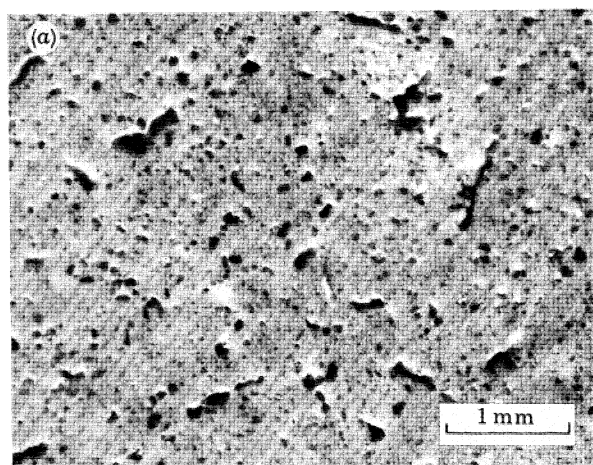
flex strength, $\sigma = 1.5\,FL/bd^2$

FIGURE 4. (*a*) Optical micrograph of a polished sample of Portland cement paste showing the large voids decorated black. (*b*) The flex testing arrangement. (*c*) Results for hardened Portland cement, w/c = 0.22. The curve derived from equation (7) is drawn as a solid line.

where E_0 and R_0 were the values at zero porosity volume. By calculating the energy U associated with a crack of length $2c$ (equivalent to an edge crack of length c) in an infinite sheet under a tensile stress σ, and applying the condition for energy conservation (given in Lawn & Wilshaw 1975, for example)

$$\mathrm{d}U/\mathrm{d}c = 0, \tag{6}$$

the criterion for crack extension was found to be

$$\sigma = \left[\frac{E_0 R_0 (1-p)^3 \exp(-kp)}{\pi c} \right]^{\frac{1}{2}}. \tag{7}$$

This equation was plotted in figure $3c$ to compare with the experimental results for porous silica glass, and was found to give reasonable agreement.
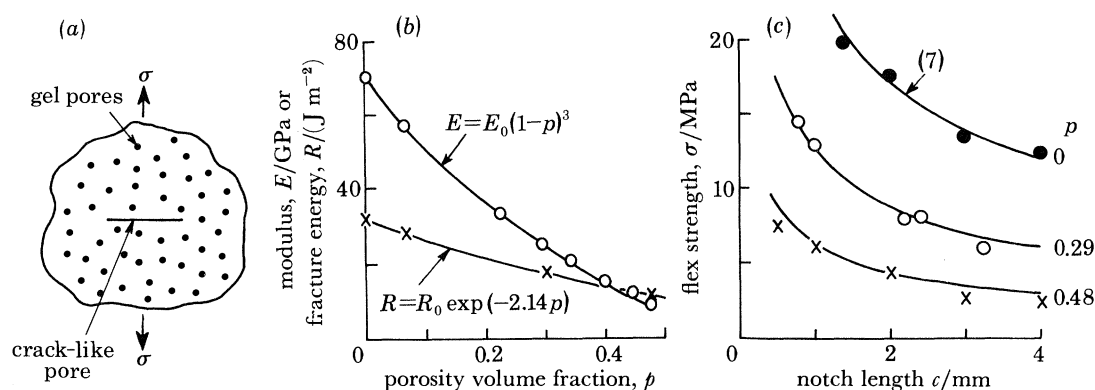

FIGURE 3. (a) Theoretical model showing two types of pore; the small gel pores of volume fraction p, and a long crack-like pore of length $2c$ causing fracture. (b) Variation of Young modulus E and fracture energy R with volume fraction of pores in porous silica glass. (c) Flexural strength as a function of notch length and pore volume for porous silica glass. This graph shows good agreement with equation (7), which is plotted as solid lines.

Equation (7), derived from thermodynamic considerations, is interesting for several reasons. It demonstrates that strength is a function of two independent variables, volume of porosity and length of a crack-like pore. Thus, the plotting of strength against pore volume p, a common error in the cement literature, is not sensible unless pore length c remains constant. Nor can strength be plotted against crack length unless porosity volume is constant. However, the main benefit of equation (7) is that it reveals two methods for strengthening porous materials such as hardened cement; the reduction of the volume of pores from 30 % to zero increases strength by a factor 2 (figure $3c$); but the reduction in length of crack-like pores from 1 mm to 0.01 mm increases strength by a factor of 10. These predictions were tested experimentally on cement.

5. EXPERIMENTAL STUDY OF LARGE CRACK-LIKE PORES

It is perhaps surprising that the long crack-like pores in hardened cement have not been much studied. One possible reason for this is that mercury intrusion porosimetry, the conventional method adopted by many workers (Winslow & Diamond 1970; Diamond 1973; Beaudoin 1979), does not give a correct description of large pores in cement. Several samples of cement paste were sectioned, polished, and decorated with carbon black to reveal the large pores under optical microscopy (figure $4a$, plate 1). Measurements of several large pores gave a mean maximum pore

length of 0.83 ± 0.17 mm and a volume fraction of around 10 % of pores exceeding $15\,\mu$m in length. When tested by mercury porosimetry, the volume of large pores was seriously under-estimated, in one case by a factor 44 (table 2). The conclusion was that the large pores in cement were not detected by mercury, either because they were closed pores, or because the pores had small entrances and so were registered as pores of small size (Birchall *et al.* 1981 *a*). This conclusion has since been verified by others (Alford & Rahman 1981; Alford & Double 1982).
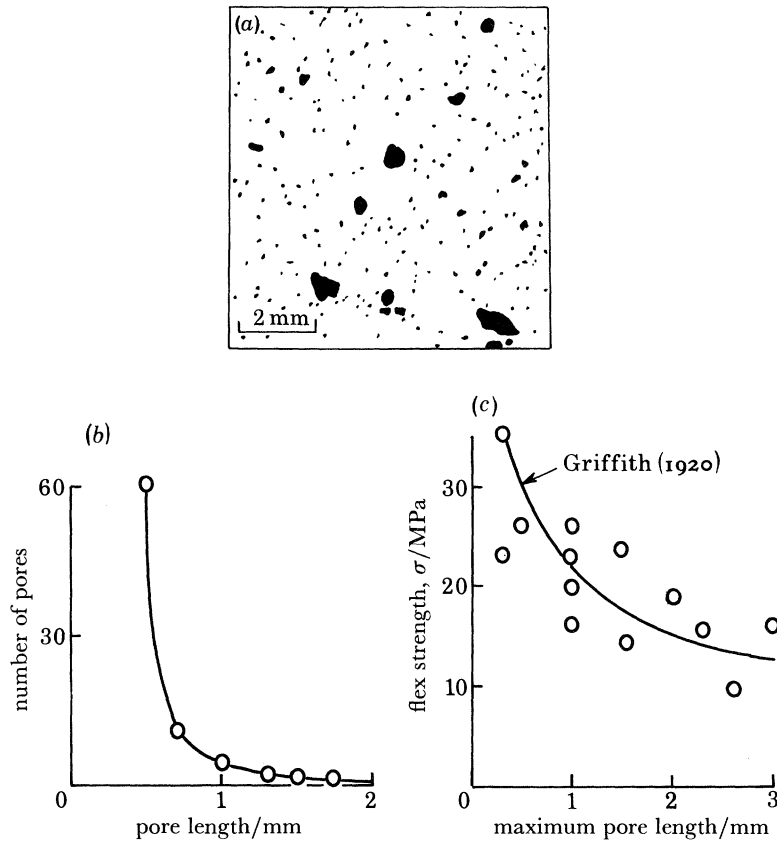

FIGURE 5. (*a*) Typical magiscan trace showing the distribution of flaws in a white cement surface (Secar 71, Lafarge, w/c = 0.35) cast against a smooth surface. (*b*) Magiscan plot of pore lengths over surface. (*c*) Bending strength dependence on length of natural flaws in white Portland cement (Snowcrete, Blue Circle, w/c = 0.25). The solid curve is drawn from Griffith's (1920) theory.

TABLE 2. VOLUME FRACTION OF LARGE PORES, GREATER THAN $15\,\mu$m IN LENGTH, MEASURED IN CEMENT SAMPLES BY TWO DIFFERENT METHODS; MERCURY POROSIMETRY, AND QUANTITATIVE MICROSCOPY

	volume fraction of pores longer than $15\,\mu$m	
sample number	mercury porosimetry	quantitative microscopy
1	0.0028	0.048
2	0.0011	0.048
3	0.0063	0.065
4	0.0097	0.114

Bending tests on notched cement samples were undertaken to see whether the long crack-like pores could be detected mechanically. A typical experimental arrangement is illustrated in figure 4*b*, which shows a cast block of Portland cement paste, notched with a diamond saw, and

loaded in flexure. For notches less than 1 mm in length, the flexural strength was not reduced (figure 5*c*), whereas notches longer than 1 mm caused the strength to diminish along the Griffith curve. Thus the natural crack-like pores in ordinary cement are about 1 mm long (Birchall *et al.* 1981*a*).

In bending tests, the surface pores are dominant, but they cannot easily be seen on ordinary cement surfaces. To enhance pore visibility, white cement was cast against an optically smooth surface such as polyester film. After hardening, the film was removed and the cement surface was seen to be mottled when viewed in reflected light, the dark areas proved to be pores when probed with a needle. The size distribution of these pores was determined by image analysis and it was discovered that approximately 0.1 area fraction of the surface consisted of pores exceeding 0.25 mm in size, some up to 2 mm in length (figure 5). The strength of the samples was found to depend on the measured pore length in the stressed region, roughly fitting the Griffith (1920) theory. It was concluded that ordinary cast cement contains pores some millimetres in length, and that these pores limit the strength in bending. Alford (1981) has verified these conclusions.

The removal of these large natural pores from cements should result in a significant improvement in cement strength, even for materials of high volume porosity.

6. ORIGIN AND REMOVAL OF LONG PORES

Long pores in hardened cement originate from the hydraulic process. The conventional process of mixing cement powder with water and casting into a mould leaves large air bubbles and packing defects in the final product. Air bubbles cannot fill with hydrate gel because there is no water to transport the material. Packing defects contain water but insufficient cement grains to fill the space with gel, thus leaving a gap in the dried product.

Two observations suffice to show why the ordinary process leads to such voids. First, consider the packing of the dry cement grains. A bag of cement contains only 30 % volume fraction of cement; the rest is air. This observation shows that the cement grains are flocculated, stuck to each other to give a bonded open structure with large voids and a distinct yield point. Wetting the grains reduces the flocculation, but not to zero. Next, consider applying a mechanical force to the wet cement mix, as in the apparatus of figure 6*a*. Cement paste is often said to be plastic or 'Bingham' in its flow behaviour (Newman 1966; Helmuth 1980), but it differs from plasticine, which fits the mathematical theory of plasticity for this geometry (Hill 1950)

$$P = \tfrac{1}{4}Y(3+w/h), \tag{8}$$

where P is the pressure applied to the ram cylinder of diameter w acting on a thickness h of plastic material (figure 6*b*). Instead, cement paste gave a rapid increase in resistance P as the gap h was reduced, and this was explained by frictional interaction between cement grains sliding across each other, giving

$$P = \tfrac{1}{4}(Y+\mu P)(3+w/h), \tag{9}$$

where μ was the friction coefficient as in the behaviour of soils (Bolton 1979). Thus there are two forces acting on grains, leading to large pores; the attractive force between grains, described by the yield pressure Y, and the frictional force, described by μ, which prevents the grains from moving into their most close packed positions when mixed.

Addition of water to cement, or vibration, or use of superplasticizers, reduced the yield pressure but not the friction coefficient. However, addition of water-soluble polymers such as hydroxypropylmethylcellulose (HPMC), poly(acrylamide), or poly(vinylalcohol/acetate)

reduced both yield pressure and friction (figure 6 *c*). Such mixtures did behave as plastic bodies and could be worked by rolling, extrusion, and dough mixing (Downing *et al.* 1976; Birchall *et al.* 1981 *b–d*, 1982 *b*).
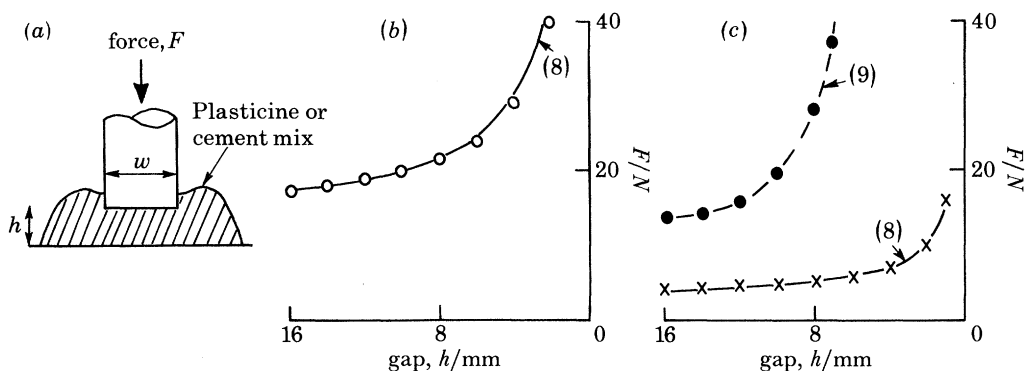

FIGURE 6. (*a*) Apparatus for determining the plasticity of pastes. A cylindrical ram was pressed into the paste at constant speed and the force measured as function of gap *h*. (*b*) Graph to show that results for Plasticine (○) fit the plastic theory (solid line drawn from equation 8). (*c*) Ordinary cement paste results (●) do not fit the plastic theory but fit equation (9) (dashed line), which assumes a friction coefficient between the grains ($\mu = 0.7$).When 3% of poly(vinylalcohol/acetate) was added the results (crosses) fitted equation 8 (solid line).
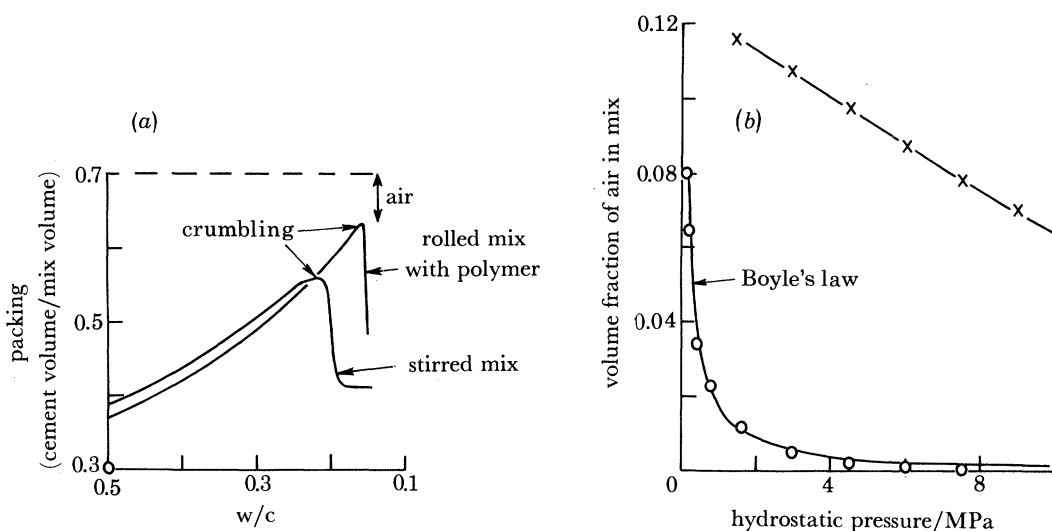

FIGURE 7. (*a*) Graph to show that increasing the packing of cement grains in a stirred mix by reducing water is limited by crumbling of the mix at about 0.22 w/c. But when polymer was added and the mix was rolled, the mix did not crumble until 0.15 liquid/cement ratio. The origin is the packing of dry cement powder. (*b*) Air in an ordinary cement/water mix (100/19) was not easily pressed out, but in a mix containing polymer (100/16/3HPMC), air was compressed according to Boyle's law. *Key*: crosses, cement/water mix results; circles, cement/water/polymer mix results.

The benefits of this dramatic change in rheology were shown in figure 7 *a*. Whereas ordinary stirring of a mixture of water and cement produced a maximum packing of 0.56 before crumbling occurred, roll-mixing of water, cement and polymer gave 0.63 packing. Both such mixes contained nearly 10 % by volume of air. But whereas the air was only compressed with difficulty out of the ordinary cement, it was readily compressed according to Boyle's law from the polymer mix, owing to lower friction. The air almost disappeared at 5 MPa pressure, giving a packing of 0.7 (figure 7 *b*).

It should be emphasized that polymer addition, by itself, did not result in good packing, nor high strength. In fact, merely adding polymer to a stirred mix at the same volume packing resulted in crumbling and low strength (table 3). The best results were obtained by polymer addition, dough mixing, and air removal. By these three operations, the microstructure of the hardened cement was much changed, with no pores greater than $15\,\mu m$ long when it was polished, stained with carbon black, and viewed in the optical microscope. For this reason, these new materials were called macro-defect-free (MDF) cements.
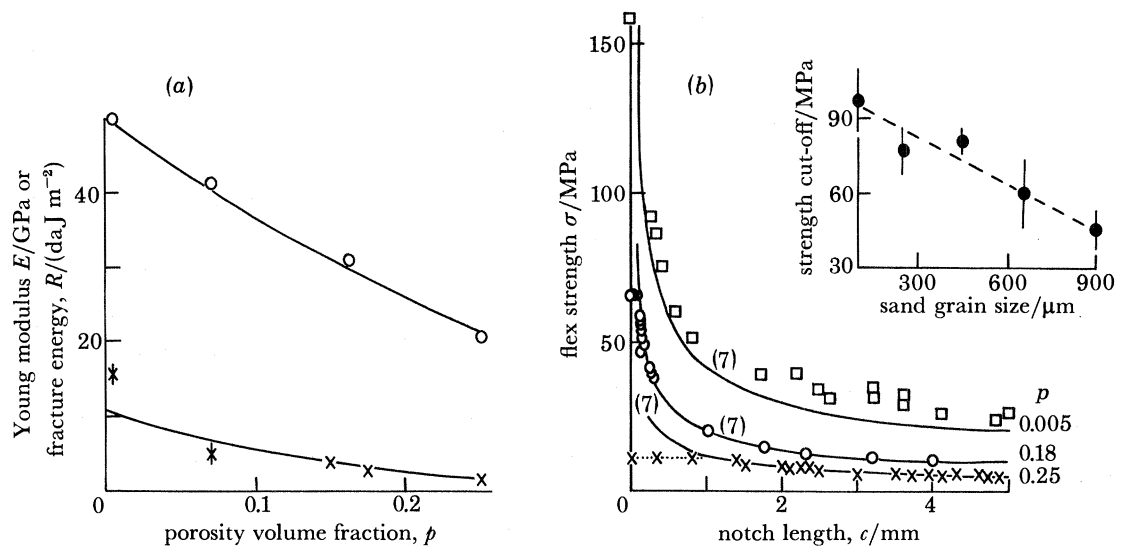

FIGURE 8. (a) Variation in Young modulus and fracture energy of cement with porosity p. (b) Flexural strength plotted against notch length for three different porosity cements compared with equation (7) (solid lines). Inset: change in the strength cut-off with grain size of sand particles sprinkled on the mix before pressing.

TABLE 3. RESULTS SHOWING THE THREE STEPS REQUIRED TO MAKE MDF CEMENT WITH CALCIUM ALUMINATE (SECAR 71, LAFARGE) AND POLYMER (CELACOL 15000 DS, CELANESE)

(Neither polymer nor pressure were in themselves sufficient to give high strength.)

mix	flex strength/MPa
control (100c/22w†, stirred, hand laid)	14 ± 2
control plus polymer (100c/18w/4p, stirred, hand laid)	1 (crumbly)
control plus pressure (2.5 MPa)	20 ± 5
control plus pressure (10 MPa)	25 ± 8
control, polymer and pressure (100c/18w/4p, 10 MPa)	27 ± 2
control, polymer plus dough mix (100c/18w/4p, twin-roll mill)	40 ± 2
control, polymer, dough mix, press set (100c/18w/4p, roll, pressure set at 5 MPa)	55 ± 3

† Note: c, cement; w, water; p, polymer.

When notched and tested in bending, MDF cement fitted equation (7) (figure 8b, middle line), but was now distinctly different from ordinary cast cement (figure 8b, bottom line). First, because less water was used and some air was removed, the volume porosity was reduced, so the strength results lay on a higher Griffith curve. Second, and more important, the results fitted the curve at smaller notch depths, down to 0.1 mm, because the large natural pores had been eliminated. Unnotched bending strength thus rose to 66 MPa. Although the visible pores were reduced far below the 0.1 mm level, the strength did not rise further. It was suggested that flaws other than

pores were becoming important at this stage. Significantly, the largest cement grains were around 0.1 mm diameter, so that elastic mismatch or poor grain bonding may have become significant. Placing sand grains of various sizes in the surface of a dough before pressing, progressively dropped the strength of the material (figure 8, inset).

7. ORIGIN AND REMOVAL OF COLLOIDAL PORES

The strength increases above were obtained by the removal of the long crack-like pores, a significant volume of colloidal pores remaining in the cement product, 0.18 volume fraction. These colloidal pores stemmed from the gel hydration product, which has been thought to be intrinsically porous to allow osmosis and continued hydration (Double *et al.* 1978; Birchall *et al.* 1978, 1980). Yet, in certain circumstances, colloidal pores can be removed from hydraulic systems. For example, silica gel on sintering at 1000 °C shrinks as the gel particles fuse together to eliminate porosity. Similarly, a latex of colloidal polymer particles shrinks at room temperature as drying occurs to pull the particles into a non-porous mass (Kendall 1980, 1982).

We have found a way of doing this room temperature sintering operation on hydraulic cements, by using particular combinations of water-soluble polymer and cement (Birchall *et al.* 1982 *b*). For example, 100 g of calcium aluminate powder (Secar 71, Lafarge) was mixed with 7 g of poly(vinylalcohol/acetate) (KH 17s, Nippon Gohsei) and 11 g of water. When stirred, this mixture formed a crumbly composition, which was twin-roll milled to a stiff dough. This dough was found to exhibit a rheology quite different from doughs made with other cements and polymers. The shear stress doubled for a tenfold increase in shear rate, whereas Portland cement mixed with poly(acrylamide) and water gave roughly constant shear stress as the shear rate was increased.

The dough was press moulded at 5 MPa to remove air bubbles, then hydrated in the mould by heating at 80 °C for 10 minutes. After removal from the mould, the hydrated sheet was dried at 80 °C in an oven, and it was observed that significant shrinkage occurred, up to 3 % linear or 9 % volume. This was thought to correspond to the coalescence of the hydrate precipitate and the collapse of the colloidal porosity in the hardened cement, equivalent to sintering the material. Polished cross sections of this product showed no large pores. The material was thus proved to be a special case of macro-defect-free cement.

When tested for porosity by soaking in organic fluid, this material was shown to be much less porous than normal MDF cement. Usually, MDF cement absorbed between 10 % and 15 % by volume of fluid, whereas the shrunk material absorbed only 0.5 %, suggesting a low volume porosity. Moreover, the Young modulus was 50 GPa (figure 8*a*) consistent with a porosity below 0.01.

The material was notched and flex tested as before (figure 8*b*, top line). Again the results followed equation 7 with a cut-off around 0.1 mm notch length, giving a flex strength of around 150 MPa. The fracture energy was somewhat higher than expected from equation (7), 160 J m^{-2} compared with the theoretical prediction of 106 J m^{-2}, and this suggested that the polymer additive was making some contribution to crack resistance. However, it may be seen from figure 8 that equation 7 gives a reasonable description of the strength properties of the three cements tested, with porosity as the only variable.

8. Feret's (1897) law

It was now possible to re-interpret Feret's (1897) original empirical description of cement strength embodied in equation 1, while recognizing that almost half the water volume in Feret's equation is converted into pores. Thus the strength is

$$\sigma = A[V_c/(V_c + V_w + V_a)]^2 = A(1 - 1.95p)^2 \quad \text{when} \quad V_a = 0. \tag{10}$$

This expression was plotted in figure 9 to compare with equation (7) calculated for several notch sizes c. Agreement was good when the notch length was taken to be 2 mm, and $A = 30.2$. Thus it seems that Feret's law describes the strength of cements at constant flaw size, that is the toughness of cement. By some happy accident, when cements were made by the conventional mixing
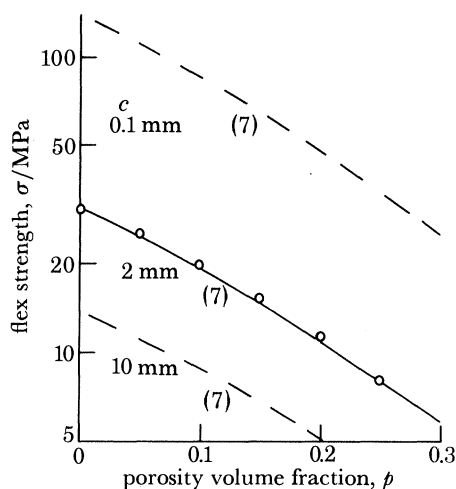

FIGURE 9. Comparison between Feret's (1897) law (○) and equation (7) (dashed and solid curves) plotted for several different flaw sizes c. Feret's law fits only at one flaw size; thus it describes the *toughness* of cement and not its *strength*.

process, the flaw size must have remained roughly constant when different water contents were used. Feret's law is therefore only partly true because it does not take into account the variation of flaw size c, which can be obtained by using different processes to mix cement. For example, freezing the mix would introduce long flaws and would give the lower curve in figure 9, whereas the MDF process would give the top curve. The true description of cement strength is equation (7), which plots onto figure 9 as a family of Feret curves, each corresponding to a constant flaw size.

9. Conclusions

A theory has been proposed to explain the connection between bending strength and porosity of hardened cement pastes. This theory indicates that the main influence on strength is the presence of macro-defects, which can initiate fracture in the material. Microscopic examination of ordinary cements has shown that such macro-defects may be identified as large pores, around 1 mm in length, stemming from imperfections in the mixing process. Improvements in mixing by (i) adding a polymer to make the mix plastic, (ii) employing high shear mixers and (iii) removing trapped air, produced a macro-defect-free product with a high bending strength of 70 MPa, even though the porosity volume remained at a high level. Thus, pore volume is not the

major determinant of cement strength as suggested by previous workers. However, the volume of colloidal pores was found to influence strength by changing the elastic modulus and fracture energy of the material. By reducing the porosity volume to low levels after removing the macro-defects, the bending strength was further increased to 150 MPa, without the need for reinforcement or high-pressure compaction. The results were in fair agreement with the predictions of the theory.

TABLE 4. IMPROVED PROPERTIES OF MACRO-DEFECT-FREE (MDF) CEMENT
COMPARED WITH ORDINARY CEMENT

	ordinary cement	MDF cement
flex strength/MPa	10	40–150
Young modulus/GPa	20	35–50
compressive strength/MPa	40	100–300
fracture energy/($J\ m^{-2}$)	20	40–200
electrical breakdown/(kV mm^{-1})	0.1	6–13
gas permeability/(mol $m^{-1}\ s^{-1}\ Pa^{-1}$).	10^{-12}	10^{-16}

The improved values of strength and toughness exhibited by macro-defect-free cements (table 4) should allow these materials to be employed in hitherto unexpected and advanced applications.

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Discussion

P. L. PRATT (*Department of Metallurgy and Materials Science, Imperial College, Prince Consort Road, London SW7 2BP, U.K.*). In their interesting series of experiments Kendall and his co-authors have shown that porous silica glass obeys Griffith's (1920) criterion for a range of porosities from 0 to 0.5. As a result of these experiments they claim to have discovered a new theory of fracture, which they express in equation (7). My first question is what is new about this theory? Surely it is a simple statement of the Griffith criterion in which particular empirical relations are used to approximate the values of E and R. As such it has been used by those interested in the fracture mechanics of ceramics for many years, although the choice of Balshin's (1949, 1950) form of the dependence of E on porosity might not be the best.

The authors claim further that the cause of the natural flaws in hardened cement paste are pores arising from air in the cement, owing to flocculation. Trapped air is present in hand-mixed cement paste and the easiest way to remove it is with a short vacuum treatment of the fresh paste. This removes the bubbles of air and increases the initial ultrasonic pulse velocity from that for transmission through air to that for transmission through water. De-airing eliminates the large pores from the microstructure but unfortunately has only a small effect on the strength and fracture toughness of well mixed hardened paste. A more likely explanation of the low tensile strength of ordinary cement paste lies in the morphology of the hydration products and their susceptibility to subcritical crack growth. Inherent flaws like inner product detached from Hadley shells (Pratt & Ghose, this symposium) are not affected by vacuum de-airing. Have the authors considered the effects of the vigorous working and limited hydration involved in the MDF process on other defects in the microstructure, like Hadley grains, and on subcritical crack growth?

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Balshin, M. Y. 1950 *Chem. Abstr.* **44**, 2425f.

K. KENDALL. We do not claim that equation (7) is new. However, we have not been able to find any reference to this equation and its experimental verification in the literature relating either to cement or to ceramics. Indeed, we have been unable to find any statement that there is a conflict between the Ryshkewitch (1953) equation and the Griffith (1920) theory. Can Professor Pratt provide some evidence of such previous work?

On the further question of large pores in cement, air is not the only source of such pores. The other major source is packing defects, that is regions of the cement mix containing water but insufficient cement to fill the space with hydrate.

Moreover, Professor Pratt is wrong in stating that removal of air bubbles has only a small effect on the strength of hardened cement paste. Removal of air has a large effect on strength, as Feret pointed out in 1897. A 20 % volume fraction of air reduces strength by a factor 3.

B. A. PROCTOR (*Fibres and Composites Department, Pilkington Brothers p.l.c., Research and Development Laboratories, Hall Lane, Lathom, Ormskirk, Lancashire, U.K.*). The apparent anomaly between the effects of pores and cracks may be explained by the approach of Inglis (1913), who analysed the stress-concentrating effect of elliptical voids, in contrast with the approach of Griffith (1920), who used the stress distributions of Inglis to analyse the energetics of propagation of infinitely sharp elliptical voids or cracks.

In the work of Inglis the sharpness of the crack tip is an important factor affecting the degree of stress concentration of a given size of crack and this was well recognized in work on the strength of brittle solids some 20 years ago. Since that time the Griffith approach concentrating on the factors governing the propagation of an already infinitely sharp crack has become more widely used, and the importance of shape and tip curvature, emphasized by Inglis, rather neglected.

Reference

Inglis, C. E. 1913 *Trans. Instn nav. Archit.* 55, 219–230.

K. KENDALL. The Inglis approach cannot possibly explain anything about the fracture of brittle materials such as hardened cement, because it implies that cracks propagate as a result of *stress*, and thus argues that the *shape* of a notch (or crack) is the only important parameter, not the *length* of the notch. This idea is false.

As Griffith demonstrated with his *energy* criterion of cracking, it is the *length* of the notch that is of prime importance for brittle materials, not the *shape*, which may be varied enormously without much effect on fracture. This result may easily be demonstrated by cutting notches of different shapes in MDF cement.

Confusion on this issue partly stems from Griffith's (1920) original paper in which he states the energy criterion, but then appears to support the opposing stress argument by stating 'rupture of an isotropic elastic material always occurs at a certain maximum tension' (i.e. stress). In fact he reverted to the stress criterion in his later paper on compressive failure (Griffith 1924).

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Griffith, A. A. 1924 In *Proceedings of the first International Congress on Applied Mechanics, Delft* (ed. C. B. Biezeno & J. M. Burgers), pp. 55–63.

S. A. JEFFERIS (*Civil Engineering Department, King's College London, Strand, London, WC2R 2IS, U.K.*). The results have shown the dramatic effect that pore size has on strength. One reason for this must be the contrast in elastic modulus between the empty pore and the matrix. If so, un-hydrated cement particles may also behave as flaws as they may be significantly stiffer than their hydration products. Such stiff flaws will have less effect than voids but could become significant in materials with low porosity and very small pores. Is cement grain size also an important factor in controlling the properties of MDF materials?

K. KENDALL. Unhydrated grains of cement are indeed stiffer than their hydration products, and therefore may behave as flaws in MDF cements. When large grains of stiff material were deliberately added to the MDF cement, the flexural strength of the material was found to be reduced.
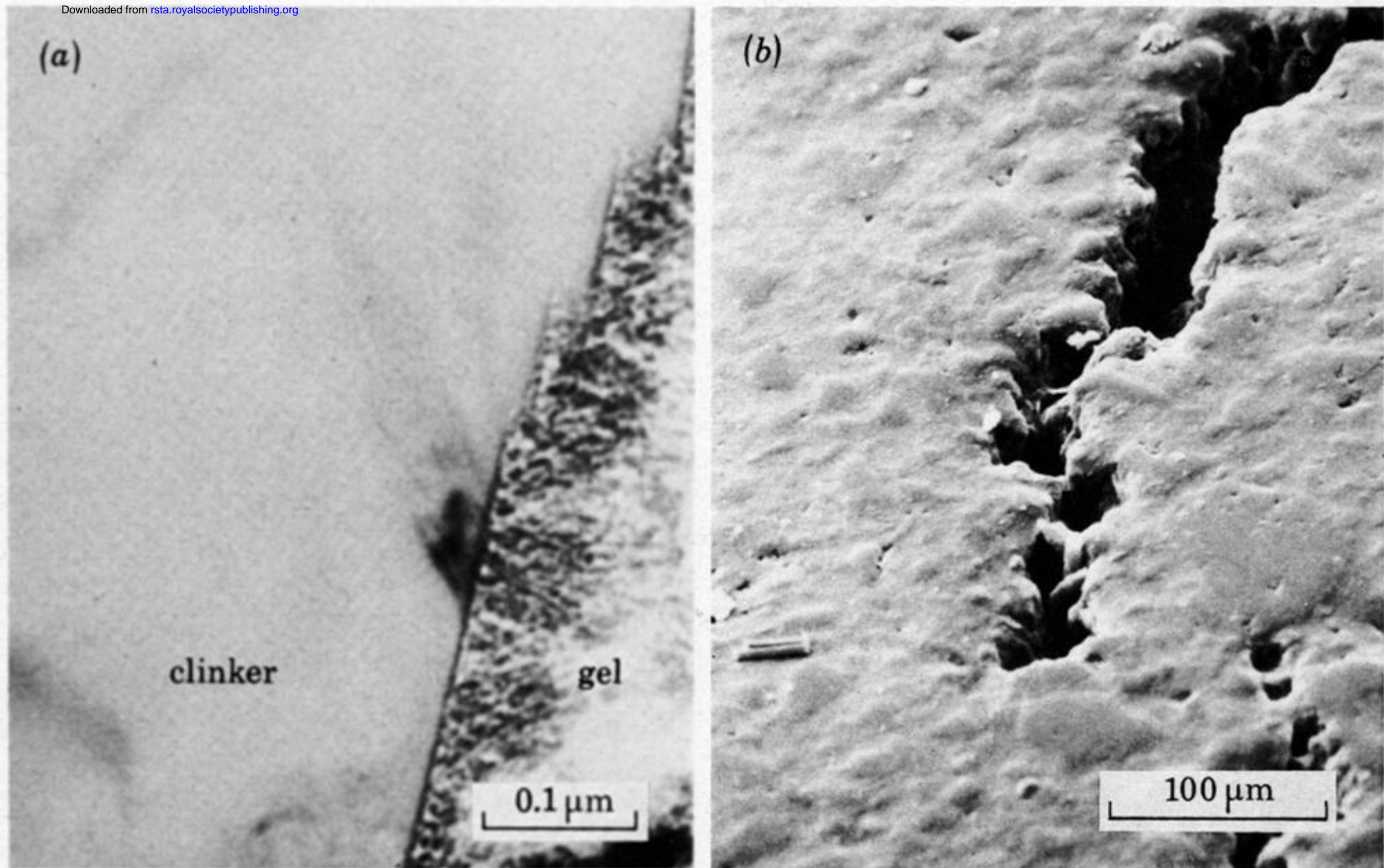
FIGURE 2. (a) Porous colloidal hydrate gel formed on an ion-thinned tricalcium silicate crystal (courtesy of Dr G. W. Groves). (b) Crack-like pore in polished cement paste; the cement grain residues can be seen protruding from the gel matrix.

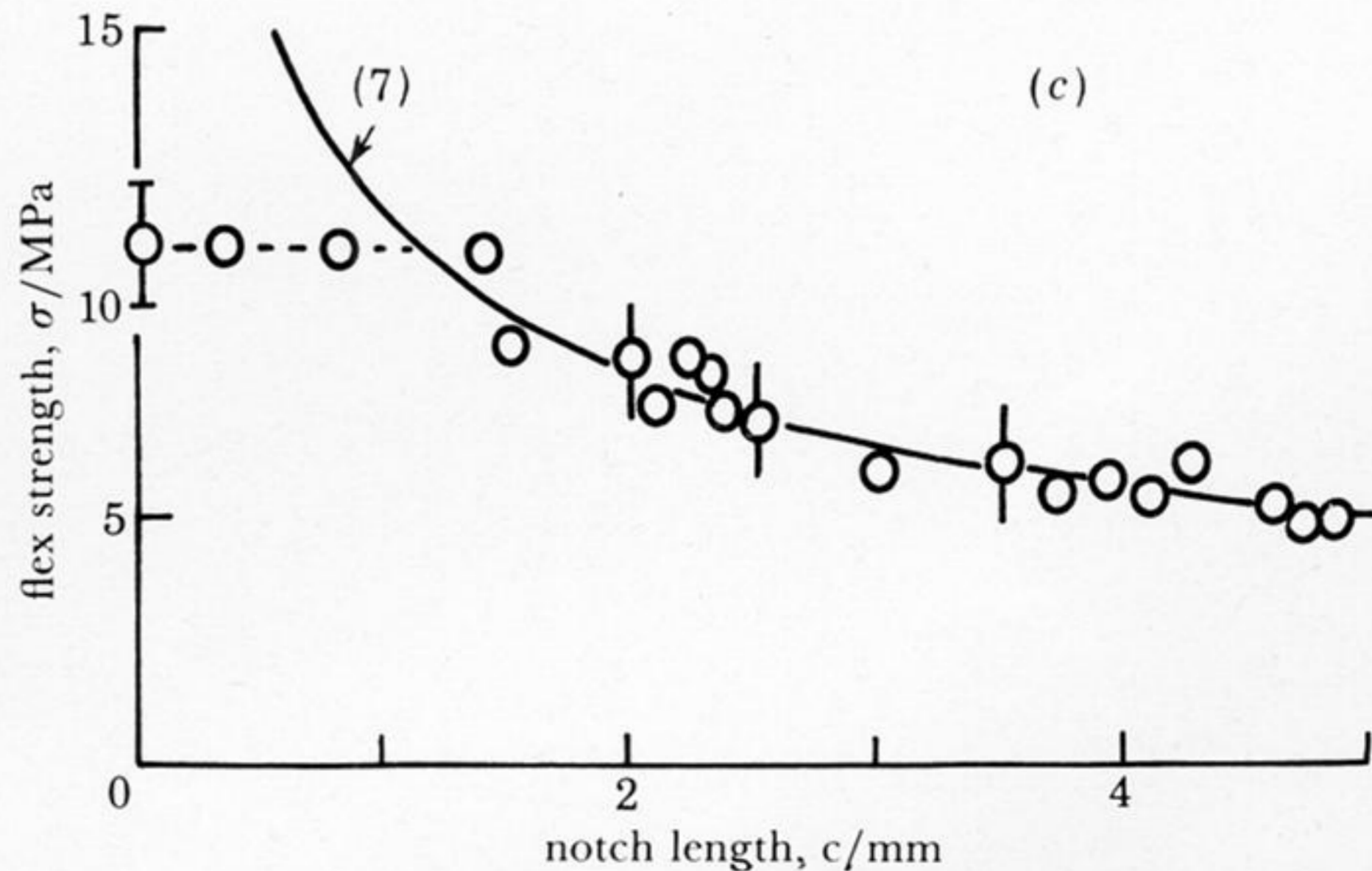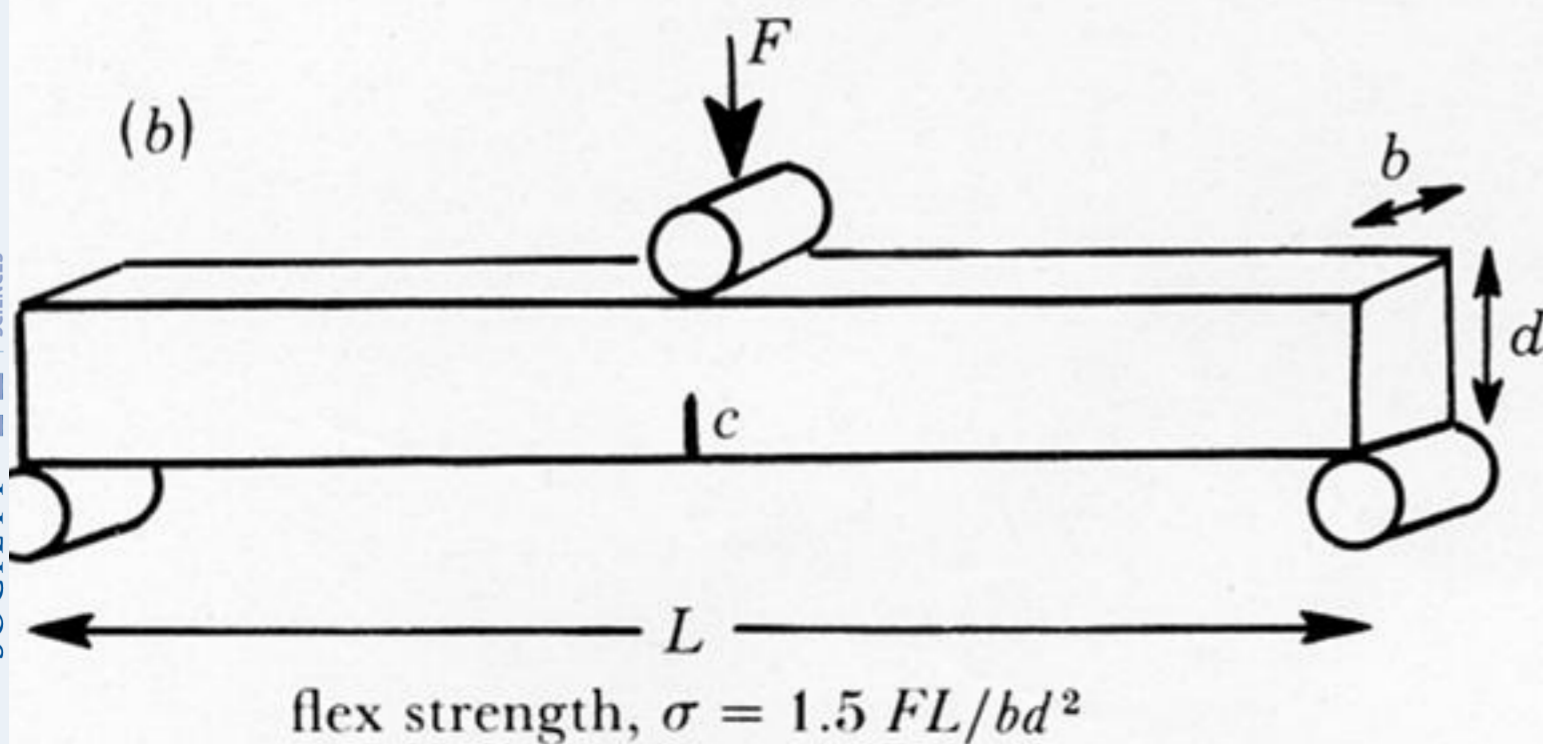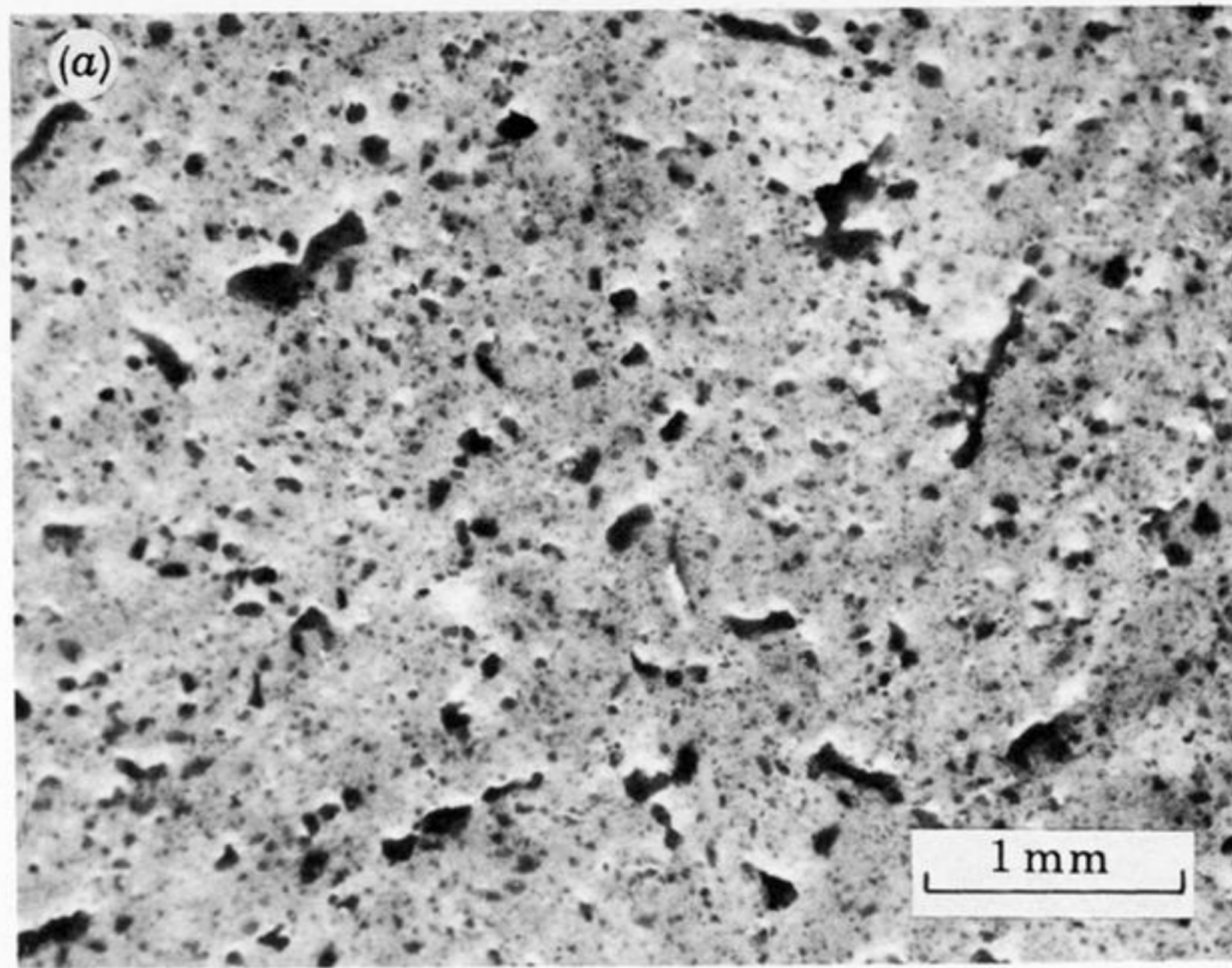flex strength, $\sigma = 1.5\,FL/bd^2$

FIGURE 4. (a) Optical micrograph of a polished sample of Portland cement paste showing the large voids decorated black. (b) The flex testing arrangement. (c) Results for hardened Portland cement, w/c = 0.22. The curve derived from equation (7) is drawn as a solid line.