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### High-strength cement pastes: a critical appraisal

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## HIGH-STRENGTH CEMENT PASTES – A CRITICAL APPRAISAL

by J.J. Beaudoin and R.F. Feldman

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## RÉSUMÉ

Les mécanismes de renforcement qui agissent dans la pâte de ciment à haute résistance sont évalués dans cet essai visant à définir les caractéristiques communes à certaines nouvelles technologies comme les pâtes de ciment pressées à chaud, imprégnées et sans défauts majeurs. Les facteurs importants modifiant la résistance des matériaux poreux sont, entre autres, la porosité, la dimension des pores, la composition C-S-H, le comportement des composites et les critères de rupture.

Cette communication traite également des effets de faibles rapports eau-ciment, des inclusions denses, des modifications des contraintes dans les zones critiques et de leur rôle dans l'amélioration et le contrôle de la fabrication de la pâte de ciment à haute résistance.

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## HIGH-STRENGTH CEMENT PASTES - A CRITICAL APPRAISAL

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### ABSTRACT

The mechanisms responsible for high strength in cement paste systems are assessed in an attempt to define features common to selected new technologies, e.g., hot-pressed, impregnated, and macrodefect-free pastes. Important factors influencing strength of porous systems include porosity, pore geometry, C-S-H composition, composite behaviour and fracture criteria. The effects of low water-cement ratio, dense inclusions, stress modification in critical areas and their role in optimizing and controlling production of high-strength cement paste are discussed.

Energy consciousness in the 1980's has increased the need for innovation in the cement and concrete industry, with the result that high-strength lightweight materials have been developed for various applications such as cladding panels and composites for retrofit purposes. The area of high strength concrete\* has also been the subject of recent symposia called to obtain consensus on priorities to be set among concrete scientists, structural engineers, and mechanics theorists (1).

Development of new materials has generally been carried out by material scientists, including research on the superplasticizers that have made possible the use of low w/c ratio concrete. Although there are many conventional ways of producing high-strength concrete (including judicious selection of aggregate, admixture and curing conditions) work has generally been related to the cement paste binder phase. New technologies resulting in high-strength concrete products have evolved from research on portland cement paste. This paper examines some of the strengthening mechanisms in operation in high-strength cement paste and considers the mechanistic features common to selected new technologies concerned with the paste.

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\* For normal weight aggregate concrete, high strength is generally defined as concrete having compressive strength exceeding that used in current design practice and is nominally  $>40$  MPa.

## 1.0 Factors Influencing Strength of Porous Cement Systems

Data indicate that both compressive and tensile strengths of cement systems are porosity dependent (2), for example, flexural strength (Fig. 1). The significance of the flexural strength-porosity relation has, however, been questioned (3) and some of the factors influencing it have been discussed (4-8).

### 1.1 Porosity

Several displacement fluids have been used in measuring the porosity of hydrated portland cement. Water is generally inappropriate because dried hydrosilicates will rehydrate on exposure to it and the apparent measured porosity will be higher than the actual value. Other media such as helium, methanol and mercury generally give similar results for most w/c ratio preparations, in general agreement with the "capillary" porosity estimations of Helmuth and Turk (8).

In helium porosity calculations, solid volume is measured and porosity is computed from the apparent volume determined by other methods. Helium flows instantly into the pores of most cement systems and the measured solid volume includes interlayer spaces. Helium can, in time, penetrate the interlayer space, the amount depending on the interlayer water present. Cement samples are usually conditioned at 11% RH prior to solid volume measurement, when most of the interlayer spaces are filled with water. Interlayer water is part of the C-S-H structure and density determinations employing helium pycnometry can detect it. If water pycnometry is employed, the density values depend on the amount of water already present; for dried samples the values approach the density of the C-S-H layers themselves.

It has been reported (9,10) that mercury intrusion porosimetry cannot detect porosity in the macropore region (e.g., 0.5 - 1 mm diam). Helium porosity values are similar to those obtained by mercury intrusion methods when w/c > 0.40. This suggests that for these preparations the macropores do not exist. At lower w/c ratios (<0.40) where compaction during sample preparation is promoted the pore size distribution shifts to smaller sizes, and lower porosity values obtained by the mercury method are attributed to the inability of mercury to penetrate trapped space. Evidence for the existence of trapped space in the C-S-H microstructure is obtained by helium diffusion and density measurements (11).

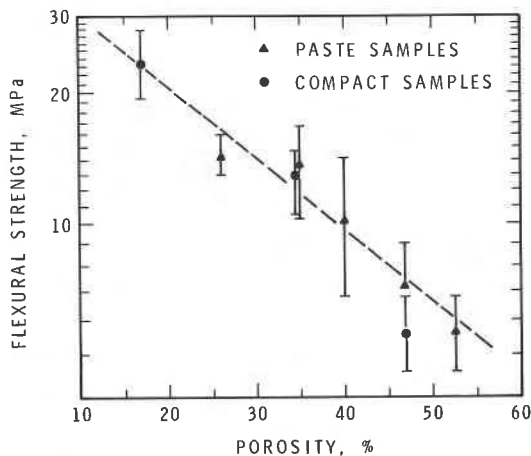


FIG. 1  
Flexural strength of hydrated  
portland cement paste and compacts  
as a function of porosity

Some authors (12) have cited the existence of macropores as a strength controlling factor in cement systems. Evidence for the existence of macropores based on differences in porosity values obtained by water pycnometry or pycnometry using other fluids is not valid in hydrated portland cement systems. Macropores in very low w/c ratio cement paste preparations (w/c < 0.20) may occur as a result of poor compaction if rheological aids, special admixtures, or special compaction procedures are not used. Such voids would undoubtedly be a source of weakness.

### 1.2 Composition of C-S-H

It is known that for the hydrated portland cement system the degree of polymerization and polysilicate content increases with time. It has not yet been demonstrated, however, that the dependence of strength on polysilicate content is independent of the type of C-S-H.

The dependence of strength-porosity relations on chemical composition of the hydrosilicates (and, hence, density and crystallinity) has been studied by the authors, who obtained a family of log strength-porosity curves from the results of measurements on a variety of autoclaved cement-silica systems (5) (Fig. 2a). In general, highest strengths appear to be obtained if the reaction product is a blend of poorly-crystalline and semi-crystalline types of C-S-H (curves for 20 and 30% SiO<sub>2</sub>, Fig. 2a). The proportion of crystalline types giving highest strength is dependent on porosity and starting material. The fly ash/cement blend (curve EF, Fig. 2a) has an increasing proportion of coarse, dense, crystalline material and has highest strengths over the porosity range studied. Very high strength obtained at low porosity (below the normal working range) with a high-density matrix material will be discussed as a special case in section 2.2.

Taylor (6) and Crennan et al. (13) presented the authors' data in another way by preparing a porosity particle-type strength diagram (Fig. 2b) for cement pastes and similar materials. Porosity is plotted against amount of coarse, dense, crystalline material for a series of constant strength contours. The lines AB, EF, and CD crossing the strength contours are for normally cured cement paste, autoclaved cement-silica products and very "high density" cement materials. The significance of the lines will be discussed in sections 2.1 and 2.2.

### 1.3 Cement Paste Microstructure

Cement paste can be considered as a composite material consisting largely of C-S-H, CH, unhydrated cement and pore space, the amount of each component depending on the degree of hydration and w/c ratio. In assessing the relative contribution of each component to strength the application of composite theory is useful; when applying binary mixture rule theory C-S-H, CH, and pore space can be considered as one phase and unhydrated cement as the other. The following form of mixing rule equation relating microhardness\* of the composite (H<sub>c</sub>) to volume fraction of the second phase provides some insight into expected composite behaviour (14):

$$H_c = H_1 \left( 1 + \left\{ \alpha V_2 / (1 + \gamma V_2) \right\} \right) \quad (1)$$

where  $\alpha = \left\{ (G_2/G_1 - 1) / (G_2/G_1) \right\} \beta$   
 $\gamma = \left\{ \alpha (E_2/E_1) + 1 \right\} / (E_2/E_1 - 1)$   
 $V_2$  = volume fraction of second phase  
 $E$  is modulus of elasticity

\* Microhardness correlates with both compressive and flexural strength of cement systems (5).

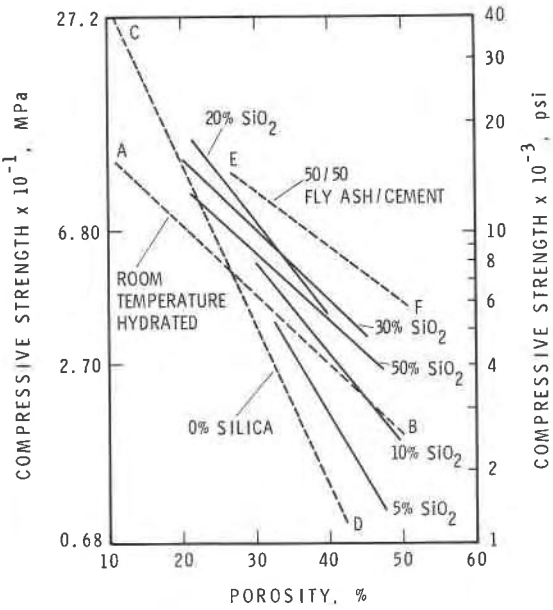


FIG. 2(a)  
Compressive strength versus porosity for various autoclaved and room temperature hydrated cement and cement-silica preparations

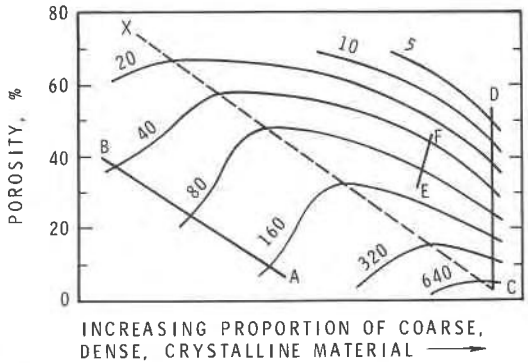


FIG. 2(b)  
Porosity-particle type-strength plot for cement pastes and similar materials. Curves of constant compressive strength are labelled in MPa. The broken line XC joins points of maximum strength at a given porosity and fraction of non-crystalline material. For significance of lines AB, CD and EF see text

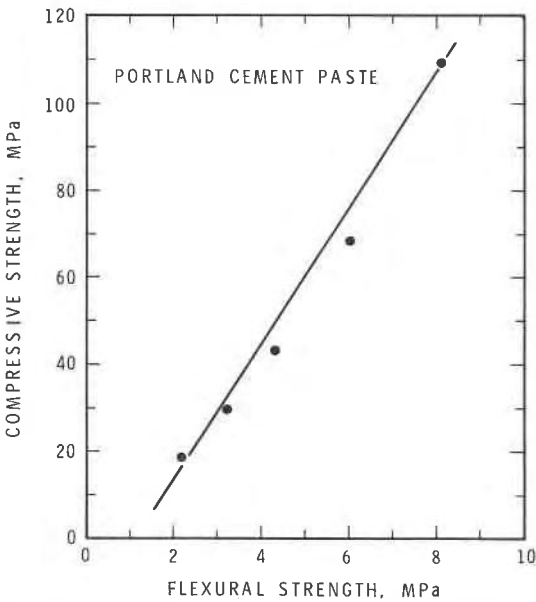


FIG. 2(c)  
Relation between compressive strength and flexural strength for normally hydrated portland cement paste

$G$  is shear modulus

$\beta$  is a stress concentration factor and is a function of  $E_2/E_1$  and geometry of the second phase (i.e. major to minor axis ratio of an elliptical inclusion)

(Subscripts refer to first or second phase and  $H_1$  is the microhardness of the first phase, usually the continuous matrix.)

An example where eq. (1) might be applied is a cement system containing large amounts of unhydrated cement separated by thin layers of C-S-H. Consider phase 1 to be the dense, unhydrated cement particles present in sufficient numbers to comprise the continuous phase, and the second, discontinuous phase to be the hydrated material including C-S-H, CH and pore space. Equation (1) indicates that the contribution of the second phase to composite strength depends on the shape of the second-phase particles, modulus ratio, and volume fraction. The inner bracketed term (negative) expresses the degree to which the strong unhydrated cement particles can contribute to composite strength. Other examples include polymer-impregnated or modified-cement systems. In general, the composite theory will be used to supplement other arguments in support of particular strengthening mechanisms.

#### 1.4 Crack Formation

Some workers have employed the Griffith equation to predict strength ( $\sigma$ ) of ceramic and cement systems (5).

$$\sigma = \sqrt{\frac{2ET}{\pi c}} \quad (2)$$

where  $E$  is Young's modulus,  $T$  is surface energy, and  $c$  is half the flaw length.

One difficulty with the direct application of eq. (2) is that work terms in addition to specific surface energy affect fracture. Secondly, neither fracture energy nor Young's modulus is constant; both are dependent on porosity, w/c ratio, environment, and other matrix properties (2,15). For example, some workers have incorrectly compared polymer-modified cement systems with ordinary portland cement paste (9), using the same value of  $T$  for both systems in eq. (2).

Equation (2) is a particular case of the Inglis solution for the stress field round an elliptical hole in an infinite plate with its major axis normal to a uniform tensile stress (16). A fundamental assumption in the Griffith equation is that the flaws are atomically sharp and the major/minor axis ratio large, i.e., that the shape of the flaw is fixed. Pores (having different pore shapes), as such, do not fit the Griffith definition of a flaw. Some ceramic scientists have approached this problem by considering pores themselves as an integral part of flaws, i.e., the length of the flaw is considered to be the pore diameter plus one grain diameter on either side of the pore (17). This is based on the concept that cracks will propagate along grain boundaries emanating from the pore wall into the body until the next layer of grains is encountered. Effects of variation in pore shape that alter the stress field in the vicinity of the pore are not considered. This concept was applied to cement paste by Wittman and Zaitsev, who modelled the system as a plate containing a cylindrical hole with two edge cracks emanating from points of maximum tensile stress (18). Verification of its validity for normally hydrated cement paste by direct measurement is difficult since grain size is extremely fine. In systems that contain large numbers of unhydrated cement grains (5 - 50  $\mu\text{m}$ ) it may be possible. It is, however, uncertain whether macropores in poorly compacted low water/cement ratio pastes, which contain large amounts of unhydrated cement, can be considered as flaws in the Griffith sense (9).



### 1.5 Applied Stress Mode

The discussion of fracture criteria has been based on specimens subjected to tensile stress. A linear correlation between compressive and flexural strengths was observed (19) for normally hydrated cement paste (Fig. 2c); the average compressive/flexural strength ratio was approximately 10. Roy and Gouda (7) found a similar correlation between compressive and tensile strengths for both hot-pressed and cold-pressed cement paste specimens and argued that most microstructural properties (such as porosity) affecting high strength in compression contribute in a parallel manner to the high strength in tension.

Failure that occurs in most compressive strength tests involves the generation of tensile stresses because of end effects. Crack growth involving a pore linkage process has also been described as occurring during compression of portland cement paste (17). It appears that there are common factors affecting crack growth in compression and flexural testing. The role pores play in fracture under compression or in tension may, however, be different. Rice has suggested that tensile (or flexural) strength may be controlled primarily by pore and grain size and by total porosity, including shape effects, as discussed previously; he further argues that, in compression, pores alone act as stress concentrators: that, in compression, crack development from pores is inhibited until much higher stresses have been reached (17).

### 1.6 Pore Shape

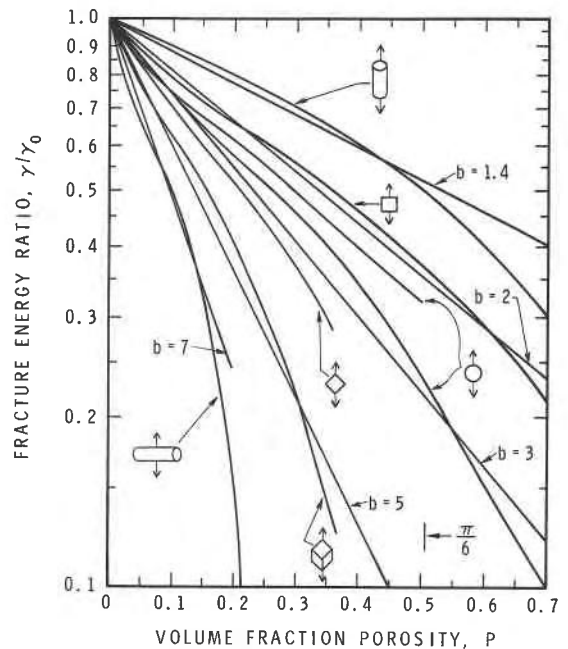
Several expressions have been used to describe the porosity dependence of strength and fracture energy for ceramic and cement systems (6,20). For example, it has been found that the role of pore shape in fracture energy can be accounted for by the following relation (21):

$$\gamma = \gamma_0 e^{-bp} \quad (3)$$

where  $\gamma$  = fracture energy,  $p$  = porosity,  $\gamma_0$  = fracture energy at zero porosity, and  $b$  is a pore shape factor (Fig. 3). Similar expressions have been used for the porosity dependence of elastic modulus and strength. A model was developed by Knudsen (22) to account for the effect of pore shape by assuming that fracture energy should be proportional to the fraction of solid area fractured, and that fracture will generally follow the path of maximum pore and minimum solid cross-sectional area. The analysis, which assumes a uniform distribution of pores, resulted in the non-linear model curves in Fig. 3. The "b" values used in eq. (3), which result in linear curves in close agreement with the model curves, are given in Fig. 3. Values of "b" derived from strength data for autoclaved cement-silica preparations vary from 4.4 to 7.7. Assuming that there is some correlation between strength ratios ( $S/S_0$ ) and fracture energy ratios ( $\gamma/\gamma_0$ ), these systems seem to have a variety of pore shapes. It might be argued that pore shape and composition of C-S-H are not two independent variables. It appears, however, that pore shape modification for a system with a given composition provides a means of increasing strength.

In addition to shape, the "b" value in eq. (3) is also sensitive to pore location and size. Fracture has generally been seen to originate in large, not small, pores in a body having both types (17). Bodies having only fine pores are generally at least as strong as comparable bodies with primarily large pores. Samples having more uniformly shaped and spaced pores tend to have lower "b" values. Local concentrations of pores can alter "b" values whether the pores are intergranular or intragranular, or mixed. In general, pores entrapped within grains are less detrimental to strength than

FIG. 3  
Fracture energy ratio,  $\gamma/\gamma_0$  vs  
volume fraction porosity for  
various simple pore shapes. The  
arrows from each pore shape  
indicate the direction of  
stressing relative to the pore  
geometry



pores at grain boundaries. The "b" value in compression tests is significantly higher. The reason for this apparent higher porosity dependence of compressive strength is not known.

It is apparent that comparison of strength data on the basis of an exponential equation similar to eq. (3) is inadequate to explain all the reasons for strength differences among various cement systems. The application of eq. (3) to strength data is, however, a useful starting point for comparing different systems.

These comments address what the authors consider to be some of the important factors in the development of very high strength cement pastes (in this review compressive strength in excess of 60 MPa). Consideration will be given to these factors in mechanistic arguments pertaining to high strength.

## 2.0 Optimization of Factors Controlling Production of High Strength Cement Paste

### 2.1 Low Water-Cement Ratio

As discussed, higher strengths can be achieved with normally hydrated low-porosity cement paste.\* This is usually accomplished by keeping the w/c ratio as low as possible, but it should be recognized that low w/c ratio cement paste (usually w/c  $\leq 0.25$ ) has a characteristic microstructure different from that of paste with higher w/c ratio. The low w/c ratio paste is a more heterogeneous composite material than normal cement paste because it contains significant amounts of anhydrous cement particles embedded in a C-S-H matrix. This, in turn, has characteristics different from those produced at higher w/c ratio (23). The C-S-H matrix and the unhydrated cement particles both

\* An important assumption is that the low porosity pastes are well compacted and do not contain large voids that may occur due to poor consolidation.

contribute to strength. This C-S-H differs from that prepared at higher w/c ratio in that it is less dense, contains trapped microspace between sheets, has a different C/S ratio, a significantly lower  $N_2$  surface area, a pore size distribution skewed towards smaller pore sizes, and contains pore space that cannot be penetrated by mercury. In these pastes, effects described as aging are more prominent, i.e., rearrangement and consolidation of C-S-H layers, generally resulting in strength increases. The relative contributions of the C-S-H matrix and cement inclusions is important in developing high strength, and these special characteristics of low w/c ratio pastes play a role in determining the extent of their contribution.

Several papers describing the preparation and properties of a well-consolidated, low porosity matrix with a relatively high degree of hydration have been published by Yudenfreund et al. (24-30). A typical composition of a cement paste prepared by them is as follows: w/c = 0.20, type I cement with fineness 600 - 900  $m^2/kg$  (much finer than normal), a grinding aid, e.g., diethylcarbonate at 0.5% by weight of cement, 1% by weight of dry-mixed calcium lignosulphonate and 0.5% potassium carbonate (a set-controlling additive). This typical cement paste (degree of hydration  $\leq 70\%$ ) has a compressive strength of about 204 MPa at 28 days. Porosity determined by water pycnometry was recalculated by the present authors to give an equivalent value of approximately 5% corresponding to that which would have been obtained by helium pycnometry. The data point for this preparation lies on the strength porosity curve for normally hydrated cement paste (line AB, Fig. 2a). In this case, the ability to achieve low porosity by means of grinding and rheological aids (without which effective consolidation would be difficult to achieve) appears to be responsible for high strength.

## 2.2 Effect of Dense Inclusions

Strengths significantly higher than 204 MPa can be obtained at low porosities by increasing the contribution of dense phases such as unhydrated cement. Roy et al. (31) demonstrated that with "hot-pressing" techniques strengths as high as 644 and 63 MPa (compressive and tensile strengths, respectively) can be achieved. These low porosity materials, pressed at up to 1020 MPa, and temperatures greater than 150°C contained large amounts of unhydrated cement (degree of hydration ranged from 29 - 37%). There are several other examples of very strong cement paste systems at low porosities. These include several of the hydrated aluminate cement minerals, e.g.,  $C_4AF$ ,  $C_3A$ ,  $CA$  (32-34).

Low strength of aluminate cements hydrated at elevated temperatures is often attributed to the formation of the  $C_3AH_6$  phase. Contrary to general opinion, however, the curing of aluminate systems at higher temperature actually results in improvement in strength, provided the water-solid ratio is low. Higher strengths at very low w/s ratios may be attributed to direct formation of the cubic  $C_3AH_6$  phase on the original sites of the cement minerals. This results in intimate contact between dense particles that form a closely welded, continuous network with enhanced mechanical strength. An analogous explanation is offered for enhanced strength of low porosity, autoclaved, cement-silica mixtures at low silica content. These pastes contain significant amounts of dense  $\alpha C_2SH$  and are weak at high porosities where the interparticle contacts are fewer, weaker, and possibly have sharp boundaries that can contribute to higher local stresses. At low porosity, the contribution to strength of the  $\alpha C_2SH$  particles - formed in close proximity to one another - is reflected in the large increase in strength of the material.

All of these high-strength, low-porosity systems containing large

amounts of dense crystalline material demonstrate the principle expressed by the mixture rule, i.e., eq. (1). The conditions of formation of the dense inclusions, however, determine the relevance of what is predicted by eq. (1).

### 2.3 Stress Modification in Critical Areas

Failure in brittle materials, including cement pastes, is often the result of initiation and propagation of cracks originating in high stress regions. Modification of the stress field in these regions can result in high strength. Fibre reinforcement of brittle matrices can result in significant increases in flexural strength and is a practical example of crack control through stress modification processes. This modification can also be achieved in unreinforced matrices, for example, by changing the geometry of a crack tip, pore, or void space between particles. This can be done in several ways: (1) deposition of a small amount of additional C-S-H binder in high-stress regions, (2) impregnation of a porous system with a second phase, (3) molecular bridging of microspace by an impregnant, (4) integral mixing with a low-modulus polymer emulsion, and (5) filling macrodefects and modifying their geometry.

Figure 4 is a schematic illustration of some of these concepts. The "hot-pressed" samples (7), which had additional moist-curing for 28 days, had significant increases in strength although the increase in degree of hydration was marginal. It is suggested that the small amount of additional hydration (although total porosity is effectively unchanged) is sufficient to "glue" the dense clinker particles together and modify the stress field at regions of interparticle contact (Fig. 4a). The mechanism of stress modification probably involves change of pore shape due to the first concept and reduction of the "b" factor in eq. (3).

Increases in strength due to impregnation of pores with a solid, which itself has good engineering properties, appears also to be (in addition to porosity reduction) the result of a stress modification mechanism controlling behaviour in regions of high stress. Figure 4b illustrates how pore shape in regions of high stress may be modified. Large increases in strength as well as high total strength are obtained for compositions containing dense particles, e.g., high porosity systems containing  $\alpha\text{-C}_2\text{SH}$  particles, when these compositions are impregnated with a second phase. The mechanism responsible for strength increase (at least in part) is similar to that suggested for the "hot-pressed" systems. Another strengthening mechanism is possible when the impregnant is filling microspace between surfaces separated by distances of molecular dimension; for example, it is arguable that a polymethylmethacrylate molecule could bridge two surfaces of a micropore, thus utilizing the strength of covalent bonds rather than the strength of the interconnections of several of the polymethylmethacrylate molecules themselves (Fig. 4c).

Microscopic evidence supports arguments that polymer emulsions, e.g., latex systems, bridge microcracks with a polymer film (35), resisting crack growth and increasing tensile strength and failure strain (Fig. 4d). Increased ductility is dependent on the type and amount of polymer. When the polymer forms a film in a region of high stress, the arguments presented for stress modification also seem to apply. With respect to water soluble polymers, if the concentration of polymer in the pore space available is high, then the polymer will have a direct reinforcing effect on the cement system and behave the same as latexes.

For a given polymer-cement ratio the concentration of polymer in the pore solution is inversely proportional to the w/c ratio. This can be a significant factor in very low porosity systems. For latex-modified portland

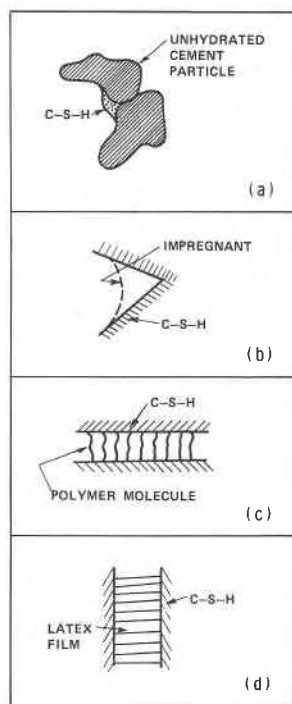


FIG. 4  
Schematic illustrations of various stress-modifying mechanisms

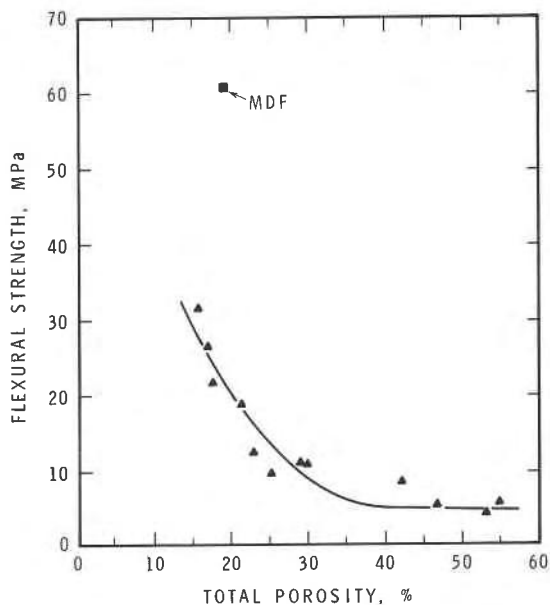


FIG. 5  
Flexural strength vs porosity for ordinary portland cement paste. MDF = cement paste

cement paste published data indicate that (for constant polymer content) tensile strength is porosity dependent over a wide range of porosity and strength increases as porosity decreases (36). It appears then that total porosity is one of the controlling factors that determine the tensile strength of these materials.

An example of a polymer-modified cement system (having high flexural strength) in which mechanisms illustrated in Fig. 4(a, b and d) are operative is a system referred to as Macro-Defect-Free (MDF) cement paste (37-42). This paste system is prepared at very low w/c ratios (0.08 - 0.20). In general, composition comprises the following: hydraulic cement, water, one polymeric or water-dispersible additive, particulate material insoluble in the composition having particle size  $\leq 0.1 \mu\text{m}$ . A typical composition is as follows: 100 parts portland cement, 0.7 part silica powder ( $0.04 \mu\text{m}$ ) and 16.5 parts aqueous solution containing 3.5 parts polyacrylamide. Hydroxypropyl methyl cellulose and hydrolyzed poly(vinylacetate) have been used in lieu of polyacrylamide.

Figure 5 is a flexural strength vs porosity plot for cement paste, including a plot point for MDF cement paste (41). The porosity values determined by water pycnometry are probably higher than actual, but the general trend of the data would be similar if correct porosity values were used. The plot point for MDF cement paste is significantly higher than the value on the curve at the same porosity. The stress-modifying characteristics of the polymer enable the dense unhydrated cement particles to contribute more

fully to the strength of the composite in accordance with eq. (1). This is the principal reason why the MDF system is stronger than normal paste and does not fit the strength-porosity curve for the latter.

The flexural strength value of the MDF paste (Fig. 5) is about 60 MPa, a value approximately the same as that obtained by Roy and Gouda<sup>7</sup> for the maximum tensile strength of hot-pressed cement paste. In both cases the unhydrated cement appears to contribute an optimum amount to composite strength in accordance with mixture rule theory and eq. (1). It is suggested that a stress modification mechanism is primarily responsible. A significantly lower compressive strength/flexural strength ratio (approx. 3) for polymer-modified cement systems appears to support this suggestion (36). The effect of macrovoids in the MDF polymer cement system has not been determined.

### 3.0 Concluding Remarks

The mechanisms discussed are those the authors believe to be relevant and apparently responsible for the high strength of many products described in recent patents. One of the principal mechanisms appears to be the modification of stress in areas of high stress (for example, crack tips) by chemical and physical means. It is hoped that the opinions expressed will provide insight for further development.

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