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Beaudoin, J. J.

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By J.J. Beaudoin

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PROPERTIES OF PORTLAND CEMENT PASTE REINFORCED WITH MICA FLAKES

J.J. Beaudoin
Division of Building Research, National Research Council Canada
Ottawa, Ontario K1A OR6, Canada

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ABSTRACT

Results of an investigation of the use of high-aspect-ratio mica flakes in hardened portland cement matrices are reported. Increases in flexural strength by a factor of 2 and in fracture toughness by a factor of 4, depending on matrix porosity, are obtained by the addition of small amounts of mica. The dependence of these properties on matrix porosity is determined and the effect of mica flake addition on matrix characteristics discussed, e.g., porosity, surface area, non-evaporable water content.

Introduction

In recent years the technology of fibre-reinforced cement has become an important segment of research and development activity in the concrete industry (1). Incorporation of inorganic and organic fibres in cement matrices has resulted in increased flexural strength and toughness (2). Intensive research effort has been directed towards the development and use of glass-fibre-reinforced cement products (GRC) (3). Alkali-resistant (AR) glass fibres have attractive properties that favour their selection as reinforcement because of high values of modulus of elasticity and tensile strength. There remains, however, concern about long-term durability. After a few years of natural weathering, original values of flexural strength and toughness of GRC materials are significantly reduced (4), and there is concern regarding its use in spite of attempts to modify and improve AR glass fibres (5).

Mica flake reinforcement has received some attention from the precast concrete industry because of its ready availability and stability to alkali attack and for economic considerations as well (6). Recent studies have also demonstrated that high alumina cement matrices reinforced with high-aspect-ratio mica flakes show significant increases in flexural strength and fracture toughness (7).

It is the object of this study to determine the effect of mica flake addition on strength, toughness and other properties of portland cement paste in order to assess its potential as a replacement for glass fibres in cement matrices.

Experimental

Materials

Cement: Portland cement composition was C_4AF = 6.7%; C_3A = 12.7%; C_3S = 51.4%; C_2S = 20.3%; and $CaSO_4$ = 5.4% as calculated by the Bogue method. Blaine fineness was 300 m^2/kg.

Mica: It is phlogopite type and high-aspect-ratio reinforcing grade, marketed as "Suzorite Mica" (Marietta Resources International Ltd., 5083 St. Denis Street, Montreal, Quebec). The average aspect ratio of the flakes is approximately 80. They are generally of irregular shape, with a mean width varying between 250 and 1400 μm. Physical and chemical properties of the flakes have been published (7).

Mixes: Eight series of cement paste mixes were made using a conventional Hobart mixer, each series with a different volume concentration of mica flakes varying from 0 to 7% in increments of 1%. For a given volume concentration of mica flakes, mixes with the following water/cement ratios were prepared: 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50. It was not possible to produce low w/c mixes when volume fraction of mica, V_f, equalled 7%. They were cast in two sample geometries: 5.1 cm cubes for compression tests and 2.5 × 2.5 × 25.4 cm long prisms for flexural tests. Three cubes and three prisms were made with each mix. Samples were demolded after one day and moist cured for approximately 32 days prior to testing.

Techniques: Flexural tests (mid-span loading) were carried out on a Tinius Olsen testing machine using a cross-head speed of 0.127 cm/min. Load deflection traces were obtained from machine records and used to determine flexural strengths and relative fracture toughness. Areas under load deflection curves were determined and used as indices of fracture toughness.

Compression tests were also carried out on a Tinius Olsen testing machine using a loading rate of 0.2 MPa s^{-1}.

Porosity measurements were made on small chunks from each specimen. Samples were conditioned to 11% RH and then pumped in a vacuum desiccator for about 45 min prior to testing. A methanol displacement method employing Archimedes Principle was used for all porosity determinations (8). Pore volumes were expressed as percentages of matrix volume, i.e., volume occupied by mica flakes was excluded from total apparent volume to provide a basis for comparing composites with different amounts of mica.

Pore size distributions were determined on selected samples by mercury intrusion at 408 MPa, using an American Instrument Co. porosimeter. Surface area measurements were made on selected samples using a Numinco-Or surface area analyser with N_2 as adsorbate.

Non-evaporable water determinations were made by oven drying samples at 110°C for 3 h and determining the loss on ignition at 1000°C. The weight of mica present in the specimens was subtracted for determining non-evaporable water content.

Results and Discussion

Logarithm of flexural strength versus porosity curves for cement matrices containing 0 - 6% mica flakes are presented in Fig. 1. Data for 7% mica content were incomplete owing to difficulties in sample fabrication and are not presented. At matrix porosities greater than about 21% all curves (with the exception of the curve for mica volume fraction, V_f = 6%) lie above the curve for V_f = 0%. At porosities <21% all curves lie above the V_f = 0% curve except those for V_f = 2 and 4%. The curve for V_f = 4% crosses the V_f = 0% curve at about 18% porosity. Logarithm of compressive strength versus porosity curves are plotted in Fig. 2. All the curves lie below the V_f = 0% curve. In general, compressive strength decreases with mica flake content over most of the porosity range. Similar results have been observed for glass-fibre-reinforced cements (9). Regression analysis data for curves in Figs. 1 and 2 are given in Tables 1 and 2.

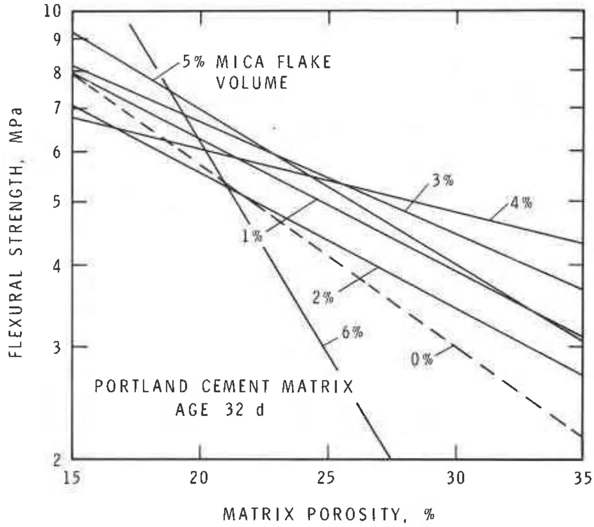

FIG. 1

Flexural strength versus matrix porosity for mica-flake-reinforced portland cement paste

The following equation, based on composite theory, has often been used to estimate composite compressive or flexural strength values at different porosities for fibre-reinforced cement composites (10):

$$\sigma_{cf} = (1-V_f)\ \sigma_m + \phi\ \sigma_f V_f \qquad (1)$$

where σ_{cf} = composite strength

σ_m = matrix strength

σ_f = maximum fibre or flake stress when composite peak stress is obtained

V_f = volume fraction of fibre or flake reinforcement

ϕ = efficiency factor used to account for fibre length and orientation.

TABLE 1

Regression Analysis of Flexural Strength-Porosity Curves for Portland Cement-Mica Flake Composites

Volume Mica Flakes, %	Flexural Strength (σ_{cf}) MPa	Correlation Coefficient, %
0	σ_{cf} = 21.04 exp (-0.064)p*	74.6
1	σ_{cf} = 15.90 exp (-0.046)p	86.6
2	σ_{cf} = 14.39 exp (-0.047)p	90.1
3	σ_{cf} = 14.26 exp (-0.037)p	96.7
4	σ_{cf} = 9.60 exp (-0.022)p	76.1
5	σ_{cf} = 20.55 exp (-0.054)p	91.8
6	σ_{cf} = 123.02 exp (-0.148)p	94.1

* p = matrix porosity

Matrix strength is expressed in terms of porosity by the following expression:

$$\sigma_m = \sigma_{mo}\exp(-bp') \qquad (2)$$

where p' = porosity of unreinforced cement paste (p' is dependent on p, the matrix porosity of the reinforced cement paste and to a first approximation $p = p'$)
b = constant
σ_{mo} = matrix strength at zero porosity.

The value of σ_{mo} is obtained by extrapolating to zero porosity the V_f = 0% curve in Fig. 2. For portland cement paste there is some evidence

TABLE 2

Regression Analysis of Compressive Strength-Porosity Curves for Portland Cement-Mica Flake Composites

Volume Mica Flakes, %	Compressive Strength (σ_{cc}) MPa	Correlation Coefficient, %
0	σ_{cc} = 400.10 exp (-0.090)p*	89.4
1	σ_{cc} = 120.23 exp (-0.059)p	89.2
2	σ_{cc} = 131.83 exp (-0.068)p	96.7
3	σ_{cc} = 79.43 exp (-0.048)p	80.3
4	σ_{cc} = 87.50 exp (-0.058)p	83.4
5	σ_{cc} = 86.49 exp (-0.056)p	91.5
6	σ_{cc} = 86.70 exp (-0.063)p	99.1

* = matrix porosity

of the validity of the extrapolation to zero porosity (11). Estimates of microhardness (there is a good correlation between microhardness and strength of cement paste) of the non-porous cement paste samples made by employing composite theory on cement paste samples completely impregnated with another phase were similar to values determined by extrapolation.

The strength ratio σ_{cf}/σ_m (which expresses the change in strength of the composite relative to the unreinforced matrix) is obtained by dividing equation (1) by equation (2) in which $p' = p$

$$\frac{\sigma_{cf}}{\sigma_m} = (1-V_f) + \frac{\phi \frac{2\ell\tau}{t} V_f}{\sigma_{mo}\exp(-bp)} \qquad (3)$$

The stress in the fibre $\sigma_f = \frac{2\ell\tau}{t}$,

where τ = interfacial shear stress between reinforcement and matrix,
ℓ/t = aspect ratio, obtained by dividing average length of flake by its thickness (ℓ/t = 80 for the mica flakes in this study;
σ_{mo} = 21.04 MPa and
b = 0.064, both of which have been obtained from curve for
V_f = 0%).

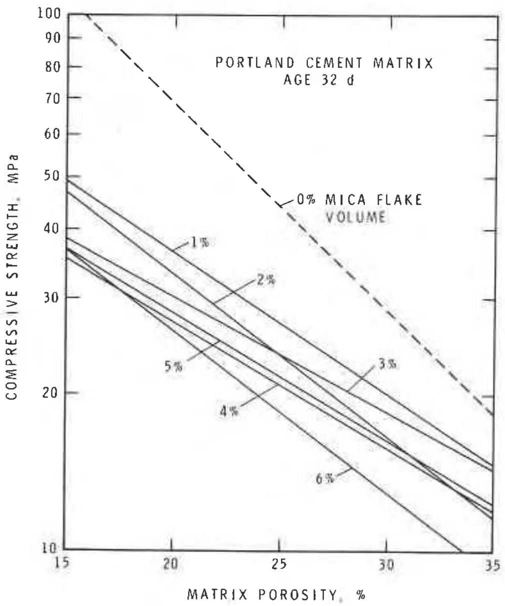

FIG. 2

Compressive strength versus matrix porosity for mica-flake-reinforced portland cement paste.

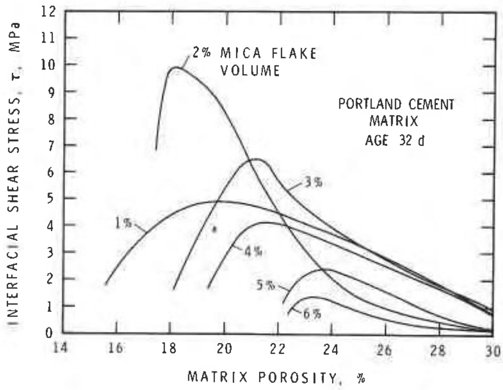

FIG. 3

Calculated values of interfacial shear strength versus matrix porosity for mica-flake-reinforced portland cement paste.

The following expression for $\phi\tau$ was used to fit equation (3) to $\left(\frac{\sigma_{cf}}{\sigma_m}, p\right)$ data obtained experimentally (p = porosity of the matrix in reinforced sample).

$$\phi\tau = K \exp\{-\alpha(p-a)\} \left[1-\exp\{-\alpha(p-a)\}\right] \exp(-bp) \qquad (4)$$

where K, α and a are constants and other terms are as previously defined.

The $\frac{\sigma_{cf}}{\sigma_m}$ versus porosity curves (not presented) increase to a maximum and then decrease as porosity increases. It was noted that mica flakes modify characteristics of the matrix, including pore structure (to be discussed later); the pore systems in reinforced and unreinforced cement pastes are therefore different. The difference in total porosity for the reinforced and unreinforced systems is not large, and as a first approximation they have been considered equal. The term exp(-bp) cancels out when equation (4) is substituted in equation (3) and $\frac{\sigma_{cf}}{\sigma_m}$ becomes a function of the matrix porosity, p, all other terms being constant.

Using a value of $\phi = 1/6$ for a random distribution of flakes in three dimension (12), values of τ were calculated and are plotted against matrix porosity in Fig. 3. There is a separate curve for each volume fraction of mica flakes. For each curve the shear stress increases to a maximum and then decreases as porosity increases. The largest value of maximum shear stress was obtained for 2% volume fraction of mica flakes.

Fracture toughness/porosity curves are plotted in Fig. 4. Toughness values for each curve decrease to a minimum value as porosity increases, then increase with further increases in porosity. Toughness values also increase as mica flake addition is increased; the curves are clustered together between 2 and 6%, suggesting that in some cases 2% addition may be sufficient to give the desired results. The shape of the toughness/porosity curve is similar for the control containing 0% mica flakes. It is suggested that inclusions such as unhydrated cement particles, $Ca(OH)_2$ particles, and pores may play a role in the fracture behaviour of hardened cement paste and affect the shape of the toughness/porosity curve.

The curves for interfacial shear stress versus porosity (Fig. 3) and for fracture toughness versus porosity (Fig. 4) have inverse shapes. It is known that increases in flexural strength due to increases in interfacial shear stress are often achieved at the expense of fracture toughness. A balance between the two properties can apparently be achieved by controlling matrix porosity, and intentional modification of the matrix-mica flake interface would have to take this into consideration.

Matrix properties may be affected by mica flakes. Nitrogen surface area measurements were made on samples containing 0 - 7 % volume fraction of mica flakes. Corrections were made to the ignited weights to account for the mica present. Surface area versus volume fraction of mica flakes is plotted in Fig. 5 for preparations with w/c = 0.35 and 0.50; it shows a decrease in surface area as mica flake addition increases. The decrease in surface area is accompanied by a decrease in the non-evaporable water content of the cement paste, indicating that the degree of hydration is lower because of flake addition. Similar observations were reported by Mikhail in his work with glass-fibre-reinforced cement (9). Typical figures for decrease in non-evaporable water content are, for example, 0.181 g/g for a sample made with w/c = 0.50 and 0% mica, decreasing to 0.155 g/g for a similar sample containing 6% mica. The hydration period was 32 days for both. The reasons for these results are not clear, but $Ca(OH)_2$ rich zones were observed in the interfacial regions between flakes and cement matrix and it is suspected that this influences the hydration process.

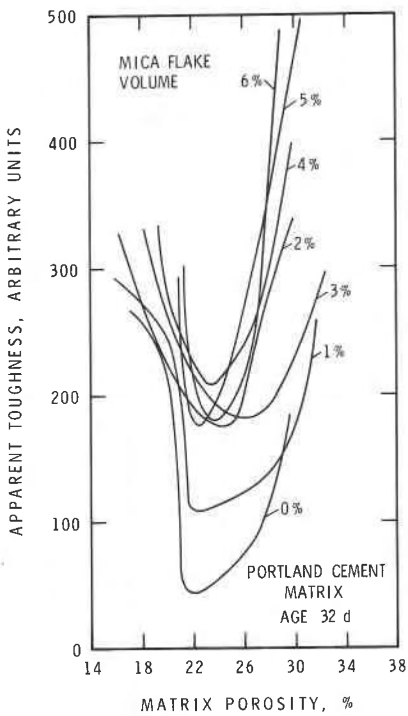

FIG. 4

Fracture toughness values versus matrix porosity for mica-flake-reinforced portland cement paste

Mica flake addition also has an effect on the pore system of hardened cement paste. To illustrate this, pore size distribution data for the w/c = 0.35 sample series will be summarized as follows. The maximum flexural strength ratio, $\frac{\sigma_{cf}}{\sigma_m}$, for a w/c ratio of 0.35 occurs at about 3% volume fraction of mica, and at this w/c ratio this paste has the lowest porosity. At mica flake volume fractions of 3% or greater the volume fraction of fine pores (0.01 - 0.003 μm) increases significantly. It appears that low porosity and high concentration of fine pores gives maximum flexural strength. At 6% volume fraction, however, total porosity and fraction of large pores (10 - 1 μm).are both higher, resulting in lower strengths. The unreinforced matrix has a greater volume concentration of pores in the medium pore size range (0.1 - 0.01 μm and 1 - 0.1 μm) than the material with 6% mica. This may account for the small but real increased flexural strength, relative to unreinforced material, for some high mica content materials. Differences in the pore size distribution may account for some aspects of the strength of these composites, but other factors such as product density, strength of matrix-flake interface and degree of crystallinity must also be considered.

Total porosity values for the various preparations are tabulated in Table 3. It is apparent that flake addition changes total porosity and that these changes are dependent on the value of V_f. High values of V_f, e.g., $V_f \geq 5\%$, generally leads to increased porosity for w/c 0.45. It was difficult to prepare samples containing V_f = 7% at w/c = 0.25.

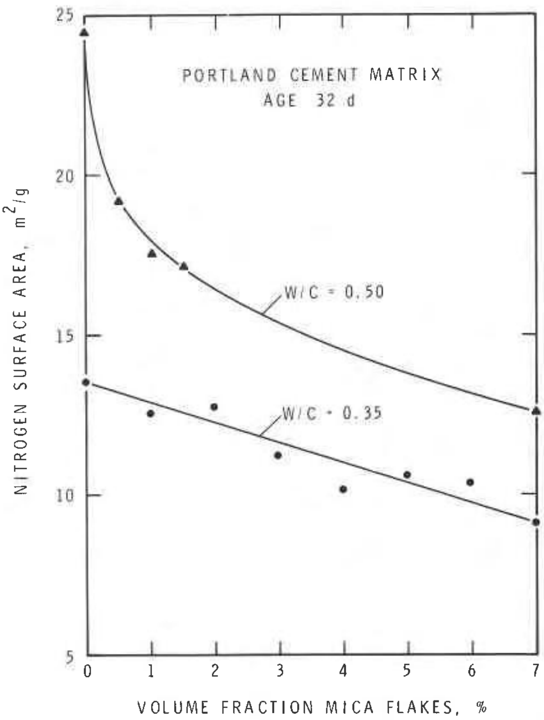

FIG. 5

Nitrogen surface area of portland cement paste reinforced with mica flakes

TABLE 3

Porosity Values of Mica-Flake-Reinforced Cement Paste Samples Hydrated For 32 days

	Water/Cement Ratio					
V_f, %	0.25	0.30	0.35	0.40	0.45	0.50
0	17.4	20.6	21.3	25.4	26.8	29.8
1	16.5	20.1	21.6	27.6	28.3	31.9
2	16.9	19.6	21.2	26.0	25.9	30.3
3	18.5	20.1	19.9	28.1	28.5	32.5
4	18.5	20.3	22.1	22.7	27.6	30.5
5	21.8	22.9	22.3	25.6	26.9	30.4
6	21.7	21.9	22.6	26.1	25.2	29.5
7	-	25.2	27.6	30.7	29.9	31.3

Aging in hydrated portland cement systems can be described as time-dependent physical and chemical processes, other than hydration, that result in microstructural change, e.g., silica polymerization, layering of silicates, etc. In the presence of admixtures that influence hydration rates surface area changes may be caused by silica polymerization (13). As mica flakes also influence the rate of hydration, it is possible that silica polymerization may be only one of the factors causing decrease in surface area.

It is apparent that factors affecting composite strength include mica content, efficiency of the reinforcement, total porosity, pore size distribution, aging, and shear stress at the matrix-mica interface. One or more of these may be the predominant factor controlling strength. The amount of mica for highest strength is porosity dependent, and at a given porosity it is probably influenced by all the above factors. Any predominating factor is difficult to determine, except that at high mica contents a greater content of large pores may be the main factor contributing to decrease in strength.

Further work is in progress to determine whether mica has potential for use in various industrial products, including those with binders containing fine aggregates.

Conclusions

1. The increase in flexural strength of mica flake-reinforced cement paste is dependent on the volume fraction of flakes and porosity and is significantly increased by a few percent of mica flakes.
2. Compressive strength of portland cement paste decreases with addition of mica flakes.
3. Fracture toughness of portland cement paste is significantly increased by the presence of mica flakes and is dependent on matrix porosity.
4. Characteristics of the matrix such as surface area, pore size distribution, and non-evaporable water content are modified by the presence of mica flakes. This modification is dependent on the volume fraction of mica added to the cement paste.
5. A balance between changes in flexural strength and fracture toughness can be achieved by controlling matrix porosity.

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