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PROPERTIES OF HIGH ALUMINA CEMENT PASTE REINFORCED WITH MICA FLAKES

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ANALYZED

ABSTRACT

The influence of small amounts of high aspect ratio mica flakes on the high alumina cement matrices is reported. Significant increases in flexural strength and fracture toughness were observed in mica-high alumina cement composites; the dependence of strength and fracture toughness of these composites on porosity and volume concentration of mica flakes was established. Compressive strength decreases with the addition of mica flakes.

RESUME

On décrit l'influence de petites quantités de paillettes de mica (dont le rapport longueur moyenne: épaisseur est élevé) sur les matrices de ciment alumineux. On constate une augmentation importante de la résistance à la flexion et de la ténacité des composés de ciment alumineux micacé; il a été démontré que la résistance et la ténacité de ces composés dépendent de la porosité et de la concentration volumique des paillettes de mica. La résistance à la compression diminue lorsqu'on ajoute des paillettes de mica.

Introduction

In recent years there have been many developments in cement composite technology (1). Fibre-reinforced cement products, including repair materials which form a significant part of this technology, generally have increased flexural strength and fracture toughness values relative to unreinforced materials. The inorganic and organic fibres utilized include asbestos, glass, steel, and polypropylene and are suitable for different applications depending on their mechanical properties. A high modulus of elasticity ratio (fibre:matrix) facilitates stress transfer between matrix and fibre and contributes to increased flexural strength.

Fibres with low modulus of elasticity but high extensibility (e.g., polypropylene) are used mainly to increase fracture toughness. Steel fibre has been used mainly with concrete and mortar, whereas glass and asbestos fibres have been associated mainly with production of thin sheet products.

Durability deficiencies of glass-fibre cement systems (including alkali-resistant glass and its modifications) have been the subject of much research, although there remains uncertainty as to the operative mechanisms responsible for observed time-dependent decreases in fracture toughness (2).

Use of asbestos fibre is coming under closer scrutiny owing to growing awareness of potential health hazards. Developments incorporating significant amounts (>10% by volume) of mica flakes as a partial replacement for asbestos fibre in some portland cement compositions have been undertaken in Canada and Japan (3,4). Mica flakes have a high modulus of elasticity relative to most cement matrix materials and are apparently less prone to the alkali-reactivity problems often associated with glass fibres (5). Mica flake reinforcement may therefore be a practical alternative to glass fibre reinforcement in many systems, particularly where the latter fibres have not proved satisfactory in the long term. It appears that economic factors will favour use of mica flakes if mechanical behaviour of mica-flake reinforced cement composites is comparable to that of glass-fibre cement composites.

High alumina cement composites have fast setting and high early strength characteristics and are used in various repair systems, e.g., bore hole plugging and anchoring grouts, where tensile strength and fracture toughness are important. A time-dependent decrease in flexural strength and fracture toughness has been observed for glass fibre-reinforced high alumina cement matrices (6). Mica flake reinforcement, which is relatively stable at temperatures up to 1200°C, may well be a suitable alternative to glass fibres in these systems. It was the objective of this study to assess the strength and fracture toughness of high alumina cement paste matrices reinforced with small amounts of mica flakes.

Experimental

Materials

Cement: Composition of the high alumina cement was as follows:

$Al_2O_3 = 40.02\%$; $Fe_2O_3 = 17.71\%$; $CaO = 37.26\%$; $SiO_2 = 3.46\%$; $MgO = 0.91\%$; $SO_3 = 0.08\%$; $Na_2O = 0.08\%$; $K_2O = 0.08\%$. Blaine fineness was $394\text{ m}^2/\text{kg}$.

Phlogopite mica: This is a high-aspect ratio reinforcing grade mica marketed as "Suzorite Mica." (Marietta Resources International Ltd., 5083 St. Denis Street., Montréal, Québec.) The flakes are generally of irregular shape with a mean width varying between 250 and 1400 μm (Fig. 1). Selected physical and chemical properties are given in Table I.

Mixes: Eight series of cement paste mixes were made using a conventional Hobart mixer. Each series contained 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 have the following water/cement ratios were prepared: 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50. They were cast in two sample geometries: 5.1 cm cubes for compression tests and $2.5 \times 2.5 \times 25.4$ cm long prisms for flexural tests. Three cubes and three prisms were made for each mix. Samples were demolded after one day and moist cured approximately 30 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. Integration of the areas under load deflection curves were used as indices of fracture toughness.

Compression tests were also carried out on a Tinius Olsen testing machine using a loading rate of 0.20 MPa s^{-1} .

FIG. 1

Optical micrograph showing size and shape of typical flakes of phlogopite mica

Porosity measurements were made on small chunks of material from each specimen. Samples were conditioned to 11% RH and then pumped in a vacuum dessicator for about 45 min prior to testing. A methanol displacement method employing Archimedes principle was used for all porosity determinations. 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.

For some samples porosity and pore size distributions were determined by mercury intrusion at 408 MPa, using an American Instrument Co. porosimeter.

TABLE I

Physical and Chemical Properties of Phlogopite

Chemical composition:

Specific gravity: 2.90

Aspect ratio $\ddagger\ddagger$: (20 flakes) 87 ± 90 (1 standard deviation)

Mean long axis of flakes: $1019 \mu\text{m} \pm 550$.

Mean short axis of flakes: $714 \mu\text{m} \pm 156$.

$\ddagger$ Chemical analysis is by Marietta Resources International Ltd

$\ddagger\ddagger$ Aspect ratio is defined as mean width of a flake divided by its thickness

Porosities determined by mercury intrusion were in general agreement with those determined by methanol displacement.

Microscopy: Examination of the microstructure of some of the samples was carried out on fractured surface using a Cambridge Stereoscan Mark 2A.

Thermal Analysis: Differential thermograms of the samples were obtained by a differential scanning calorimeter (DSC) supplied as a module to Dupont 900 thermal analysis system. The heating rate was 20°C min⁻¹.

Results

The ratio of composite flexural strength, σ_c , to matrix flexural strength, σ_m , is plotted against volume fraction of mica flakes in Fig. 2. In general, σ_c/σ_m increases to a maximum and then decreases as volume fraction of mica flakes increases. The maximum value of σ_c/σ_m also increases with water/cement ratio (w/c) up to w/c = 0.40; it then decreases. At w/c = 0.40 there is a significant increase in σ_c/σ_m (approx 90%) for as little as 1% volume fraction of mica flakes. Maximum values of σ_c/σ_m for all w/c ratios occur from 2 to 4% volume fraction of mica flakes.

The dependence of flexural strength on matrix porosity is demonstrated by the curves plotted in Fig. 3. Regression analysis is summarized in Table II. Each curve represents results for a constant volume fraction of mica flakes. All flexural strength-porosity curves for the cement pastes containing mica flakes lie above the curve for cement paste without mica flakes. The curves for 2, 3 and 4% mica flake reinforcement are close together and lie above the other curves for most of the porosity range.

Figure 4 is a plot of apparent fracture toughness versus volume fraction of mica flakes for mixes having a constant w/c ratio. The apparent fracture toughness for all w/c ratios increases to a maximum and then decreases as

FIG. 2

Ratio of composite flexural strength to matrix flexural strength versus volume fraction of mica flakes

FIG. 3

Dependence of composite flexural strength on matrix porosity for HAC-mica flake composites

TABLE II
Regression Analysis of Flexural Strength-Porosity
Curves for HAC-Mica Flake Composites

Volume Mica Flakes, %	Flexural Strength (σ_c) MPa	Correlation Coefficient, %
0	$\sigma_c = 7.96 \exp (-0.041p)^*$	91.3
1	$\sigma_c = 10.84 \exp (-0.033p)$	87.1
2	$\sigma_c = 17.35 \exp (-0.047p)$	81.9
3	$\sigma_c = 14.10 \exp (-0.032p)$	85.4
4	$\sigma_c = 10.95 \exp (-0.033p)$	75.6
5	$\sigma_c = 10.05 \exp (-0.023p)$	81.2
6	$\sigma_c = 10.86 \exp (-0.040p)$	70.0
7	$\sigma_c = 8.91 \exp (-0.029p)$	90.9

* p is matrix porosity

volume fraction of mica flakes increases. Maximum apparent fracture toughness is achieved for mixes having w/c ratios = 0.35 and 0.40. The optimum volume fraction of mica flakes for maximum apparent toughness generally increases with w/c, although there are no significant differences in optimum flake volume between w/c ratios of 0.30 and 0.35 and 0.40 and 0.45.

The dependence of apparent toughness of these HAC composites on matrix porosity is illustrated by the curves in Fig. 5. Generally, apparent toughness increases to a maximum and then decreases as matrix porosity increases. Apparent toughness-matrix porosity curves for all volume fractions of mica flakes, with the exception of some low porosity values at 1% volume fraction, lie above the reference curve for HAC paste containing 0% mica flakes. The matrix porosity at maximum toughness for all composite mixes is greater than the porosity for the reference mix.

The effect of mica flake addition on the compressive strength of HAC cement pastes is different from its effect on flexural strength: there is a general decrease in compressive strength at all water/cement ratios. This is illustrated by Fig. 6, which is a plot of volume fraction of mica flakes versus the ratio of composite compressive strength, σ_c , to matrix compressive strength, σ_m . The decrease, greater than 50% at w/c = 0.25, 4% mica, is less at higher water/cement ratios and for w/c = 0.40 compressive strength appears to be independent of mica flake addition up to 4% by volume.

The effect of matrix porosity on compressive strength is shown in Fig. 7 and the value is generally lower than the reference mix for all mica flake concentrations. Results of the regression analysis of the curves in Fig. 7 are given in Table III.

Discussion

This study demonstrates the advantage of reinforcing high alumina cement paste with high-aspect ratio mica flakes. Flexural strength and fracture toughness of the composites can be significantly increased and compare favourably with those of glass fibre-reinforced HAC paste (7,8). Factors that affect the strength and fracture toughness of these composites include matrix porosity, pore structure, product composition, density and morphology-related

FIG. 4

Dependence of apparent fracture toughness on volume fraction of mica flakes for HAC-mica flake composites

FIG. 5

Dependence of apparent toughness on matrix porosity for HAC-mica flake composites

Fig. 6

Ratio of composite compressive strength to matrix compressive strength versus volume fraction of mica flakes

FIG. 7

Dependence of composite compressive strength on matrix porosity for HAC-mica flake composites

TABLE III

Results of Regression Analysis of Compressive Strength-Porosity Curves for HAC-Mica Flake Composites

Volume Mica Flakes, %	Compressive Strength (σ_c) MPa	Correlation Coefficient, %
0	$\sigma_c = 153.50 \exp (-0.078p)$	98.5
1	$\sigma_c = 65.11 \exp (-0.040p)$	70.1
2	$\sigma_c = 88.00 \exp (-0.050p)$	78.9
3	$\sigma_c = 50.29 \exp (-0.029p)$	96.3
4	$\sigma_c = 83.85 \exp (-0.068p)$	71.2
5	$\sigma_c = 59.58 \exp (-0.034p)$	74.5
6	$\sigma_c = 53.58 \exp (-0.027p)$	72.0
7	$\sigma_c = 53.95 \exp (-0.047p)$	83.0

features, e.g., number and strength of interparticle contacts. Some of these factors have been demonstrated in other cementitious systems (9).

In the HAC composites containing higher volume fractions of mica flakes the volume concentration of large pores (1 to 20 μm) is greater and the volume concentration of small pores is less (0.01 to 0.003 μm). For a given porosity, strength generally increases with increase in the volume of small pores and decreases with increase in the volume of large pores. This may account, in part, for decreases in strength at high volume fractions of mica flakes. Strength of reinforced composites should also depend on the strength of the matrix-reinforcement interface, and it would be expected that the porosity and pore structure of the matrix at the interface would play a role in strength development. The effect of interfacial porosity on this dependence is difficult to assess, however, and has not been determined. In some instances the presence of flakes resulted in a decrease in matrix porosity, e.g., at the optimum w/c ratio (0.40) there was a significant decrease in total porosity at flake volume fractions of 2 to 4%. This reduced porosity may partially explain maximum strengths for these mica-flake concentrations. Porosity reduction due to flake addition did not, however, occur at all w/c ratios, suggesting that other factors affect maximum strengths.

The effectiveness of fibre or flake reinforcement is dependent on orientation, i.e., maximum effectiveness occurs when reinforcement is aligned parallel to the direction of stress and minimum when alignment is perpendicular to the stress. In this study a visual examination of fracture surfaces indicated that the mica flakes are randomly distributed in the matrix in three dimensions. Orientation of flakes is dependent on process variables, e.g., preferred orientation may be achieved in production of cement boards or sheet using spray suction methods.

Hydration of calcium aluminate (a predominant compound in HAC) at 21°C leads to the formation of hexagonal and cubic phases along with gibbsite (10). The loss of compressive strength in HAC pastes due to conversion of hexagonal to cubic phase is explained by increased porosity due to formation of dense cubic product. In this study all samples have approximately similar composition, i.e., the same amounts of hexagonal and cubic phases as detected by DSC. Differences in measured properties are apparently due to factors other than composition.

Examination of SEM photomicrographs for the unreinforced HAC pastes (Fig. 8) revealed that at low w/c ratios (e.g., w/c = 0.25) the aspect ratio of the globular particle is low. As w/c ratio increases the aspect ratio of the predominately platy material increases. SEM photomicrographs of mica flake composites, e.g., w/c = 0.40 samples (Fig. 8), indicate that the flakes act to decrease the aspect ratio of the particles at volume concentrations to 4%, perhaps diminishing the contribution to fracture toughness of the hydrated particles themselves. These photomicrographs are records of the predominate microstructures observed and are believed to be representative. At volume concentrations greater than 4%, aspect ratio of particles again increases. This is in concert with an increase in coarse porosity at high volume fractions. It is suggested that the aspect ratio of the particles themselves may influence fracture behaviour. If the particle-aspect ratio is sufficiently high, the particles may assume a role similar to that of reinforcement, i.e., the tortuosity of the crack migration around particles would result in increased energy requirements for fracture.

Fracture toughness-porosity curves increase with porosity to a maximum value of fracture toughness and then decrease. The maximum value of fracture energy may be a result of several factors: inclusions of dense cubic phase material in the matrix that modify the stress field in the material and possibly act as crack arrestors; changes in aspect ratio of hydrated particles; and crack-arresting properties of both mica flakes and the pores (11). At high porosities low fracture values may be due to the relative ease of crack initiation and propagation through points of interparticle contact.

A compressive strength decrease has been observed when asbestos or glass fibres are added to hydrated portland cement paste (12) similar to that observed when mica-flakes are added. The advantage of increased flexural strength of the systems overrides any disadvantage of decreased compressive strength. Compressive strength of hydrated cements is generally more than adequate for practical purposes. The compressive failure mechanisms of fibre-reinforced cement composites in general is unresolved, although it has been suggested that fibres may fail in a buckling mode (13).

Conclusions

1. Addition of small amounts of high aspect ratio mica flakes to a high alumina cement paste matrix significantly increases flexural strength and fracture toughness.
2. Mica flake addition to high alumina cement paste results in a decrease in compressive strength.
3. Mica flake addition decreases the aspect ratio of the calcium aluminate hydrate particles for concentrations less than 4%.
4. Flexural strength, compressive strength and fracture toughness of mica-flake reinforced high alumina cement composites are dependent on porosity and volume concentration of the mica flakes. The dependence of the logarithm of compressive and flexural strength on porosity is linear.
5. The porosity dependence of fracture toughness is non-linear. Non-linearity may result from energy dissipation processes due to pore-crack interaction.
6. Mica flakes have potential as possible replacement for glass or asbestos fibre in high alumina cement paste.

- (a) $W/C = 0.25$, 0% MICA
(b) $W/C = 0.40$, 0% MICA
(c) $W/C = 0.40$, 1-4% MICA
(TYPICAL)
(d) $W/C = 0.40$, 5% MICA
(e) $W/C = 0.40$, 7% MICA

FIG. 8

SEM photomicrographs of HAC-mica flake composites

References

1. C.D. Johnston. Progress in Concrete Technology, (Ed. by V.M. Malhotra), Dept. Supply and Services Canada, Chap. 12, 451 (1980).
2. A.J. Majumdar and R.W. Nurse. Mats. Sci. and Eng. 15, 107 (1974).
3. Marietta Resources Int., Information Sheet T-10 (1976).
4. S. Kin and T. Makimoto. Japan Kokai 79-99, 131, 4 Aug 1979; Chem. Abstr. 91 197877 (1980).
5. P.E. Grattan-Bellew and J.J. Beaudoin. Cem. Conc. Res. 10, 789 (1980).
6. A.J. Majumdar, B. Singh, A.A. Langley and M.A. Ali. J. Mats. Sci. 15, 1085 (1980).
7. F.J. Grimer and M.A. Ali. Mag. Conc. Res. 21, 23 (1969).
8. H.C. Chan and W.A. Patterson. J. Mats. Sci. 6, 342 (1971).
9. P.J. Sereda, R.F. Feldman and V.S. Ramachandran. 7th International Congress Chemistry Cement, Paris, VI-1, 3-44 (1980).
10. V.S. Ramachandran and R.F. Feldman. Cem. Conc. Res. 3, 729 (1973).
11. J.J. Beaudoin. To be published.
12. R. Sh. Mikhail, M. Abd-El-Khalik and A. Hassanein. Cem. Conc. Res. 8, 765 (1978).
13. R.N. Swamy and P.S. Mangat. Cem. Conc. Res. 4, 451 (1974).

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