NRC Publications Archive Archives des publications du CNRC

Effect of mica addition on the microstructure of Portland cement paste Beaudoin, J. J.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

[https://doi.org/10.1016/0008-8846\(86\)90093-1](https://doi.org/10.1016/0008-8846(86)90093-1)

Cement and Concrete Research, 16, July 4, pp. 554-560, 1986-07-01

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

<https://nrc-publications.canada.ca/eng/view/object/?id=3662cd60-6354-468f-97b8-8b36ede41335>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=3662cd60-6354-468f-97b8-8b36ede41335>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Ser
TH1
N21d
no. 1407
c. 2
BLDG

**National Research
Council Canada**

**Institute for
Research in
Construction**

**Conseil national
de recherches Canada**

**Institut de
recherche en
construction**

Effect of Mica Addition on the Microstructure of Portland Cement Paste

by J.J. Beaudoin

ANALYZED

Reprinted from
Cement and Concrete Research
Vol. 16, No. 4, 1986
p. 554-560
(IRC Paper No. 1407)

Price \$2.00

NRCC 26401

NRC - CISTI
IRC
LIBRARY

FEB 25 1986

BIBLIOTHÈQUE
IRC
NRC - CISTI

RÉSUMÉ

Pour déterminer l'effet de l'addition de mica sur la microstructure de la pâte de ciment, on a observé les modifications survenues dans des éprouvettes hydratées pendant des périodes atteignant cinq ans au niveau de la répartition des pores par tailles, de la porosité, de la teneur en eau captive et de la répartition des particules CH selon la dimension. Les changements microstructurels dépendaient du rapport eau-ciment et de la quantité de mica ajoutée.

CISTI/ICIST

3 1809 00210 5861

EFFECT OF MICA ADDITION ON THE MICROSTRUCTURE OF PORTLAND CEMENT PASTE

J.J. Beaudoin

Institute for Research in Construction, National Research Council of Canada,
Ottawa, Canada, K1A 0R6

(Communicated by F.H. Wittmann)

(Received April 24, 1986)

ABSTRACT

In assessing the effect of mica reinforcement on cement paste microstructure, modifications to pore-size distribution, porosity, non-evaporable water content, and CH particle size distribution were observed for samples hydrated for up to five years. Microstructural changes were dependent on water-cement ratio and amount of mica added.

Introduction

There has been in the past decade a proliferation of new products marketed for concrete repair (1). In recognition of the serious state of deterioration of concrete structures such as parking garages and bridge decks, many of these products include fibre-reinforced cement systems. The addition of a reinforcement (fibre or flake) to a portland cement-based matrix generally results in an increase of either or both flexural strength and toughness, properties highly desirable in a repair. Composite theory, usually some form of mixture rule, is generally applied to predict the behaviour of the materials (2).

Composite theory, however, has normally been applied without consideration for changes to the matrix, including microstructural changes brought about by the reinforcement. Such changes may determine durability as well as strength and toughness. As mica flakes have been found to be a useful reinforcement for portland cement matrices (3), it was the objective of the present work to define their effect on the matrix microstructure of cement composites moist cured for periods of up to five years.

Experimental

Materials

Cement: Portland cement composition: $C_3S = 51.4\%$; $C_2S = 20.3\%$; $C_3A = 12.7\%$; $C_4AF = 6.7\%$ and $CaSO_4 = 5.4\%$ as calculated by the Bogue method.

Mica: A phlogopite type mineral with high-aspect ratio; physical and chemical properties of the flakes have been published (3).

Mixes: Cement paste mixes with water-cement ratios of 0.25-0.70 and mica content of 0-7% by volume were hydrated in lime-saturated water for up to five years. Mix details are provided elsewhere (3).

Technique

Porosity and pore-size distributions were determined by mercury intrusion under pressures up to 408 MPa, using an American Instrument Co. porosimeter.

Non-evaporable water content was determined by TGA, employing a 1090 Dupont Thermal Analyzer containing a 951 TGA accessory.

Leaching of CH from mica-cement specimens (sliced 0.030 μm thick) was accomplished with partially-saturated lime solutions according to the method developed by Ramachandran and Polomark (4). Leaching time was at least 30 days; its efficiency was checked by TGA.

Estimations of CH content were verified by DSC. A Dupont 1090 thermal analysis system was used.

Results and Discussion

Pore-size distribution

Pore-size distribution for mica-reinforced cement paste specimens hydrated for five years is presented in Figure 1. Mica addition generally results in greater pore volume above a pore diameter greater than 0.10 μm . The threshold value of the control samples (pore size at which the initial mercury intrusion rate changes significantly) also increases with w/c ratio from 0.05 μm at w/c = 0.35 to 0.30 μm at w/c = 0.70. Pores greater than 0.30 μm were detected only in mica-reinforced material (w/c = 0.70). Many pores exist in the interface zone, between the bulk matrix and the mica surfaces where properties are dependent on w/c ratio and curing conditions (5).

Total porosities expressed as pore volume per unit volume of paste (corrections are made for the volume of mica in a given sample) are given in Table 1. The cement matrix (w/c = 0.70) containing 5% mica has less total pore volume (over the entire pore size range) than matrices containing less mica (1-3%), indicating that mica does not necessarily increase total porosity at higher w/c ratios. The total pore volume of specimens having w/c = 0.35 and the highest

FIG. 1. Pore size distribution of cement paste samples (with and without mica) hydrated for five years with different amounts of mica.

(V_f = volume % mica)

FIG. 2. Non-evaporable water versus mica content for cements hydrated for (a) five years and (b) 35 days

mica content is also less than that for the control sample containing no mica.

Non-evaporable water content

Plots of W_n (non-evaporable water content) versus mica content for samples hydrated for 35 days and five years are presented in Figure 2. In general, W_n decreases with mica flake addition, although at the lowest w/c ratio (0.25) W_n appears to be independent of it. Regression curves of W_n versus matrix porosity (for 35 d hydration) are given in Figure 3 for w/c = 0.25-0.50, for which correlation coefficients were greater than 90%. Values of W_n over most of the porosity range were generally less when mica was added to the paste. At a given porosity, W_n decreased with percentage of mica. A similar effect has been observed with addition of glass fibers (6).

Some workers have postulated that CH particles in cement paste act as nucleation sites for C-S-H growth (7). Mica affects the distribution of CH particles in cement paste, e.g., interface regions in mica cements are CH-rich (2). A modification of this nucleation process in the presence of mica reinforcement may be one explanation for lower rates of hydration. It is possible that mica enhances the early crystallization of CH so that the nucleation effect of CH (with large surface face energy) is reduced.

Table 1. Porosity (%) of Mica Cements Hydrated for Five Years

Mica %	0.70	0.60	0.50 w/c	0.40	0.35
0	32.0	26.0	17.0	11.5	8.0
1	35.9	25.8	18.7	12.8	8.6
2	38.3	25.3	18.4	15.5	10.2
3	34.0	28.4	19.1	12.9	5.7
4	30.2	30.2	-	14.1	-
5	30.0	29.5	20.0	-	-

CH Particle Size Distribution

The size distribution of CH particles in paste was determined in the following manner. A pore-size distribution curve was obtained using a sample from which CH had been removed by leaching with a partially-saturated lime solution (4). It is assumed that mercury enters all the spaces formed when CH is removed, and that CH particle size is equivalent to the size of the vacated space. A corresponding pore-size distribution curve for an unleached companion sample was also obtained. A CH particle size distribution curve was then constructed by plotting the difference in cumulative pore volume from the pore-size distribution curves so obtained versus the particle size. Typical pore-size distributions for leached and unleached cement pastes containing 4% mica are given in Figure 4; the constructed CH particle size distribution is also given. In general, the curve has three regions: one of increasing pore volume, 0-1; one with essentially no increase in pore volume, 1-2; and a fine pore region with increasing pore volume, 2-3.

CH particle size distribution curves for five-year mica-reinforced pastes are given in Figure 5. The volume of CH in control and mica-reinforced samples generally increases with w/c ratio for particle sizes greater than $0.20\ \mu\text{m}$. Several curves exhibit a low slope between 0.2 and $0.02\ \mu\text{m}$ and an increasing slope between 0.02 and $0.004\ \mu\text{m}$. Many samples, therefore, contain small amounts of CH in the former size range and, apparently, larger amounts in the latter.

CH particle size histograms (over the size range $2\text{--}0.2\ \mu\text{m}$) for $w/c = 0.75$ are presented in Figure 6. The largest volume of CH particles occurs in the size range $0.8\text{--}0.6\ \mu\text{m}$ for mica additions up to 2% and is greatest for the control samples. The range for maximum CH volume shifts to $0.6\text{--}0.4\ \mu\text{m}$ for 3 and 4% mica. The particle size ranges for maximum CH volume for $w/c = 0.60$, 0.50 and 0.40 (histograms are not plotted) are $0.6\text{--}0.4$, $0.4\text{--}0.3$, and $0.3\text{--}0.2\ \mu\text{m}$, respectively. Control samples for these w/c

FIG. 3. Non-evaporable water versus matrix porosity for mica cements hydrated for 35 days. V_f = volume % mica

FIG. 4. Typical pore size and CH particle size distribution for mica-reinforced cement paste, $w/c = 0.60$, 4% mica, hydrated for five years. V_f = volume % mica

ratios generally have the largest CH volume in these ranges.

Volumes of CH determined by mercury porosimetry were nearly always higher than those determined by DSC methods. The two were approximately equal, however, if the "fine pore" volume (region 2-3 of the constructed curve, Figure 4) was subtracted from the total volume determined by porosimetry. DSC values of CH volume are plotted against volumes determined by the corrected mercury porosimetry method in Figure 7. It appears that leaching of CH from cement composites "opens up" fine pores previously inaccessible to mercury.

Volumes of CH determined by the mercury intrusion method are given in Table 2. Nearly all the free lime was removed from most samples by the leaching process, as verified by thermal methods, but in a few samples some remained, e.g., $w/c = 0.40$. The volume of CH generally decreases with mica addition for $w/c > 0.50$. The exception is at 4% mica content, at which the particle size curve does not flatten (Figure 5) and the amount of CH may be overestimated. A lower amount of lime with mica addition can be explained, in part, by the lower values of non-evaporable water for these samples (Figure 8). Higher CH contents with 4% mica may be due to porosity not accounted for in applying corrections to constructed particle size distribution curves. A difference in C/S ratio of the C-S-H formed in the presence of mica would also affect the CH content and non-evaporable content.

FIG. 5. Particle size distribution of CH in mica cements. Hydrated for five years

Conclusion

1. Mica flakes modify the pore-size distribution and total porosity of the matrix in cement composites hydrated for five years. Pores of diameter greater than $0.30 \mu\text{m}$ are dependent on water-cement ratio and mica content.
2. Addition of mica flake generally retards hydration of cements. The decrease is dependent on water-cement ratio and mica addition.

FIG. 6. Particle size of CH in mica cements in the range 2.0 - 0.2 μm . Hydrated for five years; w/c = 0.70; V_f = volume % mica

FIG. 7. Comparison of CH estimation methods for mica cements. Method of estimating CH, using mercury porosimetry, and correction procedures are explained in text

FIG. 8. Volume of CH in mica cements hydrated for five years versus non-evaporable water content

Table 2. Total Volume (%) of CH Determined by Mercury Porosimetry for Mica Cements Hydrated for Five Years

w/c	Mica (%)					
	0	1	2	3	4	5
0.70	22.0 (16.5)*	19.0(12.5)	15.0(12.0)	12.5(11.5)	24.0(15.0)	17.0(12.0)
0.60	20.0 (13.0)	19.0(12.5)	18.0(13)	18.0(12.5)	20.0(14.0)	17.0(12.5)
0.50	22.0 (17.0)	19.0(15.0)	17.5(15.0)	15.0(11.5)	22.0(17.0)	10.0 (9.0)
0.40	12.5**(12.5)	-	12.5**(12.5)	17.0(17.0)	16.0(16.0)	-

*Estimates in brackets obtained by correcting particle size distribution curves (see text).

**Not all lime leached out.

3. Mica flakes modify the size distribution of CH particles in the matrix of cement composites hydrated for five years. Maximum particle size increases with water-cement ratio.
4. The volume percentage of large CH particles increases at mica contents greater than 2%.
5. CH in cements prevents mercury from entering some of the micropores. When the CH is removed, the pores are accessible to mercury.
6. Consideration should be given to the effect of fiber or flake reinforcement on the cement matrix when making long-term predictions of strength and durability.

Acknowledgement

The author wishes to thank R. Myers and F. Guertin for assistance with the experimental work. This paper is a contribution from the Institute for Research in Construction, National Research Council of Canada.

References

1. P. Hewlett, Construction Repairs and Maintenance, 1, 3 (1985).
2. V.S. Ramachandran, R.F. Feldman and J.J. Beaudoin, Concrete Science, Heyden & Son, 427 p. (1981).
3. J.J. Beaudoin, Cem. Concr. Res. 13, 153 (1983).
4. V.S. Ramachandran and G.M. Polomark, J. Chem. Tech. and Biotech., 32, 946 (1982).
5. A. Bentur, S. Diamond and S. Mindess, J. Mats. Sci. 20, 3610 (1985).
6. R. Sh. Mikhail, M. Abd-El-Khalik and A. Hassanein, Cem. Concr. Res. 8, 765 (1978).
7. J. Skalny and J.F. Young, Proc. 7th Int. Congr. Chem. Cem., Paris, Paper II-1, 3 (1980).