

MECHANICAL PROPERTIES OF HIGH PERFORMANCE CEMENT BINDERS
REINFORCED WITH WOLLASTONITE MICRO-FIBRES

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ABSTRACT

Factors that influence the flexural strength characteristics of the cement-water and the cement-silica fume-water systems reinforced with inorganic wollastonite micro-fibres are discussed. The effect of the wollastonite micro-fibres on matrix pore structure was investigated using mercury intrusion porosimetry and helium gas pycnometry. Fibre-matrix interaction was also examined using the conduction calorimetry method. Results indicated that natural wollastonite micro-fibres are effective in improving both pre-peak and post-peak load behaviour. The results are discussed in terms of composite theory and matrix microstructure.

Introduction

The study of high performance cement-based material systems has intensified in recent years. Research and development activities in this area have coincided with a national focus on infrastructure renewal. The development of high performance cement-based material systems generally involved the use of silica fume as these composite products are found to have low permeability to aqueous solutions. The achievement of improvement in the strength characteristics, however, does not necessarily insure the attainment of high performance. Durability and long term service requirements have become a more important concern for both new construction and rehabilitation projects in the construction industry. Repair materials must be compatible with the new genre of concretes. In recent years, many potential cement composites for repair have been developed and they are commonly reinforced with fibrous materials. This is due to the fact that these fibre-reinforced composites can be designed to have specific strength and toughness characteristics [1,2].

Cement paste matrices reinforced with carbon and steel micro-fibres have been found to have significant improvements in both pre-peak and post-peak load behaviour [2,3]. These micro-fibres are generally very fine with fibre size in the same range of the cement particles (about 25-40 μ m) and the fibre length usually does not exceed about 5-6 mm. Micro-fibres were found to be a convenient material to mix in a cement matrix at relatively high concentrations (up to 15% by volume). These composite materials are suitable for grouts and repair material formulation. Thus far research and development activities have concentrated on the use of carbon and steel micro-fibres. There are a number of other inorganic fibrous minerals that are readily available for possible applications. Natural wollastonite, a silicate mineral (β -CaO-SiO₂), is crystallized in a fibrous form. It has been used in the pottery industry and to a limited extent in the cement product industry for the manufacturing of cement board and tile [4]. The use of natural wollastonite micro-fibres for the development of high performance repair cement composites promises to offer some economic benefits compared to steel or carbon micro-fibres which are generally more expensive. A systematic investigation has been carried out to explore the potential of the natural wollastonite micro-fibres as a reinforcing material in cement matrices. The objective was to examine various factors which affect composite behaviour and to develop new high performance cement-based materials. The results of the first phase of the study are presented. The feasibility of utilizing wollastonite micro-fibres as a reinforcing material component in the cement-based systems is discussed.

Experimental

Materials

Type 10 Portland cement^{*} was used as the base component. The natural wollastonite micro-fibres which appeared in the form of rectangular shape rods or needles, as shown in the SEM micrograph in Figure 1, were obtained from a local supplier[†]. The size of most of the fibres is estimated in the range of about 25-30 μ m in the transverse dimension and the length is in the range of about 0.4 - 0.6 mm. The silica fume^{**} was confirmed to be an amorphous material by X-ray diffraction analysis. The superplasticizer solution^{***} is made up of about 48% solids and 52% water.

Specimen Preparation

Seven different concentrations varying from 2% to 15% by volume of the wollastonite micro-fibres were used. The wollastonite micro-fibres were first manually blended with cement in a steel mixing bowl until a uniform mixture was obtained by visual inspection. The superplasticizer solution equivalent to about 1% by weight of the solid mixture was then added to the water solution gauged to provide a water/cement ratio of 0.35. The liquid water containing the superplasticizer solution was first placed in the mechanical blender and mixed for about 2 minutes. The solid mixture of the cement and the wollastonite micro-fibres was then added to the water solution and blended for a period of about 5 minutes. The cement composite mixture was then cast into a plastic mould which measured about 40 x 130 x 4 mm. The cement mixture was allowed to harden in a moisture controlled room at saturation for a period of 24 hours. The hardened cement specimen was then de-moulded. After the de-moulding process, the specimens were kept in a calcium hydroxide solution to continue the normal hydration for a period varying from 7 days to 28 days. The composite specimens were sliced into small beams measuring about 4 x 65 x 4 mm after the selected period of hydration treatment. These test specimens were used for flexural strength determination and characterization of other physical properties.

Similar compositions of the wollastonite micro-fibres were mixed with the cement-silica fume matrix in the preparation of the cement-silica fume-wollastonite composite system. The mixture consisted of 85 parts cement and 15 parts silica fume. The cement and the silica fume powder were first manually mixed together to obtain a uniform mixture. The superplasticizer solution, equivalent to about 1% of the solid mixture, was blended with the water solution (based on a similar water/cement + silica fume ratio of 0.35). Similar procedures were followed in the preparation of the composite specimens for evaluation.

Test Measurements

Flexural strength of the composite specimens was determined using a computer controlled Material Testing System[#] based on a three-point loading method. The test specimens were maintained in the calcium hydroxide solution after slicing and prior to the bending test. The excess water from the specimen surface was first removed by a water absorbent *type* paper and was then installed on the specimen support.

The porosity in the specimens was determined using a mercury intrusion porosimetry method and a helium gas pycnometric method. The mercury porosimeter^{##} was operated at pressures up to 414 MPa



Figure 1. SEM micrograph of the natural wollastonite micro-fibres.

(60,000 psi). The specimens used in the mercury porosimetry measurements were those specimens which had been tested for their flexural strength in the bending test experiments. The helium gas pycnometer^{###} was operated at a gas pressure of about 0.21 MPa (30 psi). Separate and slightly larger specimens were used for the helium pycnometry measurements. The reference cement paste and the composite specimens were oven-dried at 105°C for a period of at least 72 hours prior to use for both mercury porosimetry and helium pycnometry measurements. The dried composite specimen was broken into 7 to 8 small pieces of solid and weighed about 0.5 grams for porosimetry measurement. The dried composite specimen was maintained as a whole piece and weighed about 1.2 grams for the helium pycnometry measurement.

The fractured surface and the internal microstructure of the cement composite specimens were examined using a scanning electron microscope^{####}.

Possible fibre-cement matrix interaction was investigated using a computer controlled calorimeter^{####}. A water solution based on a water/cement ratio of 0.35 was mixed with the composite matrix and the hydration reaction was monitored for a period of about 24 hours.

^{*} Type 10 Portland cement was supplied by the St. Mary's Cement, Quebec, Canada.

^{**} The natural wollastonite micro-fibres were of the NYAD G grade and obtained from Prescott & Co., Mississauga, Ontario, Canada.

^{***} The silica fume powder used in the investigation contained 95.2% SiO₂, 1.6% carbon, 0.27% K₂O, and 0.10% Na₂O.

^{****} The superplasticizer solution was the Atlas Mighty 150 RD2 grade.

[#] The Material Testing Systems is the MTS Model 810 apparatus manufactured by MTS Systems Corp., Mpls, MN, U.S.A.

^{##} The mercury porosimeter is the Model 60,000 psi Porosimeter manufactured by American Instrument Co., Maryland, U.S.A.

^{###} The helium gas pycnometer is the Beckman 930 Comparison Pycnometer manufactured by Beckman Instrument, Inc., California, U.S.A.

^{####} The scanning electron microscope is the Cambridge Steroscan Model S250 manufactured by Cambridge Instruments, England.

^{#####} The computer controlled calorimeter is the Cement - Calorimeter model manufactured by the T-D Institute of Applied Physics, Netherlands.

Results and Discussion

Flexural strength and microstructural characteristics of cement composites reinforced with wollastonite micro-fibres were observed to vary depending on the composition of the matrix. The experimental results are analyzed and discussed in terms of difference in the observed properties.

[A] Flexural Strength

The flexural strength of the Portland cement paste prepared with a water/cement ratio of 0.35 and a superplasticizer (solution equivalent to about 0.3% of the solids) increased gradually in the range of 10.3 - 13.7 MPa (1500 - 1990 psi) after hydration in calcium hydroxide solution for 7 to 28 days. The flexural strength of cement paste prepared with 85 parts Portland cement and 15 parts silica fume with superplasticizer solution also equivalent to about 0.3% of the solids and a water/solid ratio of 0.35 also increased gradually in the range of 4.0 - 8.5 MPa (585 - 1233 psi) from 7 to 28 days after hydration in the calcium hydroxide solution.

Addition of wollastonite micro-fibres to cement paste significantly modified the physical characteristics and the strength properties of the composite system after normal hydration. The flexural strength of the cement-wollastonite composites was observed to vary from 10.7 MPa (1550 psi) to 22.60 MPa (3150 psi) depending on the mixture composition and the hydration period, as shown in Figure 2. The matrix generally displayed a small increase in the flexural strength as the hydration period increased from 7 days to 28 days. A relatively large and linear increase in the flexural strength was, however, observed when the amount of the wollastonite micro-fibres incorporated into the cement matrix was increased from 2% to 11.5% by volume. A maximum flexural strength in the composite system was observed when the composite system contained about 12.5% by volume of the wollastonite micro-fibres. Further increase of the wollastonite micro-fibres in the cement matrix up to 15% by volume resulted in a slight reduction in the flexural strength of the composite system. This trend was maintained in a similar manner when the hydration period was increased from 7 days to 28 days.

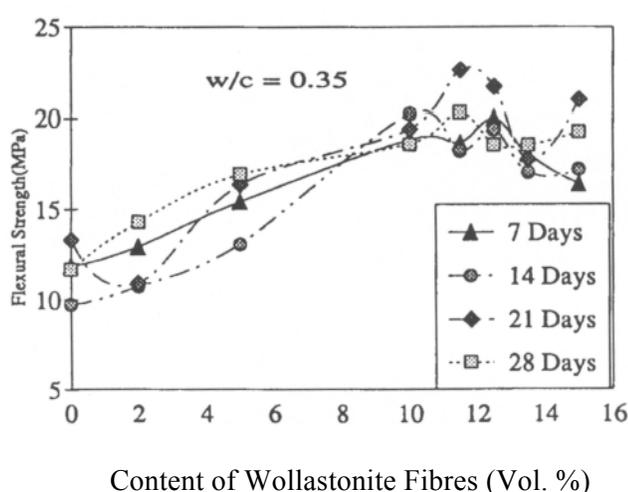


Figure 2. Flexural strength of cement-wollastonite composite versus volume fraction of wollastonite fibres.

Wollastonite micro-fibres incorporated into a matrix consisting of cement and silica fume particles modified strength properties of the cement-silica fume-wollastonite composite system in a similar manner. The variation of the flexural strength with mixture composition and hydration period, however, covered a much wider range, 5.4 - 24.0 MPa (780 - 3480 psi), as shown in Figure 3. A similar trend of linear increase in the flexural strength was also observed when the amount of wollastonite micro-fibres incorporated into the cement-silica fume matrix was increased from 2% to 11.5% by volume. A maximum flexural strength in the composite system was also observed when the composite system contained about 12.5% by volume of wollastonite micro-fibres. Further increase of wollastonite micro-fibres in the cement-silica fume matrix up to 15% by volume also caused a slight reduction in the flexural strength of the composite system.

The incorporation of wollastonite micro-fibres into the cement matrix was also observed to improve the post-peak load behaviour in both the cement-wollastonite and the cement-silica fume-wollastonite composite systems. A typical load-deflection curve is shown in Figure 4. An initial linear region O - A is followed by a non-linear region A - B with a continuous increase in load to a maximum at B. This is followed by a strain softening region B - C. The non-linearity in region A - B has been attributed to strain hardening phenomena due to multiple crack formation [3]. Fibre pull-out processes predominate in region B - C. Fracture and total failure in a pure hydrated cement matrix generally occur abruptly with a straight drop in the load-deflection plot when point A is reached. Fracture and failure in the cement composites reinforced with the wollastonite micro-fibres occur gradually and the drop in the load-deflection plot (region B - C) occurred in a steady manner demonstrating improved ductility characteristics. This modification in post-peak behaviour was observed to vary slightly depending on the concentration of the wollastonite micro-fibres mixed with the cement or the cement-silica fume matrices.

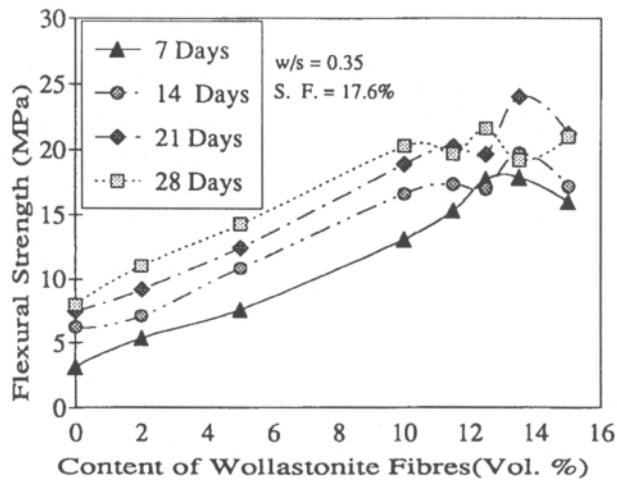


Figure 3. Flexural strength of cement-silica fume -wollastonite composite versus volume fraction of wollastonite fibres.

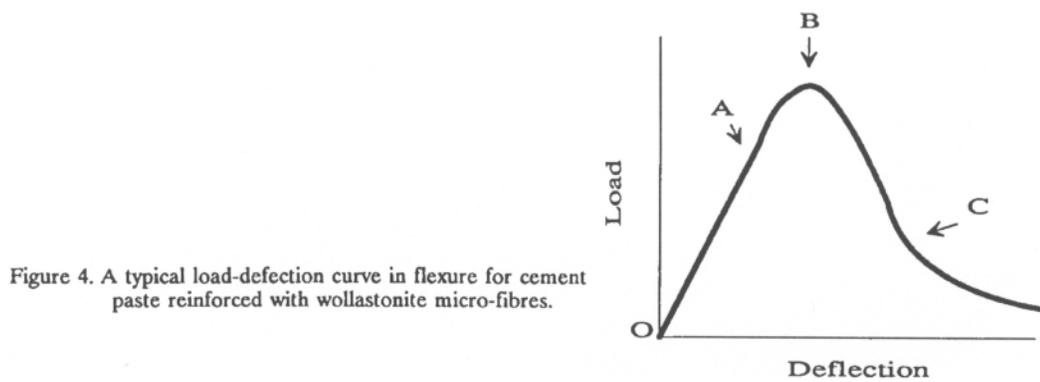


Figure 4. A typical load-deflection curve in flexure for cement paste reinforced with wollastonite micro-fibres.

Results showed that in both composite systems 12.5% by volume is the optimum concentration of wollastonite micro-fibres to maximize the flexural strength. The significant improvement of the flexural strength characteristics in the pre-peak region resulting from incorporation of the wollastonite micro-fibres can be partially attributed to the relatively high modulus of elasticity of the wollastonite inorganic mineral (ie 200 GPa). The improvement of the post-peak load behaviour is attributed to the multiple cracking and fibre pull-out process. Pull-out of wollastonite fibres is clearly illustrated in Figure 5.

[B] Microstructure of the Cement Composites

The microstructure of the cement paste matrices and of the cement-silica fume paste matrices reinforced with the wollastonite micro-fibres is significantly different in the two composite systems. The results are discussed in terms of pore structure parameters and physical characteristics as determined by the mercury porosimetry and the helium gas pycnometry measurements.

Specimens hydrated for 21 days were selected for characterization of the microstructure. These samples had the highest values of flexural strength in half the systems studied. Mercury intrusion porosimetry showed that the total porosity in the hydrated cement-wollastonite composite matrix is in the range of 18.3 - 21.5%. However, if the wollastonite micro-fibres are assumed to be non-porous and the porosity is concentrated

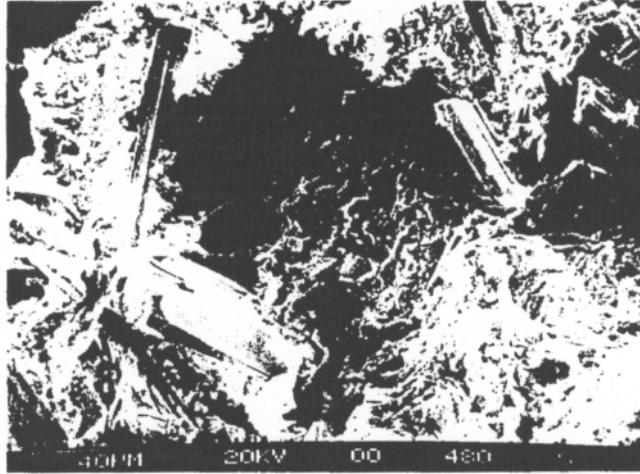


Figure 5. SEM micrograph of the fracture surface of a cement-wollastonite composite illustrating pull-out of wollastonite micro-fibers from the cement matrix.

only in the cement paste matrix portion, the total porosity in the composite system expressed as a percentage of the paste fraction is in the range of 20.5 - 23.6%. There is a very narrow range of variation with change in mixture composition. These results are consistent as all composite samples in the cement-wollastonite system were prepared with the same water/cement ratio of 0.35.

Mercury porosimetry also indicated that the total porosity in the cement-silica fume-wollastonite composite is in the range of 15.4% - 18.5% and the corrected total porosity is in the range of 15.5 - 21.5%. Porosity in both data sets increases gradually with the amount of wollastonite micro-fibers (2% to 15% by volume). Measurements indicate that the overall total porosity in the cement-wollastonite composite system is larger than that in the cement-silica fume-wollastonite composite system. This result is clearly dependent on the assumption that mercury intrusion gives true porosity values for both systems. This has been questioned by some investigators and will be discussed later [5].

Close examination of the test data showed that the distribution of pore sizes in these two composite systems is significantly different. The content of the pores larger than $1\mu\text{m}$ in both composite systems is very similar. However, pores in the range of $0.5 - 0.1\mu\text{m}$ in the cement-silica fume-wollastonite composite system is significantly higher than those in the cement-wollastonite composite system. Furthermore, the pore volume in this size range was observed to increase gradually as the content of the wollastonite micro-fibers in the composite was increased from 0% to 15% by volume. The distribution of pore sizes after correction on the basis of the cement matrix volume is shown in Figure 6 for the cement-wollastonite system and in Figure 7 for the cement-silica fume-wollastonite system. There are striking similarities in character of the pore size distribution data for the two cement systems reinforced with the wollastonite micro-fibers and mortars prepared with similar binders containing silica sand inclusions [6]. It has been reported that pores in the $0.5 - 0.1\mu\text{m}$ range are formed at the sand particle-paste interface in mortars. These pores increase with sand-cement ratio in mixes with and without silica fume. Silica fume addition to mortars results in an increase of pores in this range at the sand-paste interface. Silica fume addition to mortars therefore had the general effect of increasing the volume of coarse pores.

Processes associated with transition zone formation in the vicinity of inclusions such as wollastonite micro-fibers affect the deposition of cement reaction products (such as CH, C-S-H, and ettringite) in this region. The pore structure in this region is generally coarser and is affected by the quantity, size and nature of the inclusion [7]. Inclusions can affect rate and extent of hydration in addition to CH formation and matrix permeability [8]. Silica fume reacts with CH. The removal of CH from the matrix and interface decreases the permeability of the system and degree of hydration of the cement, thus resulting in a higher porosity. Low permeability is achieved despite higher porosity due to a higher degree of discontinuity in the pores [8]. The

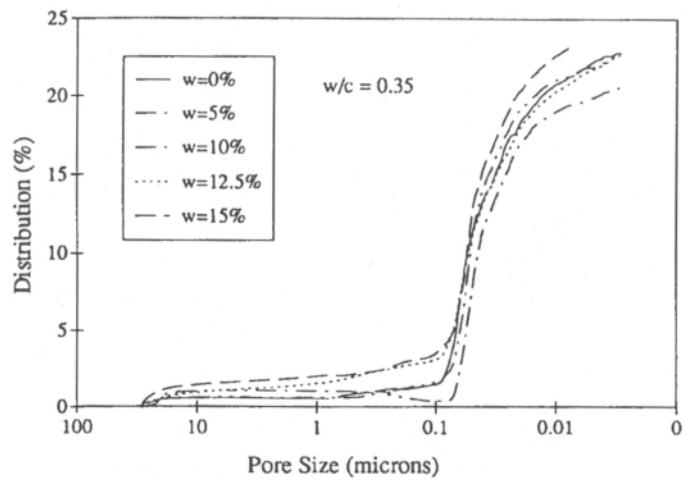


Figure 6. Pore size distribution in the cement-wollastonite composite system.

effect of wollastonite micro-fibres on the pore structure of cement matrices described above also appears to account for the strain-softening behaviour described earlier. A fibre pull-out mechanism was observed to be operative. The pull-out process is likely affected by interfacial pore structure resulting from addition of wollastonite micro-fibres.

Solid density of the cement-wollastonite composite samples determined by the helium pycnometry measurements is in the range of 2.11 - 2.34 g/ml; no trend with the mixture compositions was observed. The solid density of the cement-silica fume-wollastonite composite system is in the range of 1.872 - 2.026 g/ml. A gradual increase with the content of the wollastonite micro-fibres was observed. It is apparent that helium does not enter all the pore space in systems containing silica fume. The total porosity of the two and of the three component composite systems determined by helium pycnometry was significantly lower than values determined by the mercury intrusion porosimetry. A correlation between the porosity values determined by the two different methods is shown in Figure 8. Porosity values determined by helium pycnometry are significantly lower for both composite systems containing wollastonite micro-fibres than values obtained by

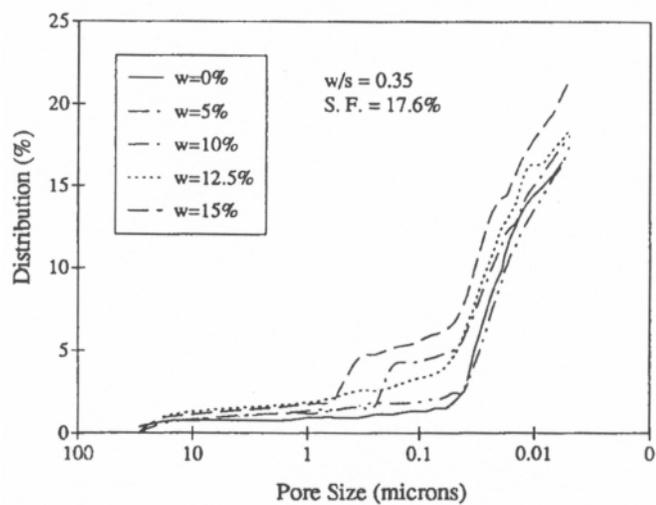


Figure 7. Pore size distribution in the cement-silica fume-wollastonite composite system.

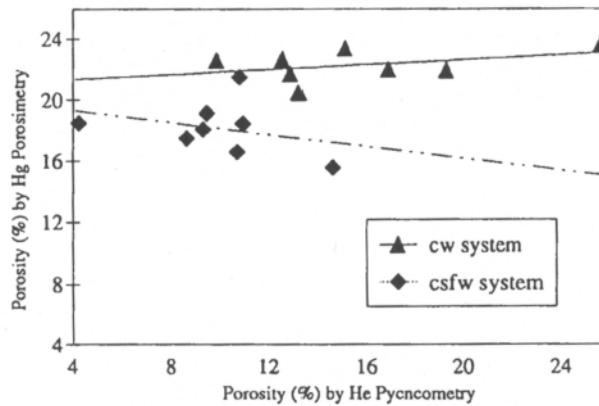


Figure 8. Porosity of cement and cement-silica fume pastes containing wollastonite micro-fibres: Values determined by Hg intrusion porosimetry versus values determined by He gas pycnometry.

mercury intrusion porosimetry. This suggests that mercury at high pressures damages the microstructure and enters into space inaccessible to helium. This effect appears to be more pronounced for the two component cement-wollastonite system. Addition of wollastonite micro-fibres appears to have a similar effect to that of silica fume in promoting pore discontinuity.

[C] Scanning Electron Microscopy

Scanning electron microscopic examinations showed that the wollastonite micro-fibres were uniformly and randomly dispersed in the cement and in the cement-silica fume matrices. No preferential segregation of the fibres in the cement matrix was observed. Pull-out of the wollastonite micro-fibres from the hydrated cement matrix was evident, as shown in Figure 5. Close examination revealed that the surface of wollastonite micro-fibres pulled-out from the cement-silica fume matrix appeared to be coated with amorphous reaction products. Wollastonite micro-fibres pulled-out from the plain hydrated cement matrix showed no deposition of products on the surface.

[D] Calorimetry Measurements

Interaction between the wollastonite micro-fibres and the cement matrix was investigated using conduction calorimetry. A plain cement-water mixture and two samples containing wollastonite micro-fibres were reacted simultaneously in a computer controlled calorimeter apparatus for a period of 24 hours. The amount of heat released from the hydration process in each mixture was separately and continuously monitored with a data acquisition system. Two different composite mixtures were used: one sample contained 98% cement and 2% by volume of the wollastonite micro-fibres (sample CW020) and another sample contained 87.5% cement and 12.5% by volume of the wollastonite micro-fibres (sample CW125). The selection of the latter mixture was based on the observation that this specific composition exhibited the maximum flexural strength. All three samples contained an appropriate amount of water to give a water/cement ratio of 0.35. Results indicate that there is no apparent chemical reaction between the wollastonite micro-fibres and the cement matrix, as shown in Figure 9. The calorimetric curves for the three samples showed similar characteristics. The small difference in the peak intensity between the two composite samples (CW020 and CW125) is probably attributed to the different amount of cement and water which were used in the sample materials due to the dilution effect.

Conclusion

The experimental results obtained in this investigation support the following conclusions:

1. Natural wollastonite micro-fibres are effective in modifying the flexural strength characteristics of hydrated cement and cement-silica fume composite matrices.

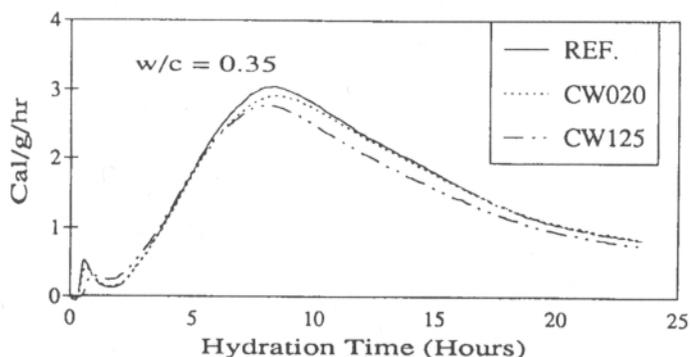


Figure 9. Conduction calorimetry curves of a reference cement paste and cement paste containing 2% and 12.5% by volume of the wollastonite micro-fibres.

2. Incorporation of the wollastonite micro-fibres into cement and cement-silica fume matrices improves both the pre-peak and post-peak load-deflection response resulting in higher flexural strength and better ductility characteristics.
3. Incorporation of wollastonite micro-fibres into the cement matrix modifies the microstructure of the cement-based composite systems.
4. Porosity, pore size distribution and solid density of the hydrated phases were significantly different in the cement- wollastonite and in the cement-silica fume-wollastonite composite systems.
5. Porosity determined by mercury intrusion porosimetry is generally greater than that determined by the helium gas pycnometry.
6. Wollastonite micro-fibres and silica fume addition appear to promote pore discontinuity in cement systems.
7. It is suggested that on the basis of conduction calorimetry measurements there is no apparent chemical interaction between the wollastonite micro-fibres and the cement matrix during the hydration process.
8. Natural wollastonite micro-fibres are an effective reinforcement for improving the flexural strength characteristics of the cement systems. The relatively lower cost of the wollastonite micro-fibres compared to other micro-fibres may result in more widespread use of this natural mineral in the construction industry.

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