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Impedance studies of wollastonite micro-fibre-reinforced cement paste systems

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The impedance behaviour of wollastonite micro-fibre-reinforced cement-based composites at various degrees of hydration has been investigated. The observation of larger high-frequency arcs accompanying wollastonite micro-fibre addition to the Portland cement system at a hydration time greater than 3 days is an indication that the fibre matrix interface zone is less porous than the matrix itself. This conclusion is supported by SEM examination and porosimetry determinations. It is demonstrated that differences in the value of R_2 (the diameter of the high-frequency arc) for pastes with and without fibre reinforcement can be explained by the contribution to pore structure of both the fibre-cement interface and the cement matrix.

Introduction

In the last decade much attention has been given to the use of fibres in cement-based systems, owing to a great improvement in mechanical properties. These reinforcing materials are often made of steel, glass, polymer, etc.¹ Natural fibres and mineral materials such as mica flakes and cellulose fibres have been reported to have positive results in terms of increased flexural strength and toughness.¹ It has been understood that the addition of fibres has a crack-arresting function. The extent of the improvement depends on the mechanical properties of the reinforcing fibres, the microstructure of the fibre-matrix interface and the interaction between the fibres and the cement matrix.

Natural wollastonite, a silicate material with the chemical formula $\beta\text{-CaO}\cdot\text{SiO}_2$, is an economical

reinforcing material used in the pottery industry and in certain cement products.² It has been reported that the addition of a small percentage of wollastonite micro-fibres can reduce shrinkage in cement-based composites.² A recent study by Low *et al.*,^{3,4} reported the results of an investigation into the mechanical properties of cement composites with wollastonite addition of 2–15%. It was argued on the basis of the large differences in porosity values measured by mercury intrusion, helium and isopropanol displacement that wollastonite micro-fibre addition produces a highly discontinuous pore network. It was also concluded for cement and cement-silica fume systems that the natural wollastonite micro-fibres are an effective reinforcement which improves the flexural strength characteristics. This significant improvement of the flexural strength is attributed to the relatively high modulus of elasticity of the wollastonite fibres, and the multiple cracking mechanism associated with the fibre pull-out process. As the wollastonite fibres are relatively inert, the cement-fibre bonding is probably physical and mechanical rather than chemical in nature. The microstructure of the cement-fibre interface zone therefore has an important influence on its mechanical properties. It has been demonstrated in previous studies^{5–15} that the impedance behaviour of cement systems is dependent on the microstructure of the solid and the liquid phase, e.g. the porosity and pore size distribution of the matrix, etc. The application of impedance spectroscopy to characterize the microstructural characteristics of wollastonite micro-fibre reinforced cement systems is described in this Paper.

Impedance behaviour of cementitious materials

Impedance spectra recorded over a wide range of frequencies (from MHz to Hz) have provided new information and insight into cement paste microstructure and hydration. A typical impedance spectrum for a cement system plotted in the real versus imaginary plane (Fig.

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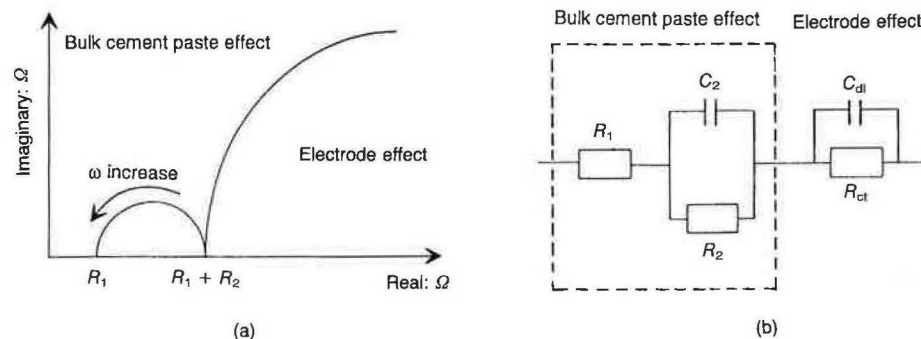


Fig. 1. (a) Schematic plot of high-frequency arc in impedance complex plane obtained for cement paste systems. (b) Simplified electrical equivalent circuit for hydrating cement systems

1(a)) shows a single arc in the high-frequency range, with a small part of a second arc in a relatively low frequency region. From previous investigations¹⁰⁻¹⁵ it is suggested that the high-frequency arc (HFA) may be attributed to the bulk paste impedance behaviour, and that the second arc may be due to the cement-electrode surface capacitance contribution. The intercepts R_1 (at the high-frequency end) and $R_1 + R_2$ (at the minimum between the electrode arc and bulk arc) are important parameters which provide information related to the cement paste microstructure profile. The interpretation of an impedance spectrum (IS) is usually carried out through modelling with an equivalent circuit (Fig. 1(b)) until the electrical response of the elemental microstructure of the cement paste is well simulated.

Previous investigations¹³⁻¹⁵ have indicated that the impedance behaviour of the hydrating cement system depends on the ionic concentration of the pore solution and the porosity. The high-frequency resistance R_1 and the high-frequency arc diameter R_2 may be expressed as

$$R_1 = \kappa' \left[\frac{1}{1 - \alpha(1 - P)} \right] \left[\frac{1}{\lambda_0(1 - \beta\sqrt{[C]})[C]} \right] \quad (1)$$

$$R_2 = \frac{k_1}{\sigma_f} \left[\delta_{st}' + \frac{k_2}{\sqrt{[C]}} \right] \left[\frac{1}{Pr_0} \right] \quad (2)$$

where κ' is a constant related to the cell geometry, λ_0 is the equivalent conductivity of the pore solution at infinite dilution, and β is an experimental constant associated with ionic interactions and the viscosity of the pore solution, etc. The term $[C]$ is the concentration of ions in the bulk pore solution. The thickness of the Stern layer is represented by δ_{st} . The specific constants k_1 and k_2 are functions of temperature and the valences of the ions in the pore solution. The (area fraction)–(volume fraction) ratio of the pores is given by α . P is the porosity of the cement matrix and r_0 is the mean pore size, determined from a pore size distribution curve obtained by mercury intrusion porosimetry. From equations (1) and (2) the following points may be drawn.

The high-frequency resistance R_1 is an inverse function of both porosity and ionic concentration in the pore solution. If the pore solution concentration remains essentially unchanged, an increase of R_1 value may then

be considered to be due to the reduction of porosity as the hydration products fill the capillary pores.

The high-frequency arc diameter (or chord) R_2 is an inverse function of the porosity, mean pore size and ionic concentration of the pore solution. If the concentration term remains unchanged, an increase of R_2 value must be due to the change of porosity and mean pore size as the hydration time increases.

Both R_1 and R_2 are affected by the ionic concentration of the pore solution. An increase in the concentration will lead to lower R_1 and R_2 values.

Experimental

Materials

Type 10 Portland cement was used. The chemical composition (wt%) was as follows: $\text{SiO}_2 = 19.83$; $\text{CaO} = 61.21$; $\text{Fe}_2\text{O}_3 = 3.20$; $\text{Al}_2\text{O}_3 = 4.18$; $\text{MgO} = 4.09$; $\text{SO}_3 = 3.93$; $\text{Na}_2\text{O} = 0.45$; and $\text{K}_2\text{O} = 0.82$. Wollastonite micro-fibres were supplied by Prescott & Co. USA. The shape of natural wollastonite micro-fibres is needle-like, and they are estimated to be 25–30 μm in diameter and 0.4–0.6 mm in length.

Specimen preparation

Four specimens were prepared containing 0, 5, 10 and 15% by volume of wollastonite. The fresh cement-based mixtures were mixed in a conventional Hobart mixer with a water : cement ratio of 0.35, and they were placed in a 1.2 cm \times 1.5 cm stainless steel cylindrical cell described in references 8 and 9. The sample was left in a 100% relative humidity environment for 24 hours and subsequently immersed in saturated lime solution for the remainder of the test period.

Instrumentation

A 1260 Impedance Gain-Phase Analyzer from Schlumberger Technologies was used for the impedance measurements. Data were collected using a frequency scan from 20 MHz to 1 Hz with 10 readings per decade. SEM micrographs were obtained using a Cambridge Stereoscan S250. Pore size distributions were determined by mercury intrusion at pressures up to 408 MPa using an American Instrument Co. porosimeter.

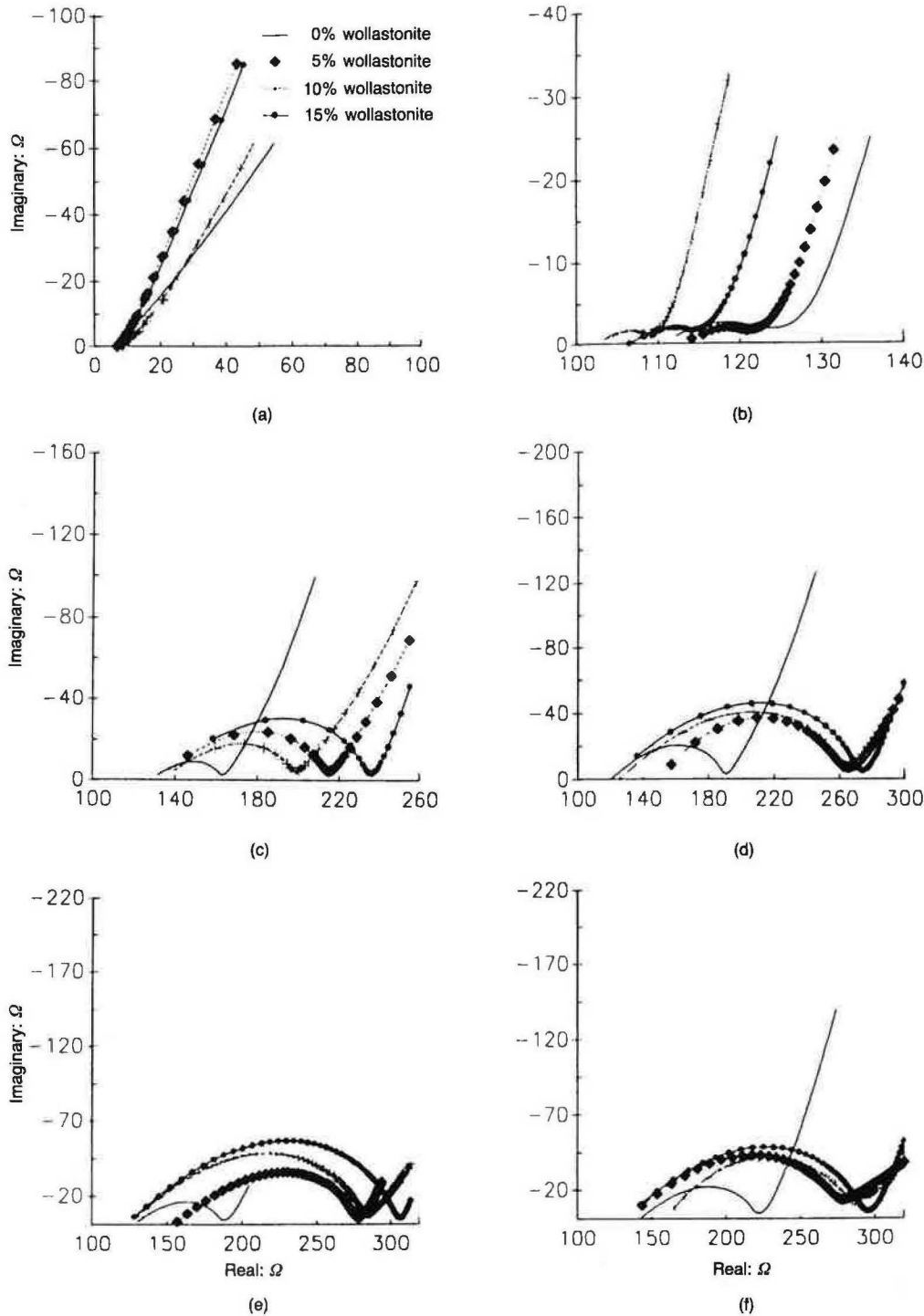


Fig. 2. Impedance plots in real versus imaginary resistance complex plane for cement-based composites with and without wollastonite micro-fibre addition; hydration times: (a) 4 h; (b) 3 d; (c) 13 d; (d) 25 d; (e) 35 d and (f) 41 d

Results and discussion

Impedance behaviour of wollastonite–cement systems

The impedance behaviour of three cement paste–wollastonite micro-fibre reinforced cement systems, with various wollastonite additions from 5 to 15% by volume, was examined. A control sample without fibre addition was also prepared. Figs 2(a)–(f) depict the impedance

data in the real versus imaginary plane for the four specimens at various hydration times ranging from 4 hours to 41 days. At the early stage of hydration, e.g. 4 h, only part of the second arc was observed for all the specimens. At hydration times longer than 3 days high-frequency arcs were observed for all the specimens. The control sample appears to have the largest arc at 3 days (the diameters are 24, 16, 12 and 14 ohms for the 0, 5, 10 and 15%

wollastonite micro-fibre reinforced cement systems). However, at later hydration stages the control sample appears to have an arc smaller than all those of the wollastonite reinforced systems, and the size of the arc for the control specimen remains substantially smaller than the arc for the wollastonite systems. The differences in size with age is an indication of changes in microstructure development. The appearance of the high-frequency arc (HFA) is due to the microstructure of the solid phase and the ionic conductivity of the pore solution. Analysis of cement hydration by impedance spectroscopy relies on the extraction of useful parameters from the data, e.g. high-frequency resistance (HFR) R_1 , interfacial resistance R_2 and interfacial capacitance C_2 . In the following sections, these model parameters are discussed.

High-frequency resistance R_1 . Figure 3 is a plot of the high-frequency resistance R_1 , versus hydration time for the four systems investigated. The observations are similar to those obtained earlier by the Authors^{10–12} and others.^{8–9} R_1 increases at early hydration times and then reaches a relatively constant value at a hydration time of about 20 days. This tendency coincides with the relationship between hydration degree and time. According to equation (1) the high-frequency resistance R_1 is a function of the ionic concentration of the pore solution and of the matrix porosity.^{13,14} The change of R_1 with hydration time correlates with the cement hydration process. In the early hydration process a rapid increase of R_1 at early hydration (shorter than 3 days) is attributed to the rapid consumption of free water and the reduction of porosity. Once hydration has reached a certain degree the hydration rate becomes diffusion-controlled and the porosity change becomes insignificant (the alkali ionic concentration also remains relatively unchanged at the late hydration stages if leaching does not occur). The high-frequency resistance therefore remains relatively unchanged. Comparing the four curves in Fig. 3, the R_1 values for the paste containing 10% wollastonite micro-fibre addition are slightly larger than for other samples at the later hydration stages. There is no apparent indication that the optimum dosage of wollastonite addition

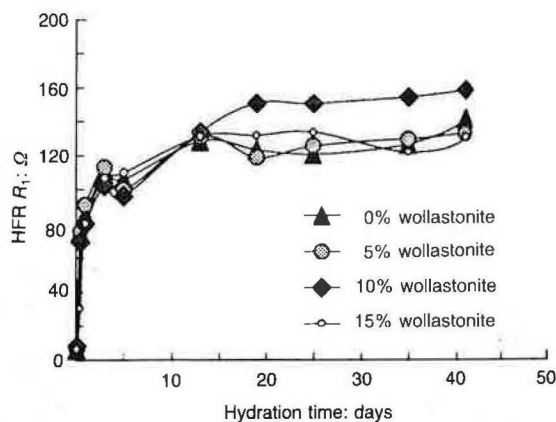


Fig. 3. Plot of high-frequency resistance R_1 versus hydration time

is around 10% by volume, i.e. the value which corresponds to the maximum flexural strength.³ The improvement of flexural strength is attributed to processes associated with fibre pull-out, the high modulus of elasticity of the fibres and the control of crack growth.

Interfacial resistance R_2 and capacitance C_2 . The change of the interfacial resistance R_2 with hydration time for the four systems is shown in Fig. 4. The shape of the R_2 versus hydration time curves is similar to that for curves of hydration degree versus hydration time. The value of R_2 is determined by the intercepts R_1 (at the high-frequency end) and $R_1 + R_2$ (at the minimum between the electrode arc and bulk arc). The increase of R_2 may be due to the accumulation of porous hydration products (C–S–H gel, etc.), which increase the density of interfaces and internal surface area. If the ionic concentrations in the liquid phase, i.e. in the pore solution, are similar in these systems, the slope may be used to characterize the hydration rate. These are affected by the ionic concentration in pore solution,¹⁵ which is determined by the soluble alkali component in the cement. The fast increase of R_2 at the early hydration stages is due to the initial fast hydration rate; the slow increase of R_2 at the later hydration stage beyond 21 days is in concert with surface diffusion processes controlling the overall hydration rate. Further experiments indicated that at hydration times greater than 41 days the value of R_2 approached a relatively constant value. Some relatively small decreases in R_2 values were also observed; these may be due to slow leaching of the alkali ions during the curing process. The decrease of the interface capacitance with hydration time for the wollastonite systems is given in Fig. 5 (the inserted picture shows an enlarged scale). A rapid decrease of the capacitance values of the samples was observed. This is due to the increase in the amount of hydration products, which increase the total interface density. Small capacitance values usually correspond to a large interface resistance, indicating a denser matrix.

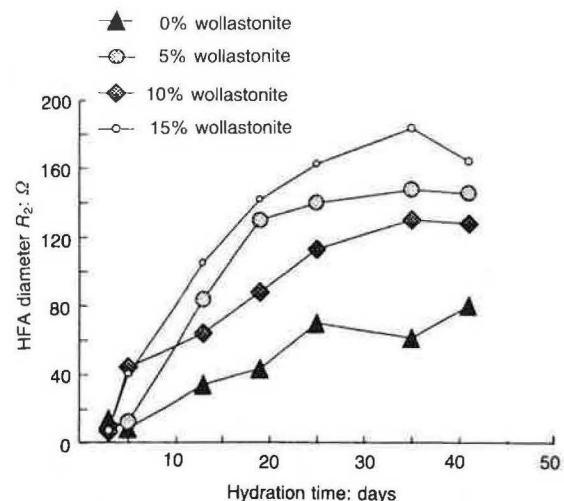


Fig. 4. Plot of interface resistance R_2 versus hydration time for cement paste containing wollastonite micro-fibres ($w/c=0.35$)

They are also a function of porosity, the mean pore size diameter and the ionic concentration of the liquid.

Fibre-matrix interface microstructure

To complement the AC impedance study, the fibre-matrix interface microstructure of the wollastonite

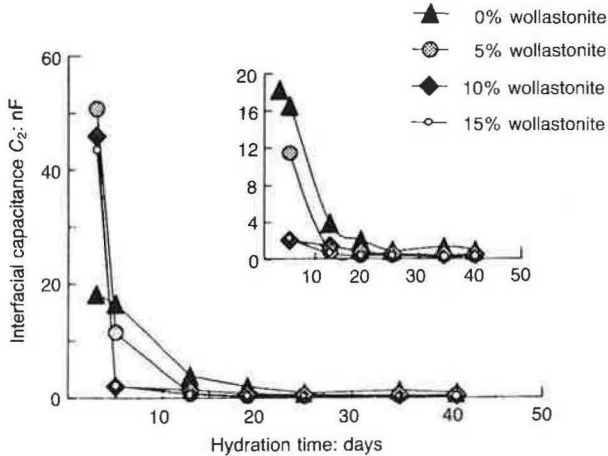
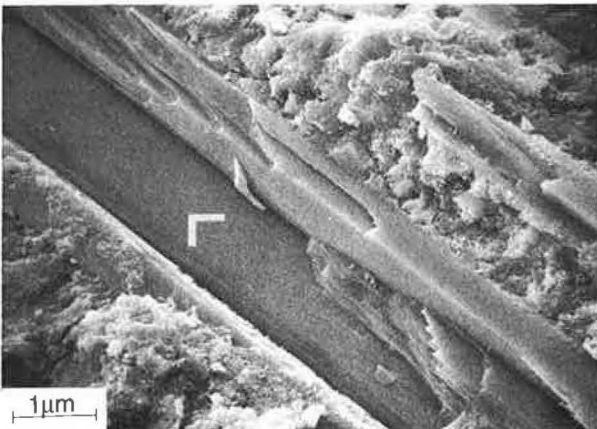


Fig. 5. Plot of interface capacitance C_2 versus hydration time



(a)



(b)

Fig. 6. SEM micrograph ($\times 1500$) for cement paste containing wollastonite fibre ($w/c=0.35$): (a) at 1 day of hydration; (b) at 21 days of hydration

Table 1. Total porosity of wollastonite micro-fibre-reinforced cement pastes determined by mercury intrusion porosimetry

Hydration time	Wollastonite content: %			
	0	5	10	15
1 day	31.5%	32.48%	34.14%	33.32%
21 day	24.79%	22.81%	23.28%	22.21%

reinforced cement systems was also investigated by SEM and mercury intrusion porosimetry. Two hydration times (1 and 21 days) were selected for the examination in order to examine microstructural differences at the fibre-cement interface. Figs 6(a) and (b) are SEM micrographs at these two hydration stages for a paste containing wollastonite micro-fibres. It is clear that the fibre-cement paste interface was quite porous at an early hydration age and then became much denser. Porosity measurements also indicated a significant variation for the two hydration stages. Table 1 lists the total porosity values for the investigated samples at two hydration ages. It is noted that the control sample has a smaller porosity than all the fibre-reinforced systems at 1 day of hydration, but it is larger at 21 days of hydration. An explanation for this observation is that the transition zone at the interface contributes to porosity at early hydration times. The transition zone becomes dense (Fig. 6) at later ages, and its contribution to porosity appears to be much less significant.

Figures 7(a) and (b) depict the pore size distribution for the pure cement paste and paste containing various percentages of wollastonite micro-fibres at 1 and 21 days of hydration. There is a significant difference in the most probable pore size diameters between the wollastonite micro-fibre-reinforced ($0.05\text{--}0.2\text{ }\mu\text{m}$ — 15% wollastonite system $0.05\text{--}0.3\text{ }\mu\text{m}$) and plain paste ($0.04\text{--}0.09\text{ }\mu\text{m}$) systems at 1 day of hydration. Pores larger than $0.09\text{ }\mu\text{m}$ appear to be the result of micro-fibre addition.¹⁶ It is also noted that at 21 days of hydration the pore size distribution for the specimens with and without fibre addition is very similar. The most probable pore size diameters are around $0.05\text{--}0.08\text{ }\mu\text{m}$. The similarity of pore size distribution curves for specimens at 21 days of hydration is also evidence that the porosity at this stage is mainly contributed by the bulk cement matrix rather than the transition zone.

In general, the addition of wollastonite micro-fibres tends to increase the total porosity at early ages. This has been demonstrated by impedance, SEM and porosimetry studies. However, at hydration greater than 3 days the arc diameters of the wollastonite-reinforced specimens become significantly larger than those for the control sample (about 3 times at 41 days for 15% wollastonite). These differences indicate that the transition zone due to the addition of wollastonite tends to become denser than the cement matrix itself. This is compatible with flexural strength results. Flexural strengths increase with wollastonite addition. Strength values at 28 days

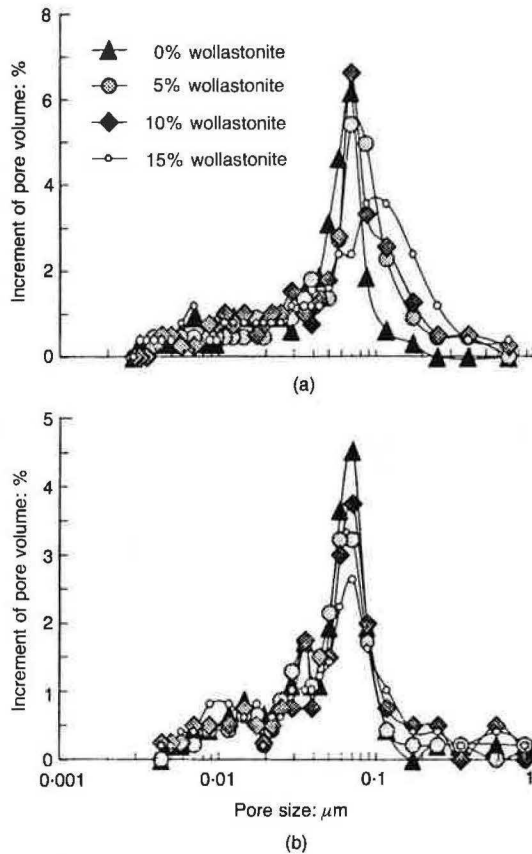


Fig. 7. Plot of increment of pore volume versus pore size diameter determined by mercury intrusion porosimetry for cement-based composites with and without wollastonite micro-fibre addition: (a) at 1 day of hydration; (b) at 21 days of hydration

(w/c=0.35) are 10 and 20 MPa, respectively, for control paste and paste containing 11% wollastonite micro-fibre by volume.^{3,4} Also, wollastonite does not appear to participate directly in the hydration process. There is no apparent chemical reaction between the wollastonite micro-fibres and the cement matrix as determined by calorimetry measurements up to 25 hours of hydration time.³ Nucleation of C-S-H at wollastonite micro-fibre surfaces and the resulting pore structure change may lead to the formation of a denser transition zone than the matrix.

Conclusions

At early hydration times (less than 3 days) the high-frequency arcs obtained by AC impedance spectroscopy for wollastonite micro-fibre-reinforced cement paste systems are smaller than those for the pure Portland cement system. This implies that the porosity at the fibre-matrix interface area is significant.

At the later hydration time (greater than 3 days), the high-frequency arcs obtained by AC impedance spectroscopy for wollastonite micro-fibre-reinforced cement paste systems are larger than those for the pure Portland cement paste system. Evidence suggests that the

porosity at the fibre-cement interface area is less significant than the porosity of the matrix itself.

Differences in high-frequency arc diameter R_2 for pastes with and without fibre addition can be explained by the pore size distribution and the values of total porosity determined by mercury intrusion porosimetry, as well as by SEM examination.

The increase of R_2 at later hydration times is due to the cement hydration products filling the existing pores, and nucleation of C-S-H at wollastonite micro-fibre surfaces. The resulting pore structure changes appear to lead to the formation of a denser transition zone than the matrix.

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