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RHEOLOGY OF HIGH-PERFORMANCE CONCRETE: EFFECT OF ULTRAFINE PARTICLES

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ABSTRACT

The effect of ultrafine particles used as partial replacements for cement on the rheology of high-strength concrete (HSC) was investigated. Various proportions of 3 μm and 0.7 μm mean particle size limestone fillers, a finely ground silica, and silica fume were individually used as partial replacement for cement in 0.33 water/binder (w/b) ratio concrete mixtures. In addition, concrete mixtures were made with triple-blended composite cements containing different proportions of limestone filler and silica fume. A rheometer and the slump test were both used to measure the rheological properties at different ages, and the induced bleeding of the various concrete mixtures was investigated. An effort was made to explain why the production of HSC is made rheologically easier when ultrafine particles are added to the concrete mix. The effect of ultrafine particles on the superplasticizer requirement and the effect of time on the rheological characteristics of HSC were also examined. Likewise, the advantages of using triple-blended binders containing microfillers of various particle sizes were investigated. *© 1998 Elsevier Science Ltd*

Introduction

The incorporation of microfillers and supplementary cementing materials in concrete as partial replacements for Portland cement continues to increase. Most of these blending materials are either industrial byproducts or unprocessed materials. They provide environmental relief because industrial byproducts are being recycled, hazardous emissions released into the atmosphere due to cement production are reduced, raw materials are preserved, and energy is saved (1). Most importantly, some of these microfillers have the potential to impart superior properties to cement-based materials. Perhaps this is the reason why the European Standards (2) have recently specified 25 varieties of cements, among which only Portland

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cement is not made from two or more components including several fillers and mineral admixtures.

Because the properties of hardened concrete depend strongly on the early stages of concrete production, the effects of fillers on the rheological properties of cement based materials should be clarified. The effects of blending materials on the rheology of cement pastes and concretes have been previously addressed (3). However, the focus there was only on fly ash, slag, and silica fume. Nearly inert fillers, such as limestone, and blends of pozzolanic and inert fillers have not been fully investigated, especially in HSC where these effects may be more significant. More recent work (4) has addressed the effects of fillers on the rheological properties of HSC. However, the types of fillers used and the design of the experiments made this work of limited relevance for the rheology of composite cements (5).

Nehdi et al. (6) have investigated the effect of adding ultrafine particles to cement on the rheology of composite cement pastes. The flow time of cement pastes, the flow of corresponding mortars, the yield stress and plastic viscosity, the induced bleeding, mini slump, and superplasticizer efficiency were statistically modeled as a function of the microfiller addition rate and the w/b ratio. In later work, Nehdi et al. (7) have statistically modeled the flow resistance, the torque viscosity, and the slump loss over time of HSC made with triple-blended composite cements containing microfillers.

The present work aims at a deeper insight into the filler effect on the rheology of HSC in an attempt to answer questions such as: Why is the production of HSC made rheologically easier when ultrafine particles are added to the concrete mix? How is the superplasticizer requirement affected by adding microfillers? How do the ultrafine particles affect the slump loss of fresh HSC? What happens to the rheological characteristics of fresh HSC while it stiffens with time? Is it rheologically advantageous to use triple-blended binders containing microfillers of various particle sizes?

Experimental

Apparatus

The rheometer used was developed at the University of British Columbia (8). A computer drives a motor from rest to the desired speed and then back to rest, which causes a planetary motion of a four-finger impeller. A tachometer is used to measure the impeller speed, and a torque measuring device equipped with four strain gauges measures the torque from the deflection of a small beam in bending (Fig. 1). The impeller speed and torque data are acquired by a data acquisition system. A computer program allows the user to customize test parameters, such as the number of readings, the speed increment, the speed decrement, the sampling interval between the readings, etc. In this work the rheometric test consisted of an impeller speed loop starting from rest and going up to about 1.08 rev/s in 10 increments. The speed was then gradually reduced to zero in 30 decrements. A total of 50 measurements of speed and torque were made in approximately 0.06 s followed by a waiting period of 1.2 s for each increment. The test duration was 2.8 min., a compromise between accuracy and the segregation due to longer tests. The slump test was carried out according to the ASTM C143–90 requirements (Standard Test Method for Slump of Hydraulic Cement Concrete). The induced bleeding test consisted of applying a controlled pressure of 2.1 MPa on a cylindrical sample of concrete which was placed in an airtight cell, and measuring the water

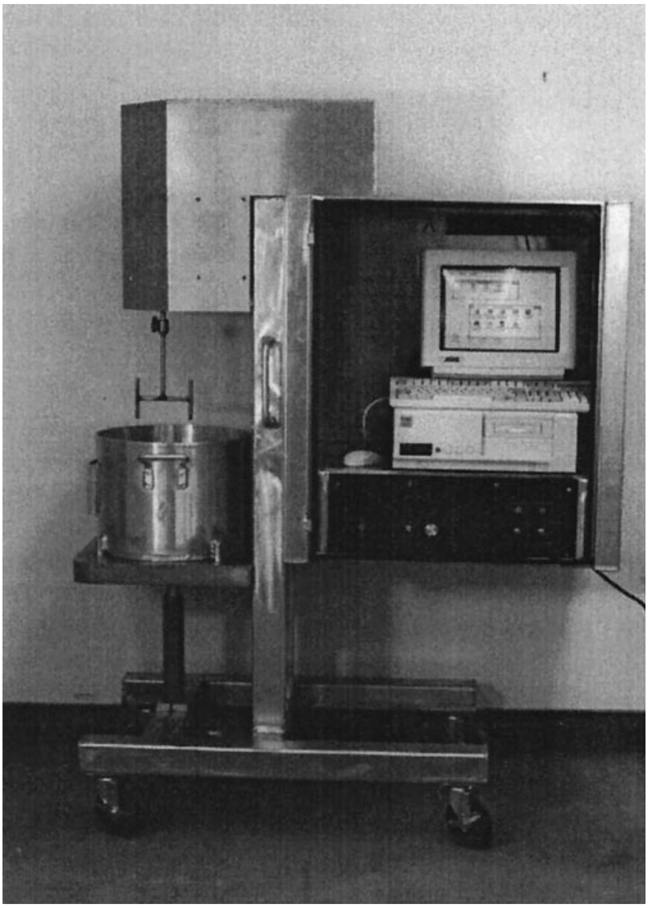

FIG. 1.
Illustration of the UBC Rheometer.

collected from a bleed hole over time. The test setup and procedure are described elsewhere (8).

Materials and Procedure

Ordinary ASTM Type I Portland cement was used. Two high purity limestone fillers having mean particle sizes of 3 μm and 0.7 μm (LF1 and LF2, respectively), finely ground silica (GS), silica fume (SF), and concrete sand were used as partial substitutes for cement. Some chemical and physical properties of the cement and fillers are given in Table 1. Washed 10-mm gravel was employed as coarse aggregate and silica sand having a fineness modulus of 2.3 was used as fine aggregate. Tap water and a naphthalene-sulfonate superplasticizer (41% solids) were employed for the mixing.

TABLE 1
Chemical and physical properties of the cement and fillers.

Chemical Composition of Cement (%)		Physical Tests	OPC	SF	LF1	LF2	GS
SiO_2	21.5	Initial set time (min.)	125				
Al_2O_3	4.6	Final set time (min.)	230				
Fe_2O_3	3.2	Autoclave expansion (%)	0.04				
CaO (total)	63.2	Air content of mortar (%)	7				
CaO (free)	0.6	f'_c (MPa)					
		3d	24.6				
		7d	30.0				
		28d	38.5				
SO_3	2.7	Passing 45 μm sieve (%)	87.7	100	100	100	100
MgO	3.0	Specific surface Blaine (m^2/kg)	350				
$Na_2O + K_2O$	0.84	Specific surface BET (m^2/kg)		17500	2300	10000	1250
Loss on ignition	0.7	Mean particle size (μm)	25.6	0.26	2.9	0.7	13.8
Insoluble residue	0.2	Residue on 325 mesh (%)		≤0.005			
		Specific gravity	3.16	2.23	2.71	2.71	2.65
Potential composition of cement (%)		C_3A	7				
		C_4AF	10				
		C_3S	51				
		C_2S	23				

Results

Superplasticizer Requirement

The superplasticizer requirement to achieve a slump of 220 ± 20 mm for the 0.33 w/b concrete mixtures is shown in Figure 2. Replacing proportions of the cement with concrete sand reduced the superplasticizer requirement, probably due to an increase in the w/c ratio and a reduction of the wettable surface area. Partial substitution of GS and LF for cement reduced slightly the superplasticizer requirement. However, SF replacement of cement increased the superplasticizer required to achieve a constant workability. It is interesting to note that 20% replacement of cement by LF2 (mean particle size = 0.7 μm) reduced slightly the superplasticizer requirement, while a 5% SF (mean particle size = 0.26 μm) replacement of cement increased the superplasticizer requirement. This implies that the high surface area of SF may not be the sole factor affecting the increase in the superplasticizer demand for SF mixtures, and supports the idea that SF may have an affinity for multi-layer adsorption of superplasticizer molecules. Previous work (6) has shown that while using a 3 μm LF tended to reduce the superplasticizer required to achieve a constant flow for cement pastes, SF increased the latter significantly. Figure 3a illustrates the statistical modeling using a factorial experimental plan (7) of the superplasticizer demanded to achieve a constant slump for concretes (w/b = 0.33) made with OPC-LF2-SF triple-blended composite cements. It is observed that LF2 tended to reduce the superplasticizer required, while SF tended to increase it significantly.

TABLE 2
Mix proportions of the concrete mixtures (kg/m^3).

Replacement Rate (%)	0	5	10	15	20
Cement	500	475	450	425	400
Sand	0	21.0	42.0	63.0	84.0
or					
GS	0	21.0	42.0	63.0	84.0
or					
LF1	0	21.5	43.0	65.0	86.0
or					
LF2	0	21.5	43.0	65.0	86.0
or					
SF	0	17.7	35.4	53.1	70.8
10 mm aggregate	1050				
Sand	715				
Water	165 L				
Superplasticizer	Adjusted to obtain 200 ± 20 mm slump				

*Replacement by volume, fillers added individually (table includes 21 mixtures).

Flow Resistance

The flow resistance, *g*, was measured at 15, 30, 45, 60, and 90 min. after mixing for 0, 5, 10, 15, and 20% partial replacement of cement by GS, LF1, LF2, SF, and concrete sand. An example of results is illustrated in Figure 4. For all the mixtures, *g* tended to increase with time, reflecting the stiffening behavior of concrete. Partial replacement of cement by concrete sand reduced *g*, probably because the w/b ratio was increased and the wettable surface area was reduced. Likewise, substituting various fine fillers for cement also reduced *g*. In the latter case, the surface area, and thus the wettable surface, were increased. This may imply that

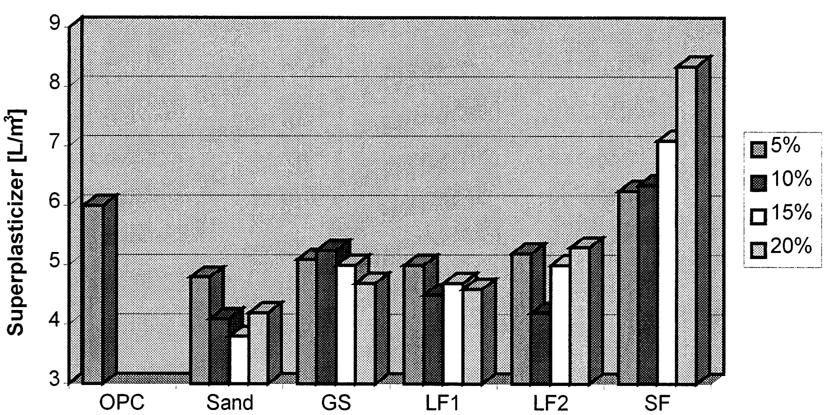

FIG. 2.
Superplasticizer requirement for a constant workability.

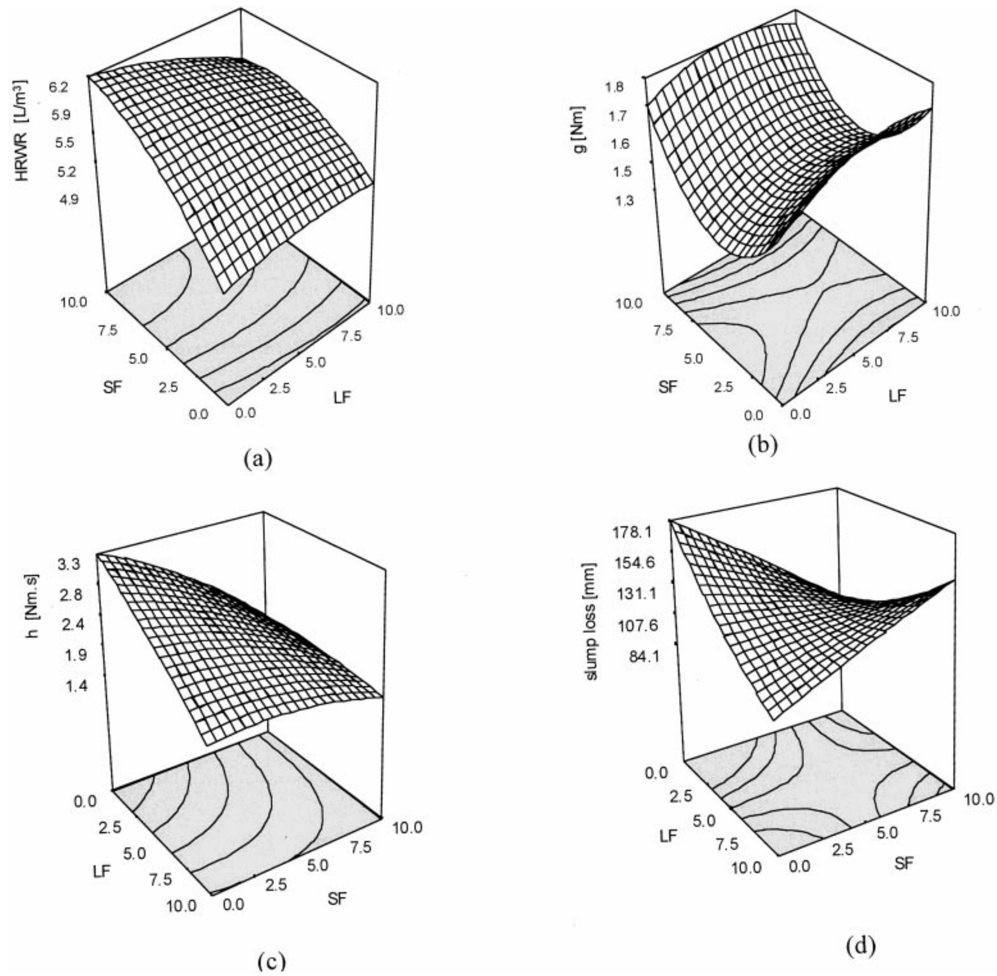

FIG. 3.
Statistical modeling of various rheological responses for OPC-LF2-SF triple-blended composite cements.

another mechanism, rather than the surface area, is involved in reducing *g*. The improved gradation of the binder and the lubricating effect imparted by the fine particles could possibly reduce the aggregate interlocking, and reduce *g* as a result. The finer and the more spherical the filler, the more *g* was reduced. It may be argued, however, for the SF mixtures, that the superplasticizer requirement was higher and *g* might thus be expected to be lower. This was not true for the GS and LF mixtures, which required less superplasticizer than the reference pure OPC mix. Figure 3b shows that in a triple-blended composite cement, *g* at 15 min. was optimal for a moderate combination of 5% SF with LF2. This suggests that a certain gradation and fineness that ensure an optimal particle packing of the binder may enhance the flow of concrete.

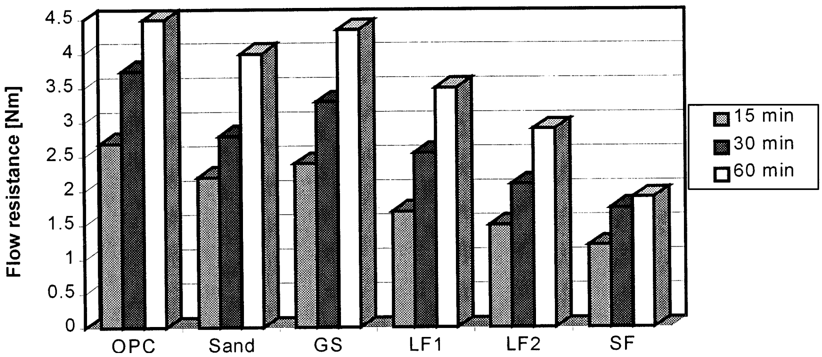

FIG. 4.
Flow resistance at various ages for concretes made with 15% of various fillers.

Torque Viscosity

The torque viscosity, *h*, at different ages for mixtures made with 15% filler replacement is illustrated in Figure 5. Replacing part of the cement with concrete sand reduced *h*, probably because more water was free and could participate in lubricating the mixture. Generally, the finer and the more spherical the microfiller, the more *h* was reduced. Higher proportions of filler replacement of cement were more effective in reducing the torque viscosity. It was observed earlier that higher filler proportions reduced the plastic viscosity of cement paste in both silica fume and non-silica fume systems (6). Yet, this effect was more significant in concrete than in cement paste, probably because the ultrafine particles played a more important lubricating role via a reduction of the aggregate interlocking. This is illustrated more clearly in results of the statistical modeling of the filler effect on the torque viscosity of HSC made with triple-blended composite cements (Fig. 3c); the higher the microfiller substitution rate, the more *h* was reduced. The torque viscosity did not, however, reflect the stiffening behavior of the fresh concrete with aging. Because concrete was allowed to rest between consecutive rheological tests, the torque requirement for the low impeller speeds increased more than that for the high impeller speeds, probably due to flocculation of binder particles, growth of hydration products, and exhaustion of superplasticizer molecules in the complex chemical processes. This resulted in a reduction of the slope of the shear stress vs. shear rate curve, which may explain why the torque viscosity did not increase with time and tended to decrease slightly in some cases. Induced segregation may also contribute to this behavior. It should also be remembered that the torque viscosity is a “dynamic” value as opposed to the flow resistance and slump test, which can be regarded as “static” values.

Slump loss

Although superplasticizers are effective in dispersing the cement particles through a deflocculation process, this action is time-dependent and very low w/b concrete undergoes a rapid slump loss. There are two concerns regarding this issue: first, that the cement should have the lowest rheological reactivity, that is, that the amount of water fixed immediately after mixing should be minimal; and second, that the superplasticizer should not compete with the calcium sulfate to neutralize the C_3A (9).

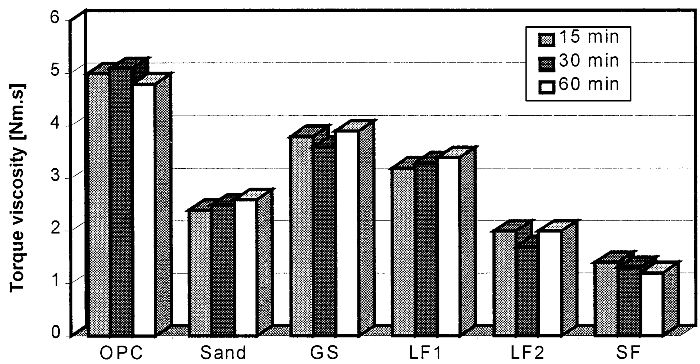

FIG. 5.
Torque viscosity at various ages for concretes made with 15% of various fillers.

The changes in the slump loss behavior that occur upon partial replacement of cement by microfillers of various mineralogies and mean particle sizes are not yet clear. Figure 6 illustrates the slump variations of 0.33 w/b concretes with 15% of various fillers at 15, 30, and 60 min. Starting at slumps of 200 $\pm$ 20 mm, all the mixtures had slumps higher than 60 mm after 60 min. The blended composite cements generally showed performance equal to or better than pure OPC.

Generally, concretes that had the highest slumps at 15 min. kept higher slumps at 60 min. It should be remembered that only the silica fume mixtures had significantly higher superplasticizer dosages (Fig. 2). Therefore, the effect of the difference in superplasticizer dosage on the slump loss is limited for the rest of the mixtures. The slump loss at 60 min. in an OPC-LF2-SF triple-blended cement is shown in Figure 3d. When added individually, increasing levels of SF or LF2 reduced the slump loss, while when combined, a moderate combination of 5% LF2–5% SF seemed to be optimal.

Induced Bleeding

It has long been known that the bleeding rate and bleeding capacity of cement paste are strongly dependent on the water content and the specific surface area of the cement (10). It can be reasonably expected that partial replacement of cement by finer microfillers would reduce the induced bleeding of cement paste and concrete. The water thus retained may participate in lubricating the concrete mixture and improving the rheology. The induced bleeding of the various concrete mixtures at 5 and 30 min. is illustrated in Figure 7. Replacing some of the cement with concrete sand increased the induced bleeding, while finer fillers reduced the bleeding both at 5 and 30 min. The finer the microfiller, the more the bleeding was inhibited, except for GS which though being the coarsest microfiller used, was the most effective in reducing the bleeding at 5 min. The reason for this behavior is not clear. It may, however, be that the GS changed the electrolytic environment, which in turn increased the inter-particle attraction. This is known to reduce the bleeding capacity while generally having little influence on the bleeding rate (10).

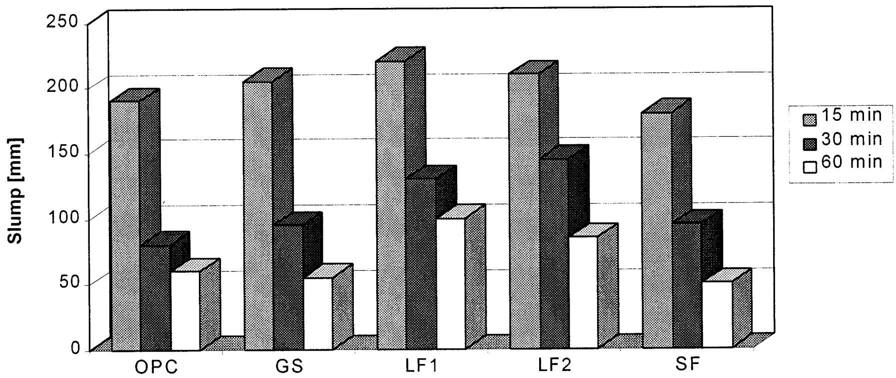

FIG. 6.
Slump variation of concretes made with different proportions of various fillers.

Discussion

Ultrafine Particles and the Rheology of Cement-Based Materials

Various kinds of forces coexist in a cement suspension. First, there is the Brownian randomizing force, which influences the spatial orientation and arrangement of particles. This force is strongly size-dependent and has a major influence below a particle size of 1 μm. The effect of microfiller substitution of cement on this kind of force is beyond the scope of this investigation.

Second, there are forces of colloidal origin that arise from mutual interactions between particles, and are affected by the polarizability of water. When the van der Waals attraction between cement grains and the electrostatic attraction between unlike charges on the surface of particles are dominant, the net result is an attraction, and the particles tend to flocculate. However, in the presence of polymeric or surfactant materials on the surface of cement grains, the net result is repulsion and the particles remain separate. In this respect, the filler material can influence the electrostatic forces depending on its mineralogical nature and the state of its particle surface charges. Because colloidal forces depend also on the average distance between nearest neighbor particles, the interposition of finer filler grains between cement particles may affect their electrostatic attraction and thus their flocculated structure. Likewise, replacing cement with a material of different specific surface area would change the wettable surface area and the amount of water adsorbed. Some fillers having a certain solubility in water may modify the electrolyte solution and thus the electrostatic forces.

Third, there are viscous forces that are proportional to the local velocity difference between a cement particle and the surrounding water, and between an aggregate and the surrounding cement paste. Because cement-based materials fall in the range of dense suspensions, particles have to move out of the way of each other, especially when flocs are formed. The filler effect on the rheology will depend on the fineness of the filler, its particle size distribution and its particle shape. Broader particle-size ranges have higher maximum particle packing because the finer particles fit into the gaps between the coarser particles. The viscosity of suspensions usually increases as the deviation from ideal grading increases, and attains a minimum at a given volume of water and at the most compact arrangement of

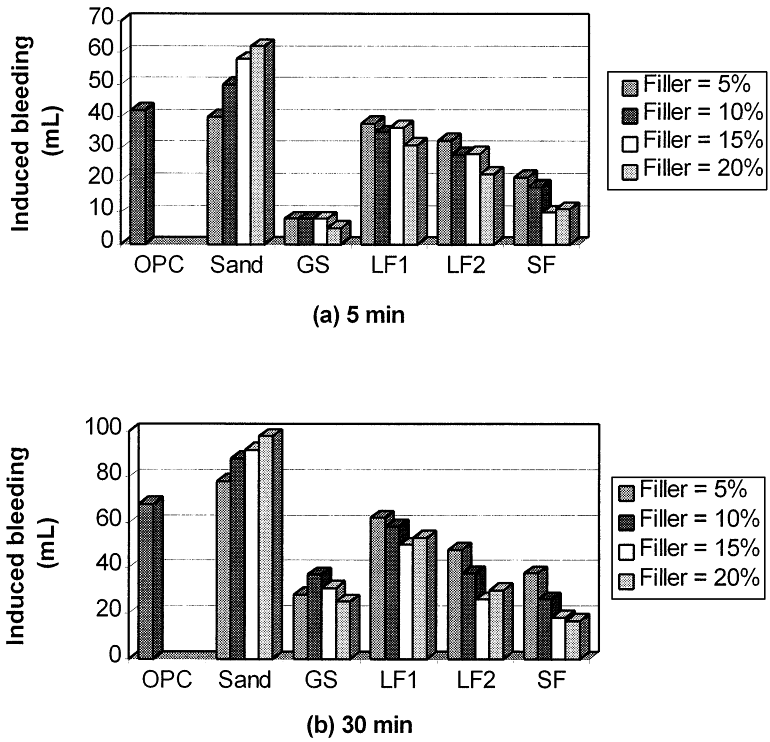

FIG. 7.
Microfiller effect on induced bleeding of HSC.

particles (11). In addition, any deviation from a spherical shape implies an increase in viscosity for the same phase volume. Thus, in the presence of fluidifiers, the finer and the more spherical the filler, the better the rheological properties. Filler materials can also have different efficiencies in the adsorption of superplasticizers. They can, if soluble, introduce certain ions that may affect the kinetics of the hydration reaction and the nucleation of hydration products.

The idea that results from the above discussion is that one can combine the effect of fluidifiers and suitable ultrafine particles to make HSC easier to place. The fluidifiers combat the electrostatic forces and ensure the dispersion of the ultrafine particles, while the microfillers reduce the viscous forces and the coulomb friction between aggregates.

Conclusions

High-strength concrete can be made easier to place by substituting proportions of ultrafine particles for cement. In the presence of superplasticizers, the finer the microfiller the lower the flow resistance and torque viscosity of the mixture. Up to 20% ground silica or limestone did not increase the superplasticizer requirement to achieve a constant workability, even though one of these fillers had a surface area as high as 10,000 m^2/kg. Silica fume, however, while being the most effective filler from a rheological point of view, increased the superplasticizer demand at a constant workability. This may suggest that a high surface area is not the sole parameter influencing the superplasticizer demand of silica fume mixtures, and that silica fume may have a strong affinity for multi-layer adsorption of superplasticizer molecules. Microfillers did not seem to reduce significantly the slump loss of fresh HSC, and were advantageous in some instances in maintaining better workability over time. Microfillers were also successful in inhibiting the induced bleeding of fresh concrete. Therefore, it is possible to design triple-blended composite cements including different fillers to achieve improved rheological characteristics.

Acknowledgments

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