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COMMUNICATIONS

DILATANT BEHAVIOR OF SUPERPLASTICIZED CEMENT PASTES CONTAINING METAKAOLIN

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ABSTRACT

Cement pastes containing metakaolin have been studied with a coaxial cylinder rotational viscometer. They show a dilatant behavior that is strongly dependent on the water/binder ratio, on the level of cement replacement by metakaolin and on the fineness of the latter. Dilatancy is caused by the angular and platelike shape of metakaolin particles. A sample with silica fume has been included for comparison. © *1998 Elsevier Science Ltd*

Introduction

Metakaolinite, obtained by thermal activation of kaolin at 700–800°C and better known as "Metakaolin" (MK), is gaining interest as a supplementary cementing material in the production of high-performance mortars and concrete (1–3). MK has a high pozzolanic activity and microfiller properties very similar to those of silica fume (SF). Both MK and SF increase the water demand of the mixes.

To date there are no reports in the literature on the rheology of cement pastes incorporating MK, although the addition of a finely divided powder is expected to have a considerable influence on the flow characteristics of the pastes. The work reported here is a first attempt to fill the gap.

Experimental

Materials

A Portland cement, classified as CEM I 52.5 R according to the European standard ENV 197/1, was employed. Its properties, together with those of two commercially available metakaolin samples (MK1, MK2) are reported in Table 1. Silica fume (SF), included for comparison, was an uncondensed powder with specific surface area (BET) of 18.2 m^2/g. A naphtalene sulphonate-based superplasticizer in powder form was used. The composition of the pastes is given in Table 2.

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TABLE 1
Properties of cement, metakaolins, and silica fume.

	Cement	MK1	MK2	SF
Specific gravity, g/cm^3	3.10	2.50	2.50	2.22
Specific surface, Blaine m^2/kg	481	—	—	—
Specific surface, BET m^2/g	—	19.8	14.7	18.2
Bulk density, kg/m^3	927	245	417	205
Composition, mass %:				
SiO_2	20.77	51.9	55.0	96.0
Al_2O_3	5.02	43.5	40.0	0.3
Fe_2O_3	2.43	1.5	0.6	0.2
CaO	64.52	—	0.1	0.3
MgO	1.23	0.5	0.4	0.5
K_2O	0.90	0.3	2.4	0.4
Na_2O	0.48	0.4	0.1	0.3
SO_3	3.43	—	—	—
LOI	1.16	0.9	—	2.0

Apparatus and Procedures

The rheological measurements were carried out with a Haake Rotovisco RV20 viscometer equipped with the CV20 measuring head and the ZA30 coaxial cylinder sensor system (gap size 1.085 mm, sample volume 5 cm^3). The pastes were mixed by using a hand-held blender with a two-loop whisk, 4 min. at lower speed (500 rpm) and 1 min. at higher speed (1000 rpm). A part of the paste was quickly transferred to the measuring cup, and the measurement could be started about 2 min. after the end of the mixing. The shearing cycle was 2 min. from 0 to 50 s^{-1} and 2 min. downward. All measurements were carried out at 20°C.

Results and Discussion

The flow curves of the pastes C, S-15, and M2–15 are reported in Figure 1, while those of M1–5, M1–10, and M1–15 are given in Figure 2. For all samples, the curve at increasing shear rates is situated above the one at decreasing shear rates, i.e., all samples

TABLE 2
Composition of the pastes (mass, g).

	C	M1-5	M1-10	M1-15	S-15	M2-15
Cement	165.0	156.7	148.5	140.2	140.2	140.2
MK1	—	8.3	16.5	24.8	—	—
MK2	—	—	—	—	—	24.8
SF	—	—	—	—	24.8	—
Superplasticizer	5.0	5.0	5.0	5.0	5.0	5.0
Water	55.0	55.0	55.0	55.0	55.0	55.0

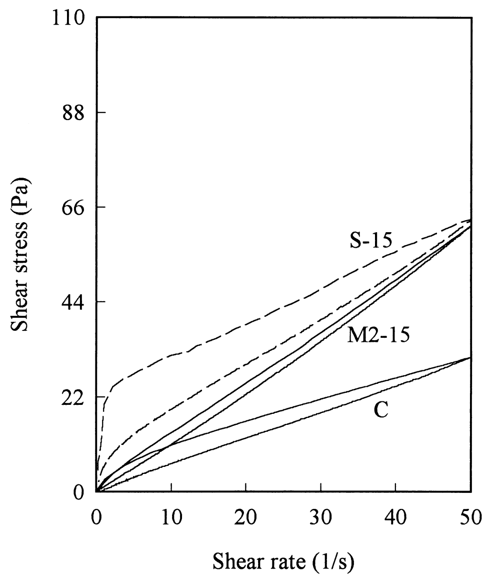

FIG. 1.
Flow curves of pastes C, M2–15, and S-15.

show a thixotropic behavior. However, while SF brings about a large increase of the thixotropy of the paste, MK somewhat decreases it. By looking at the curves recorded at decreasing shear rates an upward concavity for the samples with MK can be seen. It is present already at the 5% replacement level, is rather pronounced at 15%, and points out

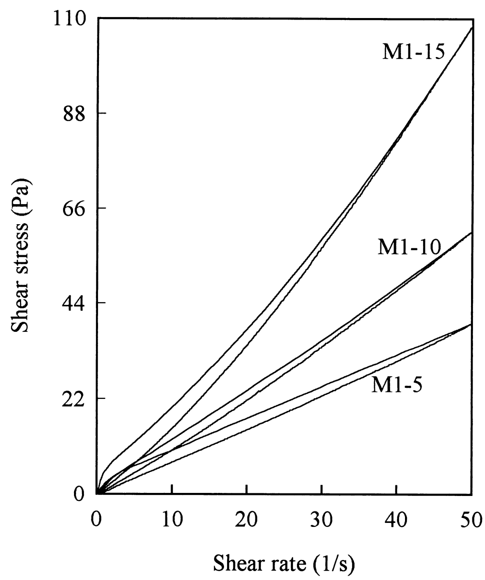

FIG. 2.
Flow curves of pastes M1–5, M1–10, and M1–15.

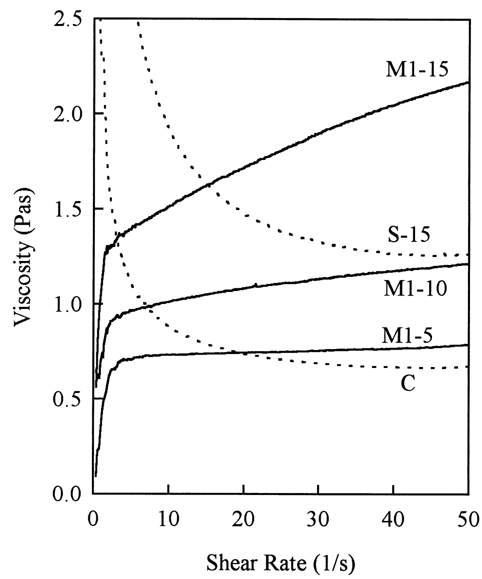

FIG. 3.
Viscosity curves of pastes C, S-15, M1–5, M1–10, and M1–15.

a dilatant behavior. MK1 is more effective than MK2 in causing dilatancy because of its higher fineness (specific surface area 19.8 vs. 14.7 m^2/g). The changes induced by a partial replacement of cement by MK or SF can be more clearly seen in the viscosity curves of Fig. 3 where only the curves at decreasing shear rates are reported. SF gives a higher apparent viscosity but does not change the pseudoplastic character of the flow curve of the cement paste, while the increasing viscosity vs. shear rate of the MK-containing samples indicates dilatancy. Figure 4 reports the flow curves of sample M1–15 with different water/binder ratios: 0.33, 0.36, and 0.42, corresponding to solids volume fractions of about 0.49, 0.47, and 0.43 respectively. The increase of the amount of water has a conspicuous effect on the flow curve, but the dilatant behavior is clearly still present at the water/binder ratio of 0.42. Thixotropy has been considerably reduced.

Dilatancy in cementitious systems has been discussed by several authors (4–8). It is caused by the attrition among solid particles when a slurry is sheared, and is enhanced by a high volume fraction of solids and by non-spherical particle shapes. It is present in slurries with a high dispersion degree and a close packing of the particles, consequently pastes with superplasticizing admixtures are likely candidates to show a dilatant behavior. On the other hand, thixotropy is due to the presence of a structure deriving from the formation of linkages among the particles, the same mechanism that originates the yield stress (6). Therefore, dilatancy and thixotropy tend to exclude each other (4,6,9). However, cement pastes are complex systems and can show both types of rheological behavior, depending on experimental conditions such as composition, dispersion state and shearing history. The progressive formation of hydration products is an additional complicating factor that goes into the direction of increasing thixotropy.

MK-containing pastes are both thixotropic and dilatant. Thixotropy is due mainly to the cement component and its hydration products and is somewhat lowered when MK is

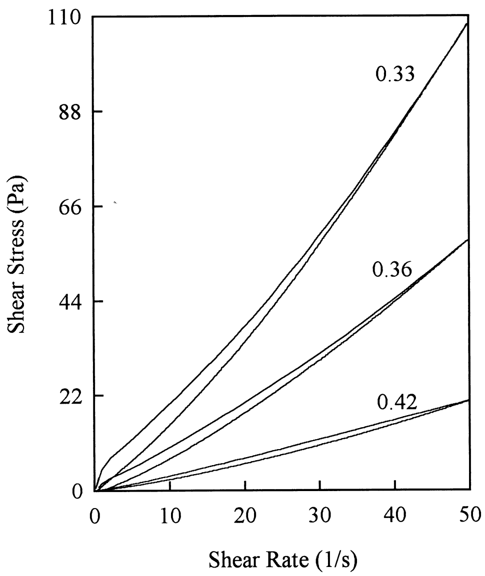

FIG. 4.
Flow curve of paste M1–15 with different water/binder ratios.

present. The curves at decreasing shear rates, when the thixotropic structure has been eliminated, clearly show dilatancy. The angular and platelike particle shape of MK and the low propensity to the formation of interparticle bonds can explain the dilatant character of the pastes. Similarly, the enhanced thixotropic behavior and the absence of dilatancy, at least at low shear rates, observed in the paste with SF is determined by the strong tendency toward structure build up and by the known spherical particle shape of this microfiller.

Conclusions

Cement pastes with metakaolin as a partial replacement of cement show a dilatant behavior.

Dilatancy is heavily influenced by the water/binder ratio, by the amount of metakaolin and by its fineness.

The thixotropy of the pastes is somewhat decreased by metakaolin, is increased by silica fume.

The dilatant properties, which are a consequence of the attrition generated in the contact of moving solid particles in sheared suspensions, can be explained by considering the angular and platelike shape of metakaolin particles.

References

1. J.A. Kostuch, V. Walters, and T.R. Jones, Proc. Int. Conf. Concrete 2000, R.K. Dhir and M.R. Jones (eds.), Vol. 2, p. 1799, E&FN Spon, London, 1993.
2. M.A. Caldarone, K.A. Gruber, and R.G. Burg, Concr. Int. 16, 37 (1994).
3. M.H. Zhang and V.M. Malhotra, Cem. Concr. Res. 25, 1713 (1995).

4. A.J. Gaskin, Proc. 4th Int. Symp. Chem. Cem., p. 744, Washington, DC, 1960.
5. C. Legrand, Cem. Concr. Res. 2, 17 (1972).
6. J.P. Bombled, Rev. Mater. Constr. 688, 137 (1974).
7. D.M. Roy and K. Asaga, Cem. Concr. Res. 9, 731 (1979).
8. R.A. Helmuth, Proc. 7th Int. Congr. Chem. Cem., Vol.3, Sub-Theme VI, p.1, Paris, 1980.
9. H. Freundlich and H.L. Roder, Trans. Faraday Soc. 34, 308 (1938).