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EFFECT OF CONTENT AND PARTICLE SIZE DISTRIBUTION OF HIGH-CALCIUM FLY ASH ON THE RHEOLOGICAL PROPERTIES OF CEMENT PASTES

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ABSTRACT

The rheological properties of high-calcium fly ash cement pastes were investigated. An increase both in yield value and plastic viscosity with fly ash content was found. It was also observed that the pastes became more fluid with the higher fly ash fineness. A more important relation was shown between the fine fractions (<24 mm) content and the degree of fluidity rather than that of specific surface area vs. fluidity. © *1997 Elsevier Science Ltd*

Introduction

The increase in fly ash content in cements brings about the modification of rheological properties of pastes and consequently influences the workability of mortars and concrete mixtures. The observed changes can be advantageous or not (1-4). This is because of many factors influencing the rheology of cement pastes.

The rheological properties of cement pastes containing fly ashes are influenced by both physical and chemical properties of the ash. The spherical shape of fly ash particles as well as the presence of glassy phase on the fly ash surface improve significantly the structure of paste. Therefore the paste is effectively densified and the water content can be reduced while the consistency is kept constant. On the other hand the reverse effect occurs, because of the lower fly ash density as compared with cement (5, 6). Consequently, at higher fly ash content in cement the water demand of paste increases.

The effect of chemical properties, in turn, results from the different fly ash reactivity as compared with that of cement and depends on the chemical and mineral composition. The physical and chemical properties differ significantly for fly ashes originating from the combustion of particular types of coal (brown, bitumious coal). The classification of fly ashes used as an admixture to cement or concrete is given in ASTM C 618-89 (7). The fly ashes from the brown coal combustion are assigned the class C with the SiO_2 + Al_2O_3 + Fe_2O_3 content lower than 50 wt.% and the CaO content exceeding 10%. Fly ashes exhibit generally a higher CaO content within the limits 15-30 wt.%. The mineral components of high-calcium fly ashes, unlike those detected in the low-calcium ones (quartz, mullite), are the same crystalline phases one may find in slags and cements, i.e. C_3A, C_2S, C_4A_3S, $C_{12}A_7$, C_2F, $CaSO_4$, free CaO (8). Therefore the high-calcium fly ashes exhibit hydraulic properties. The

TABLE 1

Chemical Composition of Clinker and Fly Ash

Component	clinkier	fly ash
	% by wt.	
Loss on ignition	0,8	1,9
SiO_2	22,7	30,0
Fe_2O_3	3,0	6,0
Al_2O_3	4,6	18,0
CaO	66,5	30,1
MgO	1,4	2,1
SO_3	0,6	10,8
Na_2O	0,2	0,2
K_2O	0,7	0,2
CaO free	0,8	3,0

phases which are susceptible to the hydration process affect the setting of fly ashes and thus the rheological properties of the cement-fly ash pastes.

Experimental

The portland cement produced in laboratory by grinding of portland cement with gypsum (5 wt.%) to the specific surface of 328 m^2/kg and the high-calcium fly ashes from the brown coal combustion were used. The chemical composition of the materials used is given in Table 1.

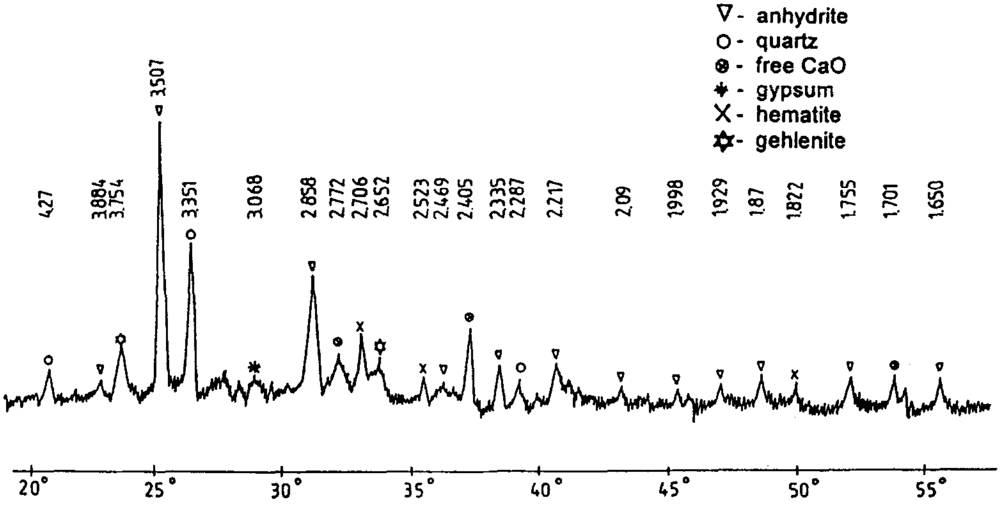

FIG. 1.
XRD pattern of a fly ash sample.

TABLE 2

Specific Surface Area of Fly Ashes (Blaine)

Fly ashes	Specific surface area of fly ashes (Blaine) [m^2/kg]
FA-0	261,9
FA-1	393,2
FA-2	430,2
FA-3	471,3

Mineralogical Composition and Particle Size Distribution of High-Calcium Fly Ash. The phase composition of fly ashes was characterized by XRD. The XRD pattern is shown in Fig. 1. The following crystalline phases have been detected: anhydrite, quartz, free CaO, calcium sulphate dihydrate-gypsum, hematite and gehlenite. Raw fly ashes were used (FA-0) as well as the ashes preliminary ground for 7 min. (FA-1), 15 min. (FA-2) and 30 min. (FA-3) to the Blaine specific surface area 393.2; 430.2 and 471.3 m^2/g, respectively.

The specific surface areas of fly ashes are given in Table 2; their grain size composition, as measured by a LAU-80 laser granulometer, in Figures 2, 3, 4, 5, respectively. The percentage of the fraction >200 μm, separated before the granulometric analysis by laser granulometer are 3,2 % wt. (FA-0), 0,9 % wt. (FA-1), 0,8 % wt. (FA-2), 0,5 % wt. (FA-3).

Rheological Measurements of Fly Ash Cement Pastes. The cement-fly ash mixtures used in the rheological investigations were prepared and homogenised in a laboratory mill within 5 hours. The fly ash content in cement was 20%, 40%, 60% and 80% wt. The rheological measurements we carried out using the rotative viscosimeter type Rheotest RV-2.1, with the modified surfaces of both cylinders. All the cement-fly ash samples were prepared and measured following the same procedure and in the same conditions. The tests were performed at a constant temperature 21°C and at a constant water to solid ratio 0.5. Measurements started 10 minutes after mixing with water. The rheological properties of pastes with fly ashes were determined from the flow curves, at growing and reduced rates of shearing in

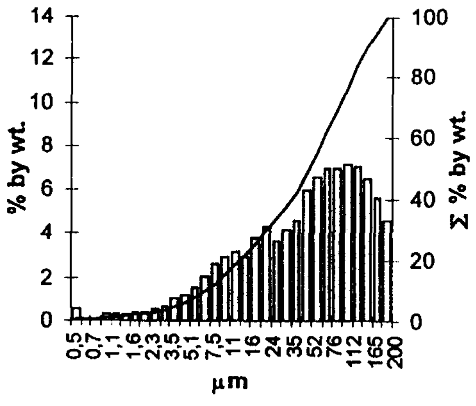

FIG. 2.
Partical size distribution and cumulative curve of fly ash FA-0.

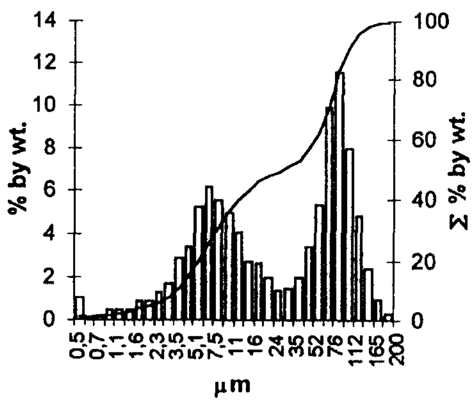

FIG. 3.
Partical size distribution and cumulative curve of fly ahs FA-1.

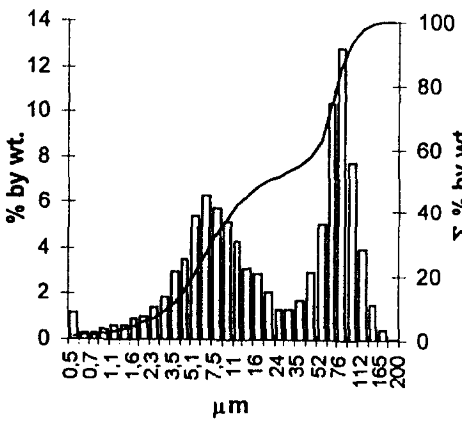

FIG. 4.
Partical size distribution and cumulative curve of fly ash FA-2.

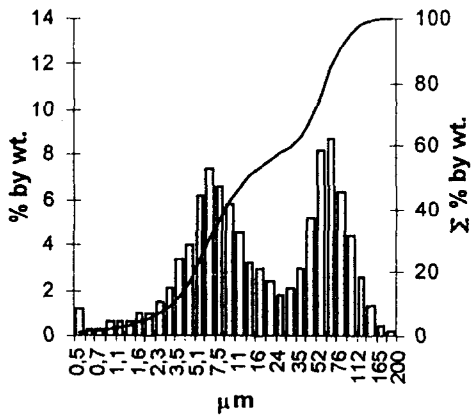

FIG. 5.
Partical size distribution and cumulative curve of fly ash FA-3.

the range from 0 to 146 s^{-1}. The yield value and plastic viscosity were determined from the descending part of flow curve, according to the Bingham's model.

Heat Evolution of Initial Stage of Hydration. A calorimetry study of a fly ash-cement paste composed of 20% wt. cement and 80% wt. fly ash (FA-0) was designed to analyse the reaction between a cement containing a high-calcium fly ash and water. Also, a similar composed fly ash-cement paste, containing bituminous fly ash (chemical composition: SiO_2-

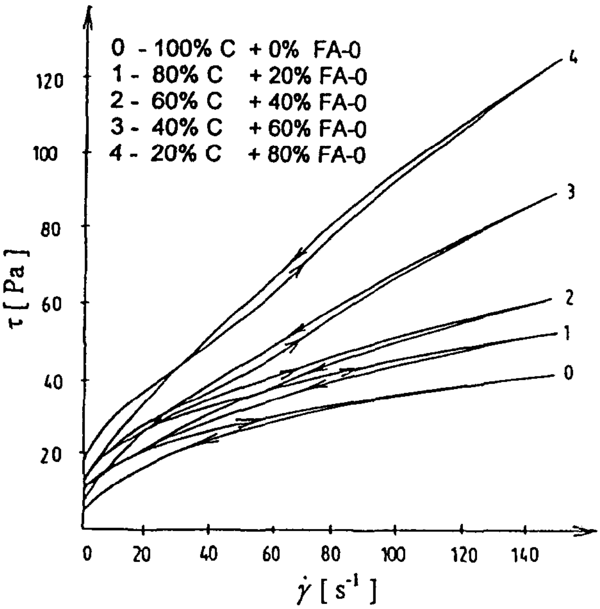

FIG. 6.
Flow curves of cement pastes containing fly ash FA-0.

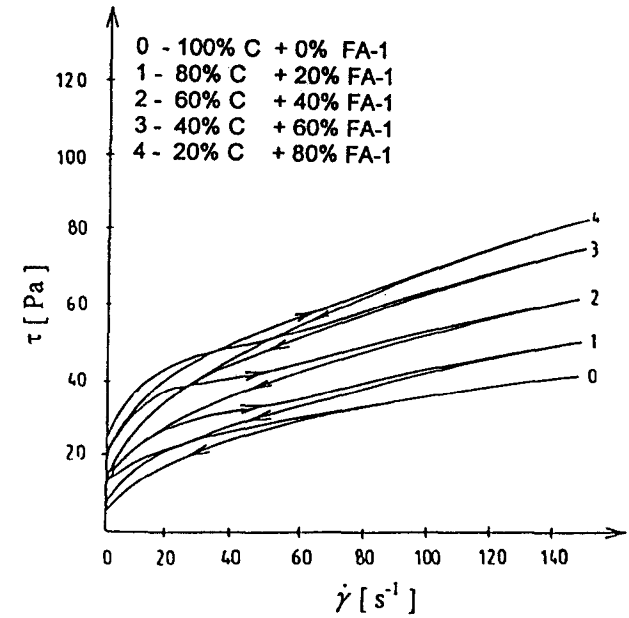

FIG. 7.
Flow curves of cement pastes containing fly ash FA-1.

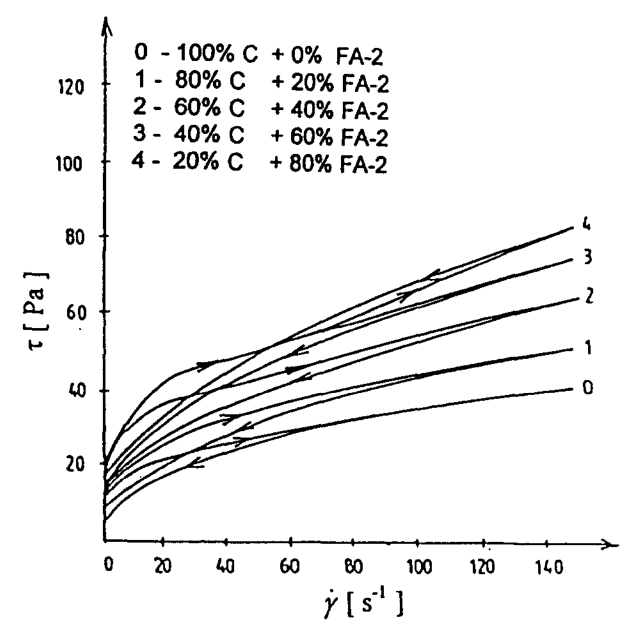

FIG. 8.
Flow curves of cement pastes containing fly ash FA-2.

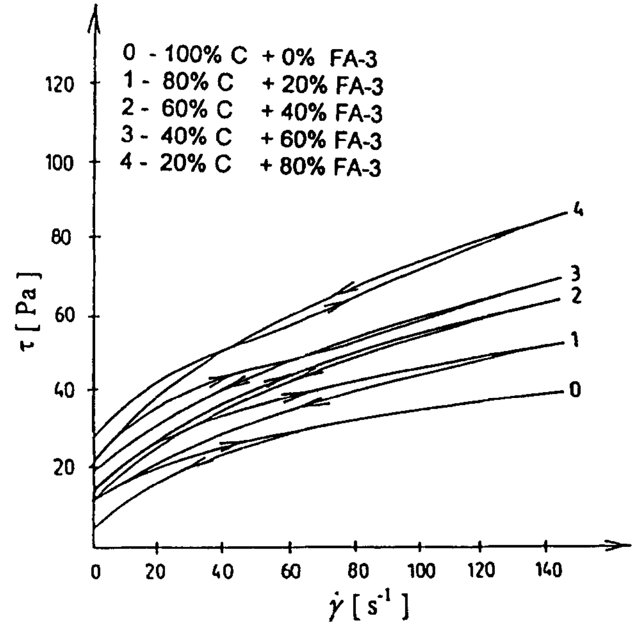

FIG. 9.
Flow curves of cement pastes containing fly ash FA-3.

51.9; Fe_2O_3-8.0; Al_2O_3-26.1; CaO-1.9; MgO-0.3; SO_3-0.8; Na_2O-3.2 wt.%.) was studied for comparison reason. A differential microcalorimeter was used in both cases and the water/solid ratio was 0.4 while the temperature was fixed at 21°C.

Scanning Electron Microscopy of Fresh Fly Ash Cement Paste. The SEM studies of cement-fly ash pastes considered those containing 20% wt. of cement and 80% wt of fly ash, i.e. of the same composition as pastes used in microcalorimetry measurements. The water/solid ratio was 0.4. The SEM observations of cement-fly ash pastes, were carried out by means of JEOL-5400 equipment after 4 hours of hydration (water to solid ratio equal 0.4).

TABLE 3

Yield Value τ_0 [Pa] and Plastic Viscosity η_{pl} [Pa · s] of Cement Pastes Containing Fly Ashes

No	Composition of cement - fly ash mixtures	FA-0		FA-1		FA-2		FA-3	
		τ_0	η_{pl}	τ_0	η_{pl}	τ_0	η_{pl}	τ_0	η_{pl}
0	100% C + 0% FA	12,8	0,26	12,8	0,26	12,8	0,26	12,8	0,26
1	80% C + 20% FA	18,6	0,29	16,4	0,28	15,4	0,30	16,6	0,30
2	60% C + 40% FA	18,8	0,45	18,9	0,32	20,6	0,35	20,7	0,36
3	40% C + 60% FA	22,9	0,55	24,4	0,36	25,6	0,39	23,3	0,37
4	20% C + 80% FA	21,1	0,74	21,5	0,41	24,8	0,47	24,7	0,48

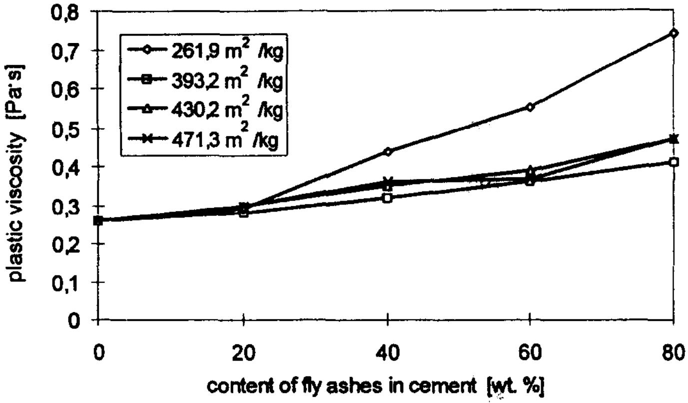

FIG. 10.
Effect of contents and specific surface area of high-calcium fly ashes on the plastic viscosity of cement pastes.

Results and Discussion

The flow curves of the cement-fly ash pastes are plotted in Figures 6-9. The calculated yield value and plastic viscosity values are presented in Table 3. The effect both of high-calcium fly ash contribution in cement and the fly ash specific surface area on the plastic viscosity of cement pastes is shown in Fig. 10.

As it results from the rheological studies, pastes prepared from cements containing the high-calcium fly ash (Table 3) reveal higher yield value and higher plastic viscosities as compared to the neat cement paste. The rheological parameters of pastes increase with the content of fly ash in the cements containing high-calcium fly ash. The plastic viscosity becomes clearly higher in pastes with 60 wt.% and 80 wt.% of raw, not ground fly ash. The plastic viscosity is thus two and three times greater than for the reference sample without fly ash. But the effect of fly ashes on the yield value is significantly less pronounced.

The grinding of the high-calcium fly ash, e.g. to 392.2 m^2/g Blaine, brings about the rheological properties improvement (increase of fluidity) as compared with the paste containing raw fly ash (261.9 m^2/g). The effect is negligible for the lowest fly ash content (20%) but becomes significant at higher values. It is clearly visible for the material containing 60 wt.% and 80 wt.% fly ash when the sharp viscosity reduction occurs (Fig. 10). The modification of rheological parameters, i.e. the increase in fluidity, is practically not influenced by a subsequent increase in the fly ash specific surface area up to 430.2 and 471.3 m^2/kg.

The analysis of the data presented in Fig. 2-5 has proved that cement pastes containing fly ashes of similar grain size distribution (FA-1, FA-2, FA-3) in the range below 24 μm reveal similar rheological properties, although they show different specific surface area values. The modification of rheological properties, consisting in the plastic viscosity decrease, observed for samples containing high-calcium fly ash ground to 393.2 m^2/kg Blaine results from the fine fraction content increase. This value rises from 33 wt.% for the raw fly ash of 261.9 m^2/kg to 50 wt.% for the ground material (393.2 m^2/kg Blaine). At higher specific surface area values of ground fly ashes, i.e. at 430.2 and 471.3 m^2/g the fraction <24 μm content is 51.6 wt.% and 57.3 wt.% respectively, so the difference is small. Similar finest

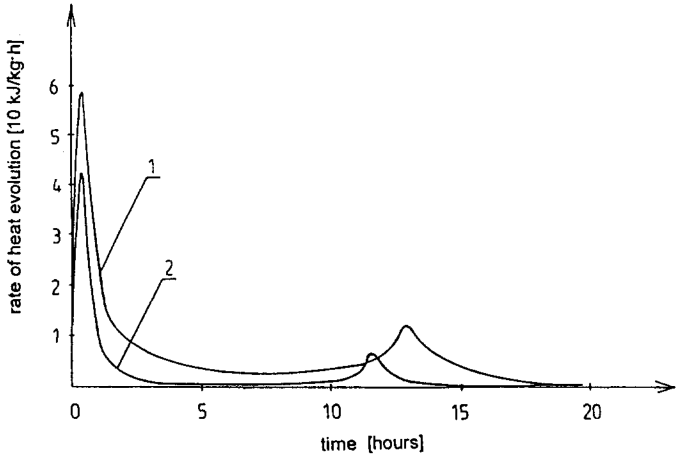

FIG. 11.
Heat evolution curves of cement pastes containing high-calcium fly ash (1) and low-calcium fly ash (2).

fractions contents in fly ashes differing in specific surface area (393.2 m^2/kg, 430.2 m^2/kg, 471.3 m^2/kg) explain the similarity in the rheology of cement-ground fly ash pastes.

As one can see from the microcalorimetric measurements, the heat evolution process is accelerated in the presence of high-calcium fly ash in the pastes, as compared when low-calcium fly ash was used. The heat evolution curves are plotted in Fig. 11. The higher values

FIG. 12.
SEM micrography structure of cement pastes containing low-calcium fly ash after 4 hours hydration time (×2000).

FIG. 13.
SEM micrography structure of cement pastes containing high-calcium fly ash after 4 hours hydration time (×3500).

of the heat released indicate for a better progress of hydration reactions in the pastes containing high-calcium fly ashes. The total heat evolved after 48 hours of hydration was 145 kJ/kg for the cement paste containing high-calcium fly ash, and 69 kJ/kg for the cement paste containing low-calcium fly ash.

As may be seen from the SEM results, there are considerable differences in morphology of the hydration products in the high- and low-calcium fly ash pastes. In the low-calcium fly ash paste the microcrystalline hydration products are present (Fig. 12) while in the high-calcium ones the ettringite needle-like products are observed (Fig. 13).

Both microcalorimetry and microscope studies revealed considerable differences in the course of the hydration process of fly ash-cement pastes, when a variety of fly ashes was applied. However, to estimate the factors affecting the paste rheology when high-calcium fly ashes were added to the cement one also needs to determine the part of hydration products in this process.

Conclusions

- A high-calcium fly ash admixture to cement results in a decrease in fluidity of pastes (higher yield value and plastic viscosity).
- Additional grinding of the high-calcium fly ash improves the rheological properties of pastes (increase in fluidity).
- The finest fractions content is a better parameter to characterize the rheological properties of cement pastes than the fly ash Blaine specific surface.

References

1. L. Massidda and U. Sanna, Il Cemento, 4, 317, (1982).
2. Ya. Ivanov and S. Zacharieva, 7 th Int. Cong. Chem. Cem., Paris, VI, 103, (1980).
3. H. Uchikawa, J. Res. Onoda Cement Company, XXXVIII, 40, (1986).
4. D.W. Hobbs, Magazine of Concrete Research, 32, 219, (1980).
5. W. Jiang and D.M. Roy, Rheology in hydratation and setting, in Hydration and Setting of Cements, Ed.: A. Nonat, J.C. Mutin, E & FN SPON, London, 1992.
6. U. Costa and F. Massazza, Il Cemento, 4, 397, (1986).
7. R.C. Joshi and R.P. Lohtia, Types and Properties of Fly Ash, in Mineral Admixtures in Cement and Concrete, Ed.: S.N. Ghosh, ABI Books Pvt. Ltd., New Delhi, 1995.
8. J.L. Alonso and K. Wesche, Characterization of Fly Ash, in Fly Ash in Concrete, Ed.: K. Wesche, E & FN SPON, London, 1991.