Computers and Concrete, Vol. 11, No. 1 (2013) 39-49
DOI: http://dx.doi.org/10.12989/cac.2013.11.1.039

Hydration and time-dependent rheology changes of cement paste containing ground fly ash

Wei Chen*[1] and Hao Huang[2]

[1]State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Luoshi Road 122, Wuhan, 430070, P.R. China
[2] School of Materials Science and Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, 430070, P.R. China

(Received September 22, 2011, Revised December 19, 2011, Accepted March 19, 2012)

Abstract. The use of ground fly ash in concrete can increase the risk of slump loss due to the drastic surface change of the particles after the grinding treatment and the accelerated reaction compared to the untreated ash. This study is aimed at the early age hydration and time-dependent rheology changes of cement paste containing ground fly ash. An original fly ash is ground into different fineness and the hydration of cement paste containing the ground fly ash is monitored with the ultrasound propagation method. The zeta potentials of the solid particles are measured and the changes of rheological parameters of the cement pastes with time are analyzed with a rheometer. A particle packing model is used to probe packing of the solid particles. The results show that the early age hydration of the paste is strongly promoted by replacing Portland cement with fly ash up to 30 percent (by mass), causing increase of the yield stress of the paste. The viscosity of a paste containing ground fly ash is lower than that containing the untreated ash, which is explained by the denser packing of the solid particles.

Keywords: hydration; ground fly ash; rheology; packing

1. Introduction

The use of fly ash in concrete has been proven effective for enhancing the fluidity of fresh concrete, improving the long-term strength of hardened concrete and its impermeability. The benefit of cost reduction makes it attractive for the concrete industry as well. However, studies and industrial experience have repeatedly shown that the advantages of using fly ash in concrete are strongly affected by the nature of the ash, such as its chemical composition, particle size distribution (PSD) and water content, according to which the untreated fly ash is classified into different grades. Normally, fine fly ashes classified into high grades are preferred for high performances. However, due to the increasing acceptance of fly ash in concrete production, a supply shortage of high-grade fly ash is often seen in practice. Thus, extra grinding treatment of the coarse fly ash to a high fineness has become an option for mitigating the supply shortage of high-grade fly ash on market (Feng 1986). Though the ground fly ash (GFA) has enhanced

∗Corresponding author, Associate Professor, E-mail: w.chen.whut@gmail.com

reactivity compared to the untreated coarse ash and is thus beneficial for the strength and durability improvement (Payá *et al*. 1997, Tangpagasit *et al*. 2005, Giergiczny 2006), it could weaken the fluidity of the fresh concrete greatly (Borsoi *et al*. 2000). Thus, the applicability of the GFA in high grade concrete is often questioned in regard to the risk of placing and consolidating difficulties.

Most of existing studies deal with the rheology of the fresh mix with knowledge established from the field of colloidal science, which involves considerations to the surface forces and inter-particle interactions (Banfill 1994, Vikan *et al*. 2005, Wallevik 2009). Even though the hydration reaction of cement is obviously a time-dependent process, efforts on associating the rheological changes with the hydration process is scarce (Struble and Lei 1995). This is especially important for cement containing fly ash, a common ingredient in modern concrete.

The morphological effects of fly ash on the properties of fresh concrete can be summarized into three different aspects, i.e., the filling role, the surface role and the lubricating role, all strongly affected by the surface characteristics and geometry of the particles (Wang *et al*. 2003). The fine particles fill the space between the clinker particles on the one hand, and on the other hand immobilize more free mixing water due to their large surface areas. The lubrication role of fly ash depends on the shape of the particles. The spherical particles lubricate better than the angular ones. The grinding process breaks the spherical particles into angular pieces and thus the lubrication effect is greatly weakened.

Payá *et al*. (1996) studied the effects of GFA on the workability of mortar by means of flow table spread test. They found linear correlations between the flow table spread values and fly ash replacing percentages. A clear diminution of workability was observed when the grinding time was increased. The workability of cement mortar containing GFA was better than the reference cement mortar without GFA. Kiattikomol *et al*. investigated the effects of GFA on the normal consistency of fresh cement paste at a replacement level of 20% by weight (Kiattikomol *et al*. 2001). It was found that amongst the five different sources of fly ash, four of them resulted in lower normal consistency after the grinding treatment and one resulted in higher values. Both the initial and final setting time of GFA blended cement paste were prolonged compared to the plain Portland cement paste. Flow of mortar sample was enhanced by the use of GFA.

This study is aimed to establish the link between the characteristics of GFA, its early age hydration behavior and the time-dependent rheological changes of cement pastes containing different amounts of GFA. The fly ash is ground into different fineness and the hydration of the cement paste is monitored with the ultrasound propagation method (Reinhardt and Grosse 2004). The zeta potentials of solid particles in the liquid suspension are measured. The rheological parameters are analyzed with a rheometer. The particle packing model of Andreasen and Andersen (1930) is used to probe the packing efficiency of solid particles and its relation to the rheological changes is discussed.

2. Experimental

2.1 Materials

A Portland Cement (PC) classified as P.I 52.5 according to the Chinese standards GB 175-2007 produced by Huaxin Cement Co. LTD is used in the experiments, which contains about 95% clinker and 5% gypsum. Density of the PC is 3.10 g/cm^3. A low-calcium fly ash with a density of

2.1 g/cm^3 is supplied by the Qinshan power plant in Wuhan. The original fly ash (FA-O) is ground in a ball mill for 15 (FA-15) and 30 (FA-30) minutes to different fineness. Oxide compositions of the PC and fly ash are listed in Table 1. The PSDs of the Portland cement and fly ash powders are plotted in Fig. 1. The Blaine fineness of the PC, FA-O, FA-15 and FA-30 are 419, 346, 495 and 592 m^2/kg, respectively. After the grinding treatment, the fineness of the fly ash is greatly increased. The PC and FA-15 have similar PSDs, as shown in Fig. 1.

The morphology of the original fly ash and GFA powders imaged with scanning electron microscope (SEM) is shown in Fig. 2. Most of the original fly ash particles are spherical. After being ground for 15 minutes, the small spheres are broken into flakes and broken shells. After being ground for 30 minutes, most of the large spherical particles remain intact while the small ones are broken and agglomerate with other broken pieces. The observation of mechanical effects on the morphology of GFA agrees well with the study of Payá *et al*. (1996).

Table 1 Oxide compositions of the Portland cement and untreated fly ash (mass%)

Material	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	Fe_2O_3	L.O.I
PC	0.13	1.61	3.92	19.37	0.81	0.59	68.3	0.32	3.69	1.09
FA-O	0.35	0.37	30.18	54.38	0.49	1.65	2.39	1.41	4.92	3.44

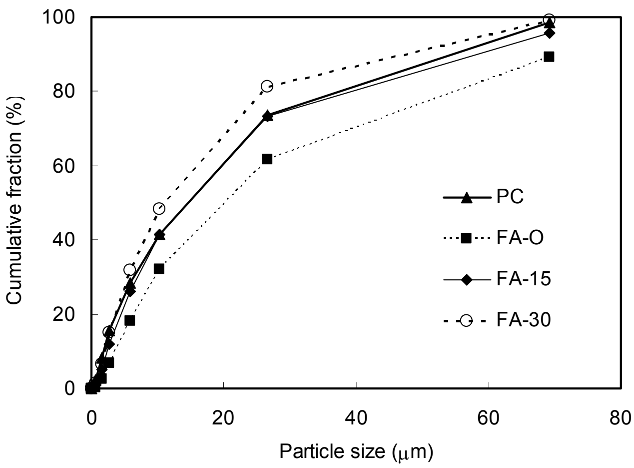
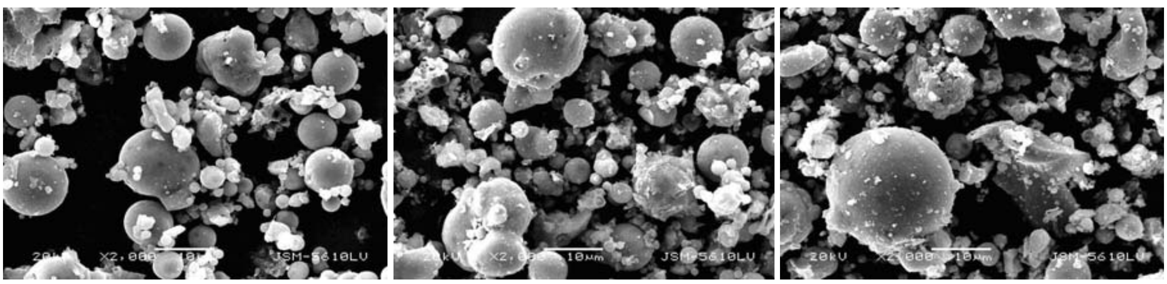


Fig. 1 Particle size distribution of PC and fly ash



FA-O FA-15 FA-30

Fig. 2 SEM images of the original and ground fly ash particles

2.2 Test methods

2.2.1 Hydration monitoring with ultrasound propagation method

Monitoring the propagation of ultrasonic pulse in hydrating Portland cement pastes has been used to investigate the early age hydration of cement paste owning to the advantages of simple operation and continuity of the monitoring process. Changes of the physical structure of a material are characterized by the ultrasound propagation velocity which is calculated from the propagation distance and time. The volume and contact area of cement particles increase with the hydration process, which provides routes for the ultrasound pulse propagation. The set-up of the device for ultrasound propagation velocity measurement is shown in Fig. 3 (Chen *et al*. 2011).

The hydration process of the PC paste and those containing 30% of FA-O or FA-30 are investigated with the ultrasound propagation methods, details of which are given in the study of Chen *et al*. (2011). By measuring the ultrasound propagation velocity (UPV) in hydrating cement paste, it is possible to probe the hydration rate and state of solids in the paste (Reinhardt and Grosse 2004, Ye *et al*. 2004). Cement pastes are prepared with water to binder (*w*/*b*) ratio of 0.40 in which the Portland cement is replaced with FA-O or FA-30 at a proportion of 0 or 30% by mass. The paste is casted into a mould of 40 × 120 × 120 mm^3 made of PMMA. The UPV is analyzed with an ultrasonic analysis system (Model TICO H-2979A by PROCEQ). The test temperature is 23^oC and the probe frequency is 54 kHz.

2.2.2 Zeta potential measurements

The zeta potential is an indication of the surface charge of a particle suspended in a solution. It can be used for a cementitious material to characterize how well the particles can be dispersed and stabilized. If a solid-liquid suspension is charged with additional electric fields, the particles will migrate between the electrodes, the speed of which (μ) is determined by

$$\mu = \frac{\zeta \mathrm{DE}}{4\pi\eta} \quad (1)$$

in which E is the potential of the electric field, D is the dielectric constant, ζ is the zeta potential and η is the viscosity of the solution. A slurry of a powder consisted of Portland cement and fly ash mixed with water is prepared with water to solid mass ratio of 1000. The slurry is stirred for 30 seconds, kept static for 10 minutes and then stirred for 30 seconds at 23^oC. The slurry is then casted into a stage for the zeta potential measurement. The zeta potential of randomly selected 15 particles is measured with a zeta meter (Model ZM3-D-G by Zeta Meter) and the average zeta potential is calculated.

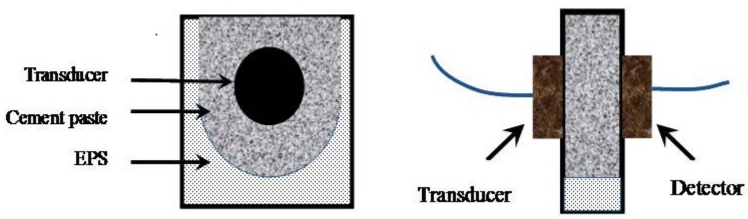


Fig. 3 Device for measuring the ultrasound propagation velocity in cement paste (Chen *et al*. 2011)

2.2.3 Rheology analysis

Cement pastes with or without fly ash are prepared with a w/b ratio of 0.45. The pastes are mixed in a 250 ml beaker for 30 seconds at 23°C and are then tested immediately with a rheometer (model R/S Plus Soft Solids Tester by Brookfield). This device uses a vane spindle lowered into the test samples. The test can be run in the beakers with minimal disruption of the initial structure. The shear rate in the rising stage is 0-200 (1/s) and that in the dropping stages is 200~0 (1/s). The test time for each stage is 120 seconds. It is found that the correlation between the shear stress (τ, Pa) and the shear rate (D, 1/s) in the dropping stage complies with the Bingham model (Hu and de Larrard 1996), which is written as

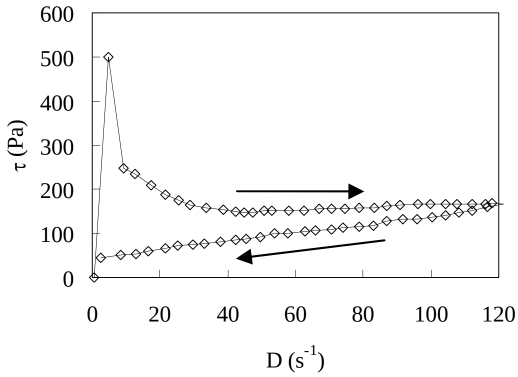
$$\tau = \tau_0 + \eta D \tag{2}$$

in which η is the plastic viscosity of the paste, and τ_0 is the Bingham yield stress. A typical test result of the cement paste with the rheometer is shown in Fig. 4. It is noted that for each recipe tested at different ages, a specimen settled in a separate beaker is used at each age to avoid the disturbance of pervious tests.

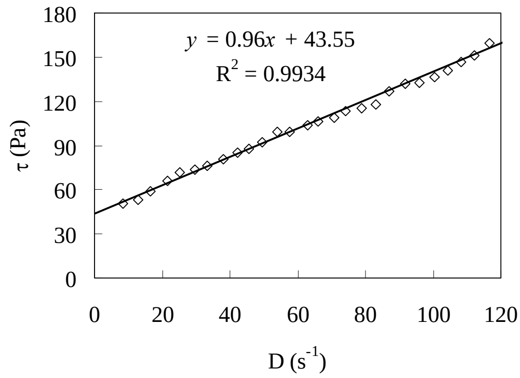
3. Test results and analysis

3.1 Zeta potential of particles

Results of the zeta potential measurements with particles suspended in a dilute solution are listed in Table 2. The surface charge of the Portland cement particle is close to neutral, observed in the study of Uchikawa *et al*. (1997) as well. This neutral surface charge renders a great potential for adsorbing chemical admixtures (Termkhajornkit and Nawa 2004). Different from the PC, the fly ash particles are strongly charged with negative potentials, and the magnitude of the potential increases with the grinding treatment. A higher fineness results in a larger potential, which is able to disperse the particles better. Hence, replacing PC with fly ash brings a lubricant effect on the rheology of cement paste.



(a) Full test range



(b) Fitting of the dropping stage

Fig. 4 Typical result of the rheological test

Table 2 Zeta potential of solid particles

Material	PC	FA-O	FA-15	FA-30
Zeta potential (mV)	-2.35	-18.6	-20.2	-24.3

3.2 Change of UPV in cement paste containing fly ash

Studies have shown that the evolution of UPV in hydrating cement paste is strongly related to the volumetric fractions of solid particles in the paste and their contact areas (Ye *et al*. 2004). The developments of UPV in hydrating Portland cement paste and those with 30% PC replaced by FA-O or FA-30 are plotted in Fig. 5. It can be seen that, even though the density of the fly ash is remarkably lower than that of the PC and the same mass of binder with or without fly ash results in different solid volume fractions in the paste, the starting UPVs of the hydrating paste are close to each other. Hence, most likely the addition of fly ash particles into the slurry enhances the dispersion force between the particles and decreases the contact areas, which is proven by the zeta potential measurement (Table 2).

Partial replacement of PC with fly ash appears to promote the early age hydration of the binder, and by replacing 30% of the PC, the threshold age of UPV increment is shortened from 50 minutes to 35 minutes for FA-O and to 30 minutes for FA-30. The promotive effects of fly ash on the PC hydration is also observed in the work of Narmluk and Nawa (2011), which is concluded as the contribution from the cement dilution effect and the promoted effective diffusion coefficient of water in C-S-H around cement particles.

The finely ground GFA reacts faster than the coarsely ground ash which is expected because of the higher specific surface area and thus more reaction fronts (Van Breugel 1997). The reaction rate of a supplementary material in a cement paste is known to be strongly related to its fineness (Chen *et al*. 2007). It is proven with the UPV measurement that the mechanical activation effect starts 30 minutes after contact with water. This is probably due not only to the increased surface area, but also the concentrated surface defects generated during the grinding process.

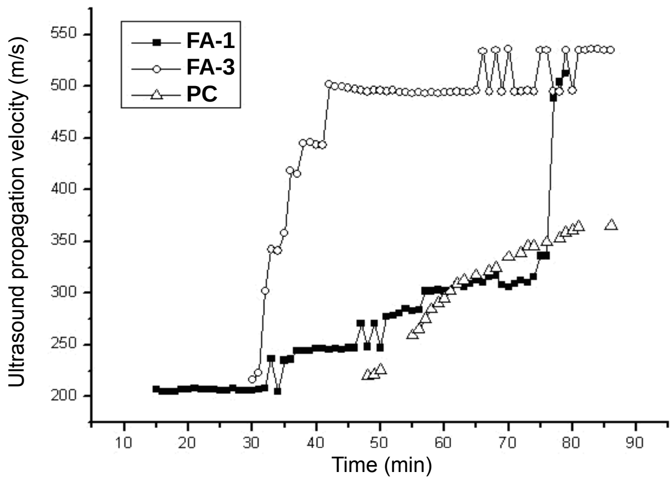


Fig. 5 Development of ultrasound propagation velocity in cement pastes (*w/c* = 0.40)

Table 3 Rheological changes with time of cement paste containing 30 percent fly ash (*w/b* = 0.45)

Fly ash	0 minutes		30 minutes		60 minutes	
	Yield stress (Pa)	Viscosity (Pa·s)	Yield stress (Pa)	Viscosity (Pa·s)	Yield stress (Pa)	Viscosity (Pa·s)
FA-O	34.15	0.85	37.64	0.79	43.55	0.96
FA-30	45.15	0.64	45.93	0.61	55.52	0.75

3.3 Rheological changes of cement paste containing fly ash

Cement pastes containing 30 percent of FA-O or FA-30 are mixed with a water-to-solid ratio of 0.45 and their rheological parameters are tested at 0, 30 and 60 minutes. The test results are listed in Table 3. It can be seen that the Bingham yield stress of the paste increases with hydration age. The rate of change increases obviously if the fly ash is ground into fine particles. Hence, it is expected that replacing the Portland cement with GFA will increase the risk of slump loss of concrete, compared to the untreated fly ash. The yield stress of the cement paste containing 30 percent of FA-30 changes very slightly during the first 30 minutes, while it increases drastically after 60 minutes. It can be concluded that the fluidity loss of cement paste containing GFA is associated to the rapid reaction of the GFA particles and the enhanced hydration of the Portland cement. As shown in Fig. 5, the grinding treatment changes the hydration process of cement paste containing GFA drastically. Hence, it is expected that the yield stress of the paste is changed as well.

The effects of replacement proportions of fly ash on the yield stress and viscosity are plotted in Fig. 6. The PSD and morphology of fly ash particles obviously influence the rheological parameters of the paste. In general, the yield stress of the paste is increased with increasing replacement percentages if GFA is used. The change of viscosity depends on the nature of the

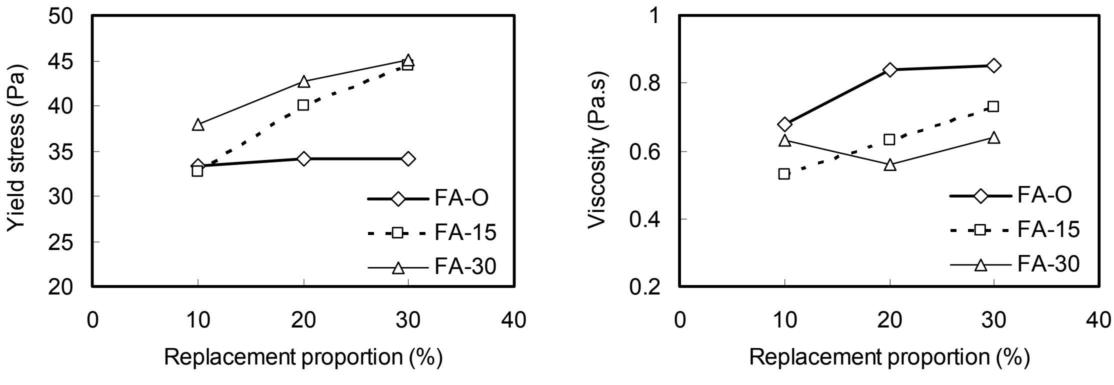


Fig. 6 Effects of GFA on the rheological parameters of cement paste (*w/c* = 0.45)

Table 4 Calculated PSD of ideally packed cement particles according to Eq. (3)

Particle size (μm)	0.71	1.52	2.70	5.79	10.27	26.68	69.30
Passed fraction (%)	16.82	21.67	26.25	33.83	40.95	56.27	77.33

GFA. It increases linearly with the replacement proportion for FA-15. However, the change of viscosity of paste containing FA-30 is not straight forward. Replacing 20% of PC with FA-30 results in a lower viscosity than the other two proportions. For the untreated fly ash (FA-O), the viscosity increases with the replacement proportions.

3.4 Effects of particle packing on the rheology changes

The rheological behavior of slurry containing solid particles suspended in a solution is not only related to the volumetric fraction of the particles and their interactions, but also to the packing of the particles that determines the mechanical interlocking of the solids. While the PSDs of the PC and fly ash are quite different from each other, it is expected that the partial replacement of PC with fly ash changes the packing of the solids, which alters the amount of free water available as lubricants (Sakai *et al*. 2009).

The packing factors of pastes containing different fly ash are evaluated with the well known Andreasen and Andersen model as

$$U(D_p) = 100\left(\frac{D_P}{D_{p\max}}\right)^q \tag{3}$$

in which $U(D_p)$ is the fraction of powder passing the sieve sizing D_p, $D_{p\max}$ is the maximum particles, q is the exponent. The exponent q is referred to as the distribution modulus and higher values of q lead to coarser blends (Brouwers and Radix 2005). By taking values of $D_{p\max}$ as 150 m and that of q as 1/3, the PSD of solid particles for ideal packing should comply with Table 4. The packing factors of mixes with different types and proportions of fly ash particles are then evaluated with the ideal PSD as

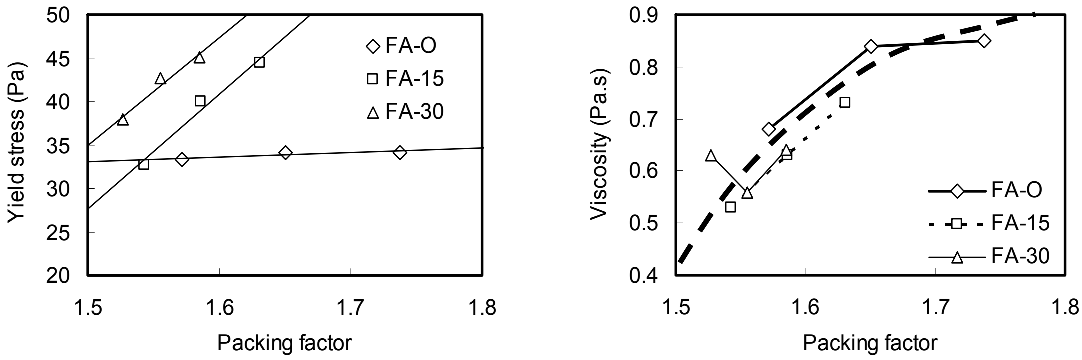
$$D = \sum_{i=0.71,n}\left(\frac{M(i) - M_0(i)}{M_0(i)}\right)^2 \tag{4}$$

in which D is the packing factor, $M_0(i)$ is the mass fraction of powder finer than sieve i, and $M_0(i)$ is that for the ideal PSD. Greater values of D indicate a larger deviation of the PSD from the ideal curve. The packing efficiently of the different mix is calculated and listed in Table 5. The packing factors are increased for all three fly ashes with increasing replacement proportions, though to a much less extent for the fine GFA (FA-30). Coarser fly ash leads to a larger value of the packing factor, indicating poor packing.

The correlation between the packing efficiency and the rheological parameters of the cement paste is plotted in Fig. 7. Larger values of the packing factor correspond generally to greater values of yield stress and viscosity. The yield stress of paste containing the FA-O is slightly influenced by

Table 5 Calculated packing factors according to Eq. (4)

Fly ash	FA-O			FA-15			FA-30		
Proportion (%)	10	20	30	10	20	30	10	20	30
D	1.572	1.651	1.738	1.543	1.586	1.631	1.527	1.555	1.585



(a) Yield stress (b) Viscosity

Fig. 7 Effects of fly ash on the rheological parameters of cement paste (w/c = 0.45)

the packing factor, due to the spherical nature of the untreated powder. The viscosity is increased with the packing factor, indicating poor packing. The dependency of the yield stress on the packing factor is highly influenced by the nature of the fly ash powder, while that of the viscosity is close to the trend shown in Fig. 7(b). Grinding the fly ash to a larger fineness increases the yield stress for the same packing factor, while the viscosity is not significantly changed.

4. Conclusions

The time-dependent rheology changes of cement pastes containing different fractions of ground fly ash are investigated together with the early age hydration processes. The results show that the early age hydration of the paste is greatly promoted by partial replacement of Portland cement with fly ash, which increases the yield stress of the paste as well. The risk of slump loss of fresh concrete is thus more serious by replacing partially Portland cement with GFA. The yield stress of cement paste containing ground fly ash is much higher than paste with the untreated fly ash and increases with the replacement proportions. The viscosity of paste containing ground fly ash is lower than that containing the untreated ash, which is explained by the dense packing of the solid particles. The yield stress of a cement paste is highly affected by the morphology of the particles, while the viscosity depends on the particle packing.

Acknowledgments

This research is financially supported by the National Natural Science Foundation of China (Project 50802067), the Scientific Research Foundation for Returned Overseas Chinese Scholars, Ministry of Education and the Youth Chenguang Project of Science and Technology of Wuhan (project 201150431086).

References

Andreasen, A.H.M. and Andersen, J. (1930), “Relation between grain size and interstitial space in products of unconsolidated granules", *Kolloid-Z*, **50**, 271-278.

Banfill, P.F.G. (1994), "Rheological methods for assessing the flow properties of mortar and related materials", *Constr. Build. Mater.*, **8**(1), 43-50.

Borsoi, A., Collepardi, S., Coppola, L., Troli, R. and Collepardi, M. (2000), "Effect of superplasticizer type on the performance of high-volume fly ash concrete", *Proceedings of the Sixth CANMET/ACI International Conference*, *SP-195*, 17-28.

Brouwers, H.J.H. and Radix, H.J. (2005), "Self-compacting concrete: The role of the particle size distribution", *1st International Symposium on Design, Performance and Use of Self-Consolidating Concrete*, **42**, 109-118.

Chen, W., Brouwers, H.J.H. and Shui, Z.H. (2007), "Three-dimensional computer modeling of slag cement hydration", *J. Mater. Sci.*, **42**(23), 9595-9610.

Chen, W., Li, Y. and Shui, Z. (2011), "Percolation of phases in hydrating cement paste at early ages: an experimental and numerical study", *The XIII International Congress on Cement Chemistry*, Palomo, A., Zatagoza, A. and Agui, J.C.L. Madrid, Editado por el Instituto de Ciencias de la Construccion Eduardo Torroja, **6,** 356.

Feng, M. (1986), "Utilization of pulverized fly ashnext term in the People's Republic of China", *Energy*, **11**(11-12), 1359-1362.

Giergiczny, Z. (2006), "The hydraulic activity of high calcium fly ash", *J. Therm. Anal. Calorim.*, **83**(1), 227-232.

Hu, C. and de Larrard, F. (1996), "The rheology of fresh high-performance concrete", *Cement Concrete Res.*, **26**(2), 283-294.

Kiattikomol, K., Jaturapitakkul, C., Songpiriyakij, S. and Chutubtim, S. (2001), "A study of ground coarse fly ashes with different finenesses from various sources as pozzolanic materials", *Cement Concrete Comp.*, **23**(4-5), 335-343.

Narmluk, M. and Nawa, T. (2011), "Effect of fly ash on the kinetics of Portland cement hydration at different curing temperatures", *Cement Concrete Res.*, **41**(6), 579-589.

Payá, J., Monzó, J., Borrachero, M.V., Peris, E. and González-López, E. (1996), "Mechanical treatment of fly ashes part II: Particle morphologies in ground fly ashes (GFA) and workability of GFA-cement mortars", *Cement Concrete Res.*, **26**(2), 225-235.

Payá, J., Monzó, J., Borrachero, M.V., Peris, E. and González-López, E. (1997), "Mechanical treatments of fly ashes. Part III: Studies on strength development of ground fly ashes (GFA) - Cement mortars", *Cement Concrete Res.*, **27**(9), 1365-1377.

Reinhardt, H.W. and Grosse, C.U. (2004), "Continuous monitoring of setting and hardening of mortar and concrete", *Constr. Build. Mater.*, **18**(3), 145-154.

Sakai, E., Masuda, K., Kakinuma, Y. and Aikawa, Y. (2009), "Effects of shape and packing density of powder particles on the fluidity of cement pastes with limestone powder", *J. Adv. Concrete Tech.*, 7(3), 347-354.

Struble, L.J. and Lei, W.G. (1995), "Rheological changes associated with setting of cement paste", *Adv. Cement Based Mater.*, **2**(6), 224-230.

Tangpagasit, J., Cheerarot, R., Jaturapitakkul, C. and Kiattikomol, K. (2005), "Packing effect and pozzolanic reaction of fly ash in mortar", *Cement Concrete Res.*, **35**(6), 1145-1151.

Termkhajornkit, P. and Nawa, T. (2004), "The fluidity of fly ash-cement paste containing naphthalene sulfonate superplasticizer", *Cement Concrete Res.*, **34**(6), 1017-1024.

Uchikawa, H., Hanehara, S. and Sawaki, D. (1997), "The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture", *Cement Concrete Res.*, **27**(1), 37-50.

Van Breugel, K. (1997), *Simulation of hydration and formation of structure in hardening cement-based materials*, Delft, The Netherlands, Delft University Press.

Vikan, H., Justnes, H. and Figi, R. (2005), *Adsorption of plasticizers - Influence of plasticizer and cement type*, Nordic Rheology Conference 2005, Tampere, Finland.

Wallevik, J.E. (2009), "Rheological properties of cement paste: Thixotropic behavior and structural breakdown", *Cement Concrete Res.*, **39**(1), 14-29.

Wang, A.Q., Zhang, C.Z. and Sun, W. (2003), "Fly ash effects: I. The morphological effect of fly ash", *Cement Concrete Res*., **33**(12), 2023-2029.
Ye, G., Lura, P., van Breugel, K. and Fraaij, A.L.A. (2004), "Study on the development of the microstructure in cement-based materials by means of numerical simulation and ultrasonic pulse velocity measurement", *Cement Concrete Comp*., **26**(5), 491-497.

CM