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Rheological properties of cementitious materials containing mineral admixtures

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Abstract

The rheological properties of cementitious materials containing fine particles, such as mineral admixtures (MA), were investigated using a Rotovisco RT 20 rheometer (Haake) with a cylindrical spindle. The mineral admixtures were finely ground blast furnace slag, fly ash and silica fume. The cementitious materials were designed as one, two and three components systems by replacement of ordinary portland cement (OPC) with these mineral admixtures. The rheological properties of one-component system (OPC) were improved with increasing the dosage of PNS-based superplasticizer. For two-components systems, yield stress and plastic viscosity decreased with replacing OPC with blast furnace slag (BFS) and fly ash (FA). In the case of OPC-silica fume (SF) system, yield stress and plastic viscosity steeply increased with increasing SF. For three components systems, both OPC-BFS-SF and OPC-FA-SF systems, the rheological properties improved, compared with the sample with SF. In the two and three components systems, the rheological properties of samples containing BFS improved much more than with FA replacement alone.

Keywords: Rheology; Workability; Granulated blast-furnace slag; Filler; Pozzolan

1. Introduction

Mineral admixtures (MA) have been used in order to increase strength and improve durability and flowability of cementitious material. Blast furnace slag (BFS), fly ash (FA) and silica fume (SF) are typical mineral admixtures for achieving these properties. These minerals significantly affect rheology of cementitous material in the fresh state, which is directly related with developing strength, durability and engineering properties of hardened structures. Generally ultra durable cement concrete structures with high strength are closely associated with densified microstructures which are strongly controlled by rheology properties in the fresh state of concrete.

Much research has been conducted for improving rheology properties and mechanical properties using various fine particles, and reported that BFS and FA could contribute to increase flowability in the fresh state, and densify microstructures and develop higher mechanical properties due to their latent hydraulic properties and pozzolanic reaction, respectively [1,2]. The silica fume, very fine particle—average particle size less than 1 ìm, was studied as a densifing additive for cementitious materials, and showed that the silica fume affected flowability in the fresh state of concrete and liberated much heat of hydration, resulting in causing drying shrinkage in the hardened state of structures [3].

Since these additive materials have their particular properties, rheological properties of cementitious materials should be controlled by mix design of admixtures. For the high performance concretes these mineral additives have been used for developing special performances, such as self compacting and leveling concrete, long-time workable concrete, low heat of hydration and high strength development concrete, high durability concrete, etc. [4,5].

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Table 1
Chemical compositions of the materials used in the study (wt.%)

Compositions	OPC[a]	BFS[b]	FA[c]	SF[d]
SiO_2	21.10	34.81	49.91	92.0
Al_2O_3	5.13	16.19	22.54	1.3
Fe_2O_3	3.30	0.47	11.37	2.4
CaO	62.51	41.25	5.84	–
MgO	2.72	8.05	1.25	0.4
SO_3	2.37	0.16	–	–
C	–	–	4.1	1.2
Na_2O_3	–	–	0.39	0.1
K_2O	–	–	0.87	1.2
Loss on ignition	1.39	0.32	0.5	–

[a] OPC: ordinary Portland cement.
[b] BFS: blast furnace slag.
[c] FA: fly ash.
[d] SF: silica fume.

As the rheology of cementitious material is closely related with developing performance of concrete, the rheology is considered one of the most important factors for the high performance concrete. For predicting concrete flowability many attempts have been carried out measuring rheological properties in the fresh state of cement paste and mortar, from conventional measurements, flow test and slump test, to more quantitative fundamental methodology, rheometer [5–9]. Recently the quantitative fundamental methodology, which was developed to assess the rheology of fluid state, has been used for analyzing cement paste and mortar. This method introduced rheological parameters, such as yield stress and plastic viscosity, for quantifying the flowability. Recent research indicated that the yield stress of cement paste showed the same trend of slump in concrete, and the plastic viscosity was associated with the stickness, placeability, pumpability, finishability and segregation in the concrete [10–12].

In this work, for developing macro-defect-free concrete highly compacted cementitious matrixes were developed using various kinds of mineral additives and investigated rheologically. The cementitious materials were prepared with OPC, two and three components systems (OPC-MAs). In order to analyze rheological properties of cementitious materials the parameters of rheology were measured and investigated. In addition, the effects of each mineral additive on the flowability of cementitious paste were discussed.

2. Experimental

2.1. Materials

Ordinary Portland cement (OPC) and mineral admixtures (MAs) were used as binder components. OPC with Blaine specific surface area 3290 cm^2/g and three types of MAs, finely ground blast furnace slag (BFS) with 5962 cm^2/g, Fly ash (FA) with 3650 cm^2/g and very fine Silica fume (SF) with 200,620 cm^2/g were used. As a superplasticizer (SP), commercial polynaphtalene sulfonate (PNS)-based product (PNS, 40% solids) was used during the mix.

The chemical compositions of OPC and MAs, and the physical properties of used materials are given in Tables 1 and 2, respectively.

2.2. Mix design

Cementitious pastes were designed as one component (OPC), two-components and three-components with replacing OPC with MAs. The mix designs in the study are shown Fig. 1, and the mix proportions of specimens are listed in Table 3. For preparing pastes the ratio of water to binder and the dosage of SP were fixed as 0.35 and 2.0 wt.% of binder (OPC+MA), respectively.

2.3. Test apparatus

Rheological properties were measured using Rotovisco RT 20 rheometer (Haake) having a cylindrical serrated spindle, which is able to plot the continuous rheological curve of paste from the relationship between shear rate and shear stress at physically defined condition. The plastic viscosity η_{pl} and the yield stress τ_o were calculated as

Table 2
Physical properties of the materials used in the study

	OPC	BFS	FA	SF
(a) Properties of binders				
Density (g/cm^3)	3.15	2.91	2.25	2.20
Specific surface area (cm^2/g)	3290	5962	3650	200,620
Mean particle diameter (μm)	18.07	8.07	19.56	0.1
Particle shape	Angular	Round edges cubic	Spherical	Spherical
(b) Properties of superplasticizer				
Main ingredient	Polynaphtalene sulfonate based (PNS)			
Color	Dark brown			
Specific gravity (20 °C) (g/cm^3)	1.3±0.05			
pH	8–9			
Solid content (%)	40±2			

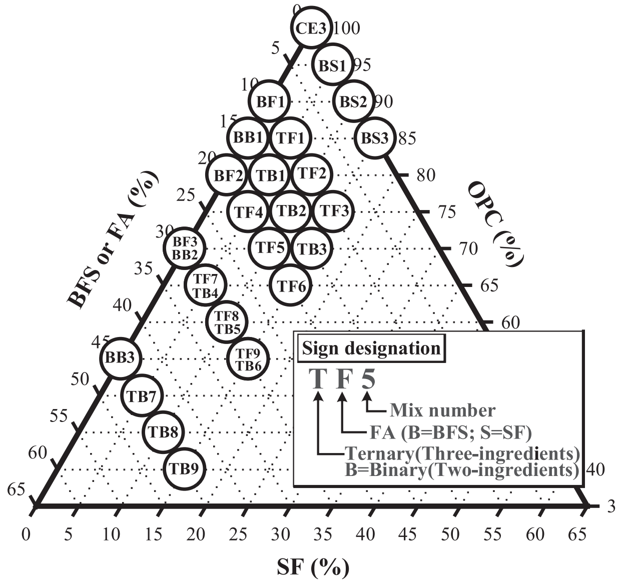

Fig. 1. Mix design of the study (wt.%).

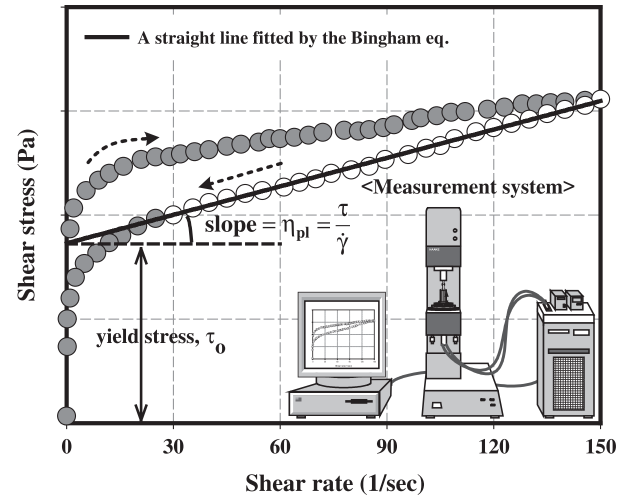

Fig. 2. Typical rheology curve described from the measurement system; a straight line fitted by the Bingham equation for the evaluation of rheological parameters.

shown in Fig. 2. Detail of the serrated spindle and the container filled with samples are depicted in Fig. 3. The spindle and the container are coaxially spaced and the spindle are serrated in the same direction as the axis.

2.4. Measurement of rheology properties

The cementitious materials pastes were prepared in accordance with the following procedures; the OPC and MAs were put in one-liter beaker, and water containing SP 2.0 wt.% was poured into the beaker, and then the mixture was stirred for two minutes. After mixing the mixture slurry was transferred into the container for measuring. In order to get an equilibrium state, the sample was placed at the stationary state for 30 s before measurement. During the measurement, the temperature of sample was maintained to 20±1 °C by an automatic controller. The applied shear rate of each paste was ranged from 0 to 150 per second and increase up and decrease down processes of shear rates were repeated at a constant rate.

2.5. Analysis of rheology properties

Typical curve of rheology property measured is represented in Fig. 2. When the shear rate was increased, the viscosity defined as the tangential slope in the rheology curve was unsteady. But when the shear rate was decreased, the

Table 3
Mix proportions of each sample (wt.% of binder)

Blended types	Notation	W/B[a]	OPC	MA		SP
				BFS(FA)	SF	
One component	CE1	0.35	100	–	–	–
	CE2		100	–	–	1.0
	CE3		100	–	–	2.0
Two components	BS1	0.35	95	–	5	2.0
	BS2		90	–	10	
	BS3		85	–	15	
	BB1(BF1)		85(90)	15(10)	–	
	BB2(BF2)		70(55)	30(20)	–	
	BB3(BF3)		55(70)	45(30)	–	
Three components	TB1(TF1)	0.35	80(85)	15(10)	5	2.0
	TB2(TF2)		75(80)	15(10)	10	
	TB3(TF3)		75(75)	15(10)	15	
	TB4(TF4)		70(75)	30(20)	5	
	TB5(TF5)		65(70)	30(20)	10	
	TB6(TF6)		60(65)	30(20)	15	
	TB7(TF7)		55(65)	45(30)	5	
	TB8(TF8)		50(60)	45(30)	10	
	TB9(TF9)		45(55)	45(30)	15	

[a] W/B: water/ binder (OPC+mineral admixtures).

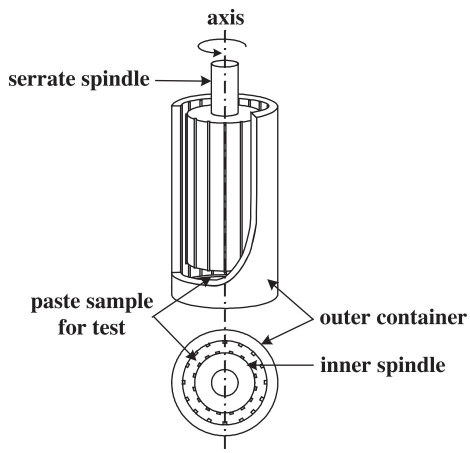

Fig. 3. Detail of the serrated spindle and the container filled with samples. The outside surface on the inner cylindrical spindle and the inside surface on the outer container are serrated to prevent the samples in the container to slip during the shear.

data, open circles, showed consistent. Especially, open circles ranging from shear rate 150 to 30/s showed more consistent and linear in all specimens, and were used for analyzing rheology properties. Thus, the plastic viscosity of paste was evaluated as a slope from the Bingham equation that was fitted to the linear portion of down curve of shear stress as a function of shear rate ranging from 150 to 30/s. The yield stress was obtained from the intercept value between the shear stress axis (at the zero shear rate) and the linear regression line of the down curve from 150 to 30/s. The mathematical form of the Bingham equation [13] is as follows:

$$\tau = \tau_0 + \eta_{\mathrm{pl}}\dot{\gamma} \tag{1}$$

Where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear strain rate (1/s), η_{pl} is the plastic viscosity (Pa s), and τ_0 is the yield stress (Pa).

3. Results and discussion

3.1. One-component system (OPC paste)

Effects of dosage of superplasticizer on the rheological properties of OPC paste and the rheological curves which were measured are shown in Fig. 4. The yield stress and the plastic viscosity stress were dramatically decreased at dosage of 1–2 wt.%, compared with the sample without SP.

The shapes of shear stresses as a function of shear rates are shown in the Fig. 4. The shear stresses of samples with SP also are dramatically decreased. The big difference between initial and final stage is shown in the sample without SP because flowability of cementitious material was changed with time due to cement hydration reaction occurred at an early time. But the samples with SP show small changes of shear stresses between initial and final stage. The sample with 2 wt.% SP shows lower and smaller change of shear stress than those of the sample with 1 wt.% SP.

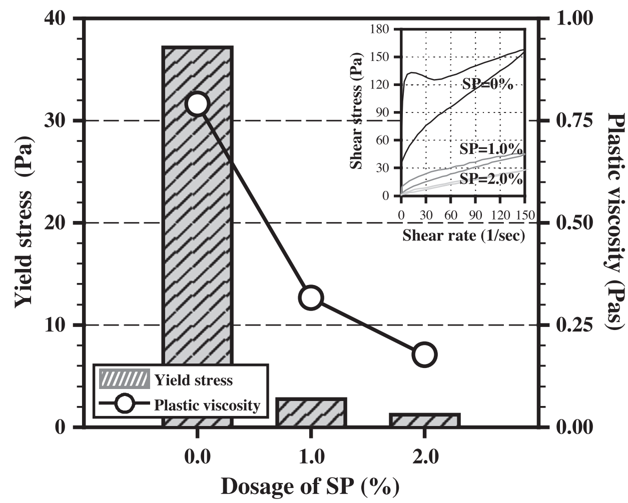

Fig. 4. Effects of dosage of superplasticizer on the rheological properties of OPC pastes and the measured rheological curves.

This phenomenon is explained by "electrostatic theory"; electrostatic repulsions between cement particles that react with superplasticizer on their surfaces [14,15]. The SP, polynaphtalene sulfonate-based superplasticizer, has an anion $-SO^{-3}$ in the molecular structure and cement particles resolve and become positive in the water [16–19]. The negative SP molecules would be around the positive cement particles and absorbed by cement particles, resulting in the electrostatic repulsion among the cement particles. As a result this repulsion induces a dispersion force among cement particles and increases flowability.

3.2. Two-components systems (OPC-BFS, OPC-FA, OPC-SF pastes)

3.2.1. OPC-BFS system

The yield stress and the plastic viscosity as a function of replacement of OPC with BFS are depicted in Fig. 5. The yield stress is decreased and increased as the BFS is

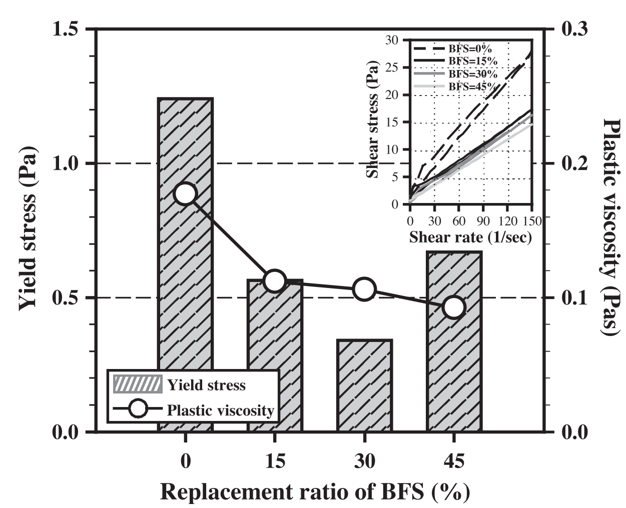

Fig. 5. Effects of replacement ratio of BFS on the rheological properties of OPC-BFS paste and the measured rheological curves.

increased, but the plastic viscosity is decreased with the BFS.

The shear stresses as a function of shear rates at between initial and final stage show lower change in the samples with BFS than the sample without BFS. The shear stresses of samples with BFS are not significantly changed as a function of the shear stresses.

The BSF acts as a good flowability aid up to 30 wt.% in this system. The BSF has a high specific surface area, average particle size 8.07 μm, and roughly spherical particles, and lower hydration reaction ability than cement. The BFS particles fill into the spaces made by larger particles of cement [3,10], average particle size 18.07 ìm, and decrease frictional forces of this OPC-BFS material. In addition, the replacement of OPC with BFS decreases hydration activity of the sample which contains little amount cement, higher hydration activity and higher absorbance of SP, as much as replacement of BFS, resulting in contributing to high flowability of this system.

3.2.2. OPC-FA system

The yield stresses and the plastic viscosities as a function of amount of FA measured are shown in Fig. 6. The sample without FA shows little bit higher yield stress than the samples with FA. For the samples with FA the yield stress is slightly increased as the FA amount increases. The plastic viscosity also slightly increases with increasing FA.

For the shear stresses as a function of the shear rates the samples with FA show very similar shapes each other, but little bit higher shear stress than the sample without FA at the higher shear rates.

The FA slightly improves flowability in this system because the spherical shape of FA reduces the frictional force among the angular particles of OPC, as called “ball bearing effect” [20]. But unburned carbons in the FA is known influencing on worse workability of cementitious materials because of adsorption of SP [21].

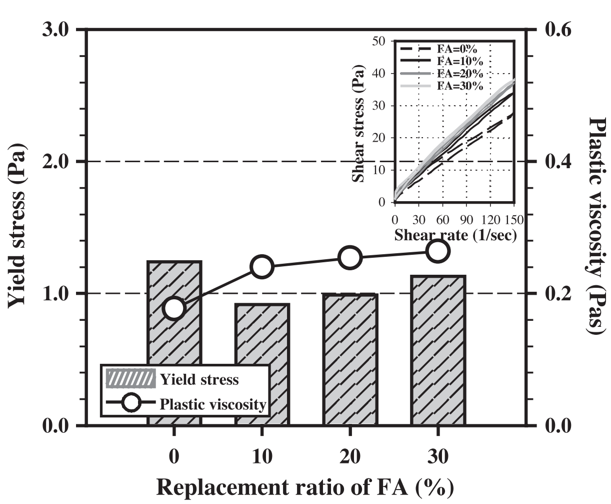

Fig. 6. Effects of replacement ratio of FA on the rheological properties of OPC-FA pastes and the measured rheological curves.

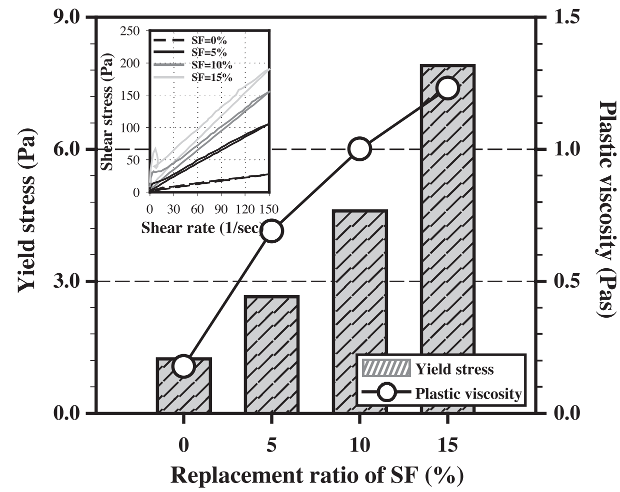

Fig. 7. Effects of replacement ratio of SF on the rheological properties of OPC-SF pastes and the measured rheological curves.

In this study the FA contains about 4 wt.% unburned carbon which actively adsorbs SP, resulting in reducing effect of SP on better flowability of cementitious material.

3.2.3. OPC-SF system

Fig. 7 shows that yield stress and the plastic viscosity as a function of SF amount measured in the OPC-SF system. The yield stress and the plastic viscosity are steeply increased with increasing SF.

The SF has very high specific surface area, 200,620 cm^2/g, and very fine particles, average particle size 0.1 ìm. The particles of SF are chemically highly reactive and easy to adsorb SP molecules with multi-layers [22,23]. As the replacement of OPC with SF increases the quantity of SP in the system decreases because much adsorption of SP by the SF was occurred. As a result the yield stress and the plastic viscosity of samples were steeply increased as the SF was increased.

The shear stress as a function of shear rate shows that SF significantly influences on rheology properties; shear stress increases with increasing SF until 15 wt.%.

3.2.4. The comparison of rheological properties of two-component systems

The yield stress and the plastic viscosity of each two-components system as a function of replacement of OPC with MAs are depicted in Fig. 8. The rheological parameters are showing different patterns according to the MAs. The yield stress, which has the same trend of slump in the fresh concrete, shows that BFS and FA act positively on flowability and SF act negatively in this system.

The SF strongly increases the yield stress and the plastic viscosity of cementitious material even though the replacement of OPC with SF is low. But the BFS shows slightly decreasing yield stress and plastic viscosity with increasing the replacement of OPC with BFS. The FA shows little bit lower yield stress and slightly higher plastic viscosity than the sample without FA.

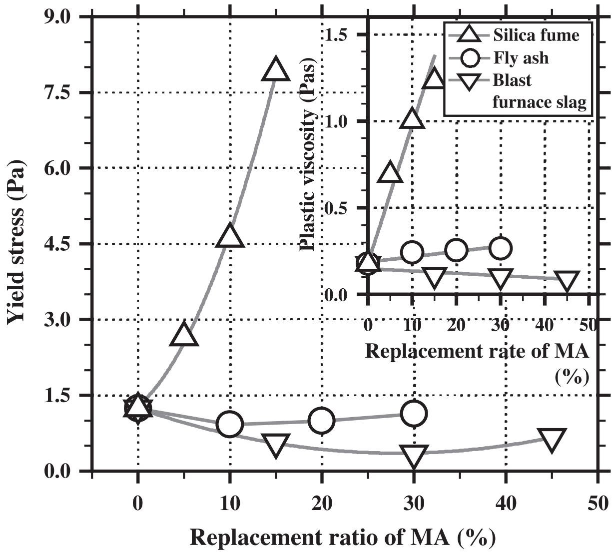

Fig. 8. The comparison of rheological properties in accordance with the replacement ratio of MA.

In the high performance concretes, especially high flowability concrete, or self-compacting and self-leveling concrete, segregation of materials is an important factor because low plastic viscosity in the fresh concrete causes segregation [5–7,22]. For designing high performance concrete moderate plastic viscosity is usually considered for avoiding segregation. From this point of view the SF may use to avoid segregation for multi-components cementitious systems which are mentioned in Section 3.3, OPC-BFS-SF and OPC-FA-SF systems.

3.3. Three-components systems (OPC-BFS-SF, OPC-FA-SF pastes)

Fig. 9 shows rheological properties of three-components pastes, OPC-BFS-SF and OPC-FA-SF systems. In these three components systems the rheological parameters are able to be controlled by MAs. Three components systems show lower yield stress and plastic viscosity than the sample with SF.

3.3.1. OPC-BFS-SF system

Fig. 9(a) shows the yield stress and the plastic viscosity as a function of replacement of OPC with MA in the OPC-BFS-SF system. The three components system shows better rheological properties compared with two components

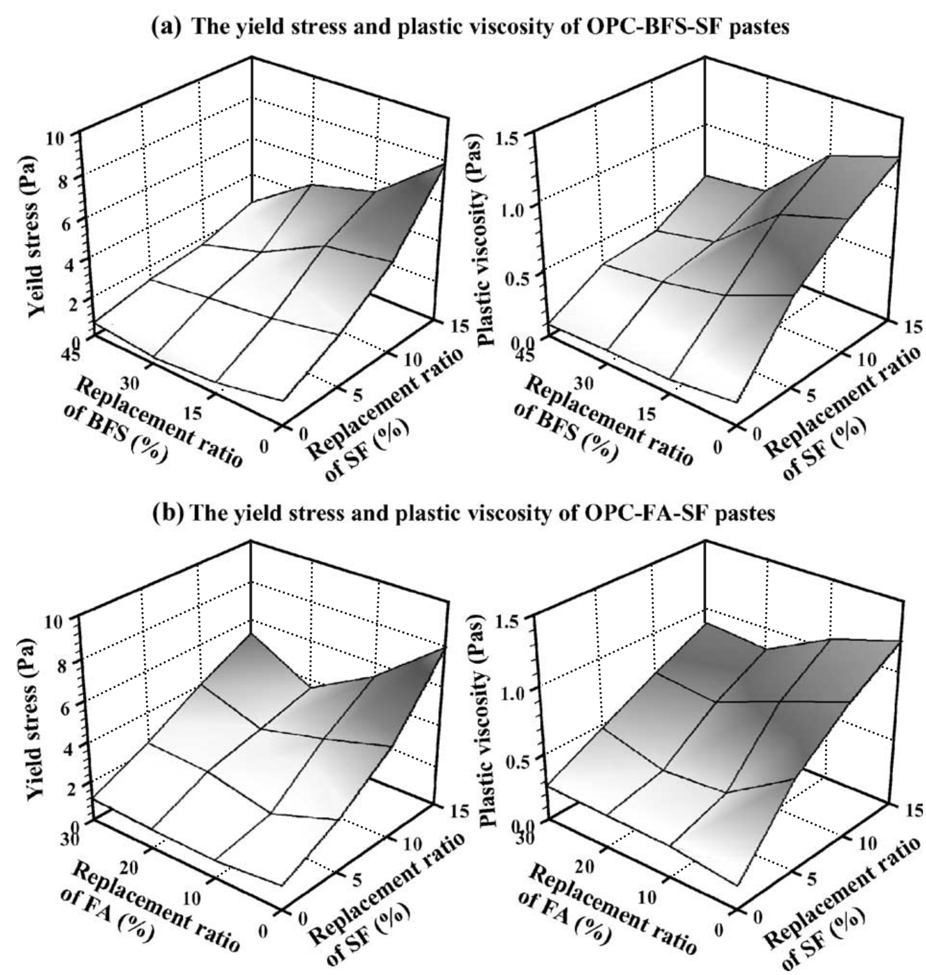

Fig. 9. Effects of replacement ratio of mineral admixtures on the rheological properties of three components systems.

Table 4
Effects of each component on rheology properties (arbitrary scale)

Blended types		Yield stress	Plastic viscosity	Remarks
One component	CE1[a]	–	–	Compare to CE1
	CE2	↓↓↓	↓	
	CE3	↓↓↓	↓↓↓	
Two components	B[b]	↓↓	↓↓	Compare to CE3
	F[c]	↓	↑	
	S[d]	↑↑↑	↑↑↑	
Three components	BF	↑	↑	Compare to B
	FS	↑↑	↑↑	Compare to S

Arbitrary scale: ↓ less, ↓↓ medium, ↓↓↓ much.
[a] CE1: OPC, CE2: superplasticizer 1%, CE3: superplasticizer 2%.
[b] B: ground blast furnace slag.
[c] F: fly ash.
[d] S: silica fume.

system; on the BFS rich area the yield stress and the plastic viscosity are increased by adding the SF, and on the SF rich area the yield stress and the plastic viscosity are decreased by adding the BFS. Along the diagonal direction from zero point the yield stress is slightly increased with increasing both BFS and SF. For the plastic viscosity, the sample with high wt.% of both BFS and SF shows about 0.5 Pa s, not so high value compared with 1.2 Pas of the sample only 15% SF.

In this system very fine particles of SF filled the spaces made by bigger particles of OPC and BFS, and absorbed SP and formed a gel [23], resulting in reducing friction forces of cementitious materials. The SF influences less on increasing yield stress and plastic viscosity, compared with the sample with only SF because of ball bearing effect and less hydration reactivity of BFS in the system.

3.3.2. OPC-FA-SF system

Fig. 9(b) shows the yield stress and plastic viscosity as a function of replacement of OPC with MA in the OPC-FA-SF system. This system is showing different pattern from the OPC-BFS-SF system.

In this system the SF affects much more significantly on yield stress and plastic viscosity; on all the areas the yield stress and plastic viscosity are steeply increased. Along the diagonal direction from zero point the yield stress and the plastic viscosity are increased more steeply, compared with OPC-BFS-SF system, but their values are lower than that of the sample with 15 wt.% SF.

In this three components system the SF may act as antimaterial-segregation agent, but its effect is not so big as act in the OPC-BFS-SF system.

Table 4 shows summary of rheology properties in the study.

4. Conclusions

This work was carried out to study the rheological properties of cementitious materials containing BFS, FA, SF, and their influences on the rheology. The conclusions of the study are as follows:

(1) For OPC paste, as the dosage of superplasticizer increases the yield stress and the plastic viscosity are much improved in the range up to at 2 wt.% SP. The dosage of superplasticizer was the crucial factor for improving the rheological properties.
(2) For two-components system, the yield stress and the plastic viscosity are decreased in accordance with an increase of BFS in the OPC-BFS system. In the OPC-FA system, the plastic viscosity is slightly increased, compared with the sample without MA. In the samples with FA the yield stress is slightly increased with increasing FA. In the OPC-SF system, the yield stress and the plastic viscosity are steeply increased. as the SF is increased.
(3) For the three-components systems, the rheological properties were improved compared with the OPC-SF system. In the OPC-BFS-SF system, the SF did not influence so significantly for increasing the yield stress and the plastic viscosity. These systems could be controlled their rheological parameters by each MA. In the OPC-FA-SF system, the yield stress and the plastic viscosity were higher than the OPC-BFS-SF system.
(4) The higher components system showed better rheological parameters than the lower components system. Especially the SF controlled the yield stress and the plastic viscosity of cementitious materials, which were important parameters for self-compacting concrete.
(5) In the two component system, BFS-OPC is better than other components. When SF is added, three components is much preferred for high performance concrete because SF acts as filler and controls rheology.

Acknowledgments

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References

[1] A.M. Neville, Porperties of Concrete, Wiley, New York, 1996, pp. 243–255.
[2] S. Mindess, J.F. Young, D. Darwin, Concrete, Prentice Hall, New Jersey, 2003, pp. 93–114.
[3] X. Zhang, J. Han, The effect of ultra-fine admixture on the rheological property of cement paste, Cem. Concr. Res. 30 (5) (2000) 827–830.
[4] M. Nehdi, S. Mindess, P.-C. Aïtcin, Rheology of high-performance concrete: effect of ultrafine particles, Cem. Concr. Res. 28 (5) (1998) 687–697.
[5] M. Cyr, C. Legrand, M. Mouret, Study of the shear thickening effect of superplasticizers on the rheological behaviour of cement pastes

containing or not mineral additives, Cem. Concr. Res. 30 (9) (2000) 1477–1483.

[6] P.-C. Aïtcin, C. Jolicoeur, J.G. MacGregor, Superplasticizers: how they work and why they occasionally don't, Concr. Int. 5 (1994) 45–52.

[7] P.F.G. Banfill, Rheology of Fresh Cement and Concrete, E&FN Spon, London, 1991, pp. 13–26.

[8] P.F.G. Banfill, The rheology of fresh cement and concrete—a review, 11th ICCC 1 (2003) 50–62.

[9] D.A. Williams, A.W. Saak, H.M. Jennings, The influence of mixing on the rheology of fresh cement paste, Cem. Concr. Res. 29 (9) (1999) 1491–1496.

[10] C.F. Ferraris, K.H. Obla, R. Hill, The influence of mineral admixtures on the rheology of cement paste and concrete, Cem. Concr. Res. 31 (2) (2001) 245–255.

[11] C.F. Ferraris, F. de Larrard, Testing and modeling of fresh concrete rheology, NIST, USA, NISTIR 6094 (1998) 1–5.

[12] C.F. Ferraris, Measurement of the rheological properties of high performance concrete, state of the art report, J. Res. NIST 104 (5) (1999) 461–478.

[13] G.H. Tattersall, P.F.G. Banfill, The Rheology of Fresh Concrete, Pitman, 1983, 356 pp.

[14] T. Nawa, H. Eguchi, Y. Hukara, Effect of alkali sulfate on the rheological behavior of cement paste containing a superplasticizer, in: V.M. Malhotra (Ed.), 3rd CANMET/ACI International Conference on Superplasticizers and Other Chemical admixtures in Concrete, SP-119, ACI, Ottawa, 1989, pp. 405–424.

[15] R.J.-M. Pellenq, J.M. Caillol, A. Delville, Electrostatic attraction between two charged surface: a (N,V,T) Monte Carlo simulation, J. Phys. Chem., B 101 (1997) 8584–8594.

[16] S. Hanehara, K. Yamada, Interaction between cement and chemical admixture form the point of cement hydration, admixture adsorption and paste rheology, Cem. Concr. Res. 29 (8) (1999) 1159–1165.

[17] M. Regourd, A review of the use of proton magnetic resonance to study superplasticizers, Mater. Res. Soc. Proc. 85 (1987) 245–254.

[18] C. Jolicoeur, P.-C. Nkinarnubanzi, M.-A. Simard, M. Piotte, Progress in understanding the functional properties of superplasticizers in fresh concrete, ACI SP 148 (1994) 63–88 (Detroit).

[19] E. Sakai, et al., Mechanisms of superplastification, Mater. Sci. Concr. 4 (1995) 91–111.

[20] P. Termkhajornkit, T. Nawa, H. Ohnuma, Effects of properties of fly ash on fluidity of paste, Cem. Sci. Concr. Technol. 55 (2001) 163–169.

[21] MA. Akgerman, M. Zardkoohi, Adsorption of phenolic compounds on fly ash, J. Chem. Eng. Data 41 (1996) 185–187.

[22] M. Nehdi, S. Mindess, P.-C. Aïtcin, Rheology of high-performance concrete: effect of ultrafine particles, Cem. Concr. Res. 28 (5) (1998) 687–697.

[23] L. Kucharska, M. Moczko, Influence of silica fume on the rheological properties of the matrices of high-performance concretes, Adv. Cem. Res. 6 (24) (1994) 139–145.