

Compatibility of Copolymer-Based Grinding Aids and Sulfonated Acetone-Formaldehyde Superplasticizer

Tailong Zhang, Jianming Gao, Xue Xie, Wei Sun

Abstract—Compatibility between sulfonated acetone-formaldehyde superplasticizer (SAF) and copolymer-based grinding aids (GA) were studied by fluidity, Zeta potential, setting time of cement pasts, initial slump and slump flow of concrete and compressive strength of concrete. ESEM, MIP, and XRD were used to investigate the changing of microstructure of interior concrete. The results indicated that GA could noticeably enhance the dispersion ability of SAF. It was found that better fluidity and slump-keeping ability of cement paste were obtained in the case of GA. In addition, GA together with SAF had a certain retardation effect on hydration of cement paste. With increasing of the GA dosage, the dispersion ability and retardation effect of admixture increased. The compressive strength of the sample made with SAF and GA after 28 days was higher than that of the control sample made only with SAF. The initial slump and slump flow of concrete increased by 10.0% and 22.9%, respectively, while 0.09 wt.% GA was used. XRD examination indicated that new products were not found in the case of GA. In addition, more dense arrangement of hydrates and lower porosity of the specimen were observed by ESEM and MIP, which contributed to higher compressive strength.

Keywords—Copolymer-Based grinding aids, superplasticizer, compatibility, microstructure, cement, concrete.

I. INTRODUCTION

NOWADAYS, superplasticizers have been one of the important ingredients in concrete technology, in improving workability, mechanical strength, and other properties of concrete [1]-[3]. Sulfonated naphthalene formaldehyde condensate (SNF), sulfonated acetone-formaldehyde co-condensate (SAF), and polycarboxylated polymers are typical superplasticizers (PCs) used commercially in China. It is reported that the dispersion mechanism of superplasticizers are: (1) electrostatic repulsive forces play a major role in SNF and SAF; (2) steric hindrance is critical for PCs [2], [4], [5].

Because of the high level energy demand of cement production, typically 95 to 110 KWh per ton of cement [6], grinding aids are extensively used in cement production to improve grinding efficiency, hence reduce energy consumption unit. In addition, grinding aids, as kinds of surface active agents, are adsorbed on cement particles to change particle surface, affect the performance of cement paste, and even the mechanical strength of produced cement [7]-[9]. Although many studies have been conducted to reveal the advantages and

application of superplasticizers and grinding aids, few studies have been done on the influences of grinding aids in cement on the performance of superplasticizers.

At present, the application of aqueous copolymer as grinding aids in cement production has attracted great attention. Compared with traditional grinding aids, copolymer-based grinding aids have more stable quality and higher cost performance, which will be summarized in our other studies. In this paper, we aimed to introduce one kind of copolymer-based grinding aids (GA) which was prepared by radical polymerization, and successfully used in cement production. Besides, SAF was selected for comparative trial. In order to avoid the influences of cement differences on results, GA was added together with SAF. Comparing with control sample only containing SAF, studies on fluidity of cement paste, Zeta potential, setting time, initial slump and slump flow of concrete and compressive strength of concrete in the case of SAF and GAF were discussed.

II. MATERIALS AND METHODS

A. Materials

The materials used include PII 42.5 ordinary Portland Cement, GA, SAF, and graded II fly ash. Cement is from the Tai Ni Cement in Jiang Su province, P.R. China. FA is from the Jianbi electric power and complies with Chinese standard GB/T 1596-2005. SAF and GA are supplied by Sika (China) Ltd. Table I lists the compositions and physical properties of cement and fly ash. Fig. 1 shows the chemical structure of GA. The properties of SAF and GA are given in Table II.

B. Fluidity and Setting Time of Cement Pastes

The test of fluidity of cement paste was conducted according to the Chinese national standard GB/T 8077-2000. 300g of cement and 105g of tap water plus SAF and GA were used in the fluidity test. The sample of cement paste was sealed in a container during test intervals of 5, 30, 60, and 90min after being mixed with water. The setting time of the cement paste was measured according to the Chinese National Standard GB/T1346-2011.

C. Zeta Potential Test

The Zeta potential of cement particles was tested during the intervals of 3, 30, 60, 90, and 120min. The cement was added into an SAF solution with or without GA. The concentrations of SAF and GA were 0.65g/L and 0.065g/L, respectively. The mass ratio of cement to solution was 1:50. The slurries were dispersed for about 30s by an ultrasonic cell disruptor. Some clearer paste solution was taken from the top side, and fed into

Tailong Zhang is with the School of Materials Science, Southeast University, Jiangning District, Nanjing 211189 China. Jiangsu Key Laboratory of Construction Materials, Southeast University, Nanjing 211189, China (phone: 86 025 52090639; fax: 86 025 52090639; e-mail: zhangtailong1976@163.com).

the electrophoretic cell to determine the zeta potential by a Zeta potential analyzer (Colloidal Dynamics, USA).

D. Preparation and Testing of Concrete

The preparation and testing of concrete were conducted according to Chinese national standard GB/T8076-2008. The maximum size of the coarse aggregate was 31.5mm, and the fineness modulus of the fine aggregate was 2.80. The mix proportion of concrete is given in Table III. The specimens of concrete were casted and taken out of molds the next day and cured in the condition of $20\pm 3^{\circ}\text{C}$ and 95% of relative humidity until the age of 28 days.

TABLE I
COMPOSITIONS AND PHYSICAL PROPERTIES OF CEMENT AND FLY ASH

Materials	Chemical Compositions (%)						Specific Surface (m^2/kg)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	
Cement	21.23	5.78	4.12	61.64	2.24	2.06	355
Fly Ash	44.38	34.50	5.21	3.40	2.85	0.53	345

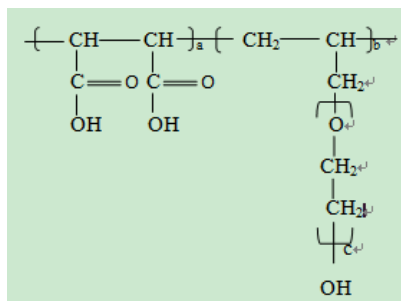


Fig. 1 Chemical structure of GA; a= moles of maleic anhydride; b= moles of APEG; c= moles of ethylene oxide

TABLE II
PHYSICAL CHARACTERISTICS OF SAF AND GA

	SAF	GA
	Solid Content(%)	27.5
Rational Viscosity(mPa.s)	180	110
PH Value	13.9	4.5
M_w	21100	6159
Na Content(ppm)	41000	3750

TABLE III
EXPERIMENT PROGRAM OF CONCRETE

Mix No.	C kg/m^3	FA kg/m^3	Agg., Fine kg/m^3	Agg., Coarse kg/m^3	SAF/(C+F) %	GA/(C+F) %
C1	320	40	814	1036	1.30	0
C2	320	40	814	1036	1.30	0.03
C3	320	40	814	1036	1.30	0.06
C4	320	40	814	1036	1.30	0.09

Water Cement Ratio = 0.5; C = Cement, F = Fly Ash

III. RESULTS AND DISCUSSION

A. Influences on Fluidity and Slump-Keeping Ability of Cement Paste

The workability properties of cement pastes containing admixtures depend on many parameters. Researchers have provided preliminary findings: charge density, side chain length, and composition of functional groups have influences

on rheological properties of cement pastes [10]-[13]. Fig. 2 and Table IV show the variation of fluidity of cement pastes versus time for SAF and SAF+GA. It is very clear that GA increases the fluidity of cement paste markedly compared to control sample only containing SAF, by about 18.8% at the initial time. With time elapsed, both fluidity of cement pastes incorporating SAF and SAF+GA decreased quickly, but the descent rate with SAF+GA was slightly slow. It is believed that there is cooperative effect between SAF and GA to get better dispersion and slump-keeping ability. This may be attributed to the fact that SAF was adsorbed on the surface of cement grains and characteristics of cement-solution interface changed, due to GA's long side chains and different functional groups which cause different dispersion mechanism of admixture.

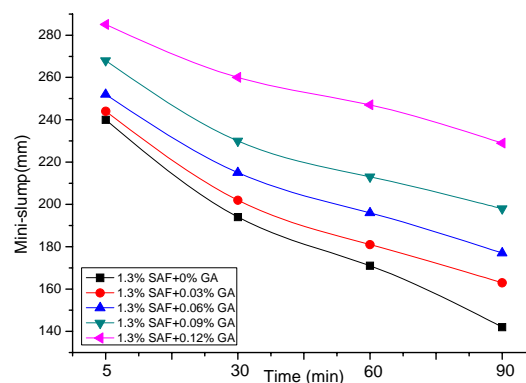


Fig. 2 Variation of minislump flow of cement pastes vs. time

TABLE IV
EXPERIMENTAL RESULTS OF FLUIDITY AND SETTING TIME OF CEMENT PASTE

Admixtures	Fluidity/mm				Setting Times /min	
	5min	30min	60min	90min	Initial	Final
1.3%SAF+0%GA	240	194	171	142	228	278
1.3%SAF+0.03%GA	244	202	181	163	232	281
1.3%SAF+0.06%GA	252	215	196	177	239	290
1.3%SAF+0.09%GA	268	230	213	198	244	294
1.3%SAF+0.12%GA	285	250	244	213	255	306

B. Influences on Zeta Potential of Cement Paste

Fig. 3 shows the variation of Zeta potential of cement particles with time in the case of SAF and SAF+GA. It is clear that GA distinctly reduced the Zeta potential of cement particles. Zeta potential of cement particle adsorbed by SAF was +3.2mv at 3min, and fluctuated in a definitive range of +3.2mv to +3.4mv with time elapsed. When GA and SAF coexisted, the Zeta potential of cement particle reduced to +2.6mv at 3min, and showed downtrend before 90min. During the next 30mins, the Zeta potential increased and reached a maximum at 120min.

The probable reason, as illustrated in Fig. 4, was that GA was absorbed on colloidal solid surface, increased the thickness of slipping layers, and reduced the counter ions concentration because of the hindrance of PEO graft chains.

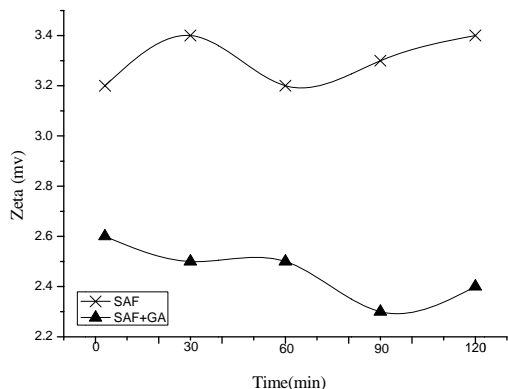


Fig. 3 Variation of Zeta potential of cement particles vs. time

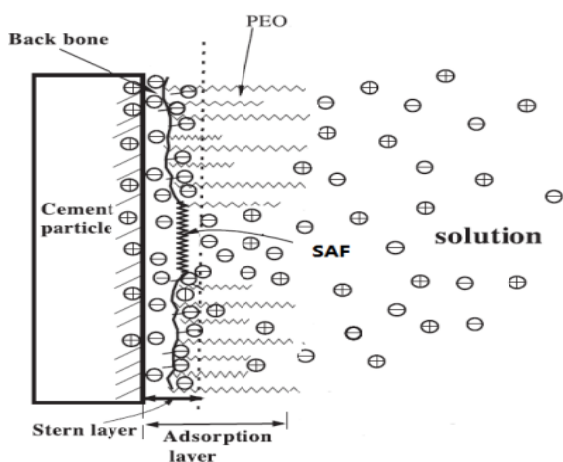


Fig. 4 Schematic figure for electric double layer of cement particle with SAF and GA

C. Setting Time

Table IV shows the variations of setting times of cement paste made with SAF and SAF + GA. It can be seen from Table IV and Fig. 5 that GA has significant influences on setting time (initial and final) of cement paste. Compared with control sample only containing SAF, initial and final setting times of cement paste increased by 11.8% and 10.1%, respectively, when GA was added at the dosage of 0.12wt. %. In addition, more GA dosage caused longer setting time (initial and final). Although the mechanism of retardation effect is not clearly understood, it is possible that (1) GA is adsorbed on the cement grains. The water film is formed to hinder water and ions diffusion across the cement-solution interface due to PEO chains; (2) the carboxylic groups in GA chelate with Ca^{2+} , which inhibit the nucleation and growth of hydrates [14]-[16].

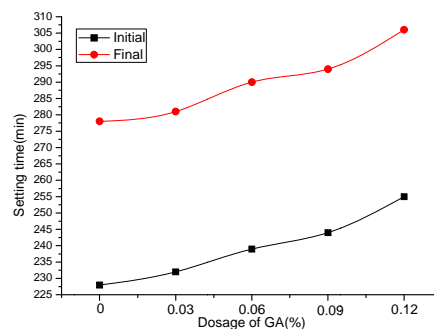


Fig. 5 Influence of GA on setting time of cement paste

D. Effects on Concrete Properties

Table III lists the mixture proportions of concrete with different admixtures. Table V shows the properties of concrete with SAF and SAF+ GA. It can be seen from Table V and Fig. 6 that GA had critical influences on the concrete compressive strength development. Compared to the control sample only containing SAF (C1), increasing of GA dosages correspondingly increase the compressive strength of concrete. Fig. 7 shows the XRD patterns of concrete specimens (28d) between C1 and C4. The results showed that there were clear diffraction peaks of ettringite and portlandite, which demonstrated that ettringite and portlandite indeed formed in the concrete. Meanwhile, the diffraction peaks of concrete in the case of GA were basically the same as the control sample made only with SAF. It seems that no new hydration substances formed when GA was used together with SAF in the concrete.

Fig. 8 shows the microstructure differences of concrete specimens (28d) between C1 and C4. It can be seen from these photos that needle-like ettringite and sheets of portlandite grow along the surface of coarse aggregates. Meanwhile, Fig. 8 (a) shows that the flocculent and porous structures of the formed hydrates as well as unhydrated grains, are available in some open space. Fig. 8 (b) shows that a more dense structure is obtained. A more dense arrangement of micro-crystalline CSH as the main hydration products and some rod-like CSH can also be observed in the micrograph. These products almost filled the pores, which can be proven by mercury intrusion porosimetry. At the same time, Fig. 9 shows the experimental results of MIP of the same concrete specimens (C1/C4). It has been discovered that the porosity decreases in the case of GA.

Table V also shows that the initial slump and slump flow of concretes are higher than that of the control sample which only contains SAF. For control sample, the initial slump and initial slump flow of concretes are 20cm and 48cm. While GA coexists with SAF, they increase to 22cm and 59cm, respectively. The results indicate that GA can improve fluidity of concrete obviously, due to better dispersion ability of admixtures.

According to the results presented above, we believe that there must have been a cooperative effect when GA and SAF were used together. GA effectively improves the dispersion of fine aggregates, which accelerates the hydration of cement clinkers and develops more dense arrangement of hydrates as well as lower porosity of specimen. Consequently, the

compressive strength of concrete made with SAF and GA increased.

TABLE V
PROPERTIES OF CONCRETE WITH DIFFERENT GAS

Mix No.	Initial Slump cm	Initial Slump Flow cm	Compressive Strength(MPa)		
			3d	7d	28d
C1	20	48	16.5	30.7	42.6
C2	21	53.5	18.1	32.1	45.8
C3	21.5	55	19.2	34.0	47.2
C4	22	59	20.8	35.4	49.8

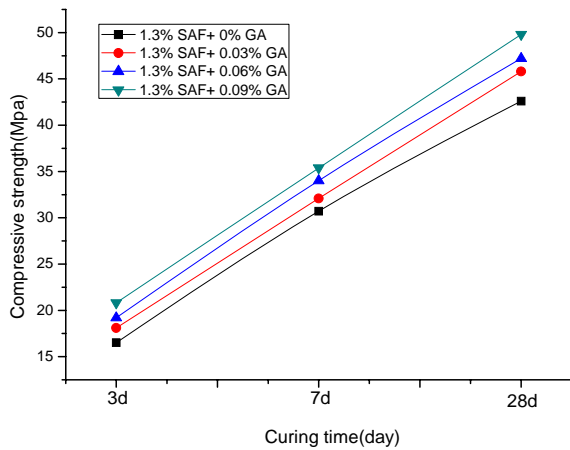


Fig. 6 Compressive strength of concrete made with SAF and SAF+GA

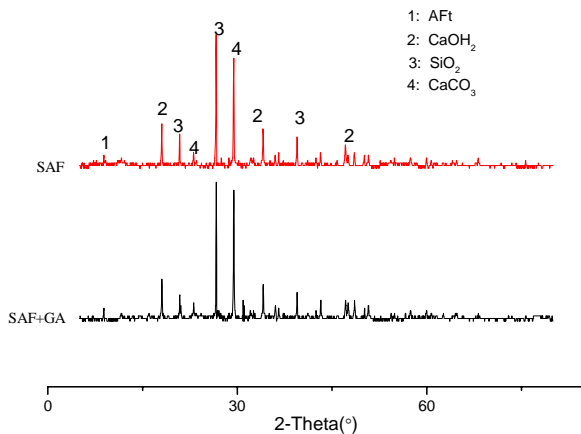
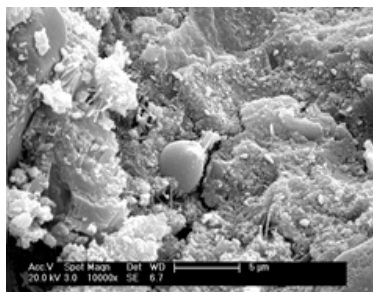
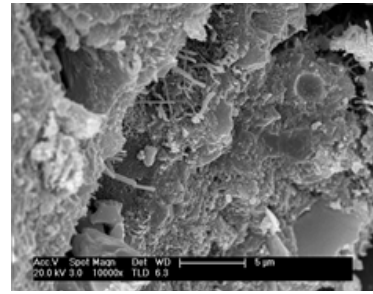


Fig. 7 XRD patterns of concrete made with SAF and SAF+GA



(a)



(b)

Fig. 8 ESEM images of expansion products of C40 concrete made with SAF (a) and SAF+ GA (b)

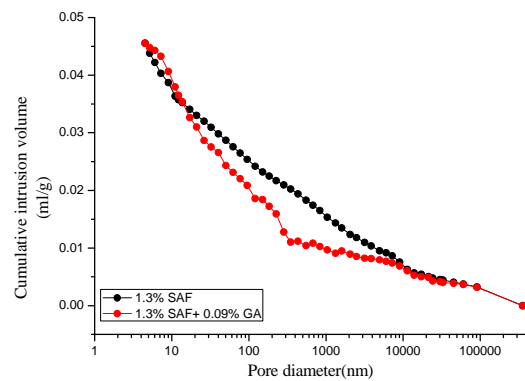


Fig. 9 Pore size cumulative distribution of concrete made with SAF and SAF+GA

IV. CONCLUSIONS

Because of cooperative effect, addition of GA has significant influences on performances of the cement paste and concrete containing SAF. The main conclusions are as follows:

The fluidity and fluid-retaining ability of cement paste increase due to GA with special molecular structure. It can be concluded that GA provides steric hindrance effect, which improves the dispersion ability of admixtures. This can be confirmed by Zeta potential values, which is lower because of the hindrance of PEO graft chains that reduce the counter ions concentration on the colloidal surfaces.

Longer setting time of cement paste was observed. This is attributed to the adsorption of GA on cement grains, which retards the hydration of cement.

The addition of GA increases the compressive strength of concrete containing SAF. Meanwhile, the higher initial slump and initial slump flow of concrete were obtained. When SAF and GA coexist, the microstructures of concrete specimen display a more dense structure and lower porosity, whereas no new hydrates were obtained. The reasonable explanation is that GA and SAF effectively improve the dispersion of fine aggregates, which accelerate the hydration of cement clinkers and reduce the porosity of concrete.

ACKNOWLEDGMENT

This work was supported by National science foundation.

The experimental work was carried out in the R&D center of Sika (China) Ltd. and the assistance of the technical staff is gratefully appreciated. The writers would also like to acknowledge the language help of Professor Yue Yu during the preparation of article.

REFERENCES

- [1] K.C. Hsu, S.D. Chen, N. Su, "Water-soluble sulfonated phenolic resins. III. Effects of degree of sulfonation and molecular weight on concrete workability," *J. Appl. Polym. Sci.* 76, 1762–1766(2000).
- [2] P.C. Aitcin, C. Jolicoeur, J.G. MacGregor, "Superplasticizers: How they work and why they occasionally don't," *Concr. Int.* 16, 45–52(1994).
- [3] R. Gagne, A. Boisvert, M. Pegeon, "Effect of superplasticizer dosage on mechanical properties, permeability, and freeze– thaw durability of high-strength concrete made with and without silica fume," *Mater. J.* 93,111 – 120(1996).
- [4] Hongming Lou, Kaibin Ji, Houkeng Lin, "Effect of molecular weight of sulphonated acetone-formaldehyde condensate on its adsorption and dispersion properties in cementitious system," *Cem. Concr. Res.*42, 1043-1048 (2012).
- [5] H. Uchikawa, S. Hanehara, D. Sawaki, "The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture," *Cem. Concr. Res.* 27, 37– 50(1997).
- [6] J. Harder, "Advanced grinding in the cement industry," *ZKG Int.* 56 (3), 31–42 (2003).
- [7] Cetin Hosten, Berkan Fidan, "An industrial comparative study of cement clinker grinding systems regarding the specific energy consumption and cement properties," *Powder Technol.* 221,183-188(2012).
- [8] M. Katsioti, P.E. Tsakiridis, P. Giannatos, "Characterization of various cement grinding aids and their impact on grindability and cement performance," *Construction and Building Mate.* 23, 1954–1959(2009).
- [9] Ion Teoreanu, Graziela Guslicov, "Mechanisms and effects of additives from the dihydroxy-compoundclass on Portland cement grinding," *Cem. and Concr. Res.* 29, 9–15(1999).
- [10] Winnefeld F, Becker S, Pakusch J, "Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems," *Cem. Concr. Comp.* 29(4),251–62(2007).
- [11] Vickers TM, Farrington SA, Bury JR, Brower LE, "Influence of dispersant structure and mixing speed on concrete slump retention," *Cem. Concr. Res.* 35(10), 1882–90(2005).
- [12] Lia C-Z, Feng N-Q, Li Y-D, Chen R-J, " Effects of polyethylene oxide chains on the performance of polycarboxylate-type water-reducers," *Cem. Concr. Res.* 35(5), 867–73(2005).
- [13] Yamada K, Takahashi T, Hanehara S, Matsuhisa M, "Effects of the chemical structure on the properties of polycarboxylate-type water reducer," *Cem. Concr. Res.* 30(2), 197–207(2000).
- [14] Kazuo Yamadaa, Tomoo Takahashib, Shunsuke Haneharaa, "Effects ofthe chemical structure on the properties of polycarboxylate-type superplasticizer," *Cem. and Concr. Res.* 30 , 197–207(2000).
- [15] Puertas F, Santos H, Palacios M, Martínez-Ramirez S, "Polycarboxylate superplasticizer admixtures: effect on hydration, microstructure and rheological behavior in cement pastes," *Adv. Cem. Res.* 17(2), 77–89(2005).
- [16] M. M. Alonso, M. Palacios, F. Puertas, "Compatibility between polycarboxylate-based admixtures and blended-cement pastes," *Cem. Concr. Compos.* 35,151–162(2013).