Comparison of fluidity of cement paste incorporating mineral admixtures with polycarboxylate superplasticizers

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Abstract. In this study, the effects of five commercially available polycarboxylate superplasticizers (PCEs), which are WP30/RM, SR/RM, ACE 8109, SKY 8705 and MG 8728 on ternary blended cement system have been studied based on the marsh cone test. Results are presented for cement pastes with Ground Granulated Blast Furnace Slag (GGBS) and Pulverised Fuel Ash (PFA) as mineral admixtures. The ratio of GGBS and PFA was fixed at 4:1 according to the optimization. The water to binder ratio was fixed at 0.30. It was observed that the behaviour of polycarboxylate superplasticizers varies from one brand to another even though their chemical family are same. By using marsh cone test, the properties of those commercial polycarboxylate superplasticizers have been compared and the optimum dosages of certain polycarboxylate superplasticizers were defined as well. Based on the result, WP30/RM possesses the best fluidity performance compared to others with the solid content of 53%.

1. Introduction

Nowadays, superplasticizer is commonly used in concrete production, especially for the high performance concrete. Addition of superplasticizer can help to improve its flow properties and to reduce the water to cement ratio in order to achieve high strength and durability[1]. However, various types of commercial polycarboxylate superplasticizers (PCEs) available on the market currently, it is essential to study each PCEs because its' compositions are not the same from different manufacturers. Its chemical structure composed of two essential parts, which are back bone that containing carboxylic groups that used to adsorb on the surface of cement particles through electrostatic interaction and side chains that containing polyethylene oxide (PEO) to induce steric hindrance effect and disperse the cement particles[2]. Different chemical structure of PCEs has different effect on concrete performance and causing differences in dosage requirement[3][4]. Another concern is the incompatibility issues between the concrete binders and different PCEs, even though their chemical family are similar. The compatibility of cement-superplasticizer can be affected by the physical and chemical characteristics of the binder used.[5]

Supplementary cementitious materials such as Ground Granulated Blast Furnace Slag (GGBS) and Pulverised Fuel Ash (PFA) are widely used as mineral admixture in the high performance concrete production. These mineral admixtures can increase the fluidity of the concrete and may reduce the dosage of PCEs that require to obtain the desire workability[6]. Nonetheless, the study about the interaction between PCEs and mineral admixture particles is very limited. It is necessary to understand the mechanism of interaction for selecting the appropriate type of PCEs at an optimum dosage for certain binders. Mineral admixture is not inert toward PCEs. M.M. Alonso[7] proved that PCEs not only adsorbed by cement particles, but by the mineral admixtures as well. But the adsorbed amounts of PCEs by cement particles were more than by mineral admixtures[3]. A. Habbaba[8] and J. Plank[9] studied on the interaction between PCEs and GGBS, they found that their dispersion mechanism is based on adsorption onto the positively charged layer of Ca^{2+} ions present on the surface of slag. However the amount of adsorbed PCEs in the fly ash blended cement paste much less extent on the nature of the fly ash, but highly depends on the replacement level of the portland cement with fly ash[10].

The purpose of this study is to compare the effect of several commercial PCEs on flow properties of cement paste that containing GGBS and PFA as mineral admixtures in order to select an appropriate compatible PCEs. Furthermore, the optimum dosages for these PCEs on ternary blended cement system were investigated as well.

2. Experimental details

2.1 Materials

In this study, Ordinary Portland cement (OPC), Ground Granulated Blast Furnace Slag (GGBS), Pulverised Fuel Ash (PFA) and Polycarboxylate superplasticizer (PCEs) were used. The OPC was obtained from Cement Industry of Malaysia Berhad. The physical and chemical properties of OPC, GGBS and PFA are given in Table 1. Five commercially available polycarboxylate superplasticizers were used in this study, which are WP30/RM, SR/RM, ACE 8109, SKY 8705 and MG 8728. The solid content of each PCEs are shown in Table 2.

Table 1. Chemical composition of OPC, GGBS and PFA used.

	% by total mass		
Chemical compound	OPC	GGBS	PFA
MgO	1.5	6.08	5.94
Al_2O_3	3.6	13.27	17.61
SiO_2	22.4	32.84	43.22
P_2O_5	0.06	0.01	0.23
SO_3	3.1	-	-
CI	n/d	-	-
K_2O	0.34	0.36	1.31
CaO	65.6	40.80	11.28
TiO_2	0.17	0.47	0.88
MnO	0.03	0.14	0.14
Fe_2O_3	2.9	0.28	13.73
ZnO	trace	-	-
SrO	0.04	-	-
PbO	0.01	-	-
CuO	n/d	-	-
Rb_2O	trace	-	-
C	n/d	-	1.80
Na_2O	n/d	0.20	0.43
C_3S	59.58	-	-
C_2S	19.6	-	-
C_3A	4.64	-	-
C_4AF	8.82	-	-
Loss on ignition (%)	2.53	-	1.80

Table 2. Solid content of each PCEs.

PCEs	Solid Content (%)
WP30/RM	53
SR/RM	52
SKY 8705	40
MG 8728	30
ACE 8109	14

2.2 Test Method

2.2.1 Mix Design Optimization

The mix design optimization started with the hybridization of OPC, GGBS and PFA without PCEs. Fully OPC mixtures as control mix, and fixed another four mixtures as 50% OPC and vary the percentage of GGBS and PFA. The optimum ratio of OPC, GGBS and PFA was determined by their mechanical strength results on 2nd, 7th and 28th days of testing ages. The mix proportions of each concrete mixture are listed in Table 3.

Table 3. Mix proportions of the concrete mixtures.

	OPC (kg/m³)	PFA (kg/m³)	GGBS (kg/m³)	SAND (kg/m³)	WATER (kg/m³)	w/b ratio
OPC 100	513	0	0	1539	256.5	0.5
OPC 50 PFA 10 GGBS 40	252.5	51.3	205.2	1527	252.5	0.5
OPC 50 PFA 20 GGBS 30	252.5	102.6	153.9	1527	252.5	0.5
OPC 50 PFA 30 GGBS 20	252.5	153.9	102.6	1527	252.5	0.5
OPC 50 PFA 40 GGBS 10	252.5	201.2	51.3	1527	252.5	0.5

2.2.2 Marsh Cone Test

The Marsh cone is a device to study the cement paste rheological behaviour. In the marsh cone test, the viscosity of a cement paste can be indicated from the time it takes a known volume of paste to flow from the base of a cone through a short tube. It depends upon cement superplasticizer compatibility. The flow time measured enables to determine the fluidity of the cement paste. The longer the flow time, the more viscous of cement paste and the shorter the flow time, the more fluid of cement paste. The optimum superplasticizer dosage also can be defined in terms of the saturation point as the maximum through marsh cone test. Beyond the saturation point, there is no significant decrease in flow time. It can be considered as incompatibility if the cement superplasticizer combinations do not exhibit a well-defined saturation point [11].

In this study, a total of 600ml paste was prepared for each mixture with different commercial PCEs. The time taken for 600ml of the paste to flow was measured and denoted as the flow time. PCEs dosage was started from 0.2% by total binder weight until 1.8% with 0.2% increment. The water to binder ratio was fixed at 0.30. The paste was prepared started by dry mix which was mixing the OPC, GGBS and PFA at low speed for 10 minutes. The ratio of GGBS to PFA was fixed at 4:1 according to the optimization result. Next, 70% of water was added and the paste was mixed for 2 minutes at high speed. In the third stage, PCE was added into the paste and mixed for 2 more minutes at high speed. In the last stage, the rest of 30% water was added and the paste was mixed for another 2 minutes at high speed.

3. Result and Discussion

3.1 Optimization of mix design ratio

The compressive strength result and flexural strength result are shown in Figure 1 and Figure 2 respectively. It was found that with 50% cement replacement by 10% PFA and 40% GGBS content yield the highest strength among the various combinations tested. It can achieved compressive strength of 8.62MPa at 2 days, 21.26MPa at 7 days and 40.67MPa at 28 days of testing ages. Flexural strength achieved was 1.96MPa at 2 days, 4.68MPa at 7 days and 6.59MPa at 28 days of testing ages.

The reaction between mineral admixtures and $Ca(OH)_2$ which formed by hydration of OPC results into C-S-H gel is responsible for gaining strength. Increase in GGBS content decreases the strength of concretes in short term as compared to control mix due to the slow pozzolanic reaction, but long term strength exhibits same of control mix because GGBS undergoes hydration reactions in the presence of water with $Ca(OH)_2$, resulting in C-S-H paste[12]. Using high content of fly ash as partial replacement of OPC reduced the strength of concrete due to the delayed hydration of pozzolanic materials[13], slow reactivity and lesser surface area of fly ash[14].

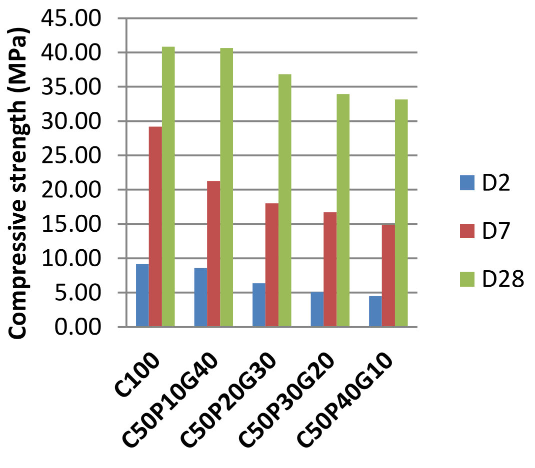

Figure 1. Compressive strength**.**

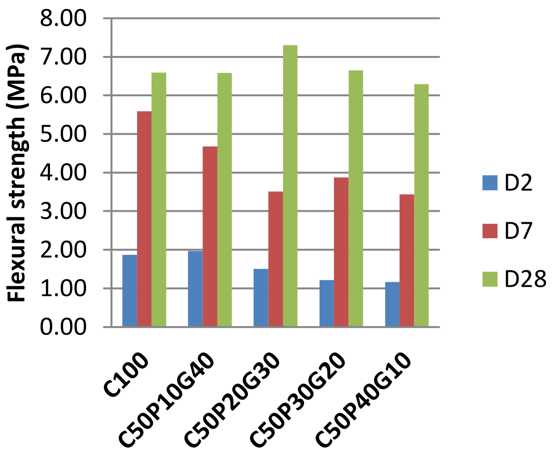

Figure 2. Flexural strength**.**

3.2 Assessment of Flow Properties

In this study, the result was presented for cement pastes that containing GGBS and PFA as the ratio that obtained from the mix design optimization, which is 50% OPC 40% GGBS and 10% PFA, with five commercially available polycarboxylate superplasticizers (PCEs), which are WP30/RM, SR/RM, ACE 8109, SKY 8705 and MG 8728. The fluidity of cement paste with those five commercial PCEs was compared by keeping water to binder ratio as 0.30 and varying the dosage of PCEs in % by weigh of binder. The result is shown in Table 4. The 600ml cement pastes that containing WP30/RM as chemical admixture took shortest time to flow out from marsh cone at different PCEs dosage, which indicated WP30/RM possesses the best fluidity performance compared to others.

IOP Conf. Series: Materials Science and Engineering **431** (2018) 052004 doi:10.1088/1757-899X/431/5/052004

Table 4. Flow time of cement paste.

PCEs dosage (%)	Flow Time (min)				
	WP30/RM	SR/RM	SKY 8705	MG 8728	ACE8109
0.20	13.00	Not flowable	Not flowable	Not flowable	Not flowable
0.40	9.45	15.28	29.10	Not flowable	Not flowable
0.60	9.43	13.30	21.27	17.39	26.52
0.80	8.41	12.52	15.10	12.47	12.20
1.00	7.25	10.28	12.57	12.53	10.22
1.20	7.31	9.44	11.40	11.41	10.15
1.40	7.33	9.52	11.49	11.20	10.05
1.60	7.00	9.34	11.52	11.18	10.36
1.80	6.28	9.17	11.11	11.18	10.35

3.3 Optimization of each PCEs

The dosage of PCEs after which no significant reduction in flow time is observed and it is called as saturation dosage or optimal dosage. For selected water to binder ratio as 0.30, the optimum dosages are 1.0% for WP30/RM (Figure 3.(a)) and ACE 8019 (Figure 3.(e)). Meanwhile, the optimum dosages are 1.2% for SR/RM (Figure 3.(b)), SKY 8705 (Figure 3.(c)) and MG 8728 (Figure 3.(d)).

PCEs works only after it adsorbed to the surface of particles, which corresponds to the surface coverage[15]. Increasing PCEs dosage can further increase the amount of adsorbed PCEs, thus improving the particle dispersion that contributes to the paste flowability. However, the dispersing ability of PCEs will not increase anymore after a complete surface coverage is obtained which means the used PCEs achieves the saturation dosage[16]. In addition, the un-adsorbed PCEs molecules may remaining in the interstitial solution in a paste that might agglomerate and form a network and provide an adverse effect on the paste flowability[17].

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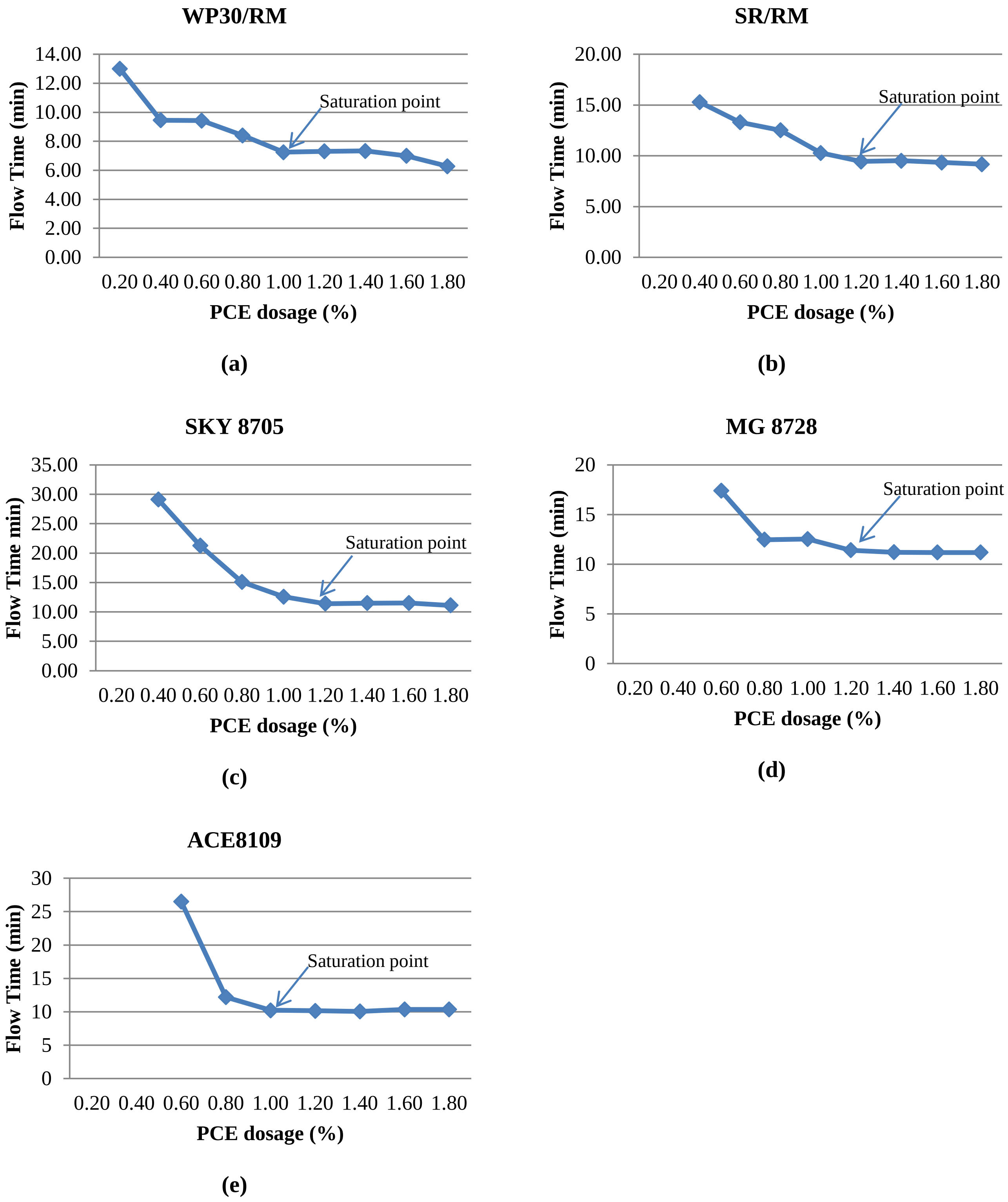

Figure 3. Optimization of PCEs dosage**.**

4. Conclusion

For selected water to binder ratio as 0.30, WP30/RM with solid content 53% is the most appropriate chemical admixture used among those five commercial PCEs for the ternary blended cement system which contains OPC 50%, GGBS 40% and PFA 10%. It possesses the best fluidity properties and optimum dosage is 1.0%.

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