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Communication

Investigation on pozzolanic effect of mineral additives in cement and concrete by specific strength index

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Abstract

In this paper a concept of contribution of unit clinker or unit cement to the strength of cement or concrete with active mineral additives was introduced. Some definitions have been given to specific strength of unit clinker in cement, specific strength of unit cement in concrete, specific strength of pozzolanic effect in cement or concrete, specific strength ratio, and contribution rate of pozzolanic effect to strength. Using these indexes and a diagram of pozzolanic effect, the magnitude, influencing factors, and regularity of pozzolanic effect during hardening of cement and concrete with active mineral additives can be analysed quantitatively.

Keywords: Pozzolanic effect; Specific strength; Contribution rate to strength

In modern cement and concrete technology, addition of active mineral additives (fly ash, silica fume, slag, natural pozzolan, etc.) is of great scientific significance [1]. It is well known that the clinker minerals C_3S and C_2S that take about 75% of the portland cement will form high basic calcium hydrosilicates (c/s $>$ 1.5) with a lime/silica ratio of 1.6–1.9 and a large amount of calcium hydroxide [2]. In comparison to low basic calcium hydrosilicates (c/s $<$ 1.5), they have much lower strength [3]. In particular the free lime has a rather low strength and poor stability, which leads to lower strength and less durability of cement paste and concrete. With the addition of a proper amount of active mineral additives, the active SiO_2 will gradually have a secondary reaction with $Ca(OH)_2$ and high basic calcium hydrosilicate in cement paste, as the so-called pozzolanic reaction, forming low basic calcium hydrosilicates.

Thus, as a result there will be an increase not only in the quality of hydrates but in the quantity as well, and the strength of cement paste and other properties can be improved greatly. However, for a long time, there have been unsolved problems as how to determine the activity of active mineral additives and how to describe the behavior of pozzolanic reaction of active mineral additives in cement and concrete. Therefore, the author has suggested a method of specific strength (SS) with which a study on pozzolanic effect of cement and concrete with active mineral additives was carried out.

1. Pozzolanic effects of active mineral additives in cement

For this study fly ash was chosen as active mineral additive. In the tests, the fly ash from Chongqing Power Plant (Chongqing, China) and the clinker from Chongqing Cement Plant (Chongqing, China) were used. Their chemical compositions are shown in Table 1. The clinker was ground to a fineness of 3300 cm^2/g with a dosage of 4% gypsum as retarder.

To overcome the disadvantages of low strength at early age of the fly ash cement, in particular for those with a large dosage of fly ash, 2% Na_2SO_4 and 3% $CaSO_4 \cdot 2H_2O$ has been added into fly ash cement.

Due to favorable water-reducing effect of fly ash, the water/cement ratio in this test on fly ash cement is taken as 0.41, although according to Chinese Standard GB175-85, the water/cement ratio for test on strength of fly ash cement mortar should be 0.46. For fly ash cement mortar with a large dosage of fly ash at water/cement ratio of 0.46, the mixture will be more flowable and the time for mould filling by compaction is much less than 20 s. As a result, during compaction by vibration, segregation would occur. Therefore, the water/cement ratio in this test was reduced to keep the time for mould filling in the range of 20–40 s. Test results are given in Table 2.

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Table 1
Chemical composition of the fly ash, clinker, silica fume, and OPC (%)

Chemical composition	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	TiO_2	SO_3	Loss of ignition
Fly ash	48.25	12.88	25.84	3.56	0.98	2.94	1.43	7.8
Clinker	20.88	3.89	5.58	61.82	2.25	0.80	1.24	1.38
Silica fume	91.27	0.45	0.17	0.45	0.92	—	—	2.88
OPC	20.50	3.10	5.90	62.0	1.80	0.60	2.17	0.80

At first we introduce a concept of contribution of unit clinker to strength of fly ash cement at different ages (that is, the contribution of 1 wt% clinker to the strength of mortar sample with this cement) and we define it as specific strength of clinker in the cement (or specific strength of cement in short). It equals the real flexural or compressive strength divided by percentage of clinker for a given composition. The results are given in Table 2, Fig. 1, and Fig. 2.

It can be seen from Figs. 1 and 2 that at 3 days of age there is a rather poor specific compressive and flexural strength of the clinker in the fly ash cement; it is without definite regularity of variation. This is due to the fact that at early ages of hydration, the degree of hydration reaction was rather low for the fly ash cement with a weak pozzolanic effect, and the strength was low. Such a weak effect is easily masked by the strength deviation due to accidental factors. At 28 days of age and in particular at 360 days of age, the specific strength of clinker in fly ash cement is much higher than that in pure clinker cement. With an increase of dosage of fly ash, the specific strength increases greatly, showing definite regularity.

It is clear as mentioned above that the specific strength of

Table 2
Mix proportion, strength, SS, and SSPE of fly ash cement

	No.					
	1	2	3	4	5	6
Mix proportion (%)						
Clinker	96	65	55	45	35	25
Fly ash	0	30	40	50	60	70
Admixture	4	5	5	5	5	5
w/c (%)	44	41	41	41	41	41
Charging time (s)	56	36	34	26	25	25
Flexural strength (Mpa)						
3 days	7.98	6.68	6.52	5.42	4.09	2.78
7 days	8.47	7.56	7.37	6.14	5.66	4.20
28 days	10.57	10.89	10.05	10.01	8.81	6.79
Compressive strength (MPa)						
3 days	37.4	27.4	24.7	20.6	14.0	9.7
7 days	45.7	30.9	28.9	26.5	20.9	15.6
28 days	61.3	46.0	48.5	43.4	36.2	28.3
Mark of cement*	525R	425R	425R	425R	325	275
Strength at 360 days (MPa) and the mark						
Flexural	11.60	12.36**	12.36**	12.36**	11.86	10.17
Compressive	71.1	75.7	75.0	66.9	57.2	44.2
Mark	625	725	725	625	525	425
Increase in mark class	1	3	3	2	2	2
SS of clinker in the cement (MPa)						
Flexural						
3 days	0.083	0.103	0.119	0.120	0.117	0.111
28 days	0.110	0.168	0.183	0.222	0.252	0.272
360 days	0.121	0.190	0.225	0.275	0.339	0.407
Compressive						
3 days	0.39	0.42	0.45	0.46	0.40	0.39
28 days	0.64	0.71	0.88	0.96	1.03	1.13
360 days	0.74	1.16	1.36	1.49	1.63	1.77
SS of pozzolanic effect of FA cement (MPa) (SSPE)						
Flexural						
3 days	0	0.020	0.036	0.037	0.034	0.028
28 days	0	0.058	0.073	0.112	0.142	0.162
360 days	0	0.069	0.104	0.154	0.218	0.286
Compressive						
3 days	0	0.03	0.06	0.07	0.01	0
28 days	0	0.07	0.24	0.32	0.39	0.49
360 days	0	0.42	0.62	0.75	0.89	1.03

* According to Chinese Standard, the series of cement marks are: 125, 175, 225, 275, 325, 425, 425R, 525, 525R, 625, 625R, 725, 725R.

** Specimen did not fail and the maximum indications has been taken.

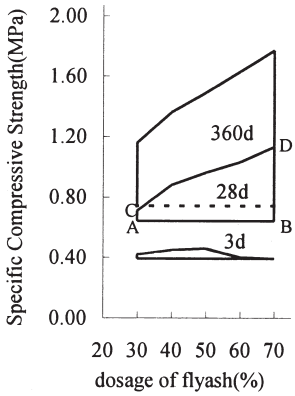

Fig. 1. Specific compressive strength of mixes.

clinker in fly ash cement is higher than that of clinker in pure clinker cement. With an increase of age and addition of fly ash, the deviation is increased, which is caused by the pozzolanic effect of the fly ash. The strength of cement with addition of active mineral additives can be considered as composed of two parts: the first part of the strength is contributed by the hydrates that are formed by the hydration of clinker in the cement, and the second part is contributed by the additional hydrates obtained from the secondary reaction between active silica and aluminum oxides in active mineral additives with free calcium hydroxide obtained from hydration of clinker. In addition, there is also a contribution to the increase of strength from an enhancement of cementitious performance by formation of low basic hydrates that resulted from a reaction between high basic hydrates with active silica oxide in additives. We call the second part the strength of pozzolanic effect for the cement. It is only this part of the strength that makes the specific strength of fly ash cement at later age become much higher than that of pure clinker cement. The difference can be called SS of pozzolanic effect (SSPE).

In Fig. 1, the zone between the line AB (SS of pure clinker cement) and the curve CD (SS of fly ash cement) indicates the diagram of specific compressive strength of pozzolanic effect (DPE) for the cement with 30~70% fly ash at 28 days. Other similar DPE also can be seen in Figs. 1 and 2. Except for DPE, which give the regularity of the pozzolanic effect based on the data of specific strength and the specific strength ratio (SSR) for the cement (or concrete) with active mineral additives at different ages and different dosages, the contribution rate of pozzolanic effect (CRPE) to the strength of the cement (or concrete) can be calculated (the formula for calculation can be found in Table 3, sections IV and V).

It can be seen from Table 4 that with an increase of dosage and age, the contribution rates of pozzolanic effect on the strengths are increased. For the dosage of 70% of fly ash, at 360 days, the contribution rate of pozzolanic effect to the flexural strengths is as high as 70.3% and the contribution to the compressive strength is 58.2%. Consequently, the pozzolanic effect is of important significance.

2. Pozzolanic effect of active mineral additives in concrete

The materials chosen are silica fume as active mineral additives (Tangshan Steel Co, Tangshan, China) and OPC of Chongqing Cement Plant mark 525R as cementitious material. Their chemical compositions are shown in Table 1. The coarse aggregate applied is crushed limestone with a maximum size of 20 mm. The fine aggregate is medium sand with fineness modulus of 2.40. The cementitious material for silica fume concrete is composed of 90% cement and 10% silica fume. In addition, under the same conditions a control concrete has been made with a pure cement. The same dosage (1.7%) of superplasticizer was added. The test results are given in Table 5 and Fig. 3*(A)*.

Here, we introduce the contribution of unit cement to the strength of concrete at different ages (i.e., the contribution of 1% cement to the strength of concrete). It is defined as SS of cement in the concrete (or SS of concrete in short). Based on Table 5, the specific compressive strength value for two mixes are given in Table 3 and Fig. 3*(B)*.

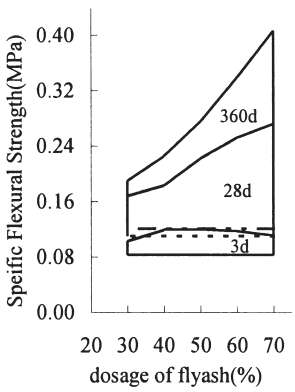

Fig. 2. Specific flexural strength of mixes.

Table 3
SS, SSPE, SSR, and CRPE of silica fume concrete

No.	Items	Formula for calculation	Age (days) 3	28	56	90
I	SS of control concrete (MPa)	$\frac{R}{100}$	0.641	0.763	0.814	0.938
II	SS of silica fume concrete (MPa)	$\frac{R}{90}$	0.763	1.169	1.244	1.400
III	SS of pozzolanic effect (MPa)	II – 1	0.122	0.406	0.430	0.464
IV	SSR	$\frac{II}{I}$	1.190	1.532	1.528	1.496
V	CRPE (%)	$\frac{II - I}{II} \times 100$	16.0	34.7	34.6	33.1
VI	CR of hydration to the strength (%)	$\frac{I}{II} \times 100$	84.0	65.3	65.4	66.9

Table 4
SSR and CRPE for fly ash cement

Index	Type of strength	Age (days)	Dosage of fly ash (%)					
			0	30	40	50	60	70
SSR	Flexural	28	1.000	1.527	1.664	2.018	2.291	2.473
		360	1.000	1.570	1.860	2.273	2.802	3.364
	Compressive	28	1.000	1.109	1.375	1.500	1.609	1.776
		360	1.000	1.568	1.838	2.014	2.203	2.392
CPRE (%)	Flexural	28	0	34.5	39.9	50.5	56.3	59.6
		360	0	36.3	46.2	56.0	64.3	70.3
	Compressive	28	0	19.9	27.3	33.3	37.4	43.4
		360	0	36.0	45.6	50.3	54.6	58.2

Table 5
Strength development of silica fume concrete

Mix no.	Composition of cementitious materials		w/c	Flowability		Apparent density at 28 days (kg/m^3)	Compressive strength R (MPa)			
	Cement (%)	Silica fume (%)		Slump (mm)	Spread (mm)		3 days	28 days	56 days	90 days
1	100	0	0.25	110	—	2553	64.1	76.3	81.4	93.8
2	90	10	0.25	235	580	2550	68.7	105.2	112.0	126.0

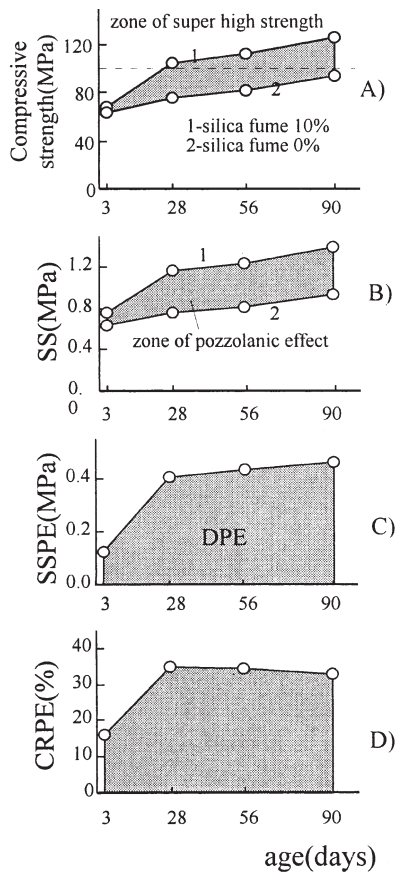

Fig. 3. Specific compressive strength value of age.

In comparison with control concrete without silica fume, there will be a higher contribution of unit cement to the concrete strength. The increment of contribution is that from pozzolanic reaction between silica fume and cement. It is defined as specific strength of pozzolanic effect for silica fume concrete. It can be seen from Fig. 3*(C)* that, with increase of age, the specific strength of pozzolanic effect increases, until 28 days. The rate of increase is higher than that after 28 days. Here, the zone between the curve and abscissa is defined as DPE for the concrete (with age). Fig. 3*(D)* gives the contribution rate of pozzolanic effect to the strength of silica fume concrete. At 28 days, the contribution rate attained its maximum (34.7%) and was followed by a gradual decrease.

It should be pointed out that with addition of active mineral additives into cement and concrete, except for pozzolanic reaction, there were other effects existing, such as water-reducing effect of fly ash, microfilling effect of silica fume, and so on. However, in comparison with the pozzolanic reaction, they are secondary. It is impossible and unnecessary to remove such effects for the specific strength study. Consequently, the pozzolanic effect given in this paper is an overall effect including the pozzolanic and these secondary ones.

3. Conclusions

The magnitude of pozzolanic effect, influencing factors, and its regularity of various active mineral additives in cement and concrete can be exactly identified and analysed by the SS, contribution of pozzolanic effect to strength, and DPE suggested by the author. It has the following advan-

tages: (a) Without application of other chemical, physical, or microscopic testing methods, an exact conclusion can be drawn by preparing a group of specimens for control cement or concrete under the same conditions; (b) The results are given as strength index, which is similar to that for cement and concrete strength estimation; and (c) There could be a quantitative comparison and analysis for the pozzolanic effect based on the test results.

With the addition of fly ash into cement, the pozzolanic effect will vary with age and dosage of fly ash. The pozzolanic effect is increased with age, and in the range studied the pozzolanic effect is increased with increase of the dosage. As for the fly ash, the pozzolanic effect is mainly expressed at later age of hardening. At 1 year of age, the compressive strength of fly ash cement is increased by 2–3 class.

Because silica fume is a highly active mineral additive with its addition into concrete, there will be pozzolanic effect at 3 days of age and the rate for pozzolanic reaction until 28 days is rather high, and then this is followed a decrease. In this study, the contribution of pozzolanic effect to strength reaches its maximum at 28 days.

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