THE EFFECT OF A NEWLY DEVELOPED HARDENING ACCELERATOR ON THE PROPERTIES OF PORTLAND BLAST-FURNACE SLAG CEMENT

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By combining some organic compounds with the ground clinker calcined at 1200-1350°C with a composition varied in $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2\text{-BaSO}_4$ system, a new type of low alkali cement hardening-accelerator has been developed. Experiments show that this accelerator can accelerate the set and significantly enhance both early and late strength of portland blast-furnace slag cement (PBSC), especially the early strength of the cement. The promotion of cement hydration, the early formation of more ettringite (AFt), the good bind among hydrates and the formation of a compact texture in the hydrate are the main reasons for the strength increment.

Key Words: *hardening-accelerator, cement, set, strength, hydration, AFt, microstructure, porosity*

1. INTRODUCTION

Nowdays admixture is called as the fifth constituent of concrete¹⁾. Although there are numerous kinds of hardening-accelerating agent, chloride or alkali is always an essential constituent as their chemical composition is considered. By using them although the early strength of concrete can be improved generally its late strength is decreased and durability is worsened. In addition, the alkali contained in the agent whether K_2O or Na_2O may cause alkali-aggregate reaction in hardened concrete. As now the importance of late strength particularly the long term durability of concret has been highly recognized and much attention is being paid to them so it seems to be urgent and necessary to develop and use alkali-free hardening-accelerators instead of the traditional alkali-contained ones.

X.J. Feng et al.²⁾ invented a method for producing barium contained sulphoaluminate cement, which is

mainly composed of $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{BaSO}_4$, $\beta\text{-C}_2\text{S}$ and C_4AF and has the peculiarities of rapid hardening and high late strength. Q.J. Yu et al.³⁾ investigated the effect of $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ ($\text{C}_{11}\text{A}_7 \cdot \text{CaF}_2$) and $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$ ($\text{C}_4\text{A}_3\bar{\text{S}}$) on the properties of portland fly-ash cement and found that the compressive strength of the cement at 28d could be raised by about 10MPa when a proper amount of $\text{C}_{11}\text{A}_7 \cdot \text{CaF}_2$ or $\text{C}_4\text{A}_3\bar{\text{S}}$ was added to the cement. Based on above researches we calcined a series of clinker which mainly contained CaO , Al_2O_3 , SiO_2 , CaF_2 and BaSO_4 but had different amount of $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{BaSO}_4$ ($3\text{CA} \cdot \text{BaSO}_4$ for short in the followings), $\beta\text{-C}_2\text{S}$, C_{12}A_7 and $\text{C}_{11}\text{A}_7 \cdot \text{CaF}_2$ in mineral composition. It was found that the clinkers could really improve the strength of PBSC but the strengthening effect were varied with their mineral components. Furthermore by optimum composition design and compositing the clinker, which had an appropriate composition, with some

Table 1 Chemical compositions of raw materials (%)

Sample	I.L.	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	BaO	SO ₃	CaF ₂	Σ
Limestone	42.60	0.30	0.48	55.43	0.03	0.68				99.52
Bauxite	13.40	4.61	72.86	0.78	1.48	0.88				94.04
Barite	0.21			0.43			59.17	29.77	6.62	96.72

Table 2 Mineral contents of clinker A, B and C (%)

Clin-ker	3CA · BaSO ₄	C ₁₂ A ₇	β - C ₂ S	C ₄ AF	C ₁₁ A ₇ · CaF ₂
A	79.5	0	15.7	2.8	0
B*	55.9	0	13.3	2.3	25.3
C**	37.9	24.6	14.7	2.6	18.0

* CaF₂--1.40%, ** CaF₂--0.98%

kinds of organic compound, a new type of low alkali cement hardening accelerator was developed. Experiments showed with an optimum addition of it to PBSC its early and late strength were increased in a large scale.

In this paper the preparation of this accelerator and its influence on the properties of PBSC are briefly introduced.

2. EXPERIMENTS AND RESULTS

(1) Raw materials

Limestone, bauxite and barite used in the experiment are industrial materials, their chemical compositions are listed in **Table 1**. The used PBSC was commercial one produced by Yiye Cement Plant, containing 65% blast-furnace slag, 30% portland cement clinker and 5% gypsum.

(2) Clinker sintering and its influence on the properties of PBSC

By trials and optimum composition design three kinds of clinker (A, B and C) which consisted of CaO 20-50%, Al₂O₃ 10-40%, SiO₂ 5-20%, BaO 10-50%, SO₃ 4-25% and slight fluoride were obtained by clinkering the mix of limestone, bauxite and barite at 1200-1350°C, in which fCaO was not found by chemical analysis. XRD patterns of the clinkers showed that the expected minerals had been formed and their contents (**Table 2**), determined by QXRD, were approximately equal to the designed. In order to investigate the effect of the clinkers on the properties of PBSC, ground A, B and C, 5% by weight, was respectively added to it. The strength specimens of 40×40×160 mm were made at a water cement ratio of 0.46 and sand cement ratio of 2.5, then cured at 20±1°C in the air of R.H.>90%

for 1d. After demoulding they were cured in water at 20±1°C to different ages. The setting time and strength of the PBSC with or without the addition of different clinkers are shown in **Table 3**.

(3) Hardening-accelerator preparation and its effect on the properties of PBSC

Table 3 shows the clinker can increase the early strength of PBSC but its effect on 28d strength improvement is not very evident. By further experiments it was found that the mixture of clinker C and an organic compound D₁ (lignin sulfonic calcium) or D₂ (β-naphthalene sulfonated formaldehyde condensates) or both of them, called F series hardening accelerator (FHA), could significantly improve both early and late strength of PBSC (**Table 4**). In which the mixture containing clinker C, D₁ and D₂ had the best promotion effect on the strength of PBSC. The experimental conditions were as same as before.

(4) Non-evaporable water in the PBSC pastes with or without clinker C or FHA addition

The content of non-evaporable water in the PBSC pastes at a water cement ratio of 0.30, with or without clinker C and FHA addition, was determined by ignition loss method^{(4), (5)}. The results are shown in **Table 5**.

(5) SEM analysis of the pastes

Fig. 1 shows the SEM images of the PBSC pastes hydrated for 3d, 7d and 28d. Although needle-like AFt had been formed in the paste hydrated for 3d, a porous structure with apparent gaps and large holes could be observed in the paste for 28d (**Fig. 1-c**).

Fig. 2-a indicates more AFt crystals grow and gather in the hole of F₄ paste for 3d, through their interlacement hydration products and unhydrated cement particles are bound together. **Fig. 2-b** also shows that plate-like hydration products play a role of bonding and bridging in the paste. From the comparison of **Fig. 1-c** with **Fig. 2-c** it can be found that the structure of F₄ paste is more compact than that of PBSC paste.

(6) Variation of the pore structure of PBSC paste after the addition of FHA

The pore size distribution, specific pore volume

Table 3 Influence of clinker A, B and C on the properties of PBSC

Sample	Setting time (h : m)		Flexural strength (MPa)			Compr. strength (MPa)		
	Initial	Final	3d	7d	28d	3d	7d	28d
PBSC	1 : 54	4 : 02	3.1/100	4.0/100	5.9/100	13.4/100	21.1/100	32.3/100
F ₁ (PBSC+5.0%A)	1 : 10	1 : 57	3.2/103	4.4/110	5.9/98	16.4/122	23.2/110	32.4/100
F ₂ (PBSC+5.0%B)	1 : 30	3 : 50	3.3/106	4.4/110	6.2/105	16.0/119	22.2/105	33.8/105
F ₃ (PBSC+5.0%C)	1 : 09	3 : 35	3.5/113	4.7/118	6.0/102	16.2/121	22.0/104	35.2/109

Table 4 Effect of F series hardening accelerator on the properties of PBSC

Sample	Setting time(h : m)		Flexural strength (MPa)			Compr. strength (MPa)		
	Initial	Final	3d	7d	28d	3d	7d	28d
PBSC	1 : 54	4 : 02	3.1/100	4.0/100	5.9/100	13.4/100	21.1/100	32.3/100
F ₄ (PBSC+4.7%C+0.3%D ₁)	1 : 00	2 : 43	3.4/110	4.4/110	5.9/100	16.0/119	26.0/123	38.0/118
F ₅ (PBSC+4.7%C+0.2%D ₂)	0 : 48	1 : 15	4.3/139	5.0/125	6.6/112	22.4/167	30.4/144	42.2/131
F ₆ (PBSC+4.7%C+0.3%D ₁ +0.2%D ₂)	0 : 57	1 : 45	3.6/116	4.8/120	6.5/110	23.4/175	31.6/150	51.4/159

Table 6 Porosimetry data of the PBSC pastes with or without the addition of FHA

Sample	Age	Pore size distribution (%)					Specific volume (cm ³ /g)	Most probable pore radius (Å)
		<300 Å	300-10 ³ Å	10 ³ -5×10 ³ Å	5×10 ³ -10×10 ³ Å	>10×10 ³ Å		
PBSC	3d	26.82	25.03	43.39	2.90	1.86	0.19	1981.1
F ₄	3d	31.84	47.15	19.12	0.72	1.16	0.12	967.9
PBSC	7d	48.51	38.40	8.89	1.79	2.40	0.14	967.9
F ₄	7d	68.97	25.40	2.35	0.61	2.59	0.08	250.9
PBSC	28d	92.39	4.04	2.45	0.40	0.48	0.11	216.0
F ₄	28d	95.93	13.61	1.34	0.55	0.76	0.06	215.9

Table 5 Non-evaporable water in cement pastes (%)

Sample	3d	7d	28d
PBSC	10.66	13.03	13.96
F ₃	11.37	14.91	17.42
F ₄	11.50	15.60	19.19
F ₆	11.85	17.30	18.72

and most probable pore radius of PBSC and F₄ pastes hydrated for 3d, 7d and 28d were analyzed by mercury penetration method. Fig. 3 shows the relation between cumulative pore volume and pore radius of the pastes, Table 6 gives the main porosity parameters of the specimens.

3. ANALYSIS AND DISCUSSION

(1) Influence of FHA on the properties of PBSC

From Table 4 it can be known when the mixture of C, D₁ and D₂ (C+D₁+D₂) was added to PBSC with an amount of 5% by weight, the compressive strength of PBSC at 3d, 7d and 28d was raised by 75%, 50% and 59% respectively, simultaneously its flexural strength was increased by more than 10%. Meantime, we also noticed that the setting time of cement was shortened after the addition of FHA, but it is still in accord with the National Standard of China for portland blast-furnace slag cement. The decrease of setting time of the cement is attributed to the addition of clinker C. Table 2 shows there are much 3CA · BaSO₄, C₁₁A₇ · CaF₂ and C₁₂A₇ in

(a) 3d

(a) 3d

(b) 7d

(b) 7d

(c) 28d

(c) 28d

Fig. 1 SEM images of hydrated PBSC

Fig. 2 SEM images of hydrated F_4

clinker C, each of the above compounds has an accelerating effect on the setting and hardening of cement. Yu et al.³⁾ observed the setting of portland fly-ash cement could be considerably accelerated by adding either $C_4A_3\bar{S}$ or $C_{11}A_7 \cdot CaF_2$ (less than 5% by weight) to it because: 1) the hydration of cement was promoted, and 2) compared with control samples more hydrates were formed in the paste

added with $C_4A_3\bar{S}$ or $C_{11}A_7 \cdot CaF_2$.

(2) Effect of FHA on the hydration rate of PBSC

Table 5 shows with the addition of clinker C to PBSC (sample F_3) or FHA to PBSC (sample F_4 and F_6) the non-evaporable water in pastes is increased, which indicates the hydration degree of PBSC is enhanced by the added clinker C or FHA.

Fig. 3 Relation between cumulative pore volume and pore radius ($\ln r$) of hydrated PBSC and F_4

Furthermore the accelerating effect of the mixture consisted of C and D_1 ($C+D_1$) or together with D_2 ($C+D_1+D_2$) on the hydration of PBSC is more evident compared with that of clinker C. This was confirmed by XRD analysis, at the same hydration age the diffraction intensity of unhydrated clinker minerals in PBSC paste is higher than that in F_3 , F_4 and F_6 pastes, but the intensity of the peak ($d=9.82 \text{ \AA}$) belonging to AFt and the peak ($d=4.91 \text{ \AA}$) for portlandite are varied in the sequence of $PBSC < F_3 < F_4 < F_6$.

(3) Mechanism of strength increment

Cement strength has a close relation with its hydration degree and the porosity and microstructure of hydrates as well as the kind, shape of hydration products. Based on this research the reasons for the strengthening effect of FHA on the strength of PBSC can be mainly attributed to the followings:

1) FHA accelerates the hydration of PBSC. At a definite age the promotion of hydration, which means the amount of hydration product is increased, necessarily leads to the raise of cement strength.

2) More AFt are formed in the paste, particularly the early formation of AFt due to the rapid hydration of $3CA \cdot BaSO_4$ contained in FHA contributes much to the enhancement of early strength. It was found that in the hydrated barium contained sulphoaluminate cement the hydration products, e.g. AFt and plate-like hydrates, were all doped with barium ions and had a characteristics of forming a well-interlaced network in the paste, which made hydrates and unhydrated particles closely bond together^{2), 6)}, this phenomenon also occurs in the paste with FHA addition. On the other hand AFt fills in the holes in the paste and makes paste structure compact, which also improves the strength of PBSC.

3) The addition of FHA to PBSC makes the pore

distribution of the paste be beneficial to strength development. Table 6 shows the specific pore volume, the percentage of the pores with radius larger than 1000 Å and the most probable pore radius in hydrated F_4 are remarkably reduced compared with those of PBSC paste, but in which the relative content of the pores with radius less than 300 Å, i.e. the mesopores, is increased, which means after the addition of FHA to PBSC not only the total porosity and the amount of large pores of the pastes are decreased but also the pores are changed to be mainly distributed in small sizes. Both of them reveal that a compact structure with low porosity has been formed in the hydrates with FHA addition, which also results in the increase of strength. From this result it can be also predicted that the addition of FHA to PBSC is possibly advantageous to the improvement of the resistance of PBSC concrete to penetration.

(4) On the corrosion of steel in the concrete added with FHA

The industrial utilization of fluor spar and gypsum as composite mineralizer in the production of cement clinker began from 1950s, then it has been widely spread in some countries, especially in China, for energy-saving consideration. The CaF_2 weight percentage of fluorine-contained clinker is about 0.5-1.0%, but up to now it has not been observed that the corrosion of the steel in the concrete made of fluorine-contained cement is considerably accelerated. The amount of CaF_2 in clinker B and C is 1.40% and 0.98%, so the corrosion rate of steel may not be increased by adding only about 5% of them to cement.

4. CONCLUSIONS

(1) At 1200-1350°C the clinker used as the main constituent of hardening accelerator can be calcined, which is mainly consisted of $3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{BaSO}_4$, $\beta\text{-C}_2\text{S}$, C_{12}A_7 and $\text{C}_{11}\text{A}_7 \cdot \text{CaF}_2$. After it is

composited with some organic compounds, a new type of low alkali cement hardening-accelerator (FHA) is developed, which can significantly increase the early and late strength of PBSC. For instance by adding 5% of it to PBSC the compressive strength of the cement at 3d and 28d were respectively increased by 75% and 59%.

(2) The strength increment of PBSC with FHA addition is attributed to: 1) the promotion of cement hydration, 2) the early formation of more AFt, 3) the improvement of the bind among hydrates and unhydrated cement particles, and 4) the decrease of the total porosity and pore size of cement paste.

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新開発硬化促進材の高炉セメントへの効果

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$\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2-\text{BaSO}_4$ 組成をさまざまに含む合成物, 1200 ~ 1350°Cで焼成された粉碎クリンカーと有機化合物に混ぜることによって, 新しいタイプの弱アルカリ性セメント硬化促進材が開発された。この促進材が凝結を促進することができ, また重要なことに高炉セメントの初期及び長期強度, 特に初期強度を高めることを実験で示した。セメント水和作用の促進, より多くのAFtの早期形成, 水和物間のすぐれた結合, そして水和物の密実構造の形成が, 強度増加の主な理由である。