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The influence of fast-setting/early-strength agent on high phosphorous slag content cement

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Abstract

In this paper, the influence of fast-setting/early-strength agent on the high-content phosphorous slag cement (PHSC) was studied by the strength tests, setting-time test, pore-structure test and XRD analysis. The components and hydration of fast-setting/early-strength agent had also been studied. Test results showed that the use of fast-setting/early-strength agent could solve the problem of poor early properties of PHSC. In addition, industry by-products had been fully utilized. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Phosphorous; Slag; Pore structure; Fast-setting/early-strength agent

1. Introduction

Phosphorous slag (PHS) has little cementing property when only water is added. Its reactivity could be activated by some activator, such as alkali or sulfate. In the portland phosphorous slag cement (PHSC), PHS was activated mainly by $Ca(OH)_2$ and calcium sulfate. It is valid to low content of PHS (less than 25%). A former study showed [1] that when content of PHS was more than 30%, it was necessary to use admixtures, such as calcine gypsum, alumstone and sodium sulfate. However, when PHS content was more than 50%, the early strength largely decreased, although using the above compound admixtures. It was established during testing that it was impossible to use the same method with low PHS content in studying high PHSC.

Because PHS is an activation material containing a glass state, it can be activated by alkali component. Shi and Li [2] studied the activation of PHS by NaOH, water glass (WG) and Na_2CO_3. Study results showed that these alkali activators all had more obvious effect on PHS, but water glass was the best. For water glass, when the M (the molecular ratio of SiO_2 and Na_2O) was 1.5, compressive strength was highest.

Because water glass is liquid, it is not suitable for cement production. Alkali (NaOH or KOH) also had a good effect on PHS, but it was short of supply and very expensive in China. On the other hand, it was easily wetted by the vapor. Therefore, using other solid admixtures was necessary to produce high-PHS-content cement.

2. Raw materials and test results

2.1. Raw materials

PHS was from Guizhou province, clinker from Qing Long mountain cement plant, gypsum from Xuzhou city in Jiangsu and alumstone from Anhui. Na_2SO_4 was the chemical reagent. Their chemical components are shown in Table 1. Fast-setting/early-strength agent was made by

Table 1
The chemical composition of raw materials (mass%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	TiO_2	P_2O_5
Alumstone	0.68	52.84	17.34	1.69	0.55	17.15	–	–
Clinker	65.4	21.28	5.34	4.63	1.47	0.9	–	–
Gypsum	32.24	–	0.16	–	–	44.97	–	–
PHS	49.02	39.33	3.94	0.42	1.6	–	0.14	1.64

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Table 2
Test contents of high-content PHSC

Number	PHS	Clinker	Anhydrite	Na_2SO_4	Alumstone	F1	F2	Fineness (m^2/kg)
PH0	30	63	4	1	3			375
PH1	40	53	4	1	3			375
PH2	50	43	4	1.5	3			375
PH3	60	33	4	1.5	3			375
PH4	70	21	4	2	4			375
PH5	50	40.5	4	1.5			4	375
PH6	50	40.5	4	1.5		4		375
PH7	60	26	6	2		6		375
PH8	60	30	4	2		4		375
PH9	60	30	4	2			4	375
PH10	70	20	4	2			4	375
PH11	70	20	4	2		4		375
PH12	70	20	4	2[a]		4		375

[a] Using solid sodium silicate.

calcination at high temperature (about 1250°C) in the lab. F1 mainly contained $C_4A_3\bar{S}$ and $C_{11}A_7{\cdot}CaF_2$. F2 mainly contained $C_4A_3\bar{S}$. Table 1 shows the chemical composition of materials.

2.1.1. Strength test

Table 2 shows the fills of PHSC. Strength test results are shown in Figs. 1–4. Fig. 1 gives the strength results of PHSC (PH0–PH4) from using compound admixtures

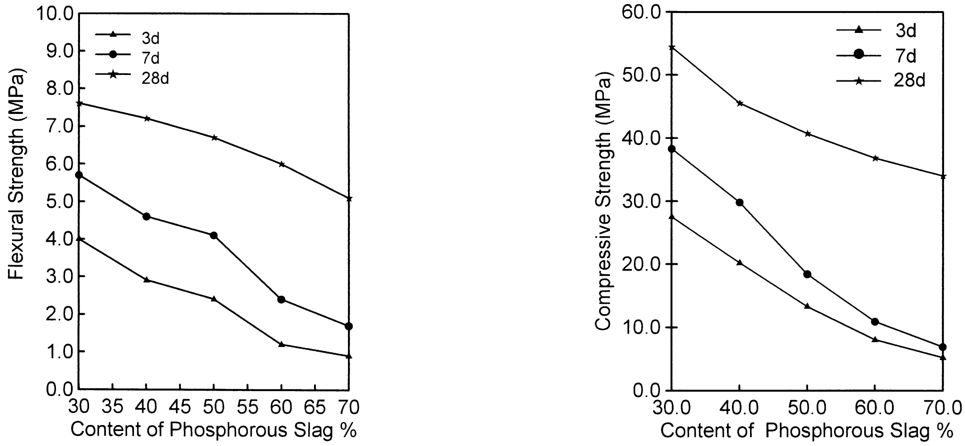

Fig. 1. The influence of PHS content on strength.

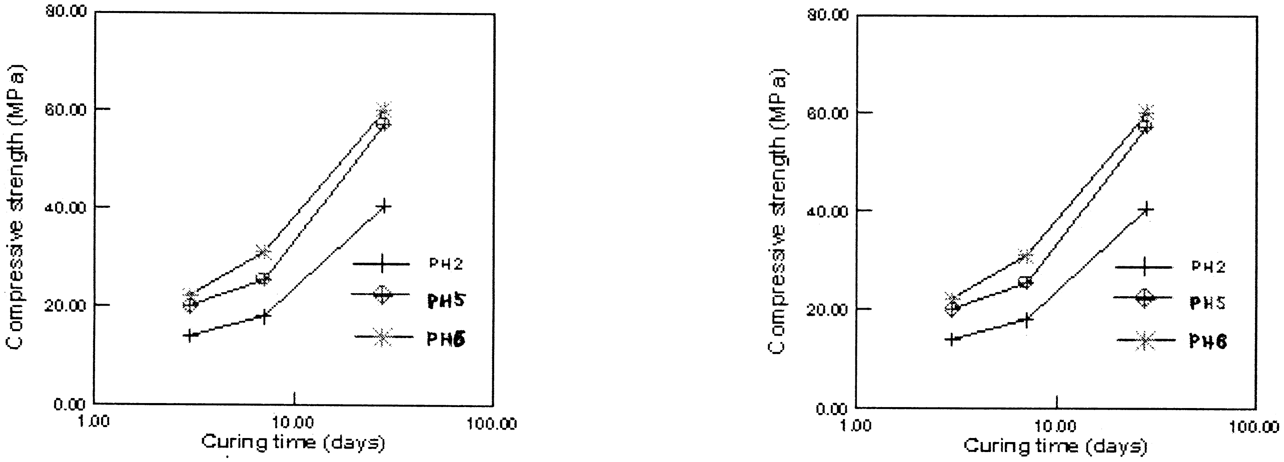

Fig. 2. Curing time vs. compressive and flexural strength (50% PHS).

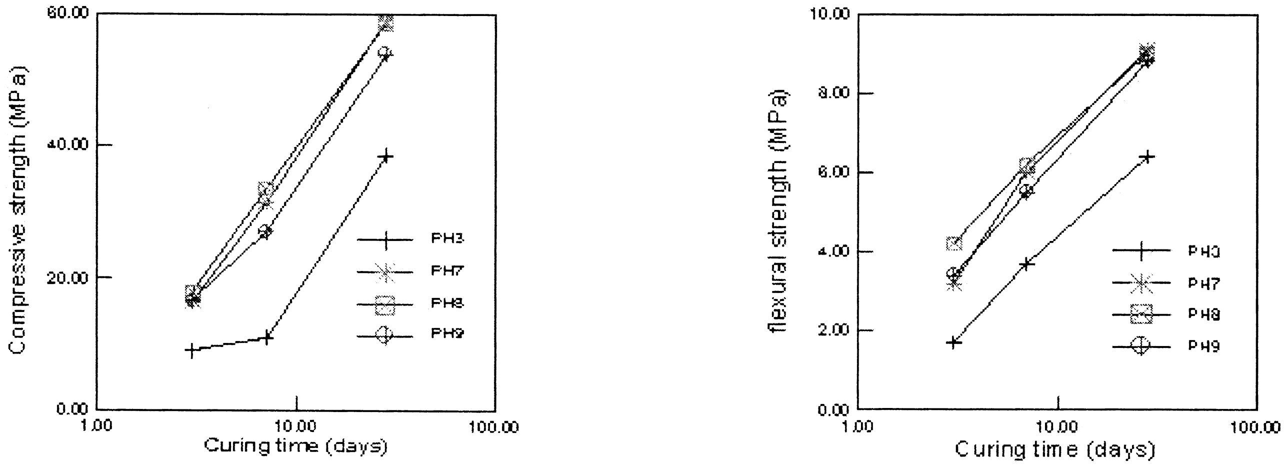

Fig. 3. Curing time vs. compressive and flexural strength (60% PHS).

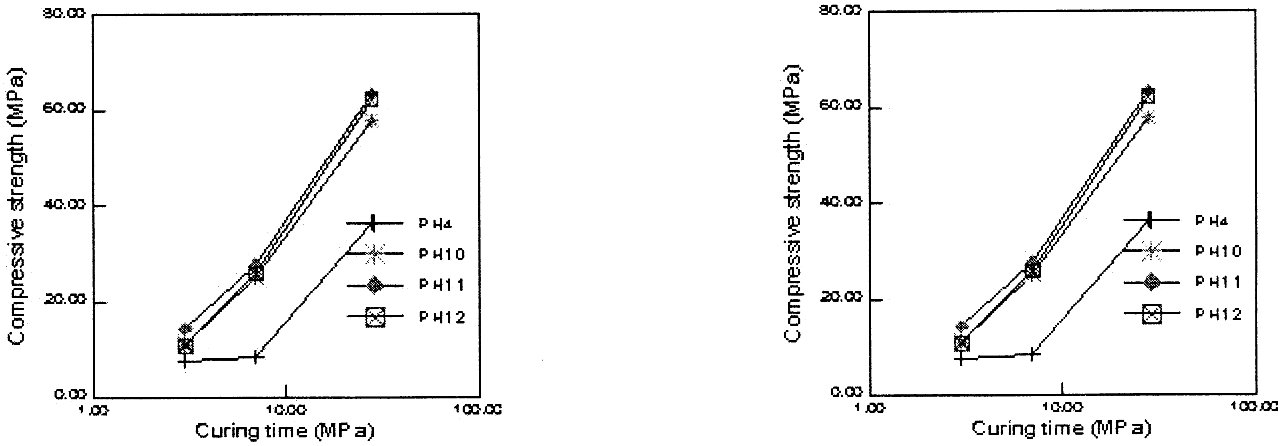

Fig. 4. Curing time vs. compressive and flexural strength (70% PHS).

(anhydrite, Na_2SO_4 and alumstone). Results showed that early strength obviously decreased, when PHS content reached 50%. When PHS content was 70%, the compressive and flexural strengths at 3 days were only 10 and 2.0 MPa. It was suitable for construction needs.

Fig. 2 shows the influence of different admixtures on PHSC, when PHS content was 50%. In these tests, anhydrite and Na_2SO_4 were fixed. Others were respectively alumstone, F1 and F2. It was well known that PH2 only reached no. 425 standard of PHSC.

Fig. 3 shows the influence of different admixtures on PHSC when PHS content was 60%. Sequence of strength was PH8 > PH7>PH9>PH3. Compared with PH3, compressive strength of PH8, respectively, increased about 125%, 133% and 57.9% at 3, 7 and 28-day hydration.

Fig. 4 shows the influence of different admixtures on PHSC, when PHS content was 70%. Results also showed that composite fast early strength had the best effect for PHSC. Using fast-setting/early-strength agent (F1 and F2), early and later strengths obviously increased. The compressive strength at 28 days increased by two grades and reached 60 MPa.

2.2. Setting time

Table 3 shows the setting time of different types of cement. For high-content PHSC, when PHS content was 70%, using common admixture, the setting time of PH4 was too long to be suitable for construction requirements.

Table 3
Results of setting times of cements

Number	Setting time		Fineness (m^2/kg)
	Beginning setting	Final setting	
Portland cement	2:13	3:10	368
PH4	13:02	22:22	350
PH11	0:51	1:10	375

Table 4
Pore structure test results of PHSC

No.		Porosity (%)	Pore volume (mm^3/g)	Medium radium (nm)	<50 μm (%)	50–100 μm (%)	>100 μm (%)	Compressive strength (MPa)
PH6	3 days	24.10	115.2	73.6	50.70	25.50	23.80	30.7
	7 days	17.90	81.5	66.8	53.6	27.7	15.8	38.1
	28 days	17.02	72.5	15.4	57.10	27.10	15.80	63.3
	90 days	14.59	66.20	22.0	80.10	16.90	3.10	69.2
PH11	3 days	31.70	162.2	146.8	42.09	17.66	40.26	16.6
	7 days	22.60	112.30	44.8	44.72	29.20	30.80	28.8
	28 days	19.03	90.2	21.6	54.82	14.64	30.56	56.80
	90 days	16.50	68.0	20.6	66.70	31.20	2.10	66.40
PC	3 days	19.32	93.3	19.80	73.31	9.43	16.83	40.40
	7 days	17.82	82.6	21.6	85.72	4.97	9.32	51.2
	90 days	14.59	67.7	17.4	84.93	7.83	8.02	70.0

When using fast early-strength reagent, PHSC showed fast setting. It is clear that the fast early agent obviously improved early properties of PHSC.

2.3. Pore structure test

Table 4 shows pore structure test results of PHSC and portland cement at different hydration times. Test results showed that portland cement had better pore structure function (including total porosity, pore volume and gel pores of less than 50 μm) at early stages of hydration (3 days, 7 days). This was because there was more C-S-H gel at early stage, which enhances the strength of cement. Compared with portland cement, although pore structure function and strength of PHSC was inferior to that of portland cement at early stage, its later pore structure function had a less significant disparity.

3. Hydration mechanism

3.1. Action of fast-setting/early-strength agent

It is well known that some calcium aluminates, such as CA, C_3A, $C_{12}A_7$, possessed fast hardening and high strength function. CA is the main component of high-alumina cement. Its 3-day strength can reach 90% of maximum strength. Because hydrates CAH_{10} and C_2AH_8 were not stable, they could transform into C_3AH_6 and aluminum hydroxide gel. At the same time, this reaction can produce free water and porosity increase, so the cement strength decreases. In order to overcome poor stability of higher aluminum cement, high early-strength cement containing anhydrous calcium sulfoaluminate was made in China. Sulfoaluminate cement has many advantages, such as fast setting, early strength and good later durability.

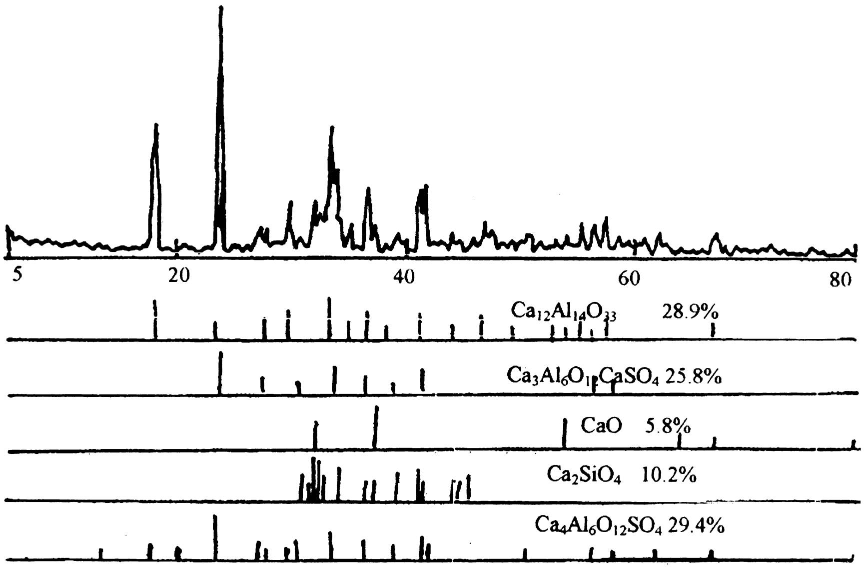

Fig. 5. XRD pattern of synthetic admixture F1.

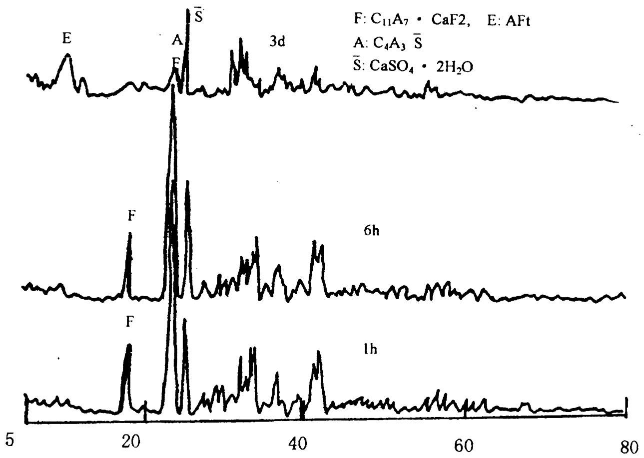

Fig. 6. XRD Pattern of cement paste of F1 + 8% gypsum.

Therefore, it was widely used as high early-strength cement, super early-strength and expansive cement [3]. Another fast early-strength cement containing calcium fluoaluminate was also used [4]. In high-content PHSC, composite fast early-strength agent containing anhydrous calcium sulfoaluminate and calcium fluoaluminate could produce the best effect.

According to theoretical calculation of raw materials, C_2F, $C_{11}A_7{\cdot}CaF_2$, $C_4A_3\overline{S}$ and C_2S were, respectively, 1.39%, 13%, 48.82% and 29.45% . Fig. 5 shows XRD pattern of synthetic early-strength agent F1. Although its mineral components differ from the theoretical calculations, as there were higher proportions of $C_4A_3\overline{S}$ and C_2F, $C_{11}A_7{\cdot}CaF_2$. It was the aim of synthetic early-strength agent.

Synthetic high early addition F1 mainly contained $C_4A_3\overline{S}$, C_2F and $C_{11}A_7{\cdot}CaF_2$. Their hydration reactions were as follows Eqs. (1)–(6):

$$C_4A_3\overline{S} + 2C\overline{S}H_2 + 34H \rightarrow C_3A\cdot 3C\overline{S}\cdot H_{32} + 2AH_3 \tag{1}$$

$$C_4A_3\overline{S} + 18H \rightarrow 2AH_3 + C_3A\cdot 3C\overline{S}\cdot H_{12} \tag{2}$$

$$3CH + AH_3 + 3C\overline{S}H_2 + 20H \rightarrow C_3A\cdot 3C\overline{S} \tag{3}$$

$$\begin{aligned} &C_{11}A_7\cdot CaF_2 + 6CH + 6C\overline{S}H_2 + 54H \\ &\quad\rightarrow 6[C_3A\cdot 3C\overline{S}\cdot H_{12}] + 2Al(OH)_2\overline{F} \end{aligned} \tag{4}$$

$$\begin{aligned} &3[C_3A\cdot 3C\overline{S}\cdot H_{12}] + 2C\overline{S}H_2 + 16H \\ &\quad\rightarrow C_3A\cdot 3C\overline{S}\cdot H_{32} \end{aligned} \tag{5}$$

$$2Al(OH)_2\overline{F} + CH \rightarrow AH_3 + CaF_2 \tag{6}$$

The above reaction showed that hydration of high early-strength agent was affected on the gypsum and limestone. If the lime was poor, AH_3 could form. Calcium monosulphoaluminate hydrate could produce while the gypsum was poor. There are many reports about the influence of gypsum and lime on hydration of fast early-strength agent [5–7].

Figs. 6 and 7 are respectively XRD patterns of hydration products of F1 of 8% and 15% gypsum content. Fig. 6 shows that $C_4A_3\overline{S}$ and C_2F, $C_{11}A_7{\cdot}CaF_2$ feature peak, still exist at 1 and 6 h of hydration. Hydrates formed C_4AH_{19} and $Ca(OH)_2$, while gypsum was also present. After 3 days

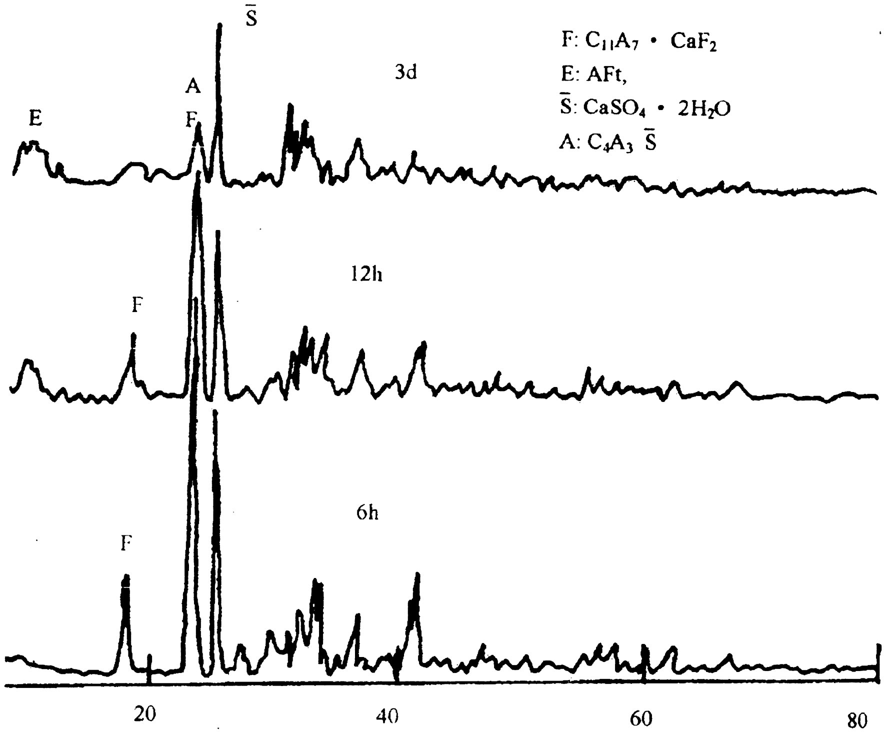

Fig. 7. XRD pattern of cement paste of F1 + 15% gypsum.

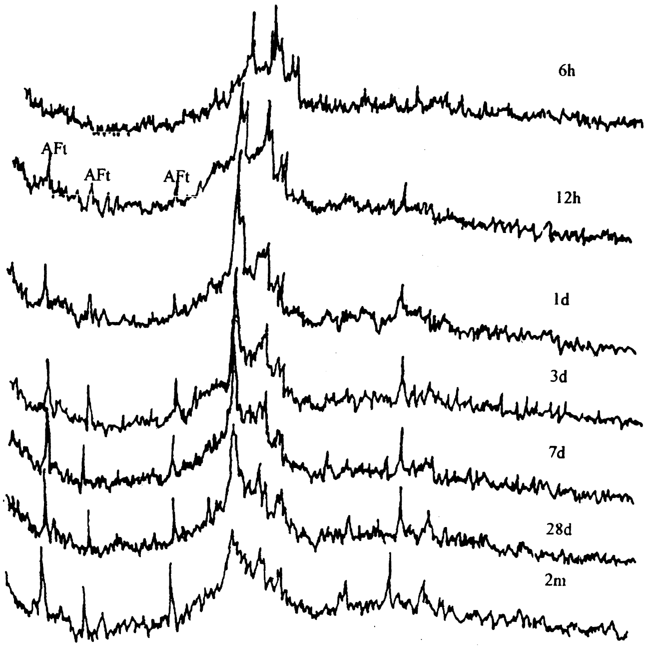

Fig. 8. XRD pattern of cement paste for PH11.

of hydration, most of $C_{11}A_7 \cdot CaF_2$ and $C_4A_3\bar{S}$ were hydrated. There was monosulfate calcium sulphoaluminate hydrate present. When increasing the gypsum content (see Fig. 7), there were ettringite and calcium monosulphoaluminate hydrate at 12 h of hydration. At the same time, hydration rate of $C_{11}A_7 \cdot CaF_2$ and $C_4A_3\bar{S}$ increased.

Fig. 8 gives the XRD patterns of PHSC (PH11). After 6 h of hydration, $C_{11}A_7 \cdot CaF_2$ feature peak did not exist. After 12 h of hydration, ettringite peaks ($d=9.23$, 5.61, 4.98, 3.84) appeared. $C_4A_3 \cdot \bar{S}$ has fully hydrated. After 7 days of hydration, ettringite content showed almost no change. However, C-S-H continued to increase because of the hydration of PHS, which made the hydrate structure more compact. Therefore, the property of PHSC was improved.

4. Conclusion

1. Fast-setting/early-strength agent is a very important factor for producing PHSC; 425- or 525-grade PHSC could be produced by using complex admixtures. The hydrates are mainly AFt and C-S-H gel, without calcium hydroxide (which is usually present in portland cement) and other hydrates.
2. The reason that these admixtures significantly enhance the early properties of PHSC is the fast hydration of $C_{11}A_7 \cdot CaF_2$. $C_4A_3\bar{S}$ increased the early hydrates. On the other hand, PHS is activated by alkali . More hydrates were produced at early stage. It is valid to improve the function of PHSC.
3. Compared with portland cement, the hardened paste of PHSC is characterized by lower porosity and less larger pores at later stage of hydration.

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