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Communication

The influence of admixtures on the properties of phosphorous slag cement

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Abstract

In China, a lot of phosphorous slag has not been used. The main reason is that phosphorous slag (PHS) lengthens the setting time of cement. At the same time, the early strength obviously decreases the setting time. Consequently, it can affect the engineering construction progress. Therefore, addition of admixtures can resolve these questions and improve the properties of PHS cement. The paper studied the influence of calcined gypsum, calcined alumstone, sodium sulphate on the strength and pore structure of PHS cement. Results show that PHS cement of 425 or 515 grade can be produced by adjusting technological parameters and using complex admixtures. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Phosphorous slag; Calcined gypsum; Calcined alumstone; Sodium sulphate; Pore structure

1. Introduction

The shortages of Portland cement (PC) have been discussed according to the policy for 'sustainable development' and the four principles of the cement industry, which include: saving natural resources and energy, reducing environmental pollution, and improving the durability of cement and concrete. Therefore, an important way has been put forward by means of partially replacing clinker by industrial waste slag, especially unused slag (such as phosphorous slag, PHS in short) to produce blended cement. PHS is an industry by-product that is similar to blast furnace slag. Although there are national standards regarding Portland PHS cement, it has not been widely used in construction. The reason is residual phosphorus of phosphorus slag has poor influence on setting time of cement, and insufficient content of Al_2O_3 also affects early properties. Therefore, its maximum was usually less than 25% in Portland PHS. In order to increase the amount of PHS and enhance early strength, it is a valid method to add alkali such as through Na_2SO_4 [1–5]. If PHS content was more than 50%, compound admixtures are necessary, especially a fast setting early strength agent. The object of this research is to fully use the PHS produced in Guizhou province due to the development of its phosphorus industry. According to the experiences and the lessons in China and elsewhere, the selection of the appropriate admixture is the major method to produce PHS cement that is based on the principle of the activation of PHS.

The research was carried out in two stages: low PHS cement (LPSC), which contains about 40% PHS and high PHS cement (HPSC), which contains about 70% PHS. This paper mainly reports the influence of admixtures on the LPHS cement. The aim is to meet the current requirement of cement plants. The results of HPHS cement studies are given in another paper.

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, alumstone from Anhui. $NaSO_4$ used was a

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Table 1
The chemical components of raw materials (wt.%)

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

chemical reagent. Their chemical components are listed in Table 1.

3. Test results

3.1. Setting time

Fig. 1 shows the influence of PHS content on the setting time, wherein as the PHS content increases, the setting time got longer. Especially when the PHS content was more than 20%, it was obvious that the setting time increased. For example, when the PHS content increased from 20% to 40%, the setting time would increase three times. Therefore, it was not suitable for use in construction. It is necessary to adapt valid methods.

4. Strength test results

Fig. 2 showed the influence of the PHS content on strength. Flexural strength showed that when the PHS content was more than 20%, flexural strength obviously decreased. Compressive strength also decreased with the increase of PHS content. It did not reach the 425 PHSC standard when PHS content was more than 30%. Therefore, PHS content was ordinarily limited to less than 25% in Portland PHS cement of our country. In comparison with PC, when the PHS content was 40%, the compressive strength for 3, 7, and 28 days, respectively, decreased by 68.7%, 63.9%, and 45.1%.

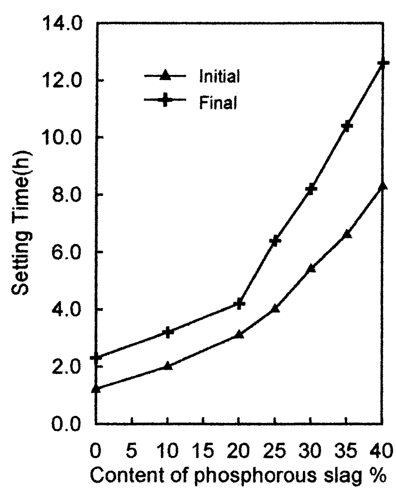

Fig. 1. The influence of PHS content on setting time.

In order to improve the strength properties of PHS cement, it is necessary to use an admixture technique. Its aims were to enhance the hydration rate, increase the content of early-stage hydrates, especially ettringite. Therefore, the following techniques were adapted. First, calcined gypsum was used as the replacement for gypsum (the results are in Table 2). From test results, it is well known that the strength properties were obviously improved by using calcined gypsum. Compressive strength can increase from 15% to 20% at early ages and flexural strength increases from 12% to 25%. Compressive strength at 28 days can increase from 8% to 15% and flexural strength increase from 6% to 10%. For example, in comparison with P_1, the compressive strength of P_2, respectively, increases by 2.1, 3.3, and 12.2 MPa at 3, 7, and 28 days of hydration, when PHS content is 30%. There are similar results with other PHS content.

Fig. 3 shows the influence of different content of calcined alumstone on strength of PHS cement. In these tests, PHS content was 30%, gypsum was 4%, and the newainden was clinker and calcined gypsum. Strength results showed that alumstone could improve the strength properties. When alumstone content was 4%, the best compressive and flexural strengths were achieved. When added alumstone content is 4%, the compressive strength at 28 days increases more than 10 MPa.

Fig. 4 showed the influence of sodium sulphate on PHS cement. There were similar strength results to calcined alumstone. Flexural strength increased with the increase of sodium sulphate (from 1% to 4%). The compressive strength is highest when the sodium sulphate content is 3%.

In order to get the best strength function, it is necessary to use compound admixtures. Table 3 shows the influence of

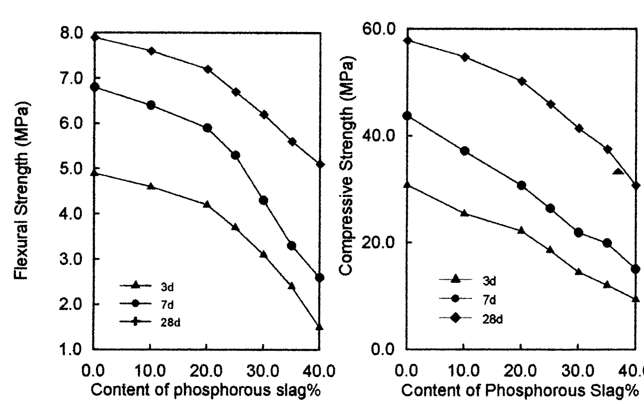

Fig. 2. Curing time vs. compressive and flexural strength of PHS cement.

Table 2
Strength results of PHSC (gypsum replaced by calcined gypsum)

					Flexural strength (MPa)			Compressive strength (MPa)		
Number	Clinker	PHS	Gypsum	Calcined gypsum	3 days	7 days	28 days	3 days	7 days	28 days
P1	66	30	4		3.1	4.3	6.2	14.5	21.9	42.1
P2	66	30		4	3.5	5.4	7.5	16.6	25.2	53.3
P3	61	35	4		2.6	3.4	5.6	12.1	19.9	37.5
P4	61	35		4	3.2	4.2	6.8	15.2	23.0	46.1
P5	56	40	4		1.5	2.6	5.2	9.4	15.1	30.7
P6	56	40		4	2.5	3.7	6.7	12.5	18.7	44.3

compound admixtures on the strength of PHSC. Results showed that the strength property of two cement with admixture was better than with a single admixture (for example, P10 and P8). The best strength function is in three parts of admixtures (for P11). In comparison with P7, compressive strength of P11, respectively, increased by 154%, 87%, and 68.6% at 3, 7, and 28 days of hydration. Flexural strength increased by 146%, 118%, and 71.4% at the same hydration time.

4.1. Pore structure tests

Relation between structure and properties dates back to the original research works of T.C. Powers. Through the

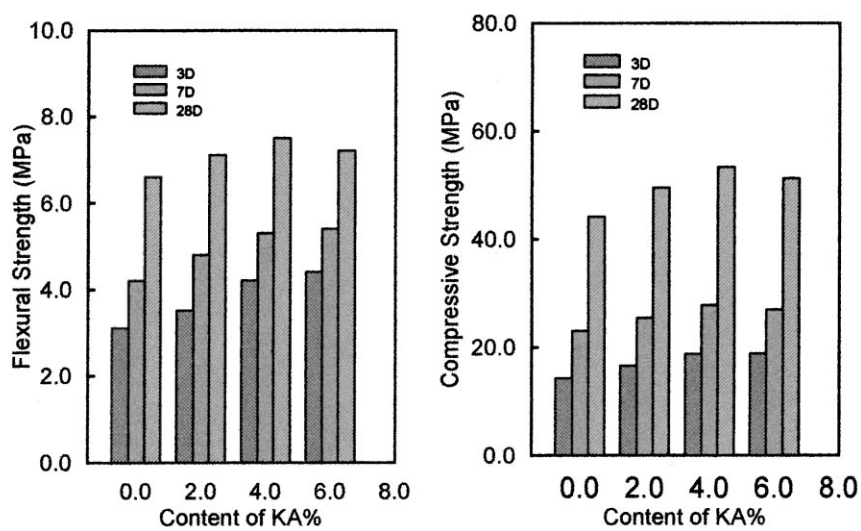

Fig. 3. The influence of calcined alumstone (KA) on strength of PHS cement.

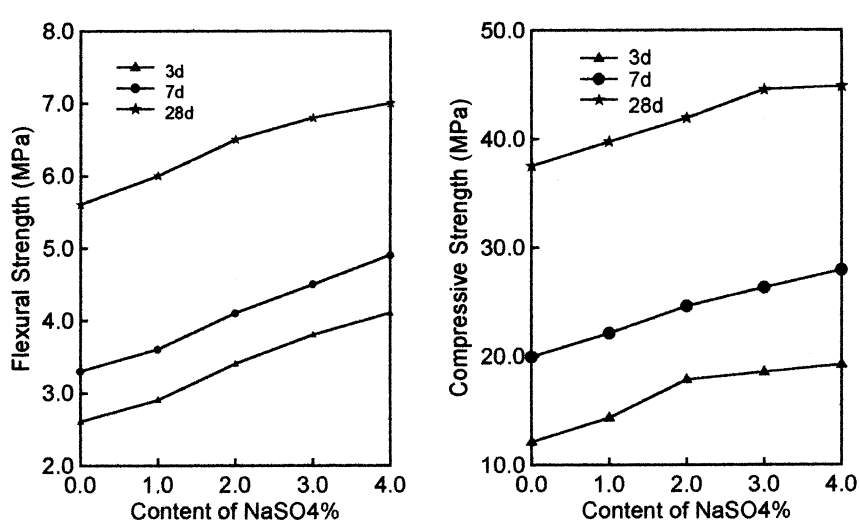

Fig. 4. The influence of sodium sulphate on PHS cement.

Table 3
The influence of compound admixtures on the strength of PHSC

Number	Clinker	PHS	Gypsum	Calcined gypsum	Calcined alumstone	Sodium sulphate	Rf (MPa)			Rc (MPa)		
							3 days	7 days	28 days	3 days	7 days	28 days
P7	61	35	4				2.6	3.4	5.6	12.1	19.9	37.5
P8	61	35		4			3.2	4.2	6.8	15.2	23.0	46.1
P9	60	35	4			1	2.9	3.6	6.0	14.3	22.1	39.7
P10	58	35	4		3		3.9	5.1	7.2	17.5	25.8	49.7
P11	57	35		4	3	1	6.4	7.4	9.6	30.7	38.1	63.3

testing of pore structure, some relations such as porosity, strength, etc., could be arranged. Pore structure tests are carried out by mercury porosimetry using auto-60 (seen in Fig. 5 (PH11)).

In Fig. 5(a)–(d), the pore volume and pore percent of less than 50 nm of Portland cement and PHS cement are shown. Fig. 5(c) showed that total pore volume decreased with the increase of hydration time. There were higher pore volumes at an early stage, but lower at later stage. The reason is that early strength of PHSC was lower, but its strength development was fast, therefore, later strength was better.

Fig. 5(d) shows the pore distribution less than 50 nm at different hydration time. The pore volume percent of PHSC was, respectively, 54.5%, 68.4%, and 76.8% at 3, 7, and 28 days of hydration. It was shown that the ratio of gel pore would increase with the increase of hydration time. Results also showed that although the pore volume of hydration at 3 days of PHSC was much larger than that of PC, the pore volume of hydration at 7 and 28 days was similar to that of PC.

4.2. Hydration mechanism

In order to fully understand the hydration mechanism of PHS cement, it is necessary to know every physical and chemical changing process. However, this is impossible because the hydration process of the system is complicated. In this way, the system of PHS cement is divided into three parts; that is PHS, clinker, and admixtures. The hydration process of PHS cement can be simply explained as follows.

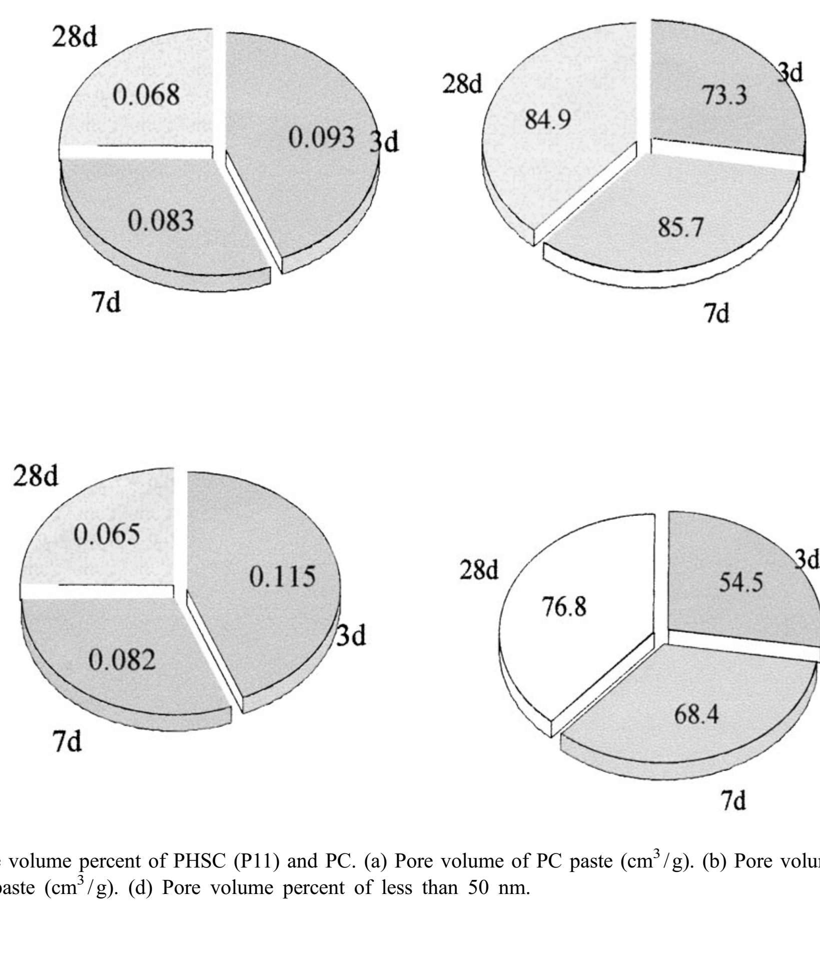

Fig. 5. Pore volume and pore volume percent of PHSC (P11) and PC. (a) Pore volume of PC paste (cm^3/g). (b) Pore volume percent of less than 50 nm. (c) Pore volume of PHSC paste (cm^3/g). (d) Pore volume percent of less than 50 nm.

4.2.1. The enhancing function of admixtures on hydration of clinker

It is well known that Na_2SO_4 is an early strength agent that is usually used by PC. The main mechanism is that the solution rate of Na_2SO_4 is very fast. When it is in contact with water, Na^+ and SO_4^{2-} are rapidly dissolved into water. The following reaction will take place.

$$Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4 \cdot 2H_2O$$

Because the reaction consumes $Ca(OH)_2$ and produces NaOH, it increases the alkalinity. The continuing consumption of $Ca(OH)_2$ speeds up the hydration of C_3S and C_2S. On the other hand, SO_4^{2-} causes C_3A to hydrate rapidly and produce ettringite. More ettringite at an early stage is beneficial because it enhances strength. Calcined alumstone provides potassium sulpho-aluminate without water and activated Al_2O_3. The components react with clinker and increase early-stage strength. The research shows that the solution of calcined degree of gypsum is greater than gypsum [6,7]. It is of benefit to the hydration of cement.

4.2.2. The enhancing function of admixtures and clinker on the activation and hydration of PHS

Because of the dissolution of admixture and hydration of clinker, NaOH, KOH, and $Ca(OH)_2$ produced this way a higher concentration of OH^- ions. The alkalinity of liquid phase is enhanced. Under highly alkaline conditions, the bonds in the glass phase of PHS are easily broken. Silicate and aluminum ions react with Ca^{2+} and produce CSH and calcium aluminate. Later, they can produce ettringite with the existing SO_4^{2-} ions. Because of the enhanced glass bond breaking and reaction rate, the properties of PHS cement are enhanced.

5. Conclusions

1. The problems of low early strength and slow setting of existing 425 grade PHS cement with more than 20% PHS could not be solved until appropriate admixtures such as calcined gypsum, calcined alumstone, and sodium sulphate are used. The dosage of PHS could be increased up to 40% and higher grade LPSC could also be made when these admixtures are mixed in certain proportions.

2. Such admixture is a more important factor for producing HPSC. The 425 or 525 grade HPSC could be produced by adjusting technological parameters and using complex admixture, which is made up of 4–5% heated gypsum, 2.5–3.5% sodium sulphate, and 5–7% especially made activator F. The hydration products are mainly AFt and C-S-H gel, without calcium hydroxide, which is usually present in PC and other hydrates.

3. The reason for the admixture's ability to significantly enhance the early properties of PHS cement could be attributed to the increased hydration of both clinker and PHS and the increase in hydrates (especially for AFt) produced.

4. Compared with PC, the hardened paste of PHS cement is characterized by a more compact structure, lower porosity, and smaller (>50 nm) pores. The study revealed that the property of resistance to sulphate corrosion of HPSC is better than that of LPSC, and PC is the worst. It is also confirmed by the experiments that PHS cement has a good ability to reduce alkali–aggregate reaction.

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