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Study on the aluminophosphate glass-rich cement

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Abstract

The phase composition, structural unit and hydration activity of glass-rich cement in $CaO-Al_2O_3-P_2O_5-ZnO$ system were studied by means of XRD and IR analysis. The results show that the main phases in this cement are glass, L phase and CA. The early strength results from the hydration of glass and CA, and long-term strength from L phase. Aluminophosphate glass-rich cement has the characteristic of stable hydrates, early strength and steadily growing long-term strength.

Keywords: Glass-rich cement; Phase composition; Hydration activity

1. Introduction

The behavior of P_2O_5 has stronger chemical activity than that of SiO_2 and Al_2O_3 by the double-bonded oxygen in $[PO_4]^{2-}$ tetrahedron [1] which brought about research on chemical bond ceramics materials proposed by Roy [2]. Certain aluminum–calcium rich regions in the $CaO-Al_2O_3-P_2O_5$ system have hydration activity, and a new ternary compound L, which contributes the long-term strength, has been synthesized in this system [3]. The studies on glass cement of $CaO-Al_2O_3-SiO_2$ [4] and $CaO-SiO_2-P_2O_5$ [5] show that the glass phase in these two systems has high hydration activity, especially early strength. Based on these studies, the combination of aluminophosphate cement with glass cement to form novel cement–aluminophosphate glass-rich cement was suggested. Thereupon, we synthesized aluminophosphate glass-rich cement by adding alkali metal and alkaline earth oxides additions [6]. In this paper, we study the synthesis of aluminophosphate glass-rich cement by adding ZnO to the $CaO-Al_2O_3-P_2O_5$ system.

2. Materials and methods

The materials used in the current study, such as $Ca(NO_3)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, H_3PO_4 and ZnO, were pure analytical reagents.

The chemical composition and ZnO content of specimens are shown in Table 1. The main mineral phases in specimen Z_o burn at 1550°C were glass, CA and $C_{12}A_7$, which is similar to that given by Li Shiqun and other previous workers [3]. Due to the transformation of the voluminous hexagonal hydrates into the more dense cubic phase, the strength slowly decreases after 28 days. The aim of ZnO addition is to modify the phase composition and stabilize the hydrates. Synthesized samples studied here have been prepared in two stages: raw samples are synthesized through the sol–gel process by $Ca(NO_3)_2{\cdot}4H_2O$, H_3PO_4 and $Al(NO_3)_3{\cdot}9H_2O$, and then mixed with ZnO and ground to the workable fineness in the laboratory ball mill, and burned at

Table 1
Chemical composition and ZnO content of the samples

Sample	$CaO/(Al_2O_3+P_2O_5)$ (mol ratio)	$(P_2O_5)/(Al_2O_3)$ (mol ratio)	ZnO content (mmol g^{-1})
Z_0	1.55	0.11	0
Z_1	1.55	0.11	0.6
Z_2	1.55	0.11	0.9
Z_3	1.55	0.11	1.2

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1450°C for 45 min, then quenched in ice and ground to pass a No. 325 sieve. The powder was mixed with water, then molded with 12.5 MPa pressure (w/c = 0.2) into specimens in sizes of 10 × 10 × 40 mm, and cured to each age for measurement of the compressive strength. The hydration was stopped by alcohol for the next analysis.

3. Results and discussion

3.1. Results

Fig. 1 shows the strength behavior of specimens Z_0, Z_1, Z_2 and Z_3 as a function of time. The compressive strength value of Z_0 and Z_1 increases up to 73 MPa and 82 MPa, respectively, at 1 year curing time. The strength value at 1 day's curing time of specimens Z_2 and Z_3 increase to 84 and 88 MPa, respectively, both increase to 100 MPa at 1 year's curing time, showing the characteristics of high early strength and growing long-term strength.

3.2. The effects of ZnO on phase composition

From Fig. 2, we can see that $C_{12}A_7$ decreases with the increasing of ZnO, and L phase has been synthesized when adding 0.9–1.2 mmol/g ZnO, which is same with that of Ref. [5] (d spaces: 0.6478, 0.3752, 0.3255, 0.290, 0.2644, 0.2165, 0.1804 and 0.1624 nm). From Fig. 2, it was observed that the baseline of XRD patterns rises with increasing of ZnO quantity, indicating that the glass content increases with increasing of ZnO and showing that ZnO is an effective cosolvent in this system.

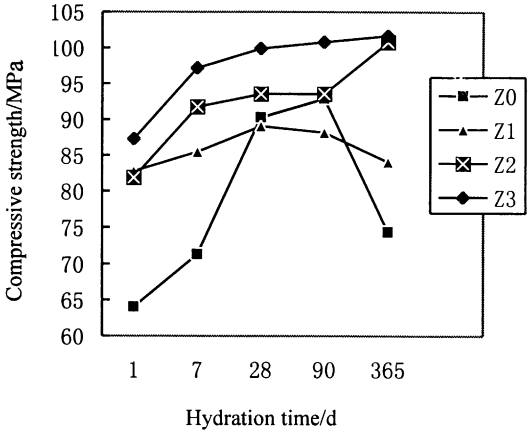

Fig. 1. Compressive strength of the samples at different ages.

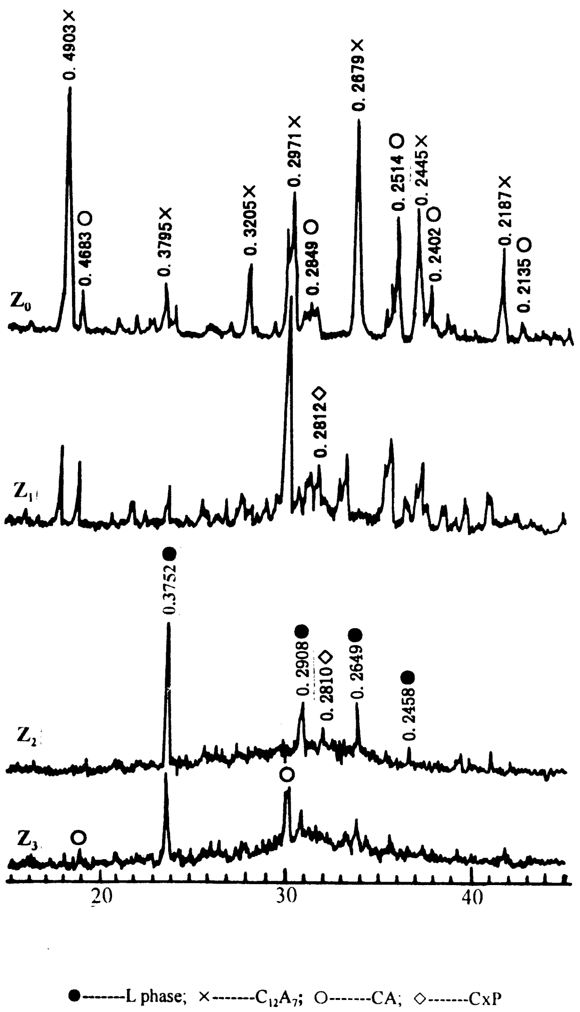

Fig. 2. X-ray pattern of the samples prepared at 1450°C. ● — L phase; × — $C_{12}A_7$; ○ — CA; ◇ — CxP.

To obtain information on how the ZnO affects the structure unit, the infrared absorption spectra of samples Z_0, Z_1, Z_2 and Z_3 were recorded; those results are shown in Fig. 3. The IR spectrum of Z_0, without ZnO, shows a band at 1058 cm^{-1}, attributed to the symmetrical stretching vibration of $[PO_4]$. The band at 868–838 cm^{-1} can be assigned to the asymmetric stretching vibration of $[AlO_4]$, and the weak band at 522–639 cm^{-1} may result from symmetrical stretching vibration of $[AlO_6]$. With increasing content of ZnO, the band of $[PO_4]$ changes, 1058 cm^{-1} lessening and 1097 cm^{-1} enhancing, indicating that the polymerization of $[PO_4]$ enhances with the increasing ZnO content. From Fig. 3, we can also see that the band at 781–838 cm^{-1} of $[AlO_4]$ obviously widen when added with ZnO. This change indicates the deformation and crystal disorders of $[AlO_4]$. The band intensities at 522–639 cm^{-1} of $[AlO_6]$ become weak when adding ZnO, as shown in Fig. 3. These differences means that the octahedral coordination of Al^{3+} ions partly transforms into tetrahedral coordination by obtaining "free O_2" provided by ZnO. As shown in Fig. 1, the hydration activity improves with the ratio of tetrahedral coordination of Al^{3+} ions.

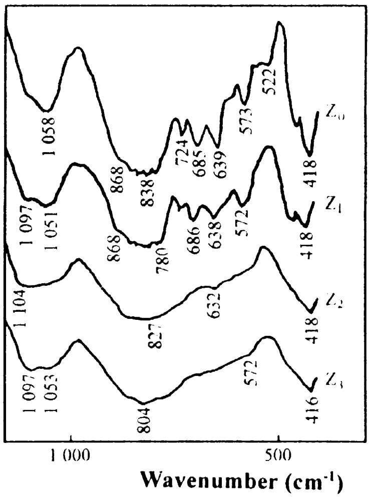

Fig. 3. IR spectra of the samples prepared at 1450°C.

3.3. XRD and infrared spectral analysis of hydration samples

As shown in Fig. 4, the early strength results from the hydration of CA and the long strength from the hydration of L phase. The main hydrates are Y phase (a new compound of Ca–Al–P–O–H_2O), a small amount of $CA(P)H_{10}$ and microcrystalline materials. Due to the substitution of P^{5+} for Al^{3+}, $CA(P)H_{10}$ is stabilized and the conversion of $CA(P)H_{10}$ into C_3AH_6 does not occur during the whole hydration process.

The infrared spectra of the hydrated sample Z_3 are given in Fig. 5. The band at 868–838 cm^{-1} of $[AlO_4]$ obviously weakens upon 1 day curing time, indicating fast hydration of the glass phase and CA. The band at 3464 cm^{-1} which results from the stretching–shrinking absorption vibration peak of water is enhanced obviously at 1 day curing time. The presence of AH_3 is indicated by the band at 560 cm^{-1}. From 1 day to 365 days, the band position of $[PO_4]$ moves from 1058 cm^{-1} to 1032 cm^{-1}. At the same time, the band intensity of $[AlO_4]$ become weaker, combined with XRD analysis this indicates the production of hydration products.

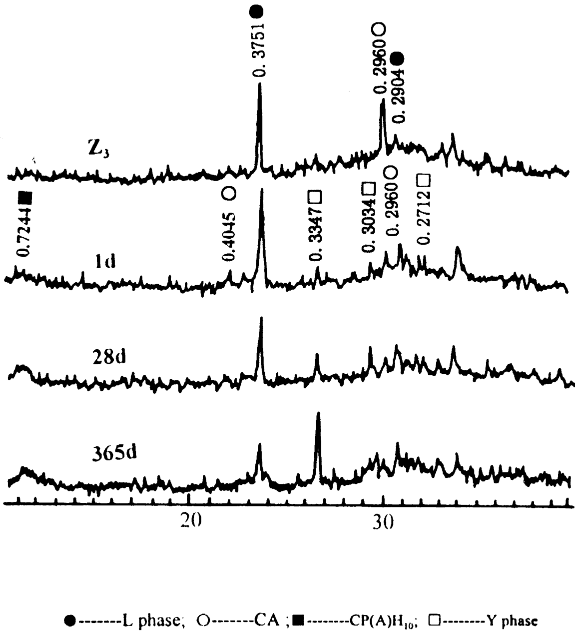

Fig. 4. X-ray pattern of the sample Z_3 at different ages. ● — L phase; ○ — CA; ■ — $CP(A)H_{10}$; □ — Y phase.

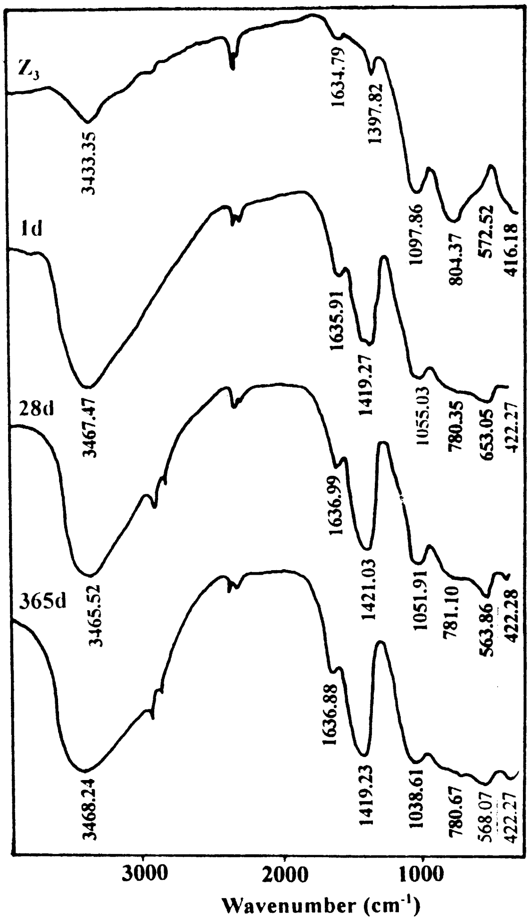

Fig. 5. IR spectra of the sample Z_3 at different ages.

By combining the information obtained from XRD and IR analysis, it is apparent that the mechanism of aluminophosphate glass-rich cement is quite different from that of high alumina cement. Glass phase and CA contribute to the early strength, and L phase to the long-term strength. The optimum link between early strength and long-term strength favors this cement with the characteristics of high early strength and steadily growing long-term strength.

4. Conclusions

1. The main phases of aluminophosphate glass-rich cement are glass, L phase and CA.

2. Glass and CA contribute to the early strength, and L phase to the long-term strength.
3. $CA(P)H_{10}$ is stabilized by substitution of P^{5+} for Al^{3+}.
4. Aluminophosphate glass-rich cement has the characteristics of high early strength and steadily growing long-term strength.

Acknowledgments

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