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Influence of phosphorus impurities on the performances of calcium sulfoaluminate cement

Yongbo Huang [a], Jueshi Qian [a,*], Congzhen Liu [a], Na Liu [a], Yan Shen [b], Ying Ma [a], Huaqiang Sun [a], Yingru Fan [a]

[a] College of Materials Science and Engineering, Chongqing University, Chongqing 400045, China
[b] College of Civil Science and Engineering, Yangzhou University, Yangzhou 225127, China

HIGHLIGHTS

- H_3PO_4 in PG significantly affects CSA cement performances.
- Phosphates in PG more or less affect early age CSA cement performances.
- H_3PO_4 in PG should be removed or transformed into a phosphate.

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ABSTRACT

When phosphogypsum (PG) is used as the added gypsum of calcium sulfoaluminate (CSA) cement, the phosphorus impurities in PG negatively affect the performances. To select an appropriate PG pretreatment method to render it suitable to serve as the added gypsum of CSA cement, it is necessary to ascertain the influence of different types of phosphorous impurities on the performances of CSA cement. Analytical reagents such as H_3PO_4, $Ca(H_2PO_4)_2{\cdot}H_2O$, $CaHPO_4{\cdot}2H_2O$, and $Ca_3(PO_4)_2$ were used to investigate the influence of phosphorus impurities on CSA cement performances. The results demonstrate that the presence of phosphate and phosphoric acid leads to an increase in the water demand for normal consistency and prolongs the setting time of CSA cement. Within 6 h, the phosphates and phosphoric acid inhibit the hydration of $C_4A_3\bar{S}$ in CSA cement, leading to a decrease in the compressive strength. In terms of inhibitory action, the following sequence is observed: $H_3PO_4 > Ca(H_2PO_4)_2{\cdot}H_2O > Ca_3(PO_4)_2 > CaHPO_4{\cdot}2H_2O$. After 12 h, $CaHPO_4{\cdot}2H_2O$ boosts the hydration of $C_4A_3\bar{S}$ in CSA cement. At 1 d and 28 d, the compressive strengths of the $CaHPO_4{\cdot}2H_2O$-added and $Ca(H_2PO_4)_2{\cdot}H_2O$-added samples exceed that of the blank sample, separately. For the $Ca_3(PO_4)_2$-added sample, the compressive strength is equivalent to that of the blank sample at 28 d, while the H_3PO_4-added sample exhibits a much lower compressive strength over 28 d. Therefore, removing H_3PO_4 from PG or transforming it into a phosphate is an effective approach to render PG suitable to serve as the added gypsum of CSA cement.

1. Introduction

Phosphogypsum (PG) is an industrial by-product generated during the production of phosphoric acid by the wet process (5 tons of PG per ton of phosphoric acid produced) [1]. Currently, the annual worldwide production of PG is estimated to be around 280 Mt, of which 55 Mt is generated in China [2–3]. However, only 15% PG is recycled. Except for gypsum and quartz, PG also contains a small amount of harmful impurities such as H_3PO_4, $CaHPO_4{\cdot}2H_2O$, $Ca(H_2PO_4)_2{\cdot}H_2O$, $Ca_3(PO_4)_2$ and fluoride [4,5]. Restrictions have been imposed on the wide application of PG because of these impurities. Therefore, the remaining 85% PG is dumped in large stockpiles, and is exposed to the environment. It not only occupies considerable areas of cultivable farmland, but also brings about severe chemical contamination to water and soil [4]. Therefore, it is extremely urgent to effectively utilize PG.

The huge consumption of building materials undoubtedly affords an avenue for the effective recycling of PG. At present, PG has been used for the preparation of gypsum plaster [6,7] and cementitious materials such as PG–fly ash (FA)–PC [8], PG–FA–hydrated lime [9,10], calcined PG–FA–lime [11], and PG–FA–PC–lime [12]. Besides, PG can also be used for the preparation of CSA cement. Due to low energy consumption, low CO_2 emission and

* Corresponding author.
E-mail address: qianjueshi@126.com (J. Qian).

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excellent performances, CSA cement is considered as an alternative to Portland cement (PC). PG can be used as a raw material and as the added gypsum for the preparation of CSA cement to satisfy the formation and hydration of the $C_4A_3\bar{S}$, separately. In general, the $C_4A_3\bar{S}$ content of CSA cement clinker exceeds 60%. Thus, around 0.4–0.5 t PG are consumed for producing 1 t CSA cement. Therefore, the utilization of PG for the production of CSA cement is also an available way for the effective recycling of PG.

When PG is used for the preparation of CSA cement, the phosphorus impurities in PG pose a great challenge. By far, PG has been used as a raw material for the preparation CSA cement clinker [13], alite–calcium sulfoaluminate (ACSA) cement clinker [14], and belite–calcium sulfoaluminate (BCSA) cement clinker [15–16]. Theses investigations demonstrated that the phosphorus impurities negatively affected the hydration of $C_4A_3\bar{S}$ [17] and slightly decreased the compressive strength of the cement. Generally, the $CaSO_4{\cdot}2H_2O$ content in PG exceeds 90%, which makes it a good substitute for natural gypsum to serve as the added gypsum of CSA cement. Additionally, the original PG is powdered, which could reduce the energy consumption of CSA cement grinding. However, when PG was used as the added gypsum of CSA cement (90% clinker and 10% PG), the early age strength development would be significantly affected by the phosphorus impurities [16]. Therefore, the pretreatment is needed for the utilization of PG as the added gypsum of the CSA cement. To lower down the phosphorus impurity content or transform phosphorus significantly affecting CSA cement performances into those slightly affecting CSA cement performances, it is necessary to ascertain the influence of different types of phosphorous impurities on the performances of CSA cement.

The phosphorus impurity content in PG is usually within the range of 0.7–2.5%. The impurities are mainly composed of phosphates and phosphoric acid, which exert different influences on the performances of CSA cement. In this study, different types of phosphates ($CaHPO_4{\cdot}2H_2O$, $Ca(H_2PO_4)_2{\cdot}H_2O$, $Ca_3(PO_4)_2$) and the phosphoric acid on the performances of commercial CSA cement were investigated.

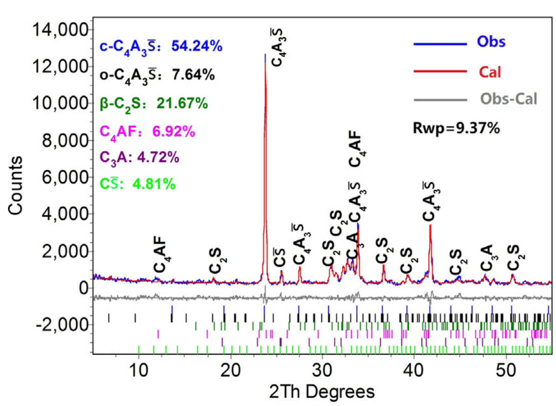

Fig. 1. Rietveld refinement plot of CSA cement clinker (The Rietveld quantitative phase analysis result is considered convincible if R_{wp} is below 15%. Note: C = CaO, A = Al_2O_3, $\bar{S}$ = SO_3, S = SiO_2, F = Fe_2O_3, c = cubic, o = orthohombic).

2. Experiments

A commercial CSA cement clinker was used in the experiment. The mineralogical composition of the clinker is shown in Fig. 1. The elemental compositions, expressed in oxide, of CSA cement clinker, natural gypsum (NG) and PG are provided in Table 1. NG from Chongqing of China and PG from Yunnan of China were used for the study. X–ray diffraction (XRD) pattern of NG is shown in Fig. 2.

The CSA cement clinker and the added NG (4:1 by weight fraction) were mixed and milled by a plate ball mill to obtain a homogeneous mixture that could pass through a 76 μm sieve with 2.3 wt% residue.

The setting time was determined by a Vicat apparatus, and the measurements were performed according to GB/T 1346–2001 standard. Based on the phosphorus content in PG (Table 1), the experiment was designed and different amount of phosphates and phosphoric acid were added into the cement paste (Table 2). The cement pastes were prepared with a constant water to cement ratio (w/c) of 0.3. The cement pastes were poured into molds with

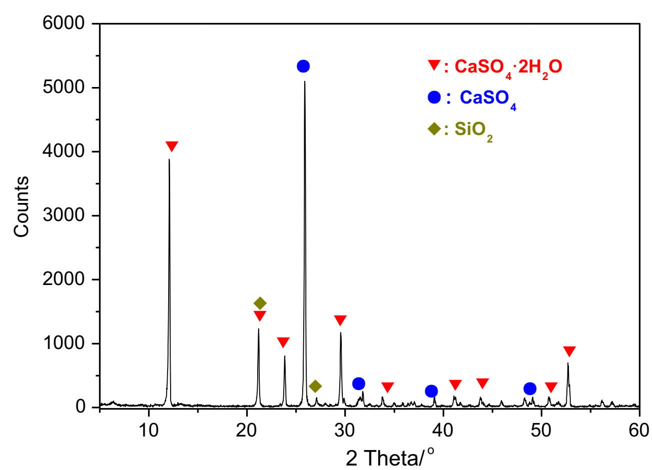

Fig. 2. XRD pattern of NG.

Table 2
Type and dosage of phosphorus in CSA cement.

Nomination	Phosphorus impurity	Content/%	Actual P_2O_5 content/%
Blank	–	0	0
A1	$Ca_3(PO_4)_2$	0.32	0.15
A2		0.65	0.30
A3		0.98	0.45
B1	$CaHPO_4{\cdot}2H_2O$	0.36	0.15
B2		0.73	0.30
B3		1.09	0.45
C1	$Ca(H_2PO_4)_2{\cdot}H_2O$	0.27	0.15
C2		0.53	0.30
C3		0.80	0.45
D1	H_3PO_4	0.21	0.15
D2		0.41	0.30
D3		0.62	0.45

Table 1
Chemical compositions (expressed in oxide) of CSA cement clinker, NG and PG/wt%.

Sample	CaO	SO_3	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	MgO	P_2O_5	s-P_2O_5
Clinker	42.33	11.10	8.04	32.91	2.85	0.30	0.16	0.68	0. 22	–
NG	28.29	39.92	6.75	1.51	0.79	0.75	0.21	3.03	0.13	–
PG	26.95	38.44	5.50	0.55	0.22	0.33	0.25	1.89	2.25	1.77

s = soluble.