

Available online at www.sciencedirect.com

ScienceDirect

Procedia Environmental Sciences 31 (2016) 970 – 976

Procedia
Environmental Sciences

The Tenth International Conference on Waste Management and Technology (ICWMT)

Hardening performance of phosphogypsum-slag-based material

Xuquan Huang*, Xiaorong Zhao, Shuangqiao Bie, Chengfeng Yang

College of Hydraulic & Environmental Engineering, China Three Gorges University, Yichang, 443002, China

Abstract

Hardening, hydration performance and mechanism of the phosphogypsum-slag-based binding material were studied in this paper. The phosphogypsum-slag-based binding material was prepared by mixing 45% phosphogypsum, 48% slag, 7% cement clinker and chemical activator at 1% relative to the binder. The compressive and flexural strength of the phosphogypsum-slag-based binding material reached the standard for compound silicate cement grade 32.5. Moreover, the softening coefficient of mortars with phosphogypsum-slag-based binding material was the same as mortars with P•C32.5. In particular, the pH value of pastes or mortars with this binding material was far lower than those with P•C32.5 and it had small impact on environment. Microscopic analysis with XRD and SEM revealed that: bar-like ettringite crystals, portlandite and the rest dihydrate gypsum crystals contacted each other as structural framework. These crystals were bonded firmly together by foil-like C-S-H gels and formed compacted body with a dense structure of high strength and water resistance.

© 2016 The Authors. Published by Elsevier B.V This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of Tsinghua University/ Basel Convention Regional Centre for Asia and the Pacific

Keywords: phosphogypsum; slag; C-S-H; ettringite ; water resistance; pH.

1. Introduction

Phosphogypsum (PG) is an industrial waste of phosphoric acid production. Its main component is referred to as dihydrate gypsum. Approximately 4.0~6.0 tons of PG are generated from the production of 1 ton, It often contains residual phosphorus pentoxide and a small amount of hydrofluoric acid, and the pH value is around 6.0 to 2.1. PG is mostly transported to waste dumps stacking and takes a lot of land and has great harm on the environment.

* Corresponding author. Tel./fax: +86 717 6392318.
E-mail address: hxq@ctgu.edu.cn

Currently, comprehensive utilization of PG resource is the best way to solve the problem of PG pollution, and the use of PG binder preparation is the main direction of resource reutilization. The related reports in literature focuses on preparing cementitious material with anhydrate PG or hemihydrate PG after high temperature or grinding treatment^{1,2}, which is not conducive to saving energy and reducing consumption. Few researches of cementitious materials preparation with untreated PG have been reported. Yun Huang^{3,4,5} studied the cementitious materials with 40–60% grinding treatment PG, but the compressive strength of the material was less than 30MPa after 28 days. And its softening coefficient wasn't studied.

In the paper, the preparation of phosphogypsum-slag-based binding material (PBM) is introduced. PBM was composed of 45% untreated PG, 3%~15% cement clinker (CC), 40~52% Granulated slag (SL) and 1% activator. The objective of this study is to analyze the strength properties, paste hardened body microscopic and phase composition of PBM, as well as compared with those of P•C32.5 cement. Finally, the hydration and hardening properties, mechanism and application prospects of PBM are discussed.

2. Materials and methods

2.1. Materials

The Blaine's surface area of untreated PG was 165m²/kg. X-ray diffraction pattern and chemical analysis indicated 85.3% dehydrated gypsum(CaSO₄ • 2H₂O). SL was ball-milled to a Blaine of 321.3m²/kg. The Blaine's surface area of CC was 386.2m²/kg. The chemical composition of original materials was seen as Table 1. P • C32.5 grade cement (PC) was from Gezhouba Group Cement Corp. Ltd. in China.

Table 1 Chemical composition of the raw materials.

	CaO	SiO ₂	Al ₂ O ₃	MgO	SO ₃	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	P ₂ O ₅
PG	37.75	8.29	0.86	0.08	50.59	0.58	0.16	0.52	0.06	0.78
SL	38.65	29.94	15.94	7.98	3.74	1.18	0.65	0.62	0.34	-
CC	65.47	20.02	4.36	1.64	1.92	3.33	0.23	1.27	0.34	-
PC	45.87	27.37	10.46	6.68	2.64	2.29	-	-	-	-

2.2. Paste preparation test

Paste prepared by cement or PBM. PBM was composed of 45% PG, 3%~15% CC, 40~52% SL, and 1% activator (Table 2). The water-binder ratio of paste was kept at 0.50 for all pastes experiments in order to ensure good workability and the same amount of water. All pastes were stirred for 4 minutes and casted in cubic moulds of 20mm, then the moulds were kept vibrating for 30s at the flat panel vibration machine and cured at 20 ± 1 °C and 95% Rh for 24h. After being demoulded, these cubic specimens were cured under water at 20 ± 1 °C to the provisions of age.

Table 2 Mix proportion of PBM (wt%)

	PBM1	PBM2	PBM3	PBM4	PBM5
PG	45	45	45	45	45
SL	50	45	40	35	30
CC	3	5	7	10	15

2.3. Mortar preparation test

Mortar mixtures were prepared according to "Method of testing cements-determination of strength GB/T 17671-1999" for uniaxial strength test, which was the same as ISO 679:1989 standard. The binder/sand and water/binder of

mortar mixtures was kept at 1:3 and 1:2 respectively. Mortar mixtures were cast in cuboid moulds of 40.0mm×40.0mm×160.0mm. After being removed from the molds, they were cured in water at $20 \pm 1^\circ\text{C}$ and 95% Rh for 3, 7 and 28 days.

2.4. pH value test

Broken tailings solidified bodies were sampled after strength test, these samples were dried at 60°C for 24h and crushed to 3mm below. The samples were mixed with deionized water (solid / water weight ratio =1:10), the supernatant was extracted to measure pH value according to “Solid waste-Extraction procedure for leaching toxicity-horizontal vibration method HJ557-2010”.

2.5. Microstructure analysis

After compressive strength test, the samples were immersed into anhydrous alcohol for 48h in order to terminate hydration. These samples were dried at 60°C for XRD and SEM tests employing a Rigaku Ultima IV diffractometer with Cu target and SEM test of these samples used for a Jeol JSM-7500F scanning electron microscope, respectively.

3. Results and discussion

3.1. CC on effects of the performances of PBM pastes

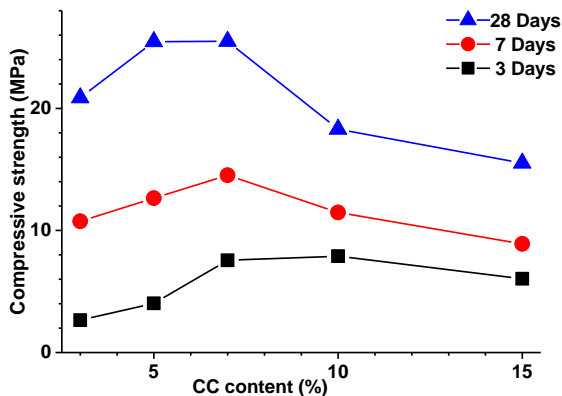


Fig.1 Effects of various CC content on compressive strength of PBM pastes

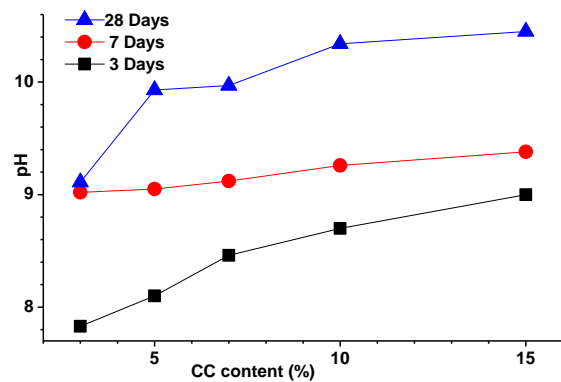


Fig.2. Effects of various CC content on the pH value of PBM pastes

Fig.1 and 2 show the evolution of compressive strength and pH value vs. CC content for the various PBM pastes. It can be observed that paste compressive strength of PBM firstly increase with the growing CC content and reached the highest point at CC content of 7%, showing the same trend at different times (3, 7 and 28 days). Then, it decreased gradually with increasing CC content. Whether the age is 3, 7 or 28 days, it can be observed the pH value of PBM pastes increased gradually with the increasing CC content from the Fig.2. The pH value of PBM pastes in 28 days are significantly higher than those in 7 days with the same CC content (5% ~ 15%). At the same time, the pH value of PBM pastes in 7 days is significantly higher than ones in 3 days. From Fig.2, it can be observed, the pH value of PBM pastes is lower than 11.0 in different days. Low pH value of pastes have little influence on environment. High strength value with lower CC content had an optimal comprehensive cost-effective. So it can be concluded that the mix proportion of PBM3 pastes was the best.

3.2. The performances comparison of pastes with PBM3 and PC

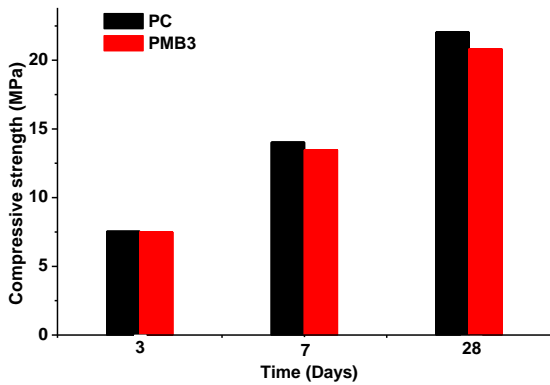


Fig.3. The compressive strength comparison of pastes with PBM3 and PC

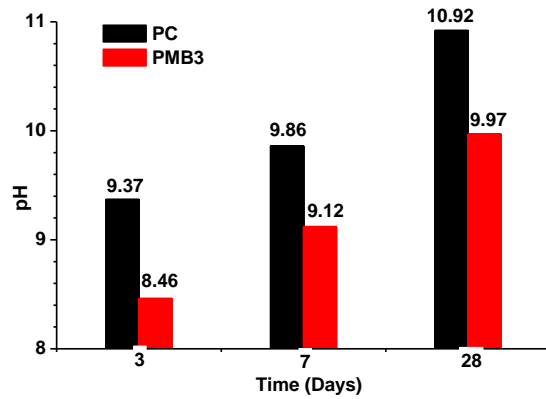


Fig.4 The pH value comparison of pastes with PBM3 and PC

The compressive strength of pastes with PBM3 and PC is almost the same in 3 days (Fig. 3). Only the compressive strengths of pastes with PBM3 are slightly lower than ones with PC in 3 and 28 days. Whether the pastes are with PBM3 or PC these pH value are all lower than 11.0. The pH value of the pastes with PC are all higher than ones with PBM3 in the same age, showing the growing trend with aging. Overall, compared with the cement, the pastes with PBM3 have some degree of damage to the environment because the slurry pH value is much lower.

3.3. The performances of mortars with PBM3 and PC

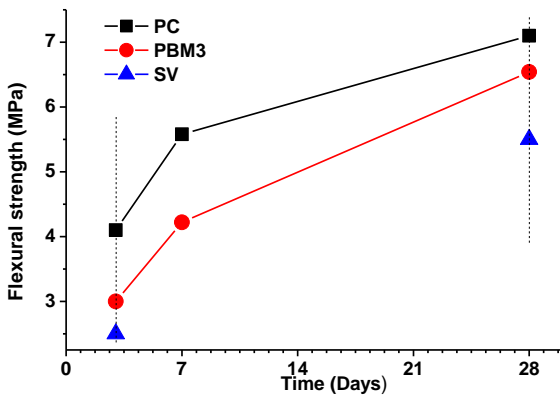


Fig.4. The flexural strength of mortars with PBM3 and PC

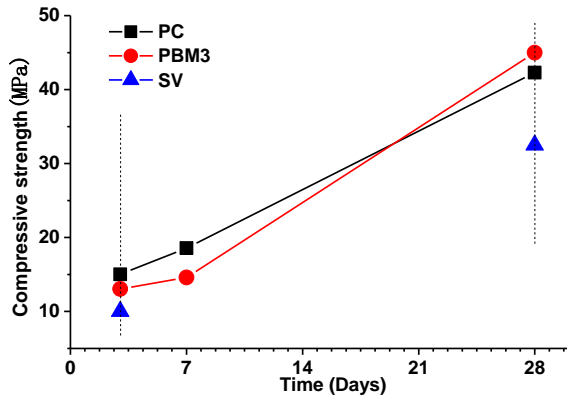


Fig.5. The compressive strength of mortars with PBM3 and PC

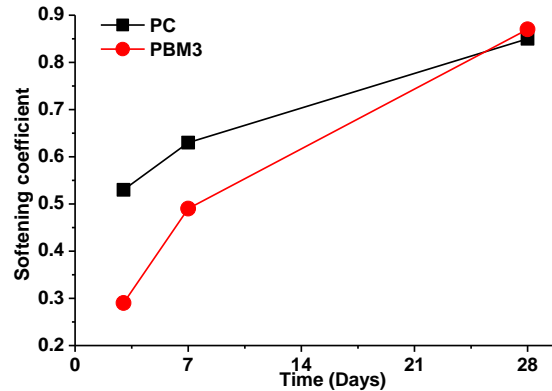


Fig.6. The softening coefficient of mortars with PBM3 and PC

Fig.4-6 summarized the main results of the performances study for PBM3 and PC. SV represents the guide line of compound silicate cement grade 32.5 in the Chinese standard “Common Portland Cement GB175-2007”, the lower bound of compressive strength of compound silicate cement grade 32.5 is 10.0 and 32.5 MPa in 3 and 28 days, respectively; the lower bound of flexural strength of compound silicate cement grade 32.5 was 2.3 and 5.5 MPa in 3 and 28 days, respectively. Although the strength of PBM3 mortars is slightly lower than PC in early ages, but it still reaches the guide line of compound silicate cement grade 32.5. Moreover, the softening coefficient of PBM3 mortars gradually increased with hydration ages and reached 0.87, which is higher than PC and indicated that this cementitious composite have good water resistance. Therefore, PBM3 is as good an alternative binder as PC.

3.4. Microscopic analysis with XRD and SEM

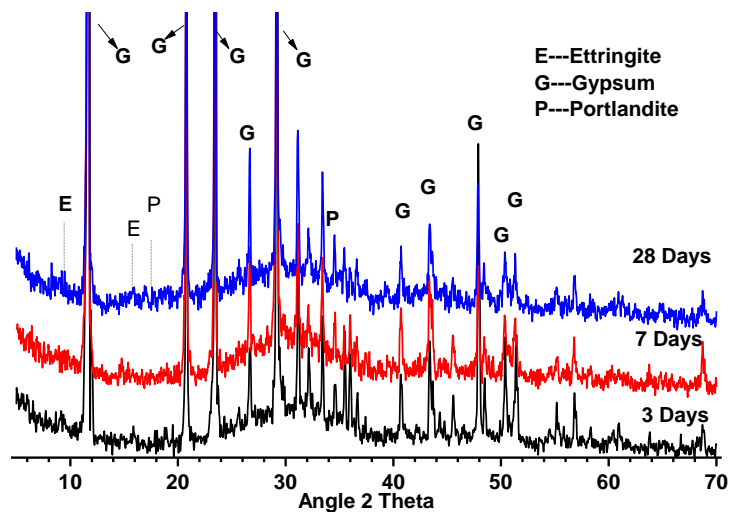


Fig.7 X-ray diffraction analysis of pastes with PBM3 at different hydration age

Fig. 7 shows XRD data after 3, 7 and 28 days for the pastes with PBM3. The hydration products of PBM3 are mainly ettringite, portlandite and the remaining gypsum crystals. The characteristic peaks of ettringite crystals and portlandite crystals could not be easily detected from XRD patterns of specimens of PBM3 pastes before 7 days, but these were very obvious in 28 days. It was possible that the water-soluble phosphate and fluoride hinder the early hydration of PC and SL. In alkaline conditions, the water-soluble phosphate or fluoride become $\text{Ca}_3(\text{PO}_4)_2$ or CaF_2 which covers the surface of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals or the hydration products and result in the whole hydration hardening of delay⁶. In addition to

participate in the generation of hydrated calcium silicate gels, excess calcium oxide mainly formed the portlandite. Due to the hydration calcium silicate does not exist in the form of crystal, so the X-ray diffraction patterns of its can't be observed.

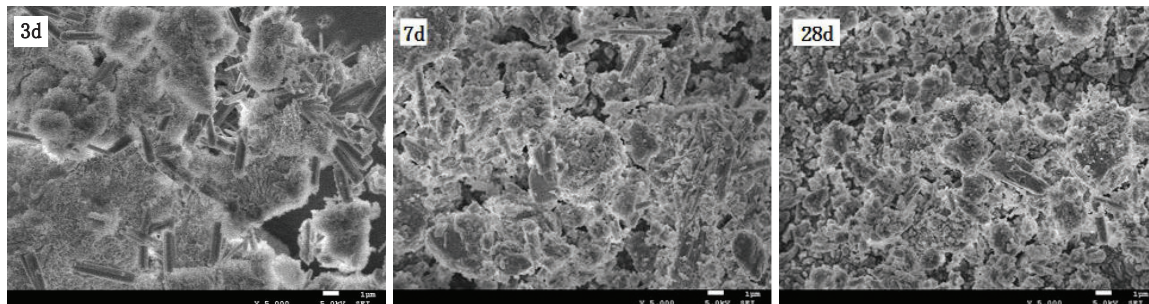


Fig.8 SEM images of pastes with PBM3 at different hydration age

The SEM images of paste with PBM3 at different hydration age are shown in Fig.8. The needle-column ettringite crystals can be clearly seen and distribute between mesh and filamentous C-S-H gels in 3 hydration days. It concludes the board-like dihydrate gypsum crystals and portlandite crystals from the previous XRD analysis, but these crystals can be identified in the SEM images. It may be because these are covered and wrapped by a large number of C-S-H gels. At this time, the whole microstructure exists obvious bulky pore and the close-grained degree is very poor. So the early strength is not high. As hydration, a large amount of hydration materials produce continuously, overlap confusedly and intertwine together. In the process of hydration products filling, it leads to the decrease of porosity and pore size. The needle-column ettringite crystals wrapped and adhered by C-S-H gels can be seen in 7 hydration days, but it has not easily been seen in 28 hydration days. All hydration products fill and intertwine with each other to form a more compact structure. That is the main reason that the later strength of PBM can be improved and the water resistance of PBM can be increased.

4. Conclusions

The phosphogypsum-slag-based binding material was mixed 45% phosphogypsum, 48% slag, 7% cement clinker and chemical activator at 1% relative to the binder. Microcosmic analyses using XRD and SEM of pastes with PBM3 reveals that: needle-column ettringite crystals, the rest board-like dihydrate gypsum crystals and portlandite crystals fill and intertwine with each other to form a more compact structure. These hydration products are embedded by a great deal of mesh and filamentous C-S-H gels, they stuck and filled in structural framework and formed compacted body. In 28 hydration days, the compressive, flexural strength and the softening coefficient of PBM3 is 6.5 MPa, 45.0 MPa and 0.87, respectively. It reaches the guide line of compound silicate cement grade 32.5. The results of mortar strength of PBM3 showed PBM3 mortars had good performances and had good water resistance. It is an appropriate alternative composite cementitious material as PC and can be used widely in infrastructure building or other domain, which could reduce CO₂ emissions and protect environment because of low PC content and high solid wastes content.

Acknowledgements

The authors would like to acknowledge Hubei Province Natural Science Foundation (Project No. 2014CFB676) and Three Gorges University talent Scientific Research Foundation (Project No. KJ2012B029)

References

1. Shen Y, Qian JS, Chai JQ, Fan YY. Calcium sulphoaluminate cements made with phosphogypsum: Production issues and material properties. *Cement Concrete Comp* 2014;48: 67-74

2. Yang M, Sun QC. Fly Ash-Calcined Phosphogypsum Cementitious Materials with Different Thermally Treated Phosphogypsum. *Adv Mater Res.*2011;261-263:816-819
3. Yun H, Zong SL. Investigation on phosphogypsum-steel slag-granulated blast-furnace Slag-limestone cement. *Constr Build Mater.* 2010;24(7):1296–1301
4. Huang Y, Lin ZS. Effect of Sodium Hydroxide on the Properties of Phosphogypsum based Cement. *J Wuhan Univ Technol.*2010,25(2):342-345
5. Mihelj N, Frankovic UN , Leakovic S, SipusicJ. Waste Phosphogypsum-Toward Sustainable Reuse in Calcium Sulfoaluminate Cement Based Building Materials. *Chem Biochem Eng Q.*2013;27(2): 219-226
6. Peng JH, Peng ZH, Zhang JX, Wan TH. Study on the form and distribution of water-soluble P₂O₅ in phosphogypsum and effective mechanism of properties. *J Chin Ceramic Soc.*2000;28(4): 309-313.