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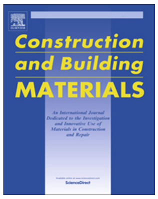

Effect of neutralization on the setting and hardening characters of hemihydrate phosphogypsum plaster

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HIGHLIGHTS

- The properties of calcined PG is different from that of FGD, causing concern in application.
- PG plaster sets slow and has a much lower strength in alkaline condition.
- Alkali has magnitude effect on the hydration process of PG plaster and gypsum morphology.
- The impurities in PG perform as retarder and microstructure modifiers in alkaline range.

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ABSTRACT

Phosphogypsum (PG) which is a waste byproduct of fertilizer production is the promising source of the gypsum industry. In order to explore the application of hemihydrate PG (HPG) as a substitute of hemihydrate gypsum, the setting and hardening characters of HPG plaster at different pH after neutralization were examined and contrasted with hemihydrate flue gas desulfurization gypsum (HFGD) plaster. Results showed that HPG plaster sets slow with a fall in strength and this effect was more pronounced after retarders were added when pH increased from 5.85 to 11.08. By contrast, HFGD plaster sets fast and without strength variation in the similar alkaline range. Microscopic studies including chemically combined water and temperature evolution curves of HPG plaster revealed that with the increase of the pH, the hydration reaction mechanism of hemihydrate and the gypsum crystal morphology were radically changed due to the fact of interaction between impurities and alkali. Consequently, HPG plaster is very different from HFGD plaster and its application in the alkaline condition was restricted.

1. Introduction

Phosphogypsum is an industrial byproduct derived from the phosphoric acid process for manufacturing fertilizers [1,2]. About 5 tons of PG is generated, for every ton of phosphoric acid made. As a result, the worldwide PG generation is estimated to be around 100–280 million tons per year[3–8]. However, only 15% of worldwide PG production is recycled. China, as a large agricultural country, consumes large quantities of phosphate fertilizers every year and its production ranked the first in the world which occupied 44.83% of the world's phosphate fertilizers [9]. Unfortunately, the reusing proportion of PG in China is even less than 10% [10]. The remaining PG is discarded into the ocean or river, or stored in ponds or dumped on land without purification, which create a need for large areas for disposal and cause serious environmental contamination [11,12].

Many researchers devoted themselves to recycle and utilize PG as a part of building materials [13,14]. For example, Yang et al. prepared self-leveling mortar mixture with original phosphogypsum without any purification [15]. Huang and Lin prepared a new type of cement combining phosphogypsum with steel-granulated blast furnace slag and limestone [17,18]. A new binder composed by phosphogypsum, fly ash and lime was also made by shen [16]. Hollow blocks were made with PG by Kuma [19] and non-calcined PG bricks without cement were manufactured by Zhou [20]. Although these results are positive, the application of PG in practise is unsatisfactory, except of being retarders in cement [21,22]. What's more, most of PG in these studies perform as fillers, only a few PG take part in the formation of AFt.

Hemihydrate gypsum is a traditional binder which can be used to produce gypsum board, gypsum block and gypsum plaster possessing fire proof, insulting and good volume stability properties.

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Naturally, the application of HPG would be more sustainable and economic. However, a lot of studies concentrated on the pretreatment and calcination process of PG. The properties of calcined PG (hemihydrate) as well as the setting and hardening of HPG plaster, particularly in presence of additives are seldom discussed. In general, HPG is obtained by thermal dehydration from PG directly at around 180 °C and only a few factories chose washing process. Therefore, HPG is still acidic, sets fast and contains impurities. In order to promote the application of HPG, neutralization is necessary. Because being acidic would lead to the corrosion of construction equipment and HPG plaster is easier to get mildewed since acid is beneficial to the growth of molds. Furthermore, cement based materials has surrounded our life, mixing with a small amount of cement-based products is inevitable. Weather alkali has influence on the properties of HPG? Besides, retarder is needed to extend the setting time of HPG plaster. How about the effect of alkali when retarder is added?

It has become almost imperative to understand the exact behavior of HPG especially with retarders after neutralization to promote the development of HPG plaster which would continuously consume a large amount of phosphogypsum. Investigations were, therefore, undertaken regarding the setting and hardening characters of HPG plaster at different pH after neutralization. Data obtained from the hydration reaction and microscopic studies in the alkaline condition were reported and discussed in this paper. Amazingly, the hydration process of HPG plaster in the alkaline condition was adversely affected.

2. Experimental

2.1. Materials

HFGD in Sichuan Panzhihua electric power plant of China was chosen and HPG was from Longmang Co., Ltd., in Deyang city Sichuan province China, which was produced after three times washing. As an industrial byproduct, the radioactivity of HPG must be take into account, the testing results was shown in Table 1. It is clear that the internal exposure index ($I_{Ra} = 0.281$) and external exposure index ($I_r = 0.686$) totally meet the requirements ($I_{Ra} \leq 1.0$, $I_r \leq 1.0$) in Chinese standard (GB 6566-2001). In fact, the radioactivity of PG is associated with phosphate rock and the radioactivity of PG in most part of china meet the requirements as reported [15]. The chemicals used as retarders were citric acid (CA), sodium tripolyphosphate (STPP), Plast Retard PE (PE), Retardan-200P (XK) and HS (made in China). The chemical compositions of the raw materials were given in Table 2.

2.2. Samples shaping

Firstly, the hemihydrate powder and the corresponding water (the water to powder which is the water requirement for normal consistency is 0.65 and 0.58 for HPG and HFGD, respectively) were weighed. After that, retarder and lime powder were the first to added into water by mass percent of hemihydrate powder when needed and stirred for 2 min, and then hemihydrate powder was added and mixed for 3 min. At last, the homogeneous slurry was poured into a triplicate molds with size of 40 × 40 × 160 mm to shape through vibration. The specimens was unmold after 24 h and then cured in a room with 60% R.H and temperature of 20 ± 1 °C.

2.3. Test methods

2.3.1. Physical properties testing

The water requirement for normal consistency is tested by consist-meter which is a steel cylinder with a height of 100 mm and a diameter of 50 mm. Hemihydrate plaster after stirring with a certain ratio of water was poured into steel cylinder and the added water is the water requirement for normal consistency when the expanded diameter of hemihydrate plaster was in the ranges of 180 mm ± 5 mm after lifting the cylinder vertically. The setting time of hemihydrate plaster were examined by Vicat apparatus specified in GB/T 9776-2008 [23] in China. The compressive strength at 2 h and 1 d were tested immediately after demolding while the specimens after curing for seven days were dried at 40 °C until the weight is constant and then the compressive strength at 7 d was tested. The chemically combined water was tested according to Chinese standard GB/T 5484-2012 [24]. About 1 g powders (m_1) of hemihydrate or grinding hydrated samples after drying at 40 °C were dried at 230 °C in the oven for 1 h and then weighed (m_2) after cooling down to room temperature. The samples were dried and weighed again and again until the m_2 keeps constant. The chemically combined water was calculated as follows: $W_{combined\ water} = \frac{m_1 - m_2}{m_1} \times 100\%$.

2.3.2. pH testing

Hemihydrate powder was stirred for 5 min after mixing with water (the ratio is 1:10) and then let it stand for 25 min. After that, the upper supernatant were used for pH testing by a Digital pH Meter Model PHS-25 (Leici, Shanghai). Lime powdered $Ca(OH)_2$, (0.1 to 0.4 by wt% of hemihydrate powder) was added to neutralize hemihydrate plaster in alkaline range (pH 7.19–11.08). The hydration degree was calculated through chemically combined water.

Table 1
The radioactivity of HPG.

No.	Nuclide	Total counts	Specific activity	Rate	Uncertainty
1	Th232	33433c	94.91 Bq/kg	11.04%	4.41%
2	Ra226	17744c	56.30 Bq/kg	6.55%	6.3%
3	K40	9590c	708.79 Bq/kg	82.42%	7.64%

Internal exposure index $I_{Ra} = 0.281(\pm 6.98\%)$, external exposure index $I_r = 0.686(\pm 3.81\%)$.

Table 2
Chemical compositions (by mass %) of raw materials.

Compositions(%)	SO_3	CaO	SiO_2	MgO	Cl	Fe_2O_3	Al_2O_3	P_2O_5	SrO	K_2O	TiO_2	Chemically combined water
HFGD	51.6	46	0.645	0.586	0.282	0.28	0.258	–	–	–	–	5.34
HPG	50.3	38.1	5.48	0.461	0.187	1.31	1.84	0.956	0.902	0.213	0.168	4.7