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Utilization of original phosphogypsum as raw material for the preparation of self-leveling mortar

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ABSTRACT

The accumulation of phosphogypsum from fertilizer industries occupies considerable land resources and causes serious environmental problem. This work aims to study the possibility of recycling original phosphogypsum as raw material for the manufacture of self-leveling mortar. Thus an experimental study was carried out to evaluate the fluidity, flexural strength, compressive strength, shrinkage, bond strength and wear resistance of self-leveling mortar prepared with original phosphogypsum, and the role of phosphogypsum in mortar was also investigated by theoretical analysis, XRD, TG-DSC and ESEM. In addition, the cost of self-leveling mortar prepared with original phosphogypsum was also discussed. The results indicate that all the properties of self-leveling mortar can meet the requirements of Chinese standard (JC/T985-2005) even when the content of phosphogypsum comes up to 55%. Phosphogypsum in mortars not only acts as fillers but also takes part in the hydration of cements. This work provides a method for the direct use of phosphogypsum and offers a high performance mortar used in civil engineering. Besides, the cost of this innovative mortar has been reduced dramatically due to the addition of waste material.

1. Introduction

China, as a large agricultural country, consumes large quantities of phosphate fertilizers every year. In 2005, the phosphate fertilizer production of China ranked the first in the world; in 2012, it reached 16.93 million tons P_2O_5 and occupied about 40% of worldwide production. The production of phosphate fertilizer cannot be accomplished without phosphoric acid. Over 90% of phosphoric acid is manufactured through the wet process technique which features dissolving phosphorus ore with sulfuric acid and phosphogypsum (PG) is a waste byproduct from this processing (Yang et al., 2013; Tayibi et al., 2009). The wet process is economical but generates a large amount of PG, about five tons of PG is generated per ton of phosphoric acid. The average annual production of PG exceeds 22 million tons in China and the worldwide PG generation is estimated to be around 100–280 million tons per year (Tayibi et al., 2009; Kuryatnyk et al., 2008; Degirmenci, 2008; Altuna and Sert, 2004; Yang et al., 2009; Sahu et al., 2014). For chemical composition, PG is primarily composed of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) but also contains some impurities, such as H_3PO_4, $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4 \cdot 2H_2O$ and $Ca_3(PO_4)_2$, residual acids, fluorides (NaF, Na_2SiF_6, Na_3AlF_6, Na_3FeF_6 and CaF_2), sulfate ions, trace metals (e.g. Cr, Cu, Zn and Cd) and organic matter as aliphatic compounds of carbonic acids, amines and ketones, adhered to the surface of the gypsum crystals (Rutherford et al., 1996; Tayibi et al., 2009). In physics, PG is a powdery material that has little or no plasticity, with particle density ranging from 2.27 to 2.40 g cm^{-3} and bulk density varying between 0.9 and 1.7 g cm^{-3}. What's more, fresh PG contains lots of free water and usually exceeds 20% in weight (Rutherford et al., 1996). From a morphological point of view, PG has a marked crystal structure, mostly in rhombic and hexagonal forms (Raјković and Tošković, 2003).

Owing to the typical characterization of PG, strong acidity ($pH < 3$) and high moisture content, only 15% of worldwide PG production is recycled as building materials, agricultural fertilizers or soil stabilization amendments and as set controller in the manufacture of Portland cement (Rutherford et al., 1996). Vast stockpiles of PG are mainly located in the US, Canada, Europe,

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Australia, Japan, India and China (Kadirova et al., 2014). Usually, PG is discarded without any treatment, which not only occupies considerable land resources but also causes serious environmental problems, including water, air, and soil pollution which can eventually damage human health and ecosystems (Rutherford et al., 1996; Kadirova et al., 2014). Recently, more and more researchers have devoted to the recycling and reuse of PG. Kadirova prepared a low-cost inorganic sorption materials using PG and kaolin (Kadirova et al., 2014); Kumar utilized PG for manufacturing of hollow blocks (Kumar, 2003); Shen prepared a new type of lime-fly ash-phosphogypsum binder (Shen et al., 2007); Cuadri proposed a novel application for PG as a modifier of bitumen for flexible road pavements (Cuadri et al., 2014); Zhou manufactured cement-free non-fired PG bricks by a novel two-step hydration process (Zhou et al., 2014); Rashad provided a potential use of PG in alkali-activated fly ash paste (Rashad, 2015), etc. Although positive results have been obtained from references, several problems still exist at present: (1) most of the available technologies are complex and the investment cost is much high; (2) PG needs to be pretreated before using, e.g., water washing, calcining, neutralizing, which increase the cost and maybe cause secondary pollution; (3) compared to natural gypsum, the actual use of PG is less satisfactory; (4) the ROI (return on investment) and economic efficiency are low, which will not draw the investors' attentions. Then, how to effectively recycle and utilize PG is a great challenge to researchers, enterprises and government.

Cement is a vital construction material and a strategic commodity, which is also considered as the most important material in terms of sheer mass in human civilization (Imbabi et al., 2012; Swanson, 2015). With the rapid development of the economy, China has become the world's largest cement production country since 1985, and its output has accounted for over half of the total in the world since 2006 (Xu et al., 2015). The fact that China used more cement (around 6.4 billion tons) between 2011 and 2013 than the US used in the entire 20th Century stunned Bill Gates (Swanson, 2015). Total world consumption of cement-based materials is in close proximity to water (Mehta and Monteiro, 2014); undoubtedly, cement-based materials have the most potential in consuming industrial waste materials now and in the future.

Self-leveling mortar (SLM), a special mortar having the ability to fill the form and consolidate under its own weight without any compaction energy, is widely used in China in recent years due to increasing labor cost and customers' demand. SLM is well known for its properties in fresh state (fluidity, cohesiveness and homogeneousness) and hardened state (rapid hardening, early strength, shrinkage compensation, smooth surface and good durability), and suitable for using in various fields, such as schools, hospitals, factories, parking lots, vessels, stores, apartments, office building and so on (Safi et al., 2013; Onishi and Bier, 2010). However, one big disadvantage of SLM is its cost associated with the use of chemical admixtures, high aluminum cement and high volumes of powders. One solution to reduce the cost of SLM is to add some waste materials as substitution. In recent literature, several waste materials have been used as raw materials for the manufacture of SLM, such as plastic waste (Safi et al., 2013), seashells (Safi et al., 2015), grounded slate from quarrying waste (Barluenga and Olivares, 2010), fly ash and brick powder (Sahmaran et al., 2006) and so on. These inspired our interest to study on utilizing phosphogypsum (PG) as raw material for the preparation of SLM. Firstly, the addition of PG in SLM instead of natural materials can reduce the total cost. Secondly, the calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) of PG reacts with aluminum-containing minerals in cements, resulting in the formation of expansible ettringite that can take the effect of shrinkage compensation in SLM (Georgin et al., 2008; Tayibi et al., 2009). Thirdly, the free water in PG is also necessary to the preparation of SLM. In addition, the residual acids in PG can retard the setting time of mortar and ensure the workability.

Thus original PG, which was not treated in any way, was directly used as raw material for the manufacture of SLM in this study. It aims to provide a method for the use and recycling of PG and offer a high performance mortar used in civil engineering. Mix proportions and properties of SLM were investigated systematically and the role of PG in mortar was investigated by theoretical analysis and experiment tests. The cost of the production was also analyzed at last.

2. Experimental

2.1. Raw materials

Ordinary Portland cement 42.5R (OPC, similar to ASTM C150 Type I cement) and Sulphoaluminate cement 42.5R (SAC) were used in this work. The chemical compositions of OPC and SAC are shown in Table 1. PG was obtained from phosphate fertilizer plant in Yun Nan with water content of 16.4% and specific gravity of 2.35 (by vacuum supply). The chemical compositions of PG are also shown in Table 1. The apparent morphology and particle size distribution of PG are shown in Fig. 1, which is a powdery material without plasticity, the particle size ranges from 1.6 μm to 208.9 μm and the mean particle size (d_{50}) is 51.6 μm. As an industrial byproduct used for the building materials, the radioactivity of PG is an important index and restricted in Chinese standard. Then, it was tested strictly in this study and the result is shown in Table 2. The internal exposure index ($I_{Ra} = 0.227$) and external exposure index ($I_r = 0.332$) fully meet the requirements ($I_{Ra} \leq 1.0$, $I_r \leq 1.0$) of Chinese standard (GB6566-2001). Quartz sands with two particle size gradings were used in this study, Class A (30–50 mesh) and Class B (40–70 mesh). Polycarboxylate superplasticizer with solid content of 40% was used. Sodium borate (AR) was added into the mixture to retard setting. Defoaming agent (Agitan P803, MUNZING-CHEMIE) was also used.

2.2. Mix proportions and preparation process of SLM

As shown in Table 3, fourteen mix proportions of SLM were designed and all raw materials were calculated by mass percent. PG was measured in dry mass though it contained 16.4% water. In addition, the dosages of superplasticizer, sodium borate and defoaming agent are 0.4%, 0.08% and 0.02% by mass of total solid, respectively. The mixtures of A-1–A-5 were used for investigating effect of SAC and OPC proportions (SAC:OPC = 4:6, 5:5, 6:4, 7:3 and 8:2) on the properties of SLM. The mixtures of B-1–B-5 were used for investigating effect of quartz sand grading on the properties of SLM, and the grading was obtained by blending Class A and Class B in proportions of 0:10, 3:7, 5:5, 7:3 and 10:0. Effect of PG content on the properties of SLM were achieved from mixtures of C-1–C-4.

In accordance with above mix proportions, all solid materials were weighed and mixed in the planetary mixer for 30 s before adding water. Then superplasticizer, sodium borate and defoaming agent with two thirds of required water were poured into the mixture and mixed again for 30 s. Next, the remaining water was added and mixed for another 30 s. After that, the fluidity of the mortar was measured and the specimens used for property test were prepared.

2.3. Test methods

The fluidity, shrinkage, wear resistance and bond strength of SLM were tested in accordance with Chinese standard (GB/T