RECYCLING OF INDUSTRIAL WASTE PHOSPHOGYPSUM FOR PRODUCING NO-CEMENT MORTAR

TÁI CHẾ PHẾ THẢI CÔNG NGHIỆP PHOSPHOGYPSUM TRONG SẢN XUẤT VỮA KHÔNG XI MĂNG

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Abstract - The present study aims to investigate the possibility of recycling phosphogypsum (PG), which is a by-product of the fertilizer industry, for producing no-cement mortar (NCM). The PG powder was mixed with ground granulated blast furnace slag (GGBFS), carbide slag (CS), calcium hydroxide (CH) at different compositions to prepare the NCM samples for the investigation. A systematical evaluation about characteristics of the NCM was reported at both fresh and hardened stages, including flowability, setting time, unit weight, and compressive strength. Additionally, microstructural properties of the NCMsamples were examined using advanced analysis techniques of a scanning electron microscope (SEM) and X-ray diffraction (XRD). Furthermore, a cost analysis was also performed to show the capability of the real application. The test results show great potential for utilizing the above materials for the production of NCM with properties that meet the requirements for real practice.

Key words - Phosphogypsum; no-cement mortar; carbide slag; compressive strength; microstructure

Tóm tắt - Nghiên cứu này nhằm tìm hiểu khả năng tái chế phosphogypsum (PG), một phế phẩm của ngành công nghiệp phân bón, trong sản xuất vữakhông xi măng (NCM). Bột PG được trộn với xỉ lò cao nghiền mịn (GGBFS) và xỉ các bua (CS) hoặc canxi hyđrôxít (CH) với các hàm lượng khác nhau để chuẩn bị mẫu NCM dùng cho nghiên cứu. Một hệ thống đánh giá đặc tính của NCM đã được báo cáo ở cả giai đoạn tươi và đóng rắn, bao gồm: độ chảy, thời gian ninh kết, khối lượng thể tích và cường độ chịu nén. Ngoài ra, các tính chất vi cấu trúc của các mẫuNCM đã được kiểm tra bằng các kỹ thuật phân tích tiên tiến của kính hiển vi quét điện tử (SEM) và nhiễu xạ tia X (XRD). Hơn nữa, phân tích chi phí cũng được thực hiện để đánh giá khả năng ứng dụng ngoài thực tế. Các kết quả thực nghiệm cho thấy một tiềm năng lớn trong việc sử dụng các vật liệu nêu trên vào sản xuất NCM với các tính chất đáp ứng các yêu cầu cho ứng dụng ngoài thực tế.

Từ khóa - Phosphogypsum; vữa không xi măng; xỉ các bua; cường độ chịu nén; vi cấu trúc

1. Introduction

Phosphogypsum (PG) is a waste material generated by the phosphate fertilizer industry, which produces millions of tons annually. Global production of this waste is from 100 to 280 million tons per year [1]. The high level of this pollutant was found and the huge occupation of stacks represents an environmental concern. The long-term burial and storage of the hazard substance expose economic as well as harmful environmental issues. The unscientific discharge of PG not only leads to serious environmental contamination but also occupies considerable land resource [2]. About 85%waste PG is directly disposed to the environment without any further treatment, which can consume considerable land resources and cause serious environmental problems [3, 4]. Therefore, strong efforts have been made in the comprehensive utilization of PG, e.g. using PG as a set retarder in Portland cement [5]. In addition, Zhou et al. [6] indicated that without adding any binder such as cement or organics, as high as 75% of waste PG is facilely prepared into non-fired bricks only with small quantities of river sand, which is significant to cost-effectively recycle the waste PG and to solve its environmental pollution.

This topic has been found necessary to cope with the above-mentioned problems. Thus, to realize the objectives of the present works, various parameters from experiments were investigated to show the potential recycling of waste PG. The main objective of the present study is to produce no-cement mortar (NCM) from 100% industrial wastes, in which using a large quantity of waste PG is in priority. Turning waste materials into construction material are found to be the most suitable way of consuming a large number of waste materials, e.g. PG. In this work, PG was used as raw material for the manufacture of NCM.

Up to now, with the restriction in terms of theoretical and practical data and not widely applied (only in some regions and some types of applications), there are few studies regarding the use of industrial wastes for producing NCM. Moreover, since the information regarding the use of blended PG, ground granulated blast furnace slag (GGBFS), carbide slag (CS), and calcium hydroxide (CH) is limited in the literature, the present study focuses on the recycling of these waste materials for manufacturing NCM. In this research, both fresh and hardened properties of the NCM were studied in order to evaluate the possible application of PG for construction products. Moreover, the advanced analysis techniques of scanning electron microscope (SEM) and X-ray diffraction (XRD) were applied to examine the microstructural properties of the NCM. Furthermore, a cost analysis was also performed in this investigation.

2. Materials and experimental programs

2.1. Materials

Binder materials used for the preparation of the NCM samples were PG, GGBFS, CS, and CH. PG is an industrial waste that is collected from the manufacture of fertilizer and phosphoric acid production process. GGBFS is a by-product of iron manufacturing in a blast furnace. CS, also known as calcium carbide residue, is a solid waste of the hydrolysis of calcium carbide. It is commonly generated from the industrial production of ethylene and polyvinyl chloride. As a kind of industrial wastes, it has no value for recovery and is commonly landfilled. CH is an inorganic compound, which is obtained when calcium oxide is mixed with water. Fine aggregate used was natural crushed sand with density, water absorption, and fineness modulus of 2650 kg/m^3, 1.4%, and 3.0, respectively. It is noted that all of the raw materials used were in air-dry condition. These materials were examined of both physical and chemical properties before being used, with the results shown in Table 1 and Table 2, respectively. Characteristics of the raw materials were presented in section 3.1.

Table 1. *Physical properties of starting materials*

Physical properties	PG	GGBFS	CS	CH
Specific gravity	2.56	2.91	2.58	2.21
Mean particle size (μm)	20.2	7.84	49.9	11.1
Specific surface area (m^2/kg)	353.9	744.3	150.0	556.5

Table 2. *Chemical composition of starting materials*

Chemical composition (wt.%)	PG	GGBFS	CS	CH
SiO_2	25.4	35.6	5.6	0.9
Al_2O_3	11.2	11.3	2.8	2.4
Fe_2O_3	9.8	0.5	1.1	0.1
CaO	45.7	41.0	86.6	93.6
MgO	-	6.5	0.3	-
K_2O	1.7	0.6	0.2	-
Na_2O	0.9	0.3	0.6	-

2.2. Mix design and proportions

Two different NCM mixtures with various compositions of PG, GGBFS, and CS or CH were prepared for this investigation using the same water-to-binder (w/b) ratio of 0.34 and aggregate content of 20% (by total weight of binder). In addition, different dosages of super plasticizer (SP) were added to the NCM mixtures in order to achieve the desired workability of the fresh mortar. The ingredient proportions (by mass) of the NCM are given in Table 3.

Table 3. *Mix proportions for the preparation of NCM samples*

Mixture	Material proportions (kg/m^3)						
	PG	GGBFS	CS	CH	Sand	SP	Water
PCS	528.3	528.3	211.3	-	253.6	4.1	430.8
PCH	574.7	574.7	-	114.9	252.9	3.6	427.9

2.3. Samples preparation and test methods

A laboratory mixer was used to mix all of the raw materials homogenously. Right after mixing, the fresh NCM mixture was checked for slump flow, setting time, and unit weight following the guidelines of ASTM C1437[7], ASTM C807[8], and ASTM C138 [9], respectively. Then, the NCM samples with dimensions of 50×50×50 mm were prepared for the test of compressive strength. These samples were cured in the lime-saturated water until the testing ages. The compressive strength test was performed at the sample ages of 1, 7, 14, and 28 days in accordance with ASTM C109[10]. The reported result was the average strength value of three samples from each mixture. In addition, broken pieces of the samples at 28 days that were taken right after the compression test were immersed in alcohol to stop hydration and then their microstructure was examined using SEM and XRD analysis.

3. Results and discussion

3.1. Characteristics of raw materials

The particle size distribution, SEM images, and XRD patterns of the starting materials are presented in Figures 1–3, respectively. It can be seen from Table 1 and Figure 1 that the particle size of the PG and CS were significantly larger than that of the GGBFS and CH particles. Generally, the smaller the particle size of the materials, the greater the potential rate of the involvement in the chemical reaction is. Moreover, it could be observed from the SEM images of the raw materials (Figure 2) that all of the materials are mostly comprised of particles with the irregular shape of different sizes. However, the homogeneous performance will be improved in a system that incorporated both smaller and larger particles size.

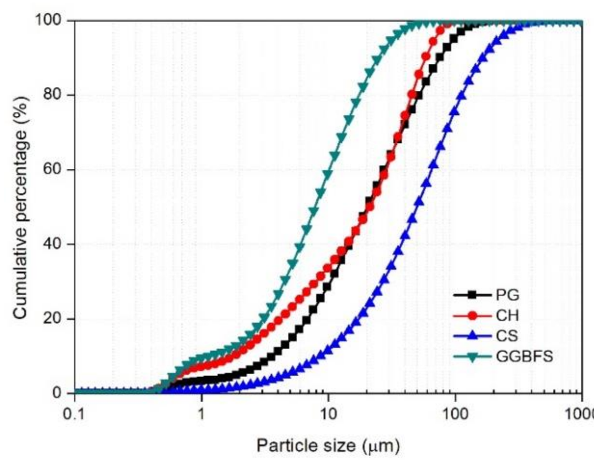

Figure 1. *Particles size distribution of starting materials*

On the other hand, as presented in Table 2, a high concentration of calcium oxide (CaO) was detected in all of the binder materials, whereas large percentages of silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) were found in PG and GGBFS. The GGBFS comprises mostly amorphous SiO_2, Al_2O_3, CaO, and MgO. The non-crystalline phases make GGBFS more active than other materials mentioned in Figure 3. The PG comprises majorly calcium sulfate hydrate and gypsum whereas the CS and CH comprise crystalline phases of ardealite and portlandite. It is well-known that the crystalline phase generally less involves in the chemical reaction.

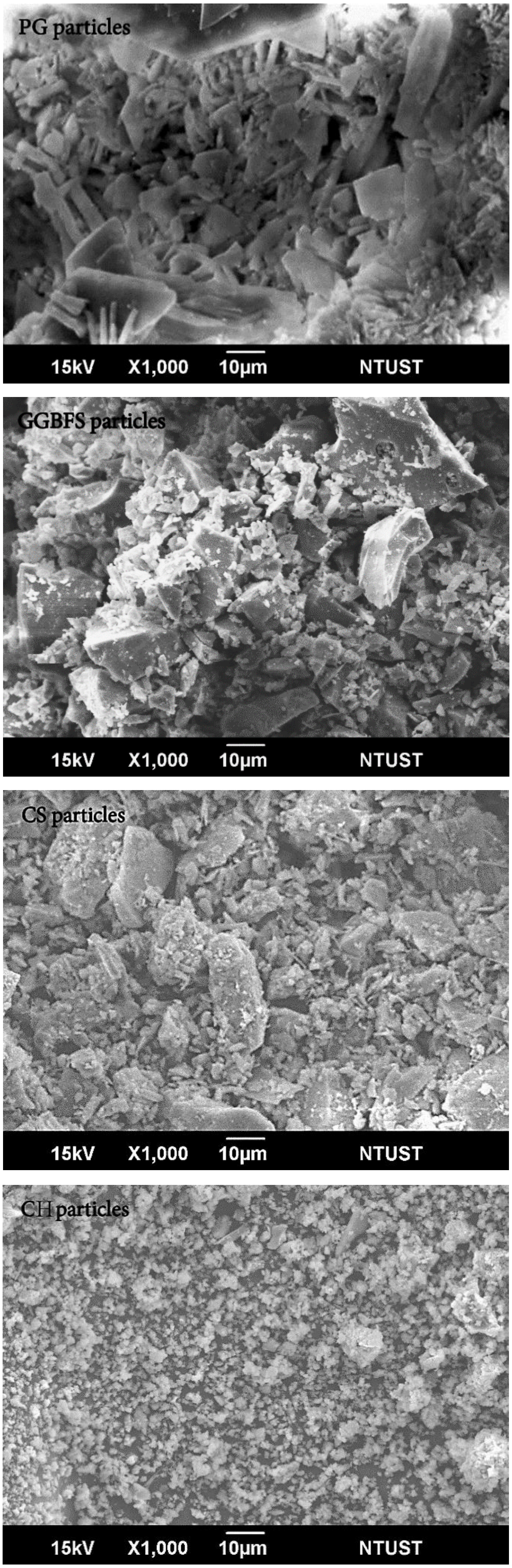

Figure 2. *SEM micrographs of starting materials*

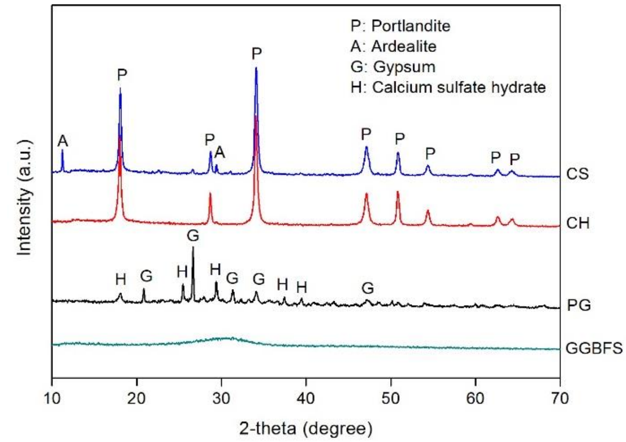

Figure 3. *XRD patterns of starting materials*

3.2. Properties of fresh mortar mixtures

Properties of fresh NCM mixtures, including slump flow measurement, unit weight, and setting time are presented in Table 4. As a result, all of the NCM mixtures exhibited good performance characteristics in the fresh stage. The PCH mixture had a slump flow value and setting time of lower and longer than that of the PCS mixture, respectively. In general, a common slump flow value of greater than 190 mm, which is acceptable for the high-flowing application, is suggested. Hwang and Huynh [11] pointed that the combined effect of both the irregular shape of slag particles (Figure 2), inhibits the lubricant effect and the very fine slag particles with a high specific surface area (Table 1), which absorbs more water on the particle surfaces and in internal pores, leading to a loss in flowability of the fresh mortar mixture.

Initial setting time (IS) and final setting time (FS) are features that are used to evaluate the pozzolan reaction. In other words, it indicates the chemical reaction rate when incorporatingdifferent materials into the nocement mixture as shown in Table 3. Table 4 lists the setting times of two NCM mixtures. As a result, the IS and FS of both PCS and PCH mixtures ranged from around 8.55 to 9.35 hours and 15.65 to 16.12 hours, respectively. It can be seen that the IS of the PCH samples is longer than the PCS samples. The increased setting time may be due to the impurities in PG, which retards the setting of the binder [2].

The unit weight of PCH mixture was also higher than that of the PCS mixture. This is due to the incorporation of more PG and GGBFS in the mixture (Table 3). The higher specific gravity values of these materials (Table 1) compared to the other materials in the mixture contribute to the higher unit weight value.

Table 4. *Properties of fresh mortar mixtures and material cost*

Mixture	Slump flow (mm)	Fresh UW (kg/m^3)	Initial setting (min)	Final setting (min)	Cost (VND/m^3)
PCS	300	1910	513	939	436200
PCH	295	1995	561	967	521400

Note: UW = Unit weight.

3.3. Compressive strength development

The development in the compressive strength of both

PCS and PCH mixture is presented in Figure 4. There is a gradual increase in mechanical properties during the curing time. It can be clearly seen that there is limited early-strength development because both PCS and PCH reached under 35% of the compressive strength in 7days. But the linear enhancement during the time testing provides reliable evidence to predict growth of strength. The results indicated that PCH mixture was stronger than PCS mixture at the same testing condition. It may be understood that the lower compressive value of the PCS due to its composition. As can see from Table 3, the higher content of PG and GGBFS help to improve the compressive strength of mortar. In the PCH, the smaller mean size particle of PG and GGBFS plays an important role in filling the void within the mixture. Additionally, the high content of SiO_2 in GGBFS and PG reacted with the appearance of CH in composition to create C-S-H which is the binder's component. Moreover, the very fine particles greatly contribute to improving the hydration rate, in which PG and GGBFS may act as an accelerator and develop the strength of the mortar samples.

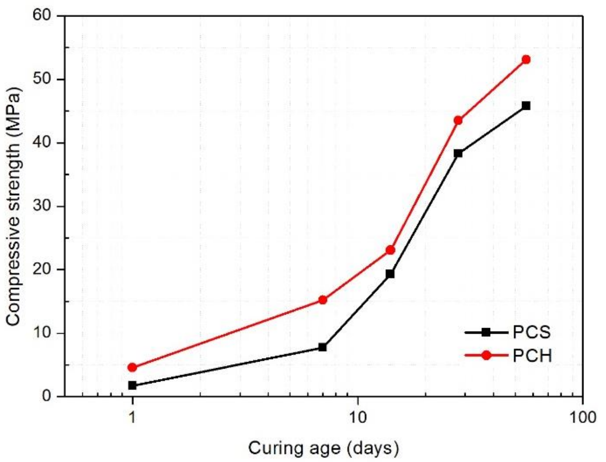

Figure 4. *Compressive strength development of the hardened mortar samples*

3.4. Microstructure analysis

The results of the chemical analysis are presented in Figure 5 (SEM) and Figure 6 (XRD). As can be seen from Figure 5 that the SEM micrographs displayed the micro-structural of the hardened mortar samples. The hydration products and the arrangement of mortar components formed a denser structure with fewer voids. A smoother and denser structure of the PCH samples could be clearly observed in comparison with the PCS samples. In fact, more voids/ pores and more incomplete reaction particles were detected from the SEM image of the PCS samples in comparison with the PCH samples (Figure 5). This characterization indicates that a homogeneous structure increases unit weight and greatly contributes to improving the mechanical strength of mortar samples.

Further, the XRD patterns of the two NCM mixtures in Figure 6 show the crystalline hydration products. The function of all materials used in this study acted not only as the pozzolanic materials but also as the filler. However, the peaks of calcium sulfate hydrate, portlandite, and gypsum were obviously detected in Figure 6, showing that the dissolution of the raw materials in the NCM mixture was not complete.

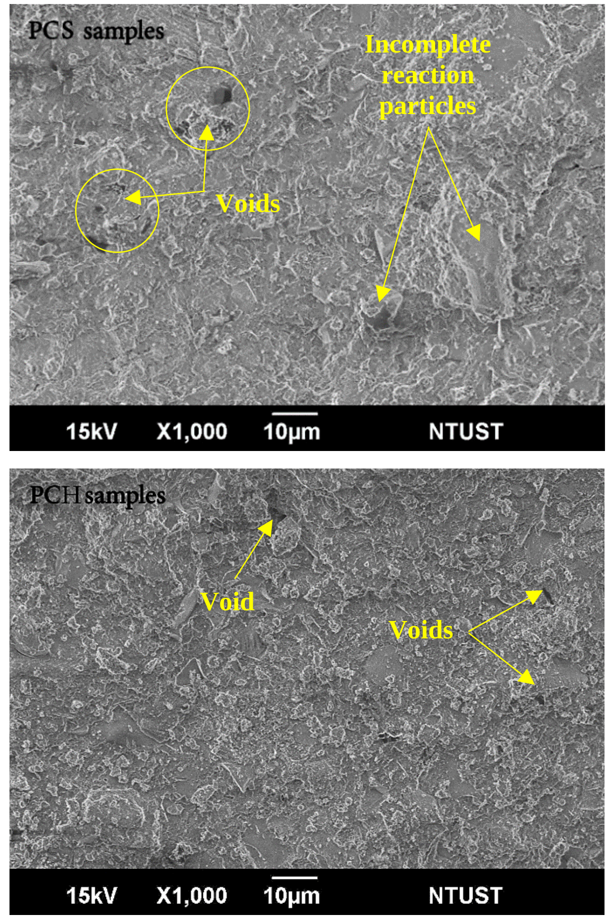

***Figure 5**. SEM micrographs of the hardened mortar samples*

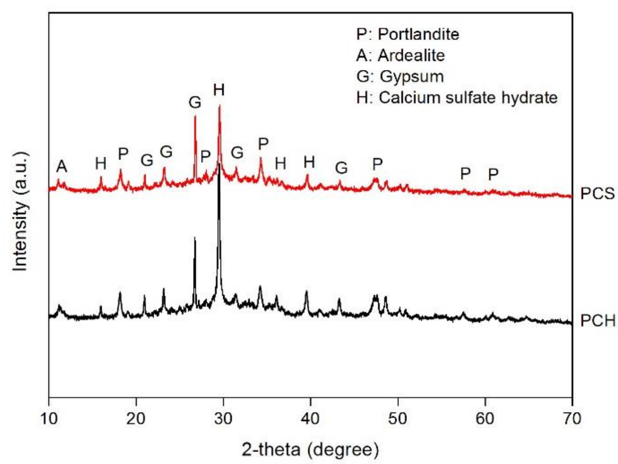

Figure 6. *XRD patterns of the hardened mortar samples*

3.5. Cost analyses

Cost is another important consideration besides the mechanical properties and quality of the mortar. Cost analysis demonstrated that the utilization of industrial wastes obtained the request for green construction material and it is the consideration for a friendly and sustainable product to the environment. So far, the cost of GGBFS is much higher than that of PG. Thus, using less GGBFS in NCM mixtures was found to have cost-effectiveness.The total material cost for both PCS and PCH was calculated with the unit cost for PG, GGBFS, CS, CH, sand, and SP were 0, 510, 272, 1020, 170, 15300 VND/kg, respectively and the final values are presented in Table 4.It is noted that the cost analysis was calculated based on the unit price of construction materials announced by the local stores in Vietnam in 2018 and the labor cost, production cost, and other costs did not include in this calculation. It can be found that the saving money was up to 593800 (VND/m^3) when replacing normal cement-based mixture (1030000 VND/m^3) with PCS. Thereby, using industrial waste materials in a positive way is necessary and important.

4. Conclusions

An experimental study was performed to evaluate the mechanical properties and microstructure of the NCM using PG-GGBFS-CS-CH blends. Based on the obtained results, the following conclusions may be drawn:

1. The loss in flowability and the increase in setting time of the fresh NCM were recorded with the incorporation of more PG in the mortar mixtures. However, for achieving acceptable workability, the addition of a sufficient SP dosage is recommended for these mixtures.

2. The incorporation of the PG in mortar mixture results in a homogeneous structure, increases unit weightand cost, and contributes to improving the compressive strength of the mortar samples.

3. The crystalline hydration products were found from the XRD patterns of the mortars. In addition, the PCH mixture showed a denser structure than the PCS mixture. This finding is in good agreement with the compressive strength development of the mortar.

4. A full benefit from the utilization of the waste materials of PG, GGBFS, CS, and CH to produce the NCM in both environmental and economic aspect was clearly demonstrated in this study. Especially, it can be indicated that PG could be potentially a good alternative to cementitious materials.

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