

Vietnam Journal of Science and Technology **58** (3A) (2020)

[doi:10.15625/2525-2518/58/3A/14246](https://doi.org/10.15625/2525-2518/58/3A/14246)



PURIFICATION OF PHOSPHOGYPSUM FOR USE AS CEMENT RETARDER BY SULPHURIC ACID TREATMENT

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Received: 18 August 2019; Accepted for publication: 23 December 2019

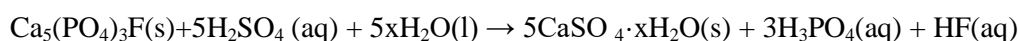
Abstract. Phosphogypsum is a by-product of the wet phosphoric acid production. In this study, chemical compositions of phosphogypsum waste (PG) in Hai Phong diammonium phosphate plant (DAP1) and Lao Cai diammonium phosphate plant (DAP2) in Viet Nam were surveyed for the purpose of gypsum recovery by P₂O₅ F removal to meet TCVN11833 for use treated gypsum as cement retarder. Studies of impurities P₂O₅, F, TOC removal by sulfuric acid 10 % at 28 °C was presented. The results found that the combination of a low concentration of sulfuric acid treatment, washing, lime neutralizing, and thermal treatment was successful in phosphogypsum treatment for use as cement retarder. The cement test proved that treated PG could partially replace natural gypsum as a retarder.

Keywords. phosphogypsum treatment, phosphorus pentoxide removal, calcium sulfate transition phase, cement retarder.

Classification numbers: 2.10, 3.7.3, 3.3.3.

1. INTRODUCTION

Phosphogypsum is a by-product of the manufacture of phosphoric acid by a wet chemical process according to the main reaction [1, 2]:



where x depends on the temperature, acid concentration and either anhydrites (AH) (x = 0), hemihydrates (HH) (x = 1/2), dihydrates (DH) (x = 2) or a combination of these is crystallized from acidic solution by a specific operation condition. About 5 - 6 % of natural gypsum used by the cement industry as a set retarder for Portland cement added to the clinker at the cement grinding stage [3, 4]. The phosphogypsum (PG) consists of 80 - 90 % of gypsum that could

replace natural gypsum in Portland cement, however a small quantity is used, the main reasons for the low demand and use are its high moisture content and impurities such as phosphorus, fluoride and organic impurities contained in phosphogypsum interfere in an unpredictable way to delay the setting time and decrease the mechanical strength development of cement [3, 4]. Up to 80 % of H_3PO_4 is produced all over the world by applying dihydrate process (DH) [5]. Hemihydrates technology of H_3PO_4 production is used rarely due to strict operation conditions. However, the dihydrate process has two shortcomings: one is the process of producing co-precipitated phosphorus in $CaSO_4 \cdot 2H_2O$, thus the loss of 4 - 6 % P_2O_5 and low H_3PO_4 grade 28 - 32 % [5] and higher impurities. Impurities in PG cause the hesitation for cement companies in its application. The improvement of existing technology of DAP fertilizer plants to create cleaner PG and resource recovery has become urgent. Our study focuses on the removal of residue P_2O_5 from phosphogypsum generated from two diammonium phosphate (DAP) fertilizer plants in Viet Nam. Phosphogypsum may not always be suitable for direct use in Portland cement and therefore it needs additional purification by using sulfuric acid. This paper aims at studying impact of different experimental parameters on P_2O_5 removal. Namely, the key parameters such as reaction temperature, H_2SO_4 concentration, reaction time, liquid/solid ratios and stirring rates were investigated and optimized.

2. MATERIALS AND METHODS

2.1. Materials and reagents

All the chemical reagents used in the experiments were obtained from commercial sources. PG waste collected at dumping sites (DAP1b, DAP2b) and newly discharged from production lines (DAP1m, DAP2m) of DAP1 and DAP2 fertilizer plants. Samples were dried at 45 °C, for 10 hours grinded to pass 200 meshes sized.

2.2. Analytical methods

pH was measured by electrometric procedure. Moisture content was measured by the sample quantity changing between before and after the oven-drying procedure at 105 °C. Metal oxide analysis was performed by X-ray fluorescence (model XRF 5006-HQ02: 30 kV, 50 uA, 23 °C). Measurements of total organic carbon (TOC) by Wiley Black method, total and soluble phosphorus pentoxide according to APHA 4500.P, soluble and total fluorine were determined by UV Vis (1800 Shimadzu); and elements of C, H, N, S by Flash 2000 – USA. SO_3 were determined by TCVN8654:2011 methods. Phase transition of $CaSO_4$ in PG was analyzed by X-ray diffraction (XRD). Effectiveness of P_2O_5 separation was calculated by equation:

$$R (\%) = \frac{C_o - C_e}{C_o} \times 100$$

where R is phosphorus pentoxide separation yield (%), C_e is concentration of dissolved phosphorus pentoxide in H_2SO_4 extraction solution (%); C_o is original concentration of phosphorus pentoxide in phosphogypsum (%).

2.3. Experiments

100 g of each of the phosphogypsum samples were stirred in sulfuric acid (0 % - 35 %) for 30 - 180 minutes at temperatures of 28 °C, 50 °C, 70 °C and 90 °C, at different ratios of sulfuric acid volume (ml) and phosphogypsum quantity (g) (L/S ratios-ml/g) from 1/1 to 5/1 (ml/g).

Samples were then filtrated and measured dissolved P_2O_5 . In some conditions, solid phase without washing/washing is stored for testing in X-ray diffraction. Solid phase was washed 3 times by the same volume of water, saturated by lime solution, dried at temperatures of 45 -140 °C. Samples were then analyzed by X-ray fluorescence and chemical analyses to determine the impurities removal, measured by X-ray diffraction to know the phase transition of the calcium sulfate at treated conditions, as well as phase transition between DH/HH, HH/DH and DH/AH forms due to acid concentration and temperature.

2.4. Cement tests

Natural gypsum, untreated and treated phosphogypsum by selected conditions were mixed with clinker in a ball mill to reach Blaine fineness of (3500 ± 100) cm^2/g for cement tests by the Institute of Science of Construction Material – Ministry of Construction and Dinh Vu Gypsum Joint Stock Company in May-July 2019. The SO_3 contents of the input materials (clinker, natural gypsum, treated/untreated PG) were first determined by chemical methods. Natural gypsum, PG and treated PG samples were then mixed with the clinker to achieve a final SO_3 content of 2.3 % in the cement. The comparative studies were made to get insights from the different impacts of treated PG (replaced for natural gypsum) on some mechanical characteristics of cement.

3. RESULTS AND DISCUSSION

3.1. Characteristics of phosphogypsum

The phosphogypsum compositions analyzed by XRF and chemical methods are shown in Table 1. The results showed that calcium sulfate dehydrate ranged from 73.1 % to 76.02 %; moisture content was from 25.2 % to 38.6 %, fluoride was from 0.62 % to 1.09 %, and total P_2O_5 was from 1.87 % to 4.83 %. Due to the low P_2O_5 recovery rate of existing wet technology, PG does not meet the requirement of TCVN11833:2017 to be used as cement retarder. Besides, PG also consisted of organic matters (measured by total organic carbon TOC was 1.24-1.51 %), iron, aluminum, acid and salt residues, as well as traces of rare elements Y, Sr measured (Table 1, Fig. 1a). XRD pattern of PG (Fig. 1b) indicated a large amount of $CaSO_4 \cdot 2H_2O$ crystals of high intensity peaks and also significant peaks of SiO_2 . SiO_2 which is consistent with the corresponding contents calculated from XRF data, i.e. from 10.5-13.92 %. P_2O_5 content in PG at dumping sites is lower than P_2O_5 on the filter conveyer.

3.2. Phosphogypsum solubility in sulfuric acid

L/S ratio (ml/g): The solubility of PG was compared when samples were dissolved in 0 - 35 % sulfuric acid. With sulfuric 5 %, L/S ratios was surveyed from 1 ml/g to 5 ml/g at 350 rpm, 28 °C in 1 hour and found the suitable L/S ratio of 3 having the P_2O_5 removal yield with the highest value at 61.89 % (Fig. 2a). The same finding was found by van der Merwea [6]. The L/S ratio was fixed at 3 during the next step. Besides, reaction time ranged from 20 to 180 minutes was carried out and it was found that 60 minutes at $L/S = 3$ is the optimal time to obtain the highest yield of P_2O_5 removal of 62 % and reaction time of 60 minutes, $L/S = 3$ used for next steps (Fig. 2b).

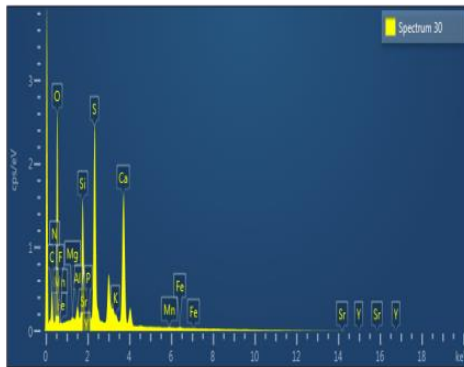


Figure 1a. EDX diagram of untreated PG of DAP1b.

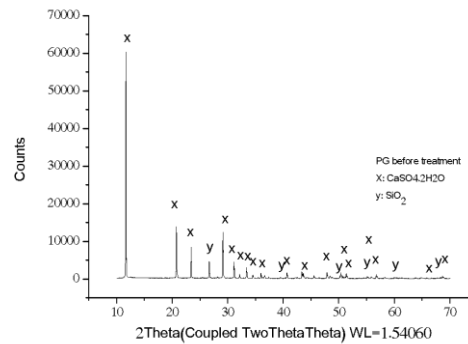


Figure 1b. XRD diagram of untreated PG at DAP1b.

Table 1. Composition of phosphogypsum in study.

Elements	Untreated PG of DAP1 (%)		Untreated PG of DAP2 (%)		Treated PG1a (%)	Natural gyps (%)
	DAP1m	DAP1b	DAP2m	DAP2b		
Moisture	38.4	25.2	38.6	27.1	20.1	-
SO ₃	35.05	36.2	33.88	34.46	41.6	42.46
P ₂ O ₅	2.35	1.15	4.32	2.03	0.4	0.02
TOC	1.24	1.44	1.34	1.51	0.5	
CaSO ₄ .2H ₂ O	76.02	77.39	73.1	74.75	87.5	92.14
CaO	25.87	26.09	24.21	24.99	31.1	30.68
F	1.2	1.012	1.29	0.86	0.41	
SiO ₂	10.485	13.92	12.3	11.55		

Treated PG1a: PG treatment at 28 °C, sulfuric 10 %, water washing 3 times (water/solid = 1), neutralization with lime milk and dried at 45 °C or sun drying for 24 hours.

Figure 2d displayed that the stirring rate of 350 rpm is the suitable rate for P₂O₅ separation.

Sulfuric concentration and temperature impacts

To study P₂O₅ separation yields the experiments were conducted at four different temperatures (28 °C, 50 °C, 70 °C and 90 °C) at stirring rate of 350 rpm during 1 hour. Then, at each temperature, the sulfuric acid concentration was set from 5 % to 35 %. The obtained results reveals that at room temperature (28 °C), P₂O₅ separation yields sharply increased when sulfuric acid concentration varied in the range of 5 % to 10 %; when sulfuric acid concentration increased beyond 10 % (from 10 % to 35 %), P₂O₅ separation yields did not change considerably (Fig. 2c). The same dependence of P₂O₅ separation yields on sulfuric acid concentration was observed for other temperatures of 50 °C, 70 °C and 90 °C (Fig. 3) At various temperatures of 28 °C, 50 °C, 70 °C and 90 °C, P₂O₅ separation yield in PG, purified accordingly with 5 % and

10 % sulfuric acid were 61.9 %, 67.6 %, 75.2 %, 79.8 % and 71.91 %, 80.56 %, 88.12 %, 92.36 %, respectively. Obviously, using of 10 % sulfuric acid was more effective than that of 5% sulfuric acid. Moreover, the impact of acid concentration on P_2O_5 separation yield was less significant compared to that of temperature (shown in Fig. 3)

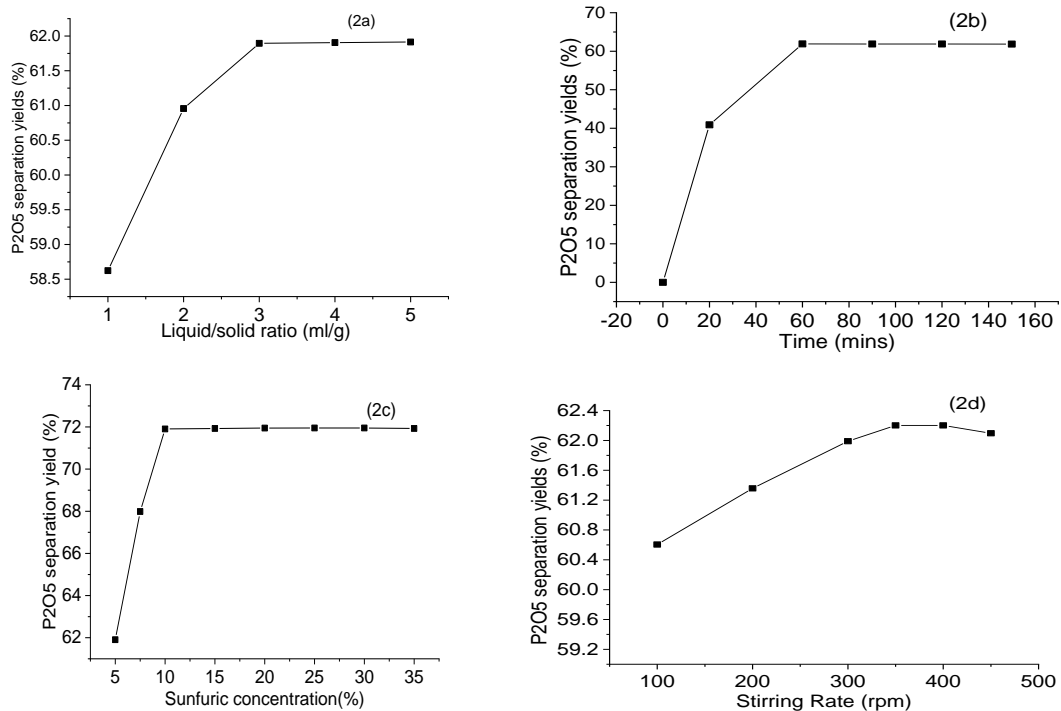


Figure 2. (a) P_2O_5 separation and L/S ratios (ml/g), (b) P_2O_5 separation and reaction time, (c) P_2O_5 separation and sulfuric concentration, (d) P_2O_5 separation and stirring rate.

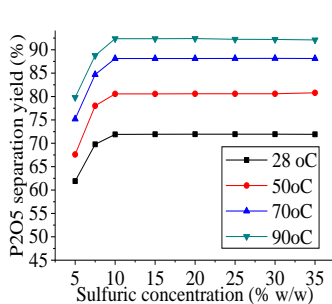


Figure 3. P_2O_5 separation - sulfuric acid concentration.

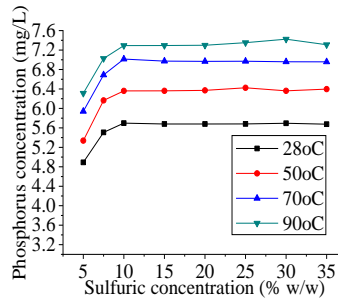


Figure 4. P_2O_5 solubility in acid solution.

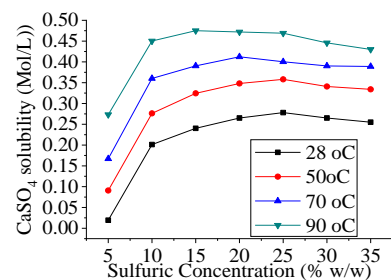


Figure 5. The solubility of $CaSO_4$ from PG in sulfuric acid.

The solubility of calcium sulfate in phosphogypsum was tested and shown in Figure 5. Figure 5 showed that the temperature factor plays an important role in the solubility of $CaSO_4$ from PG in sulfuric acid from 5 % to 35 % and at 10 % it reached the best result. Sulfuric 10 % also is the best for P_2O_5 separation yield (Fig. 3) and P_2O_5 solubility (Fig. 4). Other impurities separation yields such as F, TOC as well as the Y_2O_3 , SrO separation yields in PG was increased within the increasing of temperature (Figs. 4,5,6,7).

3.3. Phase transition between DH/HH/AH in the treatment of phosphogypsum by sulfuric acid

The CaSO_4 dihydrate of untreated PG was recognized by X-ray diffraction (Fig. 1). Dihydrate/Anhydrite CaSO_4 and gypsum/hemihydrates, hemihydrates/anhydrite were determined based on CaSO_4 solubility, under saturated, supersaturated in acid solution and temperature. Figure 5 displayed calcium sulfate solubility in sulfuric acid at differential acid concentrations and temperatures. In both normal and high temperature, CaSO_4 solubility has changed when sulfuric concentration increased from 5 % to 10 %, however when sulfuric concentration increased from 10 % to 25 %, the solubility of CaSO_4 didn't change considerably. P_2O_5 solubility experienced the same trend (Figs. 3,4 and 5). The results displayed the influence of temperature on the P_2O_5 separation, the higher temperature reached the higher P_2O_5 removed. By purifying PG with 10 % H_2SO_4 at 28 °C, washed, lime neutralized, dried 4 h at 140 °C, the obtained calcium sulfate hemihydrates phase of $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ determined by X-ray diffraction (Fig. 6a). The increase of sulfuric acid concentration to 25 % and 30 % at 90 °C created the condition for DH into AH form and the transition was recognized by X-ray diffraction (Fig. 6b, Fig. 6c), the majority of calcium sulfate was in the form of anhydrite. At sulfuric 10 %, the higher temperature showed higher impurities separation of P, F, SiO_2 and others (Fig. 7). The treated PG at normal temperature is considered for cement test.

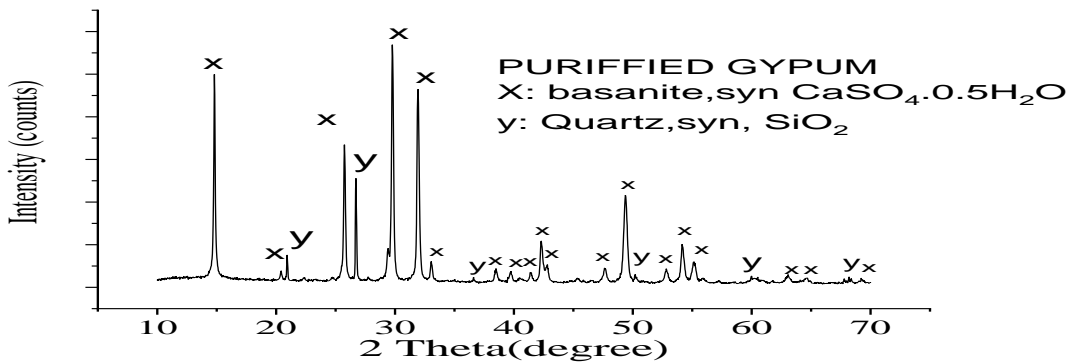


Figure 6a. XRD of PG1 – 10 % H_2SO_4 28 °C, washed, lime neutralized, filtered, dried 4 h at 140 °C, obtained calcium sulfate hemihydrates ($\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) and SiO_2 remain.

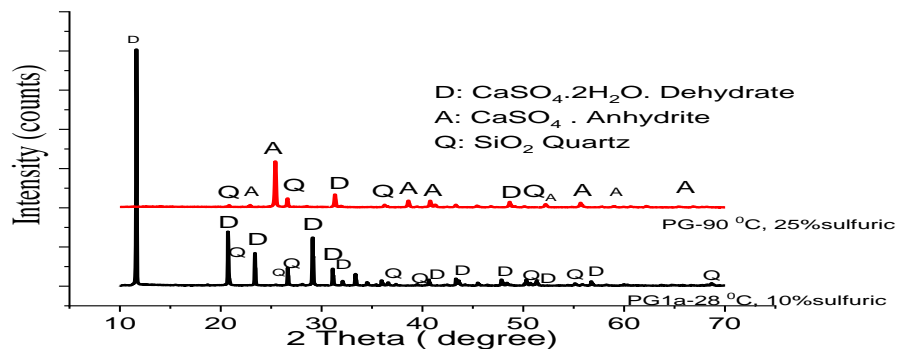


Figure 6b. XRD of PG1a treated in 10 % sulfuric 28 °C, filtered, dried 45 °C obtained $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, PG3 treated in 25 % H_2SO_4 at 90 °C, filtered, dried 45 °C, anhydrite CaSO_4 , SiO_2 .

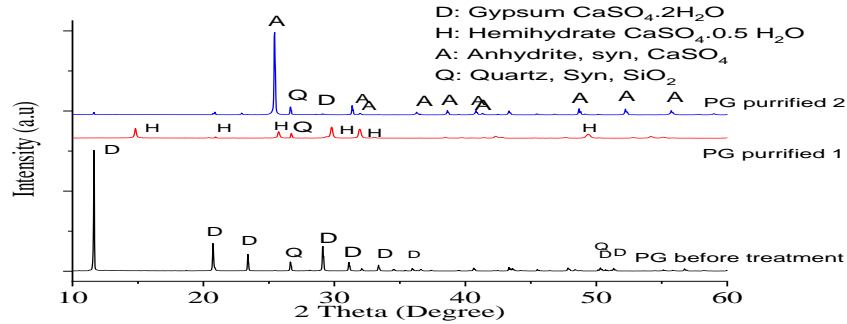


Figure 6c. Merging XRD diagrams of purified PG 1, PG2. PG1: Sulfuric 10 %, 28 °C, washed, lime neutralized filtering, drying 4 h at 140 °C. Main phase compositions are hemihydrates ($\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) and quartz (SiO_2); PG2: treated in sulfuric 30 %, 95 °C, water washing, neutralizing with lime, filtering, drying at 45 °C. Figure 6c showed that the main phase compositions of PG purified 2 are anhydrite (CaSO_4) and silicon dioxide (SiO_2).

Reported values for the gypsum/anhydrite transition temperature are 42 - 66 °C under the saturated condition with more than 40 % of water [7]. Transition temperature is very important for the production process of industrial hemihydrates materials, within the range of reported solubility data, the gypsum/basanite transition temperature may vary from less than 80 to nearly 110 °C [7]. With the sulfuric acid treatment or digestion, the CaSO_4 phase transition between DH/HH/AH, HH/AH or DH/HH and hemihydrates converted to DH, DH change phase to HH by thermal treatment 140 - 150 °C for maximal impurities removal in combination with temperature rise.

3.4. Impurity removal and cement testing



Figure 7. P_2O_5 , F, SiO_2 , TOC, Y_2O_3 , SrO separation yield.

Figure 7 displayed that treated PG with 10 % sulfuric, at both normal and high temperature at 28 °C, 50 °C, 70 °C and 90 °C in 60-minute stirring, 350 rpm are suitable for removal of P, F, TOC, SiO₂, SrO, Y₂O₃ at different impurities removal yields. After treatment at 28 °C, P₂O₅ of 0.4 %, F of 0.41 % is most feasible and met the requirements of TCVN11833: 2017 for use as cement retarder (Table 1). We chose the best condition to remove P, F, other impurities in PG by sulfuric acid 10 % at 28 °C, water washing three times and neutralizing with lime milk.

Cement testing results

Table 2 displayed the effect of retardation on cement setting in comparison among cement tests used untreated PG, treated PG and natural gypsum. The overall effect of retardation was observed. The presence of P₂O₅ and other impurities in PG make the influence on retardation that the higher impurity is, the longer setting time is. The final setting time of cement containing treated PG improved significantly compared to the final setting time of untreated PG. The final setting time of test cement made by untreated PG was from 4.7 to 4.8 hours. The final setting times of the test cement containing treated PG was from 2.75 to 2.83 hours. The final setting time of control cement was from 2.25 to 2.67 hours. Result of test cement containing treated PG was as good as control cement. The difference in final setting time between test cement and control cement was below 2 hours, responded to TCVN 11833. Table 3 displayed that the reduction of compressive strength at 3rd day and 28th day of test cement were from 4.25 % to – 5.8 % and from 1.2% to 4.7 %, according to TCVN 11833. Value -5.8 % (Table 3) means that at 3rd day, the compressive strength of test cement used treated PG is higher than control cement used natural gypsum.

Table 2. Final setting time and difference in final setting time.

Sample	Final setting time (Hour)	The difference in final setting times between test cement and control cement $\Delta T_{kt} = T_{tn} - T_{dc}$	Methodology TCVN 6017:2015 (ISO 9597:2008) Note
Test result at Institute of Construction Material Science			
Untreated PG in test cement	T _{TNo} 4.7	2.45	>2 hour
PG sulfuric (10 %, 28 °C) in test cement	T _{TNI} 2.75	0.5	< 2 hour
Natural gypsum- control cement	T _{DC} 2.25		
Test result at Dinh Vu Gypsum joint stock company			
Untreated PG in test cement	T _{TNo} 4.8	2.13	> 2 hour
PG sulfuric (10 %, 28 °C) in test cement	T _{TNI} 2.83	0.16	< 2 hour
Natural gypsum- control cement	T _{DC} 2.67		

Standard water content of cement containing treated PG and control cement were 30.25 % and 30 %, respectively. The increase of standard water content was 0.25 % was below 1 %, responded to TCVN 11833. Sample also has the constant volume stability responded to TCVN 11833:2017. Above mechanical tests of cement responded to TCVN 11833:2017 displayed that treated PG could be used as cement additives.

Table 3. Compressive strength and reduction of compressive strength.

Sample	Compressive strength (Mpa)	Reduction of compressive strength compared to control cement $Lr = \frac{R_{đc} - R_{tn}}{R_{đc}} * 100$	Methodology TCVN 6016:2011 (ISO 679:2009) Note
Test result at Institute of Construction Material Science			
PG sulfuric (10 %, 28 °C)- test cement			
3 days	R _{tn} 38.3	-5.8 %	<5
28 days	R _{tn} 60.1	+ 4.75 %	<5
Natural gyps-control cement			
3 days	R _{dc} 36.2		
28 days	R _{dc} 63.1		
Test result at Dinh Vu Gypsum joint stock company			
PG sulfuric (10 %, 28 °C)- test cement			
3 days	R _{tn} 25.18	+ 4.25 %	<5
28 days	R _{tn} 49.94	+ 1.2 %	<5
Natural gyps -Control cement			
3 days	R _{dc} 26.3		
28 days	R _{dc} 50.55		

4. CONCLUSIONS

Our research displayed that temperature and high sulfuric concentration create phase transition between $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} / \text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O} / \text{CaSO}_4$ and impurities in PG reduced as observation through this process. Phosphorus removal yield with sulfuric 10 % at 28 °C, 50 °C, 70 °C and 90 °C was 71.91 %, 80.56 %, 88.12 % and 92.36 %, respectively. Together with P_2O_5 removal, other impurities such as F, TOC, Sr, Y were reduced as the observation.

Recovery gypsum after treatment with sulfuric 10 % in 1 hour, 28 °C, the ratio L/S of 3, the stirring rate was at 350 rpm, 3 times of washing, neutralization with lime milk, dry 45 °C or sun drying 24 hours can be used as cement retarders.

Untreated PG contains lots of impurities, that doesn't meet standard to make cement as TCVN 11833: 2017. The treatment of PG with 10 % H_2SO_4 at normal temperature was most feasible and met requirements of P, F, mechanical tests according to TCVN 11833: 2017 for use as cement retarder. Fertilizer plants should organize the impurities separation process to make cement additive at the PG discharged source by reutilization of available sulfuric acid of the factory. This activity will help in reducing significantly phosphogypsum quantity and dumping sites areas.

Acknowledgements. The study was carried out with the financial support from the Ministry of Construction (code: TĐ 20-17, research contract number: 20/HĐKH CNTĐ).

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