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RESEARCH ON THE TREATMENT PROCESS OF PHOSPHOGYPSUM WASTE AND INITIAL APPLICATION OF TREATED PHOSPHOGYPSUM TO MAKE CEMENT ADDITIVES

SUMMARY OF THESIS DOCTOR OF

CHEMICAL ENGINEERING

Code: 9.52.03.01

Ha Noi - 2023

The work was completed at: Graduate University of Science and Technology - Vietnam Academy of Science and Technology

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The thesis will be evaluated by the evaluation committee of the Doctoral disertation, taking place at the Graduate University of Science and Technology - Vietnam Academy of Science and Technology at 2:00 p.m. on February 17, 2022.

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INTRODUCTION

1. The urgency of the thesis

Phosphogypsum (PG) waste is a by-product of the production of H_3PO_4. The amount of PG backlog in landfills, and factories cause the lacking of production area and the possibility of causing environmental problems due to landfill overflow, PG treatment is still a hot issue in the world. In Vietnam, more than 10 million tons of phosphogypsum are at the dump, and each year Vietnam has about 3 million tons of PG discharged from the chemical fertilizer production process of DAP Dinh Vu, DAP Lao Cai, and Bac Giang factories. PG contains impurities such as acid H_2SO_4, free H_3PO_4, phosphate salts, fluoride salts, and organic substances attached to the surface of PG crystals, these impurities need to be treated before application in building materials. The calcium sulfate content in PG is high, so it is often reused for construction purposes, but its reuse rate is less than 15% worldwide.

Research on the treatment and enhancement of PG recycling in the field of construction and synthesis of new recycled materials has always attracted the attention of many scientists worldwide and in Vietnam, but the management and utilization of phosphogypsum waste at fertilizer plants in the world and in Vietnam is still a challenging issue, so it is necessary to continue to study the scientific basis of the PG waste treatment process and make full use of treated PG in Vietnam as building materials.

The high phosphorus content in PG prolongs the setting time when PG is used as a retarder. According to the requirements of Vietnamese regulations on additives used for cement production, the soluble phosphorus and total phosphorus content in PG must be less than 0.1 % and 0.7% respectively, according to European standards, total phosphorus pentoxide should be at least 0.4%. In particular, the removal of co-precipitated phosphorus in PG requires an acidic dissolution medium to remove Phosphorus in this crystal form, allowing the total concentration of organic impurities and silicon in PG to reach the required levels, to be satisfied the demand for building materials such as cement additives, and raw materials for gypsum production. PG after acid treatment is further reacted with CO_2 gas to convert $CaSO_4$ to nano $CaCO_3$, applied as a cement additive to improve the physical and mechanical properties of cement.

From the above reasons, to strengthen the scientific basis to put phosphogypsum waste into the application as a cement additive in particular, construction materials in general, we choose the thesis topic "***Research on the treatment process of phosphogypsum waste and initial application of treated phosphogypsum to make cement additives".***

2. Research aims and objectives

+ Studying the process of removing phosphorus and impurities in the Phosphogypsum waste - a by-product of the fertilizer plant meets the standards as a cement additive according to TCVN 11833:2017.

+ Research on the process of carbonation of Phosphogypsum waste after removing impurities to obtain nano/micro $CaCO_3$ oriented as an additive to cement and building materials.

+ Initial research on the application of treated phosphogypsum after the removal of phosphorus and impurities for cement additive.

3. Research contents of the thesis

+Study on the characteristics and chemical composition old gypsum waste (PG_{old}) collected on the landfill, and fresh phosphorus gypsum waste generated on the production line (PG_{new}) of DAP plant of DAP1 and DAP2 fertilizer plants.

+Research on optimization of phosphorus removal in phosphogypsum waste (PG_{old}) at the dumping site of DAP1 plant to make cement additive to meet the requirement of TCVN 11833:2017.

+Research on obtaining nano, micromet $CaCO_3$ from phosphogypsum residue of dumping site (PG_{old}) after removing impurities.

+Research on both impurities removal and cacbonation of fresh phosphogypsum waste (PG_{new}), initial study the application of new phosphorus gypsum waste after treatment on cement mortar.

CHAPTER 1. OVERVIEW

1.1. Phosphoric acid production technology and PG waste

1.2. The role of gypsum, researching and applying PG to building materials

1.3. Studies on the removal of impurities in PG waste

1.4. Artificial gypsum regulatory and phosphorus regulatory limits

1.5. Existence forms and effects of phosphorus in PG on cement

1.6. National research on PG treatment and application

1.7. Carbonation and treatment of PG to collect $CaCO_3$ nano, micromet

CHAPTER 2. RESEARCH MATERIALS AND METHODS

2.1. Research subjects

Evaluation and survey of fresh phosphogypsum waste (PG_{new}) and old gypsum waste (PG_{old}) collected on the landfill of DAP1, DAP2 factory.

Objects of research on the treatment of impurities: Using PG_{old} from the DAP1 factory to study and determine optimal parameters in the process of removing impurities. Application of treated PG as cement additives and testing according to TCVN11833:2017 and to make $CaCO_3$ nano, micromet. Using the PG_{new} of DAP1 to study the process of simultaneously removing impurities and carbonizing PG.

2.2. Research Methods

2.2.1. Method for determination of soluble phosphorus pentoxide

The phosphorus content was determined according to the APHA 4500.P method. The principle of the method is based on the yellow complexation of PO_4^{3-} with vanadate-molipdate, the darker the yellow color, the higher the concentration of Phosphorus. KH_2PO_4 was used as a standard. Samples were optically measured at 420 nm, vanadate-molybdate is the indicator.

2.2.2. Method for determining P_2O_5 total

PG is digested according to TCVN 8563:2010, converted to PO_4^{3-} and analyzed by photometric method with vanadate-molipdate indicator at 420 nm, according to APHA 4500.P

2.2.3. Method of determination of moisture content

The moisture content of the PG sample before and after treatment was calculated based on the difference in mass of the sample at $105°C$ when the sample was dried to constant weight and weighed.

2.2.4. Method for determination of bound water content

The bound water content in the PG before and after treatment was calculated on the mass difference of the sample at $215°C$ when the sample was dried to constant weight and weighed.

2.2.5. Method to determine total SO_3 content

Break the PG sample with HCl and add 10% $BaCl_2$ to precipitate SO_4^{2-}, filter the precipitate, heat the sample at 900 ºC to constant weight and weigh, measure the change in mass of the sample to calculate the mass and amount of SO_3 obtained.

2.2.6. Method for determination of total organic matter content (TOC)

Organic matter in PG is oxidized by $K_2Cr_2O_7$ in sulfuric acid medium. The excess $K_2Cr_2O_7$ is titrated by Mohr's salt.

2.2.7. Method for determination of trace metal content on ICP-OES

PG sample is broken down with aqua regia mixture, and the received solugion is measured the heavy metal content according to the criteria in QCVN 07:2009 by Inductively coupled plasma - optical emission spectrometry (ICP-OES).

2.2.8. X-ray fluorescence spectrometer (XRF)

Metal oxides were determined on an X-ray fluorescence spectrometer (XRF) VietSpace 5006-HQ02 Institute of Materials Science - Vietnam Academy of Science and Technology

2.2.9. Energy Dispersive X-ray Spectroscopy

2.2.10. Flo content analysis

F^- content is determined by spectrophotometric method using SPADNA color reagent (HACH) at 580 nm wavelength on equipment HACH DR/2010 Institute of Tropical Engineering - Vietnam Academy of Science and Technology.

2.2.11. Elemental analysis C, H, N, S

Analyze the elemental composition C, H, N, S of the input PG sample on the FLASH 2000 elemental analyzer of the center for analysis and classification, Hanoi Customs inspection department.

2.2.12. Scanning Electron Microscopy analysis

2.2.13. Method of determining radiation safety

The level of natural radiation safety of the sample for construction materials is specified and determined according to TCVN 11833:2017, TCXDVN 397:2007. 300 grams of PG sample is analyzed on a gamma spectrometer at the Institute of Nuclear Engineering and calculated according to the formula I = Ra/300+Tho/200+K/3000 and compared with TCXDVN397:2007, TCVN 11833:2017.

2.2.14. Experimental planning method

Experimental planning and optimization of technological processes are applied according to the quadratic model of Box-Willson or Box-Behnken depending on each specific problem. After building the model, we need to evaluate the model's convergence through analysis of variance. If the model converges, we can determine the regression equation and proceed to optimize the technological parameters by the aspiration function method of Harington (1965). Design Expert 11.0 software is used to model and optimize process technology parameters.

2.2.15. XRD analysis

Crystal size and crystal composition were analysis by XRD Brucker D8 Advance with Cu- Kα (λ=1,5406Ao), Insitute of Chemistry – Vietnam Academy of Science and Technology.

2.2.16. Zetasizer analysis

Particle size distribution of a sample in solution state was analyzed by Zetasizer- Nano ZS, Malvern-UK at Insitute of Material Science, and Insitute of tropical technology- VAST.

2.2.17. CaCO₃ monitoring by UV

Qualitative method of $CaCO_3$ on UVVIS 1800 machine at the laboratory of Institute of Natural Compound Chemistry.

2.2.18. Methods for testing of building materials samples

Method of testing the flexural and compressive strength of mortar samples is based on TCVN 6016-2011. Method of testing setting time, and volume stability is based on TCVN 6017-2015. Determination of standard ductility, setting time and volume stability of gypsum is according to TCVN 4031: 1985.

2.2.19. Data analysis

Analysis results were repeated at least 3 times and were averagely calculated. Data analysis and treatment by excel. Analysisi images were drawed in origin sofware. Our analysis results were comparatively analyzed at Vietnam insitute for building material.

2.3. Experimental method

PG old of DAP1- Hải Phong is treated following lines number (1) and (4) (figure 2.3a). PG new of DAP1 Hai Phong is treated following lines number (1) (2) (figure 2.3a) and line (3) (figure 2.3b).

Research diagram on impurity removal in PG old in line (1) with purpose of receiving $CaSO_4.2H_2O$ as cement additives. C1a: sample is optimized and tested in cement mortar.

Study diagram of PG carbonation is according to the line number (1)+ (2), samples have marked as M2, M21, M22.

Study diagram of fresh PG treatment by water according to line (3), sample has marked as M3

Collected $CaCO_3$ nanomet, micromet from old PG after pretreatment is followed by line (4), marked as N.
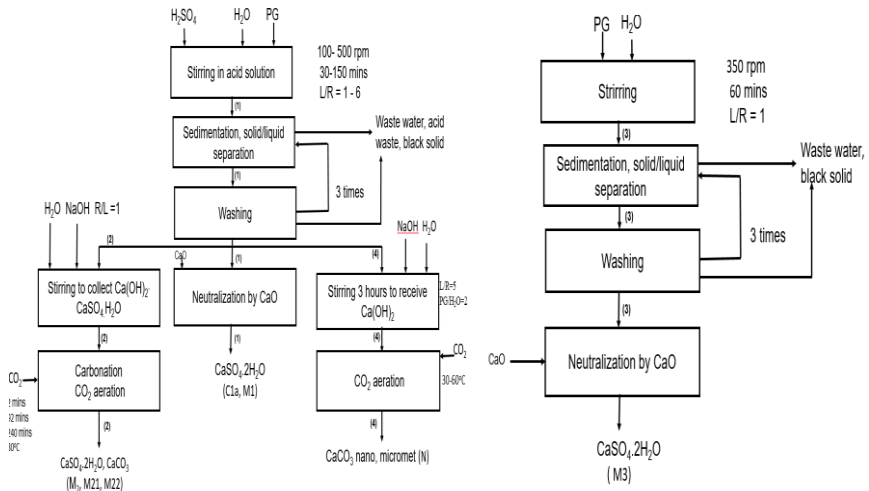
Figure 2.3. PG treament diagram with sulfuric acid (left), water(right)

2.3.1. Research methods for the treatment of P_2O_5 and other impurities

2.3.1.1. Investigation of impurity separation in PG with sulfuric acid agent

2.3.1.2.Evaluation of residual impurities and gypsum collection efficiency

2.3.1.3. Investigate the washing and neutralization process

2.3.2. Experimental planning of P_2O_5 treatment in PG to make building materials

2.3.3. Method for obtaining $CaCO_3$ nano, micromet

2.3.4. Method of simultaneously removing impurities and carbonizing fresh Phosphogypsum

2.3.5. Experimental research method on cement mortar

CHAPTER 3. RESULTS AND DISCUSSION

3.1. Analysis results of phosphogypsum waste

3.1.1. Chemical composition of PG waste from DAP1 and DAP2

Research results show that PG of DAP1 has an average $CaSO_4.2H_2O$ content of 77.82%, and an average crystalized water of 15.750%. PG of DAP2 has an average $CaSO_4.2H_2O$ content of 73.825%, and an average crystalized water of 15.255%. The average content of P_2O_5 total in PG_{new} and PG_{old} of DAP1 are 1.38% and 1.15% respectively, of DAP2 are 1.42% and 1.26%, respectively. The average flor concentraiton in PG new and PG old of DAP1 are 1.15 and 1.01% respectively, of DAP2 are 1.29% and 1.100% respectively. Phosphorus and fluorine concentrations of PG_{old} at the landfill were low than on

PG_{new} at the conveyor belt of the end of H_3PO_4 production. The PG_{old} sample of DAP2 has a higher P_2O_5 content compared to the PG_{old} of DAP1 (table 3.1).

Table 3. 1. Composition of PG waste of DAP1, DAP2 fertilizer plant

No	Parameter	PG_{new} DAP1	PG_{old} DAP1	Average DAP1	PG_{new} DAP2	PG_{old} DAP2	Average DAP2
1	Moisture, %	39,020	25,200	32,110	38,600	27,100	32,850
2	$CaSO_4.2H_2O$, %	77,860	77,790	77,825	73,100	74,550	73,825
3	Crystallized water, %	15,900	15,600	15,750	15,210	15,300	15,255
4	CaO,%	25,810	26,090	25,950	24,210	24,990	24,600
5	SO_3, %	36,520	36,200	36,360	33,880	34,460	34,170
6	SiO_2 , %	10,485	13,21	11,848	10,187	10,550	10,639
7	MnO, %	0,053	0,021	0,037	0,119	0,020	0,070
8	Fe_2O_3 , %	0,195	0,223	0,209	0,229	0,270	0,250
9	Al_2O_3, %	1,331	0,920	1,126	1,060	0,660	0,860
10	MgO, %	0,230	0,230	0,230	0,240	0,250	0,240
11	P_2O_5 tổng số, %	1,380	1,150	1,265	1,420	1,260	1,340
12	$F_{tổng số}$,%	1,150	1,010	1,080	1,290	1,100	1,195
13	P_2O_5 hoà tan,%	0,550	0,440	0,495	0,550	0,480	0,515
14	K_2O, %	0,260	0,231	0,246	0,204	0,13	0,167
15	TiO_2,%	0,192	0,267	0,230	0,180	0,21	0,195
16	SrO, %	0,09	0,182	0,136	0,084	0,183	0,134
17	Y_2O_3,%	0,010	0,022	0,016	0,010	0,001	0,006
18	TOC, %	0,130	0,110	0,120	0,150	0,180	0,165
19	C , %	1,230	1,050	1,140	0,980	1,200	1,090
20	H, %	0,900	0,610	0,755	0,560	0,700	0,630
21	N, %	0,290	0,520	0,405	0,750	2,000	1,375
22	S, %	1,100	0,830	0,965	0,900	2,450	1,675
23	Others, %	2,100	0,400	1,250	2,560	2,610	2,585

Morphology: PG residues are powdery materials. Due to the particle's voids containing residual acid, PG residues are highly acidic (pH < 2.8), the predominant particle size is < 0.045 mm in diameter, and crystal structures are mainly rectangular and hexagonal shapes (Figure 3.1b).
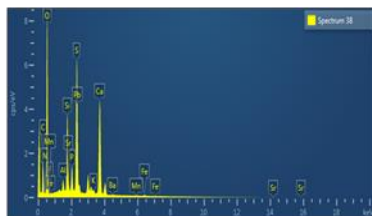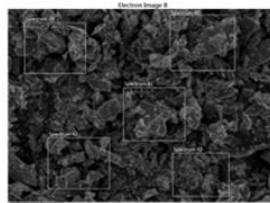
(a)   (b)

*Figure 1*EDX and SEM spectra of PG_{old} DAP1 before treatment

3.1.2. Phosphorus co-precipitated forms in PG

Phosphorus impurities in PG are in the form of compounds such as $Ca_3(PO_4)_2$, $Ca_5(PO_4)_3$ OH, $Ca(H_2PO_4)_2.H_2O$, $CaHPO_4 .H_2O$, H_3PO_4. Phosphorus impurities dissolved in water located on the surface of PG are including H_3PO_4, $Ca(H_2PO_4)_2.H_2O$; Insoluble phosphorus impurities are located in the crystal such as: $CaHPO_4.2H_2O$; and insoluble phosphorus impurities are compounds appearing after phosphate ore breaking process including $Ca_3(PO_4)_2$, $Ca_5(PO_4)_3OH$.

The results of the study on the composition of P_2O_5 in DAP1 and DAP2 in table 3.2a showed that insoluble phosphorus in the study accounted for over 61.5% of total phosphorus and a higher proportion than soluble phosphorus. Worldwide, the amount of phosphorus copper precipitated accounts for 59% of the total phosphorus.

3.1.3. Results of analysis of hazardous components in PG waste

- Inorganic hazardous components such as fluorine, pH exceeding the hazardous waste threshold according to QCVN 07:2009/BTNMT. Cr is at risk of exceeding the allowable threshold and needs further monitoring.

Table 2a. Phosphorus composition in Vietnam and other countries

	Brazil [first]	Brazil [first]	Russia [2]	PG$_{new}$ _ DAP1	P G$_{old}$ _ DAP1	PG$_{new}$ DAP2	PG$_{old}$ DAP2	Ave
P$_2$O $_{5ts}$	0.69	1.93	1.30-3.14	1.38	1.15	1.42	1.26	1.30
P$_2$O $_5$ dissolved	0.29 (42.0%)	0.72 (37.3%)	0.6-1.21 (46.1-39.4%)	0.5 6 (40,6 %)	0.44 (38.3%)	0.55 (38.8%)	0.46 (36.5%)	0.50 (38.6%)
P$_2$O $_{5 is}$ insoluble	0.4 (58%)	1.21 (62.7%)	1.06-1.94 (58.9-60.6%)	0.82 (59.4%)	0.68 (61.7%)	0.82 (61.2%)	0.78 (63.5%)	0.78 (61.5)

3.2. Effect of factors on the removal of impurities with sulfuric acid

3.2.1. Phosphorus removal research

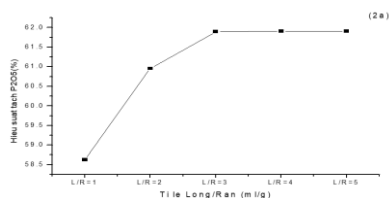*3.2.1.1. Effect of liquid/solid ratio on phosphorus removal efficiency*

Figure 3. 2. Effect of liquid/solid ratio (ml/g) on P removal

Figure 3.4. Effect of time on P removal

Low L/R ratio, poorer dissolution of PG, poor removal of P due to poor mixing of samples. The P removal efficiency did not change
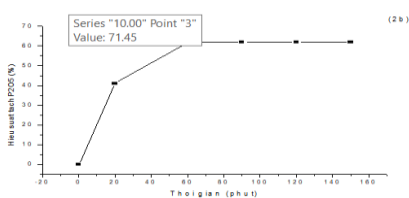
significantly when increasing the L/R ratio from 3 to 5. Therefore, we chose the L/R ratio = 3 as the best condition for phosphorus removal (Figure 3.3).

3.2.1.2. Effect of stirring time

Research results display that the stirring time at 60 minutes gives the best effect on P removal (Figure 3.4).

3.2.1.3. Effect of stirring speed

With liquid/Solid ratio =3, stirring time of 60 min, result of the best stirring speed is 350 rpm to get the best phosphorus removal (Figure 3.5).

3.2.1.4. Effect of acid concentration

The amount of soluble phosphorus increased markedly with increasing acid concentration by 5% to 10%, and there was almost no significant change of P removal efficiency with acid concentration from 10% to 35%. We therefore chose the sulfuric concentration of 10%.
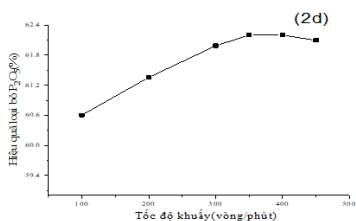
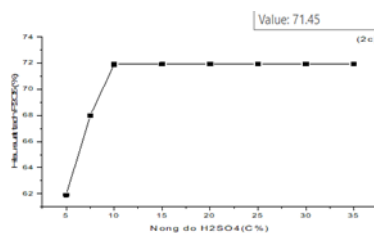Figure 3.5. Influence of stirring speed

Figure 3.6. Effect of acid concentration

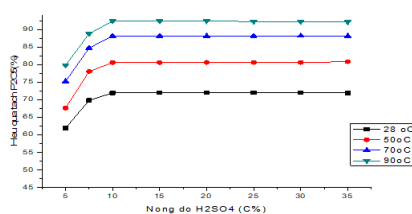### 3.2.1.5. Effect of temperature and removal of P by sulfuric acid

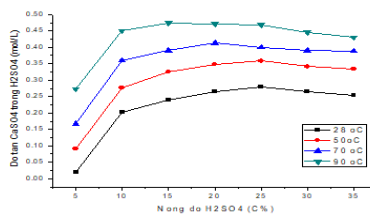Figure 3.7. Removal efficiency according to temperature and sulfuric concentration

Figure 3.8. Solubility of $CaSO_4$ in H_2SO_4 according to temperature and concentration

$CaSO_4$ is slightly soluble in water and slightly soluble in sulfuric acid at room temperature. The solubility of $CaSO_4$ has a clear change with increasing sulfuric acid concentration from 5% to 10%, however

above 10% sulfuric the solubility of $CaSO_4$ does not increase significantly. The solubility of P_2O_5 tends to be the same as that of $CaSO_4.2H_2O$. The results are obvious at 5-10% acid concentration, P_2O_5 dissociation increased fastest and best value at 10% at all investigated temperatures, the higher the temperature is, the more efficient of P_2O_5 removal is. At 5% H_2SO_4 at a temperature of 28°, the P removal efficiency is over 50%, removing the amount of $P_{co-precipitated,}$ when the concentration reaches 10%, at a temperature of 28° above it can remove 70% of the amount of P_2O_5 , at a high temperature of up to 90°C, it can remove over 90% of P_2O_5.

3.2.2. Research on the process and technique of washing PG waste

3.2.2.1. Investigate the washing process

The survey results of the number of washings after acid separation show that it is necessary to wash 3 to 4 times, as the gypsum has a P_{ht} index < 0.1%, Table 3.3 shows that it needs to be washed at least 3 times.

Table 3.3. Survey of washing times

Sample Type	10% sulfuric acid concentration	
	P_2O_{5ht} (%)	Water/PG (ml/g)
Residue after washing	1.031	
1st	0.28	1.10
2nd	0.20	2.10
3rd	0.07	3.10

3.2.2.2. Neutralization process.

After washing, suitable CaO ratio 0.09-0.11% by weight of PG is used to neutralize the treated PG

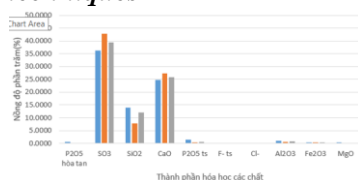### 3.2.3. Comparison of metal oxide removal capabilities of washing techniques

Figure 3.9. Comparison of the impurity removal capacity of washing techniques

Figure 3.10. Effectively remove other impurities

It is found that the technique of washing samples by gravity decantation method is more effective than the technique of filtering the samples on paper/membrane. The yield of artificial gypsum after decanting treatment is 50%. The yield of artificial gypsum after filtration is 99.8%.
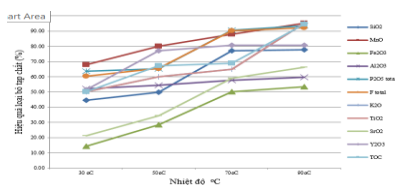
3.2.4. Investigate other impurities removal efficiency

Investigation of the removal efficiency of other metals was carried out in the same way as with P. The effective separation of most metals was 10% acid, the temperature increased 70°C-90°C, the removal efficiency of F and SiO_2 is over 70%, removal of P_2O_5 is over 90%.

3.2.5. Existence forms of gypsum in treatment process

It was found that treated PG at H_2SO_4 (25-30%) and 90°C has a phase transition to $CaSO_4$ anhydrite gypsum. The SiO_2 concentration is decreased with the increasing of temperature, compared to before treatment, SiO_2 concentration decreased by 70-77% when PG is treated at high temperature and impurities are removed by sedimentation and decantation techniques. PG is treated at high temperatures, and SiO_2 is reduced to 3% satisfying for use in gypsum board.
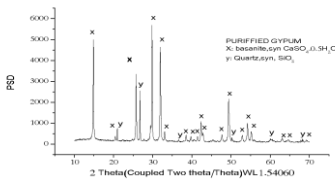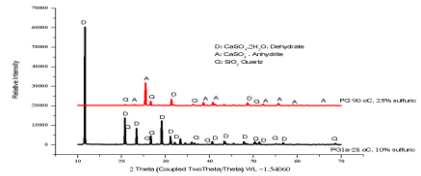

Figure 3.11. XRD spectrum of C1

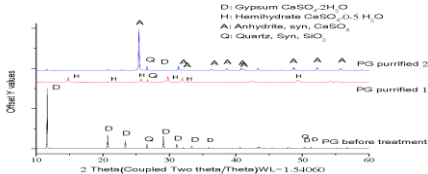Figure 3.12 XRD spectra of C1a and C1b

Figure 3.13. XRD spectrum of PG$_{old}$, C1, C1c

When the treatment temperature is increased, the ability to separate some forms of salt- containing silicon is increased, too. Based on the experimental monitoring of the phase transition of gypsum at high temperatures, the concentration and efficiency of the removal of impurities increased, but the artificial gypsum obtained changed from DH to HH or AH form, which did not meet the requirements of TCVN 11833:2017 is the acquisition of DH form gypsum used as a cement additive. Therefore, to obtain DH used as an additive to replace artificial gypsum in cement and without energy costs, it only needs to dissolve PG in sulfuric acid at room temperature.

3.2.6. Evaluation of natural radioactivity of PG

The results shown in the table show that the natural radioactivity of PG treated with acid separation process satisfies the requirements as a building material (Ii ≤ 1) according to TCXDVN 397:2007.

Table 3.7. *Natural radioactivity of PG after treatment*

Items	Ra, Bq/kg	U, Bq/kg	Th, Bq/kg
PG after treatment	102.6	98.2	11.3

3.2.7. Research on optimization of P_2O_5 removal efficiency

3.2.7.1. Set up the model and build the experimental plan matrix

From experimental data on the influence of univariate technological parameters on the objective function Y1: phosphorus removal efficiency, we choose a quadratic model, experimental planning according to Box-Wilson description. The base level (0), low level (-1) and caco level (+1) of the factors (with k=3) and the range of variation are shown in table 3.8.

Table 3.8. Experimental levels of technological variables

Variable name Range of variation			Research level				
Real variable	Code variable	Range of variation	$-\alpha$	-1	0	1	$+\alpha$
Z1: Acid concentration (%)	A	5	3.9	5	10	15	16.1
Z2: Ratio of ingredients/ consumption per	B	2	0.6	1	3	5	5.5
Z3: Temperature (ºC)	C	3	25.4	26	29	32	32.6

Using Design expert 11.0 software to build an experimental plan matrix with 15 experiments.

3.2.7.2. Check the significance of the model

The significance of the quadratic regression model of phosphorus treatment in PG residues and the coefficients was carried out by analysis of variance (ANOVA), the results of the model were determined to be compatible with the real situation. experience. After removing the elements that don't make sense. The objective function is defined and represented by a quadratic regression equation as follows: $Y = 72.22 + 3.77A + 3.997B + 3.62C - 1.15 AC + 1.475BC - 5.53A^2 - 4.15B^2 - 2.05C^2$

3.2.7.3. Optimization of P_2O_5 removal in PG waste

The optimal value of the independent variables is determined by solving the quadratic equation according to the objective function method so that the processing efficiency is maximized. The level of the selected objective function is level 4. And the value of the acid

concentration variable, the liquid/solid ratio chooses the low concentration region to reduce the cost of raw materials. The value of the processing temperature selects the normal temperature to save energy.

Table 3.11. Values of objective functions at theoretical and practical conditions

Sample	Acid concentration (%)	L/R ratio	Temperature (°C)	Theoretical phosphorus removal (%)	Experimental phosphorus removal (%)
Model 1	10 %	3	29 (°C)	72.217	72.218±0.04

Experimental results at optimal conditions show that the difference is small, once again confirming that the model has high compatibility.

3.3. Study on obtaining CaCO₃ nano, micromet size

3.3.1. Monitoring the reaction process

3.3.2. Identification of CaCO₃ on UV
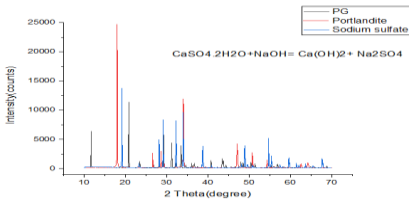
3.3.3. Detection of CaCO₃ on X-ray diffraction
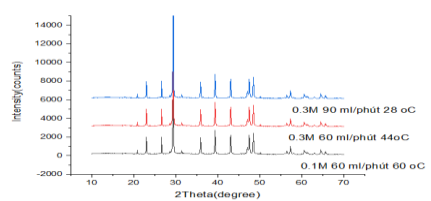

Figure 3.25. XRD spectrum PG, $Ca(OH)_2$, Na_2SO_4

Figure 3.26. XRD spectrum of $CaCO_3$ acquired

Figure 3.25 shows that the reaction process followed the reaction equation: $CaSO_4.2H_2O + NaOH \rightleftharpoons Ca(OH)_2 + Na_2SO_4$. Figure 3.26 shows that the obtained $CaCO_3$ is similar to the $CaCO_3$ standard spectrum, the obtained product contains 81.7% - 89.6% $CaCO_3$ in the form of Rhombohedral calcite and 10.4 - 18.3% SiO_2 is predominated crystalline phases.

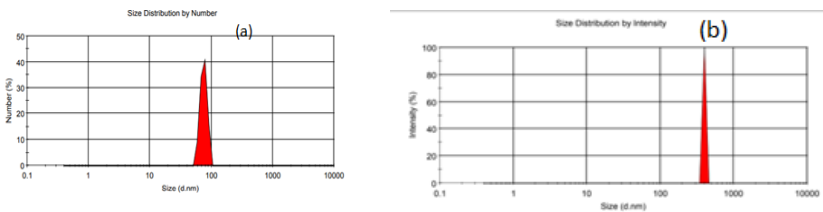### *3.3.4. CaCO₃ particle size on DLS*

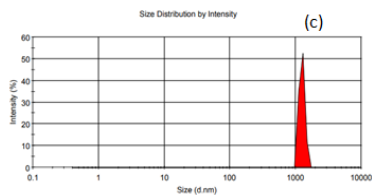*Figure 3.27. CaCO₃ sizes at $Ca(OH)_2$ (a) 0.1M, (b) 0.3M*

Figure 3.27. CaCO₃ sizes at Ca(OH)₂ (c) 0.5M

The results of measuring the particle size distribution in the solution on the zeta size machine showed that when increasing the concentration of $Ca(OH)_2$ from 0.1M to 0.3M to 0.5M, the average particle size in the solution increased significantly.

3.3.5. SEM analysis

The SEM analysis results also showed that when the concentration of $Ca(OH)_2$ increased from 0.04; 0.05, to 0.1 and 0.3 and 0.5 M the grain size increases, respectively.
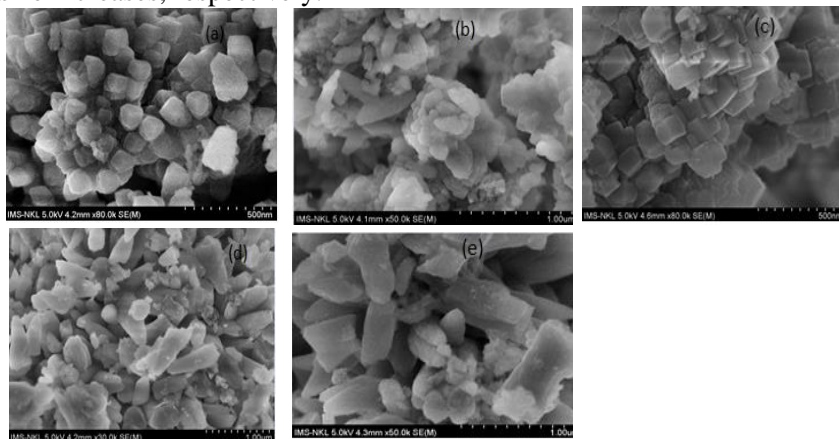

Figure 3. 28. SEM image CaCO₃ was collected at different concentrations of $Ca(OH)_2$

Note: (a) 0,04M; (b) 0,057 M; (c) 0.1M; (d) 0,3M ; (e) 0,543M

3.3.6. CaCO₃ efficiency and CO₂ capture potential of PG

The yield of nanometer-sized $CaCO_3$ is 14.8% in term of treated PG, the efficiency of micrometer-sized $CaCO_3$ is 45.08%. So from the research results, an estimate of the CO_2 capture capacity of PG is as follows: 16 million tons of PG produces 7.4 million tons of $Ca(OH)_2$ produces 10 million tons of $CaCO_3$ and PG has potential capture and could reduce 4.4 million tons of CO_2 emissions.

3.4. Simultaneously removing impurities and carbonizing PG.

3.4.1. Chemical composition of PG_new before and after treatment

Table 3.34. Chemical composition of PG_{neu} and treated PG

Items, %	PG_{new}	M_1	M_2	M_3
SiO_2	10.48	7.73	7.70	8.82
TOC	1.23	0.31	0.20	0.54
P_2O_{5ht}	0.56 _	0.03	0.024	0.1 3
$P_2O_{5\ ts}$	1.38	0.43	0.4	0.44
Removal efficiency, $P_2O_{5\ ts}$		68.84	71.01	68.11
Average efficiency, $P_2O_{5\ ts}$	69.32			
$CaSO_4.2H_2O$	77.86	86.5	86.12	84.04
Moisture	39.02	12.57	12.71	12.95

PG filter cake has total P_2O_5 content of 1.38%, $CaSO_4.2H_2O$ gypsum is 77.86 and total fluorine is 1.15%, SiO_2 is 10.48%. Total phosphorus and fluorine of filter cake PG is higher than the national standard TCVN 11833:2017.

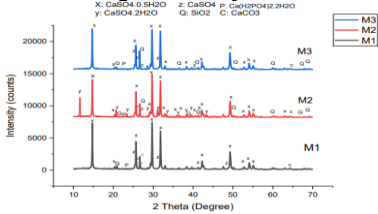### 3.4.2. Comparison of PG_new carbonated/non-carbonated treated samples

Figure 3.32a. X-ray diffraction spectrum of PG samples after treatment (M1, M2, M3)
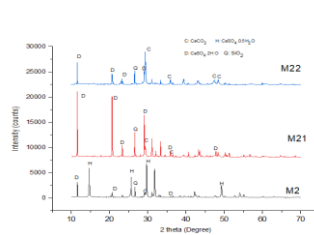
Figure 3. 32b. X-ray diffraction spectrum of PG samples after treatment (M2, M21, M22)

Sample M2 has both the removal of impurities and carbonation process, and it is observed that the $CaCO_3$ signal of M2 is higher than that of M1 and M3 (Figure 3.32a).

Table 3.16. XRD spectral signal of PG_{new} and treated PG_{new}

|	PG_{new}	M1	M2	M3
$Ca(H_2PO_4)_2.2H_2O$ $2\theta= 23.51°$ (counts)	1242	186	185	187
$CaHPO_4$ $2\theta=26.48°$ (Counts)	500	267	235	270

P_2O_5 removal efficiency was 69.32%, of which the P_2O_5 treatment efficiency at sample M2 was the best. M2 has higher intensity of $CaCO_3$, lower SiO_2 intensites in compared to M1 and M3. The characteristic diffraction signals on the XRD tool can show

that impurities such as P_2O_{5ts}, SiO_2, and $Ca(H_2PO_4)_2 .2H_2O$ of M2 are the lowest, the treatment technique option of M2 sample with dilute acid followed by excess alkali and aeration of CO_2 to neutral pH removes more P_2O_5 and SiO_2 and can generate more $CaCO_3$

3.4.3. The reactions occur when neutralization and carbonation of PG$_{new}$ in the presence of NaOH, CO$_2$

Reaction occurs. $CaO + H_2O \rightarrow Ca(OH)_2$(20a). Neutralization of PG after treatment is possible according to the reaction (20b), (20c):

$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$ (20b) ; $CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$ (20c). And $CaCO_3$ can be produced according to the reaction (16)

$$Ca(OH)_2 + CO_{2\,(air)} \rightleftharpoons CaCO_3 + H_2O\ (16).$$
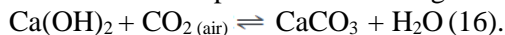
In the case of carbonation of PG$_{new}$ (M2, M21, M22) NaOH concentration (0.075M; 3.25M and 6.25M) was introduced into the gypsum solution, then CO_2 was bubbled into the solution to neutral pH, and there is a reaction between Ca^{2+} from PG$_{new}$, OH^- of NaOH, and CO_2 to produce $CaCO_3$, the ratio between the concentration of OH^- and Ca^{2+} is 0.012; 0.453 and 0.906. When CO_2 was injected into the PG solution after pretreatment with acid, the pH of the NaOH-PG solution decreased rapidly to neutral pH. Addition of NaOH and CO_2 in PG solution after acid treatment according to reactions (14) and (16) to form $CaCO_{3in\ situ}$ because $CaSO_4x2H_2O$ is more soluble than $Ca(OH)_2$, solubility constant Ksp of $CaSO_4.2H_2O$ and $Ca(OH)_2$ at 25°C are $2.4x10^5$ · respectively ; $6.5x10^{-6}$ in water. The reverse reaction of equation (14) is hardly occured. $CaSO_4.2H_2O+2NaOH \rightleftharpoons Ca(OH)_2 + Na_2SO_4 + 2H_2O$ (14) . $Ca(OH)_2 + CO_2 \rightleftharpoons CaCO_3 + H_2O$ (16). $Ca(OH)_2$ is a by-product of equation (14) which then reacts with CO_2 to form $CaCO_{3in\ situ}$ shown in reaction (16). The solubility of $CaCO_3$ ($4.5x10^{-9}$) is lower than that of $Ca(OH)_2$, the reverse reaction of reaction (16) is almost non-existent, and $CaCO_{3in\ situ}$ is observed according to equation (14) and (16). The ratio R=$[OH]^-$/$[Ca]^{2+}$ is from 0.012; 0.453; 0.906 is suitable for Ca^{2+} decomposition. The in situ $CaCO_3$ particles obtained from the carbonation process in M2, M21, M22 were observed on SEM images (Figures 3.33 b, d, e). $CaCO_3$ crystal phases of samples M2, M21, M22 are observed on XRD figure 3.32b.

M3 is obtained after stirring PG in water and residual acid is available in PG filter cake and M3 still has more impurities than M1 and M2.

NaOH is not enough in M2, M21, and M22 then these sample containe both gypsum and calcite crsytals. The SEM images of M2, M21, M22 in Figure 3.33b,d,e show the coexistence of two forms of

gypsum and calcite. The gypsum morphology is long, short columnar and calcite belongs to the rhombohedral system, appearing as a flower base. Calcite has a particle size at the nano and micro scale, located on the surface of gypsum crystals, as a result of carbonation of gypsum with CO_2 in the presence of NaOH.
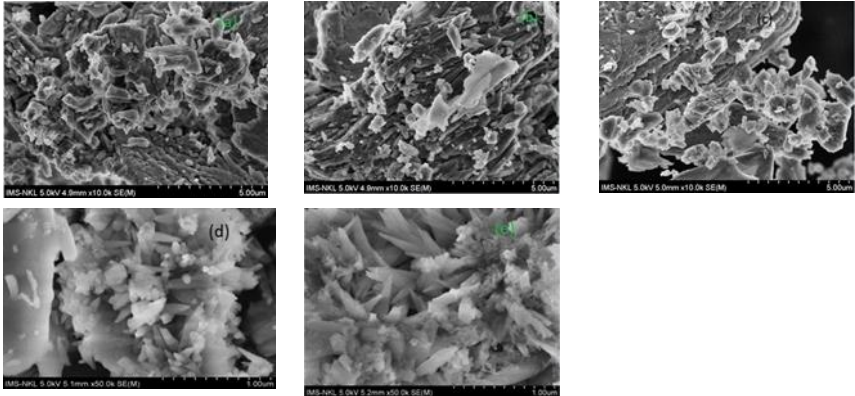

Figure 3.33. SEM PG image after processing (a)M1, (b)M2, (c)M3 , (d)M21, (e)M22

3.4.4. Initial research on hydration of cement mortar

The results show that the cementitious mortar with PG after impurities removal and carbonation (M2V mortar) has the improved mechanical and better chemical properties than that of the cement mortar without carbonation (M1V mortar), and the cement mortar without impurities removal by sulfuric acid (M3V mortar).

Table 3. 18. AFt in cement mortar

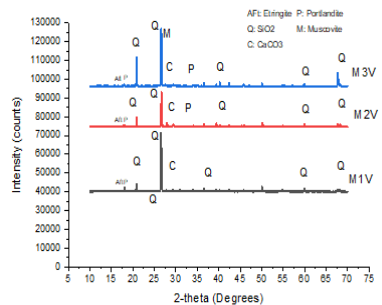| AFt at 2 = 17.7799°	M1V (mortar of PG treated M1)	M2V(mortar of PG treated M2)	M3V(mortar of PG treated M3)
AFt Intensity (counts)	550	836	516

Figure 3.35. XRD spectrum of cement mortar M1V, M2V, M3V

PG_{new} has many impurities that do not meet the requirements of cement additives according to TCVN11833:2017, so it is not tested, the

PG_{new} after treatment is mixed in cement mortar with the ratio of 2%, the results of the compressive strength test and SEM images of hydrated cement mortar samples M1V, M2V, M3V containing PG after treatment (M1, M2, M3) are presented in Table 3.19, Figure 3.34.

Table3.19.$CaCO_3$ on XRD and mortar compressive strength

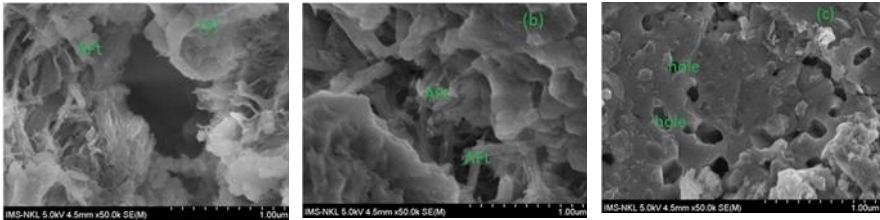| Sample	$CaCO_3$ intensity at 2theta = 29.3º (counts)	Compression strength,thirdday (N/mm^2)	Compressive strength,thirdday (N/mm^2)
M1V	813	12	17.04
M2V	854	14	17.28
M3V	686	11	10.55
Note	PDS Card No 01-071-3699	dry storage conditions	water immersion storage conditions

Figure 3.34. SEM images (a) M1V, (b) M2V clearly identify AFt (c) M3V
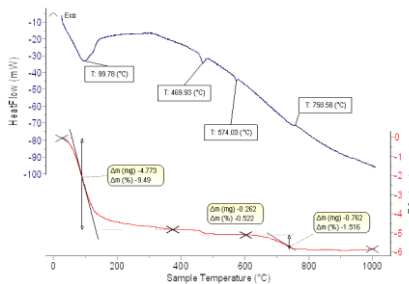
Figure 3.36. TG spectrum of M1V . cement mortar
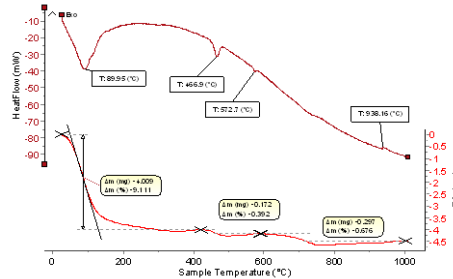
Figure 3.37. TG spectrum of M2V . mortar

The structure of the hydrated cement mortar with long needle-shaped molecules on the SEM images of M1V and M2V is observed. Figures 3.34b and 3.34a show that more needle-shaped etringite crystals (AFt) are filled in the voids of M2V mortar than in M1V and M3V, and the ettringite molecules are enhanced and longer at M2V mortar. AFt can increase the density of cement mortar and increase the compressive strength of cement mortar. The unreacted materials of the cement mortar

(Figure 3.34c) and thier voids are observed clearly in the M3V sample. The compressive strength of M1V and M2V mortar are higher than that of M3V because the mortar M1V, M2V has a denser structure than M3V.

PG after treatment contains $CaSO_4$, $CaCO_3$, treated PG is replaced with ratio of 2% of Portland cement in cement mortar (M1V, M2V, M3V). During the hydration process, $CaSO_4$, $CaCO_3$ react with the chemical components of cement (such as clinker, minerals C3S, C2S, C3A, C4AF) to form calcium silicate hydrate, etringite in homogeneous crystalline form and make the cement harder. In both SEM and XRD analysis, M2V mortar has the highest signal strength of ettringite compared to M1V and M3V.

At hydration process in the third day, the $Ca(OH)_2$ intensities of M2V mortar decreased the most in comparision to M1V and M3V, showing that the $Ca(OH)_2$ of M2V participated in the hydration of cement mortar the best. At the same time, M2V mortar also had the highest compressive strength results (Tables 3.18 and 3.19).

The intensity of AFt at 2theta 17.77 of the M2V cement mortar is the highest in comparision to M1V and M3V, showing that the amount of AFt formed from the hydration of the M2V mortar is the highest, Table 3.18, and SEM image Figure 3.34b.

Initial research results show that the addition of treated gypsum within cacbonation process can produce more ettringite and higher compressive strength. The formation of etringite produces more solid products and reduces the porosity of the hydrolyzed concrete due to the large volume expansion of the etringite and hence the strengthening of the cement mortar.

3.5. Testing of treated PG on cement mortar

Optimizing of technology parameters in PG_{old} treatment is done by Design Expert 11.0 software, the obtimal parameters of the treatment are: 10% sulfuric concentraion, 29°C, L/R=3.

Carrying PG processing at the above optimized technological parameters at the DAP1 factory, the result was foud that the actual and theoretical yield of P_2O_5 treatment were similar. The proposed process for treating PG_{old} of DAP1 to make the cement additive to meet TCVN11833:2017 and IS12679:1989 as folloiwng: 10% sulfuric acid is used, liquid/solid ratio = 3, temperature is 29°C, setting time of 10 minutes and decanting by water 3 times with water/solids ratio = 1, neutralizing by CaO 0.09-9,1%, independent test was established at the

Institute of Building Materials and the physicochemical criterias of treated PG were to meet the requirement when using PG as cement additive (Table 3.24 and Table 3.25).

Table 3.22. Cement testing- Dinh Vu gypsum joint stock company

Samples	Gradation, %		Water (%)	Initial time (minute)	Finishing time (minute)	3 days (MPa)	7 days (MPa)	28 days (MPa)
	Clanke	Natural gypsum						
Natural gypsum	95.3	4.0	30.00	120	160	27.3	32.88	50.55
C1a	95.30	4.5	30.50	130	170	25.18	32.85	49.94
C1 Filter	95.30	4.5	30.25	130	170	24.80	32.17	45.39

C1a:Separation of floating impurities, settle, 3 times whashing, neutralization by lime milk.
C1 filter: Remove impurities by filtration, 3 times whashing, neutralization by lime milk

The treated sample after being processed by the decantation washing method at optimal conditions, were tested for mechanical and physical properties at Dinh Vu gypsum joinstock company, met the initial setting time and ending time according to TCVN 11833:2017. The treated PG sample by filtration method does not meet the mechanical and physical properties according to TCVN 11833:2017 due to the presence of phosphorus and organic impurities.

Table 3.4. Compressive strength and decrease in compressive strength compared with control cement

Sample	Compression strength (MPa)	Reduced compressive strength compared to control cement $L_R = \frac{R_{dc} - R_{tn}}{R_{dc}} \times 100$	Method TCVN 6016:2011 (ISO 679:2009)
C1- filter 3 days 7 days 28 days	Rtn 24.80 Rtn 32.17 Rtn 45.39	9,157 2.159 10.2077	$L_R > 5$ $L_R < 5$ $L_R > 5$
C1a			$L_R > 5$

3 days 7 days 28 days	Rtn $_{25.18}$ Rtn $_{32.85}$ Rtn $_{49.94}$	+ 7.76% + 0.09% + 1.206%	L $_R$ < 5 L $_R$ < 5
Natural gypsum 3 days 7 days 28 days	R $_{dc}$ 27.30 R $_{dc}$ 32.88 R $_{dc}$ 50.55		

(Source: Our test results of cement at the Laboratory – Dinh Vu Gypsum Company, 2019)

Natural gypsum can be replaced with treated phosphorus gypsum in Portland cement PC40 for satisfactory properties such as standard water content, setting time, volume stability and compressive strength. requirements of TCVN 2682-2009: Portland cement - Technical requirements.

Impurites were removed in treated PG after treatment by sulfuric acid, then cement mortar contain the treated Phosphogypsum is increased the hardness when treated PG is used as an additive in cement, and therefore treated PG can be used in the construction industry to replace natural gypsum in the cement industry, cement production.

Table3.5.Test results cement samples at Institute of Building Materials

No	Targets	Unit	Result	Method
1	Increase in standard water content compared to control cement	%	0.5	TCVN 1833: 2017
2	Finishing time difference compared to control cement	Minute	30 minutes	
3	The reduction in compressive strength compared to the control cement 3 days 28 days	%	-5.8 6.2%	
4	Reduced fluidity of cement mortar compared with control cement	%	0.5	
5	Volumetric stability, Le Chaterlier method	mm	Unchanged	TCVN 6017: 2015

(Source: Our test results at Institute of Building Materials, 2019)

CONCLUSION

From the experimental research results of the thesis, the following conclusions can be drawn:

1. The chemical composition of old PG waste collected from landfills and newly generated PG on the filter line of DAP1 fertilizer factory and DAP2 plant was investigated. The gypsum content of $CaSO_4.2H_2O$ in pre-treated PG is from 74.550% to 77.825%, lower than that of gypsum in PG in the world. The average moisture content of Vietnam gypsum waste is from 32.11 to 32.85%, the average crystalized water content is acount for 15.255% to 15.750%. Impurities of P_2O_{5total}, F_{total}, and SiO_2 respectively are: 1.265 to 1.34%; 1.08 to 1.195%; and 10.369 to 11.848% and higher than the impurity content of PG waste in the world. The average P_2O_{5total} content of DAP1 and DAP2 in the PG_{new} was higher than that of the PG_{old}. The PG_{new} of DAP1 has a phosphorus content of 1.38% higher than that of the PG_{old} of DAP1 only 1.15%. The percentage of difficult-to-dissolve P_2O_5 on average accounted for 61.45%, which was higher than that of the average of soluble phosphorus (38.6%).

2. The research has found the optimal equation showing related technological parameters of the process of removing phosphorus impurities in PG_{old} : $Y = 72.22 + 3.77A + 3.99B + 3.62C - 1.15AC + 1.48 BC - 5.53 A^2 - 4.15B^2 - 2.05C^2$, optimal technological parameters suitable for removal of P_2O_5 in PG waste of DAP1: sulfuric acid concentration 10%, L/R = 3, temperature 29°C. After the treatment process, the yield of artificial gypsum reaches 50% compared to the input phosphogypsum quantity.

The proposed process for phosphorous and other impurites removal in PG_{old} of DAP1 with steps: (1) separating impurites in PG by sulfuric acid 10%, ratio of liquid/solid =3, stirring rate of 350 rpm in 1 hour, (2)sedimenting and withdrawing 2/3 vollume of impurities solution, water dacanting, adding water to the solid, ratio of water/solid =1; (3) washing the solid 3 times and collecting the solid, (4) neutralizing the solid with CaO with ratio of 0.09 – 0.11%, draying at 45° and collecting $CaSO_4.2H_2O$ to meet the requirement as cement additives according to TCVN 11833:2017.

3. Research results have obtained $CaCO_3$ nano, micromet through $Ca(OH)_2$ formed from PG in the presence of $NaOH$ and CO_2 when changing the initial concentration of $Ca(OH)_2$ suspension solution from 0.1 M to 0.5 M, temperature 28 to 50°C, CO_2 aeration rate 60 to 120 ml/min, the results show the significant effect of $Ca(OH)_2$ suspension concentration on the size of $CaCO_3$ nano, micromet. The research results obtained $CaCO_3$ particles with nanomet and micromet size of calcite morphology from old phosphorus gypsum waste without using dispersant. The efficiency of capturing nanomet-sized $CaCO_3$ is 14.8%, the efficiency of capturing micromet-sized $CaCO_3$ is 45.08% according to the treated PG quantity.

4. Initial research results on the process of simultaneously separating impurities and carbonating of new phosphogypsum show that the application of treated sample by stirring in sulfuric, carbonating by $NaOH$ and CO_2 aeration has the better role in the hardening of the cement mortar than the treated sample without the carbonation process.

NEW CONTRIBUTIONS OF THE THESIS

1)The research has found the optimal equation showing related technological parameters of the process of removing phosphorus impurities in old PG waste. Optimal technological parameters suitable for removal of P_2O_5 are sulfuric acid concentration 10%, L/R = 3, temperature 29°C.

2)One of the first study to collect $CaCO_3$ nano, micromet from old phosphorus gypsum waste dumping at DAP1 factory, Dinh Vu - Vietnam.

3) Initial study showed the role of the simultaneous process of impurity removal and carbonation in the treatment of fresh phosphogypsum on the harden of cement mortar.

LIST OF PUBLISHED ARTICLES

1. Ngo Kim Chi, **Dang Ngoc Phuong** , Chu Quang Truyen, Nguyen Mai Linh, Dang Thi Dinh, Nguyen Thi Hang, Do Thuy Tien, Phi Hoang Thuy Quynh, Tran Dai Lam, *Research on phosphogypsum gypsum residue, remove impurities , recovery of gypsum used in the production of building materials* , Environmental Journal, 2019, topic 1, 33-38.

2. **Dang Ngoc Phuong**, Ngo Kim Chi, Chu Quang Truyen, Hoang Huu Luat , Tran Dai Lam, *Research on obtaining nano $CaCO_3$ from phosphorus gypsum waste of DAP fertilizer factory* , Environmental Journal, 2020, topic 1 , 89-92.

3. **Dang Ngoc Phuong**, Ngo Kim Chi, Tran Dai Lam, Chu Quang Truyen, Tran Trung Kien, Dang Thi Dinh, *Purification of phosphogypsum for use as cement retarder by sulfuric acid treatment*, Vietnam Journal of Science and Technology, 2020, Vol.58, No.3A, 32-41.

4. **Dang Ngoc Phuong**, Ngo Kim Chi, Tran Le Minh, Hoang Huu Luat, Chu Quang Truyen, Tran Dai Lam, *Preparation of $CaCO_3$ nano and microparticles from phosphogypsum of Dinh Vu DAP plant* , *Vietnam* , Vietnam J. Chem..2021, 59 (4), 440-445 . (SCOPUS).

5. Dang Ngoc Phuong, Tran Dai Lam, Ngo Kim Chi, *Comparative study of fresh phosphogypsum treatment by sulfuric acid and neutralization with NaOH and CO_2,* Vietnam J. Chem. 2022 submitted .