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Reuse Phosphate Gypsum Waste from Dinh Vu DAP Company to Manufacture Cement

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***Abstract*— Phosphogypsum disposal from Dinh Vu DAP company was used to separate phosphate and make gypsum by (NH¬4)2SO4. The reaction time was 120 min. The percentage of P2O5 after removal was 0.72 % and met the Vietnam Standard 11833:2017 issued by Institute of Building Materials. The components in phosphogypsum could be applied to manufacture cement. The final product was mixed by PG120 : clinker : fly ash with ratio 5:80:15% (w/w), respectively to manufacture cement. The cement was tested compressive strength. The strength was 55 N/mm2 after 28 days.**

***Index Terms*— Phosphate gypsum (PG), CaHPO4.2H2O, CaSO4.2H2O, P2O5, cement, diammonium phosphate (DAP).**

I. INTRODUCTION

In the DAP company, to manufacture a ton of acid phosphoric was discharged 4 - 6 tons of dry phosphogypsum (PG) [1, 2, 3]. PG is by product of fertilizer manufacturing process from phosphate ore used by wet method [4, 5]. The capacity of Dinh Vu DAP company is 161700 tons per year. Therefore, the waste amount discharged to environment are very big comprised dry components and wet components. Presently, PG source discharged by Dinh Vu DAP company is about 1 million tons per year. This waste has been dumped.

H. Zhang et. al. was applied gypsum in cement with 4 - 5% (w/w) to reduce time of setting vicat test of cement, anti-corrugation, sulphate erosion and increase high compressive strength [6]. O. Fumie et. al. researched the effect of P_2O_5 to clinker and realized that P_2O_5 declined compressive strength and hydrolysis energy to 28 days [7]. Presently, PG was applied to improve ground [8]. Phosphate was removed by heating sand and PG in sulphuric acid environment at 250^{o}C [9]. Quang N. V. et. al. was reduced gypsum in PG waste from Dinh Vu DAP company by carbon reduction method combined silicic oxide at high temperature to strengthen mechanical strength for cement [10]. In this research, PG waste treatment was applied in manufacturing cement complied Vietnam Standard TCVN 11833:2017 for PG application in cement manufacturing [11].

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II. EXPERIMENT

PG waste: PG waste was collected from Dinh Vu DAP company in Hai Phong province. Some properties of PG waste were shown in table 1.

Table 1. Some physical properties of PG waste

Component	Signal	Unit	Result
Specific density	P	g/cm^3	2.42
Natural humidity	W_o	%	1.89
Melted limitation	W_L	%	46.69
Flexible limitation	W_P	%	40.95
Flexible index	Ip	%	5.74
Maximum void coefficient	e_{max}		1.593
Minimum void coefficient	e_{min}		0.666
Dry angular α_k	α_{dry}	angle	39°39'
Wet angular αw	α_{wet}	angle	31°29'
Maximum density of volume	γ'_{cmax}	g/cm^3	1.385
Optimum humidity	W'o	%	22.88
Permeability coefficient	K_{th}	10^{-6}cm/s	76.61

Clinker was bought from Ninh Binh Vissai company. Fly ask was collected by coal furnace of Dinh Vu DAP company and pure analysis chemicals such as standard NaOH 1N, standard H_2SO_4 10N, concentrated HCl, ammonium molybdate, ascobic acid, NaF.

The chemical to remove phosphate from PG waste was used $(NH_4)_2SO_4$ followed equation:

$(NH_4)_2SO_4 + CaHPO_4.2H_2O \rightarrow CaSO_4.2H_2O + (NH_4)_2HPO_4$ (1)

The experiment to remove phosphate from PG waste by $(NH_4)_2SO_4$ was carried out follows: 5 samples of solutions of 80 mg $(NH_4)_2SO_4$ dissolved in 200ml distilled water were mixed 10g of PG waste by magnetic stirrer during 60, 90, 120, 150 and 180 minutes.

Analysis equipments: The formation and phase modification of sample were researched by X-Ray Diffaction (XRD) in D8 Advance of Bruker (Germany) with λ = 1,5406 A^o of copper. Sample surface morphology was analyzed by scanning electron microscope (SEM) of Hitachi S-4800

(Japan). TGA-DTA diagram was measured by Labsys Evo (France). Chemical components were analyzed by S2 Puma of Bruker (Germany), spectrophotometer by Carry 60-Agilent, cement sample mold, cement sample stirrer, humidity cabinet of Daihan Labtech, compressive strength equipment was standard calibration.

III. RESULT

3.1. Some specific properties of PG waste at Dinh Vu DAP company.

PG waste was analyzed some structures, characteristics, chemical components by modern chemical physical methods such as: structure analysis, phase components by D8 Advance (Fig. 1), micro morphology by scanning electron microscope SEM-Hitachi S-4800 (Fig. 2), thermal analysis by Labsys Evo (Fig. 3), chemical component by XRF S2 Puma (Table 2). Analysis results and calculation were shown by Fig. 1, Fig.2, Fig. 3 and table 2.

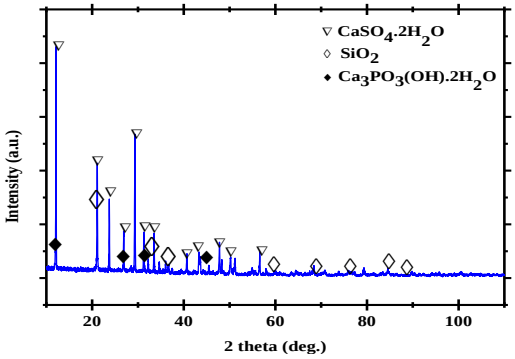

Figure 1. XRD diagram of PG waste

Based on XRD diagram, phases and structures of PG waste were $CaSO_4$. $2H_2O$; $Ca_3PO_3(OH).2H_2O$; quartz and hydrated iron oxide $FeO_2(OH)$.

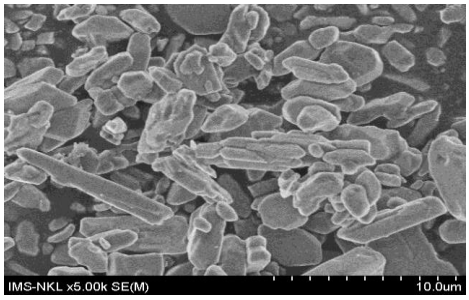

Figure 2. SEM of PG waste

Fig. 2 was shown that surface morphology of PG waste was small plate. Therefore, they were dispersed easily and blended to make additives for construction field such as bricks, gypsum mortar, panel, baffle plate, cement

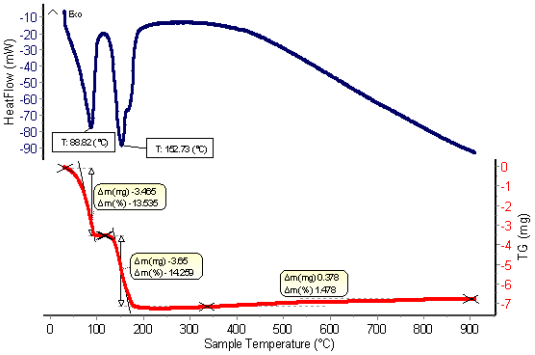

Figure 3. DTA - TGA of PG waste

Fig. 3 was shown that the weight was lost 13.54% from 114.28 to 125°C corresponded endothermic peak on DTA at 88.82°C. This reduction weight was caused by losing hydration water of $CaSO_4$. $2H_2O$ and $Ca_3PO_3(OH).2H_2O$ crystals.

From 125°C to 400°C, the weight was lost 15.75% corresponded endothermic peak at 152°C on DTA. The reduction weight was equal water crystal in $CaSO_4$. $2H_2O$ and hydrated iron oxide. When temperature was higher than 400°C, the weight was not changed. Therefore, PG waste was stable at temperature higher than 400°C and suitable to manufacture cement.

Component	% weight
Na_2O	0.06
K_2O	0.043
MgO	0.022
F	0.16
Cl	0.004
pH	2.8
CaO	25.51
SO_3	38.37
SiO_2	8.47
P_2O_5	1.02
Al_2O_3	0.58
TiO_2	0.19
MnO	0.23
Fe_2O_3	0.21
SrO	0.09
MgO	0.07

Table 2. Chemical components of PG waste

Analysis results of PG waste were shown that percentage of water was 27.7% and that of phosphate by P_2O_5 was 1.02%. This percentage of P_2O_5 was higher than limited standard 0.8% comprised by dissolved and undissolved form [11].

Otherwise, pH of PG waste was 2.8. When mixed with clinker, it was caused by thermogenic with lime.

3.2. Some characteristics of PG waste after phosphate removal by $(NH_4)_2SO_4$ from PG waste

Table 2 was shown that PG waste could not be used to manufacture cement with high compressive strength because of high percentage of P_2O_5 1.02%. Therefore, phosphate was needed to remove. $(NH_4)_2SO_4$ was applied to remove phosphate and followed by equation (1). 5 samples at different reaction times such as 60, 90, 120, 150 and 180 minutes were tested. After reaction times, samples were filtered and washed by distilled water to pH = 7. Samples were dried during 8 hours at 120°C to constant weight. Total percentages of P_2O_5 of samples were measured by following Vietnam Standard 11833:2017. Table 3 was shown the percentages of P_2O_5 at different reaction times.

Table 3. Percentages of P_2O_5 of PG after treated by using $(NH_4)_2SO_4$ at different reaction times.

Sample	Time (min)	% P_2O_5 (w/w)
PG	0	1.02
PG_{60}	60	0.83
PG_{90}	90	0.78
PG_{120}	120	0.72
PG_{150}	150	0.69
PG_{180}	180	0.66

Table 3 was shown that samples from 90 to 180 minutes had percentage of P_2O_5 lower than 0.8% [11]. Therefore, reaction time selected to remove phosphate was 120 minutes.

PG sample after phosphate treatment at 120 minutes was analyzed structures, properties, chemical components similar PG waste above. The analysis result and calculation were shown by table 4 and from Fig. 4 to Fig. 6.

Table 4. Chemical components of PG_{120} after treated by $(NH_4)_2SO_4$

Component	% weight
CaO	25.9
SO_3	38.51
F	0.028
P_2O_5	0.72
MgO	0.17
Al_2O_3	0.82
SiO_2	11.83
TiO_2	0.29
MnO	0.02
FeO	0.3
Cl	0.007

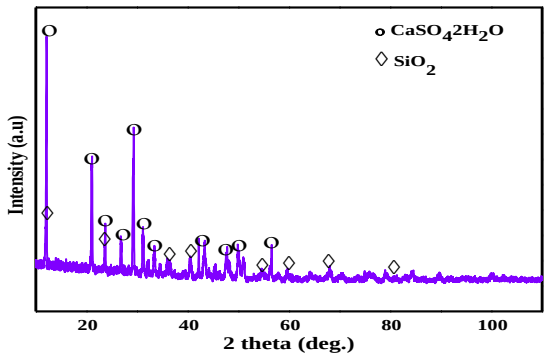

Figure 4. XRD of PG_{120}

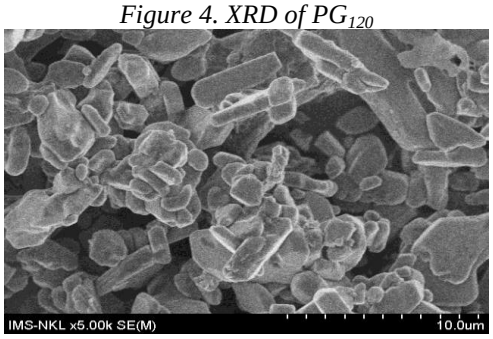

Figure 5. SEM of PG_{120}

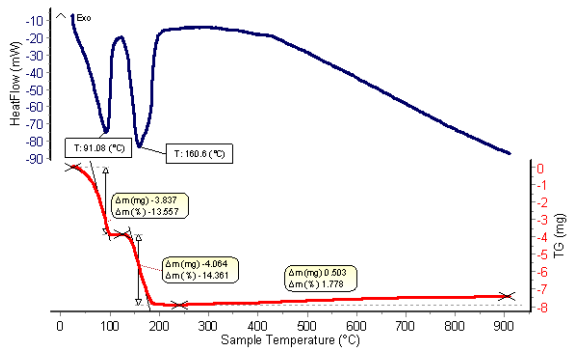

Figure 6. DTA - TGA of PG_{120}

Chemical components of PG_{120} after phosphate treatment were comprised gypsum $CaSO_4,2H_2O$ and quartz (Fig. 4). Fig. 5 was shown that morphology of PG_{120} was small uniform plate compared with PG waste. Fig. 6 was shown that the reduction weight was 14% on TGA from 125°C to 200°C corresponded by endothermic peak on DTA at 160°C. This was lost crystallization water from $CaSO_4.2H_2O$ to $CaSO_4$. From above results, PG_{120} was suitable for manufacturing cement by complying Vietnam Standard 11833:2017 [11].

3.3. Manufacturing cement by using PG_{120}

Phase components of fly ash at coal workshop of Dinh Vu DAP company and clinker at Ninh Binh Vissai company was analyzed by D2 Phaser with Topass BBQ software. Fly ash was comprised gypsum 2%, muscovite/illite 8%, microcline 2%, mullite 2%, quartz 18% and amorphous phase 68% (w/w). Higher percentage of amorphous phase, higher strength of cement was. Clinker was comprised C_3S 67.29%, C_2S 11.37%, Total aluminum 4.88%, Ferit 14.68%, CaO 0.13%, $Ca(OH)_2$ 0.23%, periclase 0.31%, quart 0.03%, Arcanite 1.05%, langbeinite 0.02%, aphthitalite 0%.

Cement was made by grinding mixture of clinker: PG_{120}: fly ash with ratio 80: 5: 15% (w/w), respectively. Compressive strength was measured by Vietnam Standard TCVN 6016:2011 [12] estimated by 3, 7, 28 days. The results and calculation were shown by figure 7.

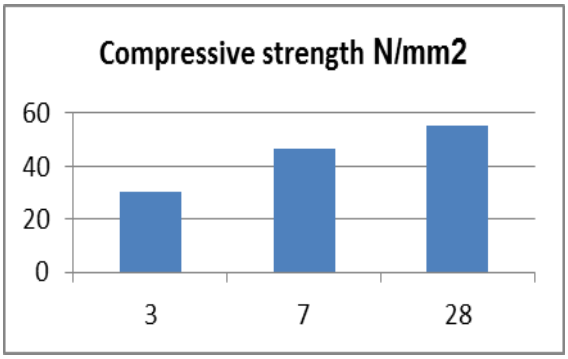

Figure 7. Compressive strength of cement used 5 % of PG_{120} at 3, 7 and 28 days

Compressive strength of cement sample of 5% PG_{120} after 3, 7, 28 days were 30, 44 and 55 N/mm^2, respectively. Compressive strength at 28 days was 55 N/mm^2 was equal PC 50 grade.

IV. CONCLUSION

Researching specific properties of PG waste by modern chemical physical analysis methods and realizing that PG waste had small plate; phase components was $CaSO_4.2H_2O$, $Ca_3PO_3(OH).2H_2O$, quartz and hydrated iron oxide; phosphate calculated by P_2O_5 was 1.02% (w/w) and pH was 2.8.

Researching to remove phosphate to PG waste by using $(NH_4)_2SO_4$ during 120 minutes and analyzing PG_{120} structures, phase components, morphology. PG_{120} had small uniform plate. Phase components were main $CaSO_4.2H_2O$; quartz. Percentage of P_2O_5 0.72% was suitable for manufacturing cement followed Vietnam Standard TCVN 11833:2017.

PG_{120} was tested to manufacture cement. The compressive strength of cement after mixed clinker: PG_{120}: fly ash with ratio 80: 5: 15% (w/w), respectively was 55 N/mm^2 after 28 days corresponded PC50 grade.

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