

# Application Floatigram V4343 to remove SiO<sub>2</sub> from phosphogypsum waste to manufacture plasterboard and reduce waste amount to environment

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**Abstract**— Floatigram V4343 was applied to separate quartz from phosphogypsum waste. After removal, quartz concentration in phosphogypsum waste was 1.90% and lower than Vietnam Standard limitation 3%. Gypsum content was 95.70% and hemihydrate gypsum in PG waste after floating was not appeared. It met the standard to make plasterboard. It was become the raw material to make plasterboard and reduce the environmental impact from Dinh Vu DAP company

**Index Terms**— Phosphogypsum (PG); CaSO<sub>4</sub>.2H<sub>2</sub>O; SiO<sub>2</sub> Floatigram V4343

## I. INTRODUCTION

Phosphogypsum (PG) is byproduct from fertilizer manufacturing process from phosphate ore by wet method [1]. The reuse of PG waste to make building materials, portland cement additives, plaster board [1÷6], soil reclamation [6] was interested in many researches. Presently, PG waste discharged by Dinh Vu DAP company is approximate 1 million tones without treatment [6,7]. Some authors researched to remove phosphate from PG waste by baking with sand in sulfuric acid environment at 250°C [9]. Quang N. V. et. al. researched to reduce gypsum in PG waste from Dinh Vu DAP company by using carbon reduction method with silicon oxide at high temperature to increase mechanical strength for cement [7]. Researches were shown that PG waste after removed phosphate had high silica content (10 - 14%). This percentage was high and could not meet the standard limitation for manufacturing plasterboard [8]. Burat F. et. al. was compared cationic G-TAP and Floatigram V4343, H<sub>2</sub>SO<sub>4</sub> modifier and pine oil froth to remove quartz from feldspar and realized that the efficiency of V4343 was higher than that of

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G-TAP [11]. Therefore, in this research, we applied floating technology to separate and purify PG waste to meet requirement of raw material to manufacture plasterboard and reduce waste amount from PG waste to environment.

## II. EXPERIMENT

Chemical and equipment:

Material: PG waste was separated phosphate by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution. The method to separate phosphate from PG waste by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> followed the chemical equation (1).  
$$(NH_4)_2SO_4 + CaHPO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + (NH_4)HPO_4$$
 (1)

A tone of PG waste were immersed in 12 kg of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in 20 m<sup>3</sup> of water and stirred during 120 minutes, filtered and washed sludge to pH 7.

The Fig. 1 was shown the process of floatation. The chemicals were used H<sub>2</sub>SO<sub>4</sub> as pH modifier, floatigram V4343 as collector and pine oil as frother.

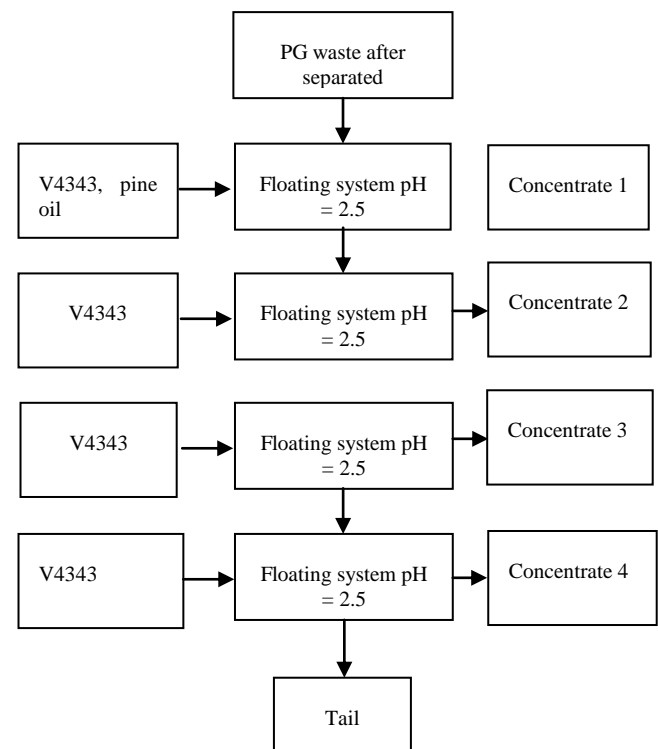


Figure 1. Floatation diagram of 4 stages

Chemical: Concentrated sulphuric acid, ammonium sulphate and pine oil were industrial grade, Floatigram V-4343 was bought from Clariant.

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Floation system: Volume was 1.2 cu. m/chamber and 4 chamber with conventional impellar speed 1200 rpm

Analysis equipments: The formation and phase modification of sample were researched by X-Ray Diffraction (XRD) in D8 Advance of Bruker (Germany) with  $\lambda = 1,5406 \text{ \AA}$  of copper. Sample surface morphology and chemical components were 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

- Determining content of CaSO<sub>4</sub>·2H<sub>2</sub>O by TCVN 9807:2013 [11].

- Determining total content of aluminum oxide and iron oxide (Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>) by ASTM C471M-17ae1 [12].

- Determining content of SiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, Cl<sup>-</sup> by TCVN 9191: 2012 [13]

- Determining content of P<sub>2</sub>O<sub>5</sub> (total and dissolved) by TCVN 11833:2017 [14].

- Determining content of fluoride (total and dissolved) by TCVN 11833:2017 [14]

- Determining pH by TCVN 9339:2012 [15].

### III. RESULT

#### 3.1. Some characteristic of PG waste before and after floating experiment

PG waste after separated phosphate by (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was analyzed structure, property, chemical components the same as PG waste. The results and calculations were shown by table 1, Fig. 2a, Fig. 3 and Fig. 4a.

Table 1. Chemical components of PG waste after separated phosphate by chemical method using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

Component	% Weight
CaO	25.90
SO <sub>3</sub>	38.51
F	0.028
P <sub>2</sub> O <sub>5</sub>	0.72
MgO	0.17
Al <sub>2</sub> O <sub>3</sub>	0.82
SiO <sub>2</sub>	11.83
TiO <sub>2</sub>	0.29
MnO	0.02
Fe <sub>2</sub> O <sub>3</sub>	0.30
Cl	0.007

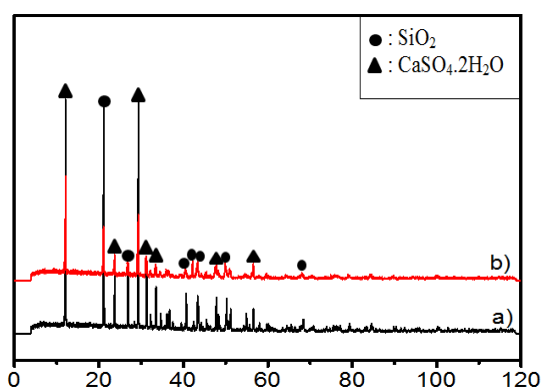


Figure 2. XRD of PG waste a) PG before floatation; b) PG waste after floatation

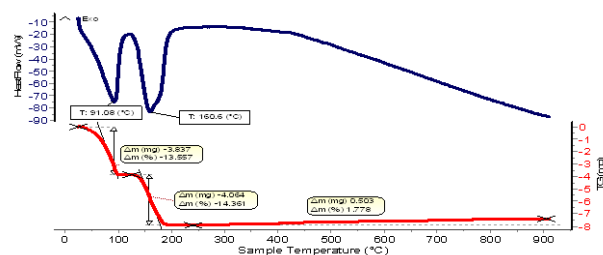


Figure 3. TGA - DTA of PG waste before floatation

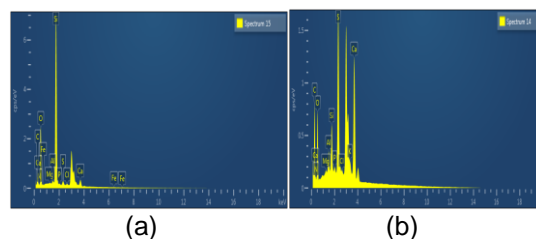


Figure 4. EDS of PG waste a) before floatation b) after floatation

From analysis results, PG after phosphate separation had phase components comprised CaSO<sub>4</sub>·2H<sub>2</sub>O and quartz (Fig. 2a). Fig. 3 was shown that the lost weight was 14% from 125°C to 200°C on TGA corresponded with endothermic peak at 160°C. This loss was crystalline water of CaSO<sub>4</sub>·2H<sub>2</sub>O to CaSO<sub>4</sub>. Otherwise, SiO<sub>2</sub> content of PG waste after separated phosphate was 11.83 % by weight. This percentage was high and could not meet requirement to manufacture plasterboard followed the Stipulation 393/QD-BXD.

#### 3.2. Separating SiO<sub>2</sub> from PG waste by Floatigram V4343.

The floation test conditions were shown in table 2 and figure 1. 10% solid of PG waste were adjusted to pH 2.5 by H<sub>2</sub>SO<sub>4</sub> and conditioned during 5 minutes for first stage and 3 minutes for each subsequent stages of collector addition. The frother was added for each stage.

Table 2. Floation condition

Parameters	Values
Collector type	Floatigram V-4343
Collector concentration	1200 g/t (300+300+300+300)
pH	2.5
% solid	10%
Conditioning time	5 + 3 + 3 + 3 min
Floation time	60 + 60 + 60 + 60 s
Frother - pine oil	(500 + 500+ 500 + 500)g/t
Medium particle sizes	41 $\mu\text{m}$

Table 3. Results of conventional floatation experiment

Dosage g/t	Product	Weight %
300	Concentrate 1	15.30
600	Concentrate 2	27.40
900	Concentrate 3	30.90
1200	Concentrate 4	15.80
	Tail	10.60
	Total	100

PG waste after floatation were determined chemical components by S2 Puma - Bruker. Structure characteristics of PG waste after floatation and tail of quartz were shown in table 4 and Fig. 2b, Fig. 4b and Fig. 5.

Table 4. Chemical component of PG waste after floatation experiment with 4 stages

Components	Weight %
CaO	30.10
SO <sub>3</sub>	45.30
F	0.028
P <sub>2</sub> O <sub>5</sub>	0.60
MgO	0.17
Al <sub>2</sub> O <sub>3</sub>	0.82
SiO <sub>2</sub>	1.90
TiO <sub>2</sub>	0.29
MnO	0.02
Fe <sub>2</sub> O <sub>3</sub>	0.30
Na <sub>2</sub> O	0.02
Cl	0.352

Fig. 2b was shown the results of XRD of PG waste after floatation. The main components were CaSO<sub>4</sub>.2H<sub>2</sub>O with 95.70 % and remain SiO<sub>2</sub> and trace. From table 3, SiO<sub>2</sub> content of PG waste before floatation was 11.83% and could see clear on Fig. 2a and Fig. 4a corresponded by high intensity. Fig. 2b and Fig. 4b were shown that the intensities of SiO<sub>2</sub> were low and corresponded SiO<sub>2</sub> content 1.90 %.

To prove the efficiency of separation of SiO<sub>2</sub> from PG waste, the tail of SiO<sub>2</sub> was determined phase components by XRD. Fig. 5 was shown that phase component of tail was main quartz. This result was the same as [10].

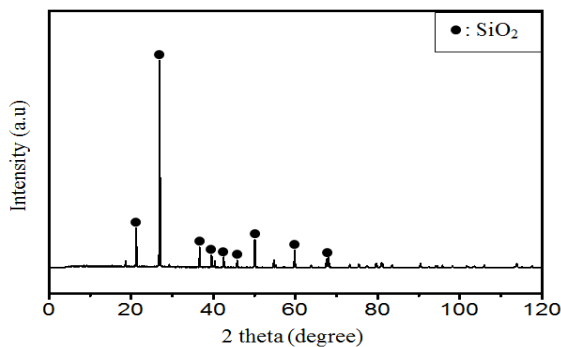


Figure 5. XRD of tail

Based on results of floatation experiment, PG waste after floatation was main CaSO<sub>4</sub>.2H<sub>2</sub>O 95.7% and SiO<sub>2</sub> 1.9%. This results met the requirement to manufacture plasterboard followed the Stipulation 393/QĐ-BXD [8]. Product CaSO<sub>4</sub>.2H<sub>2</sub>O of floatation process by Floatigram V4343 was similar as research results [1, 10]. One of important problem was that weight of waste from Dinh Vu DAP company could be reduced 10% and reduced environmental impact.

#### IV. CONCLUSION

Researching floatation of PG waste with 4 stages by collector Flotigram V4343 at pH 2.5. Collector concentration was 1200 g/t and pine oil was 500 g/t. The final product after floatation was CaSO<sub>4</sub>.2H<sub>2</sub>O 95.70 % and SiO<sub>2</sub> 1.9% and met requirement to manufacture plaster board followed the stipulation 393/QĐ-BXD. The important result was to reduce the amount of PG waste to environment to 10% of total waste.

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#### REFERENCE

- [1]H. Tayibi, M.Choura, F. A. López, F. J. Alguacil, A. López-Delgado, "Environmental impact and management of phosphogypsum". *Journal of Environmental Management*, 90 (2009) 2377-2386.
- [2]J.H. Potgieter, S.S. Poggieter, R.I. McCrindle, C.A. Strydom, "An investigation into the effect of various chemical and physical treatments of a South African PG to render a suitable as a set retarder for cement", *Cement and Concrete Research*, 33 (2003), pp. 1223-1227
- [3]M. Singh, M. Garg, C.L. Verma, S.K. Handa, R. Kumar, "An improved process for the purification of PG", *Constr. Build. Mater.*, 10 (8) (1996), pp. 597-600.
- [4]E.M. Van der Merwe, C.A. Strydom, "Purification of South African PG for use as Portland cement retarder by a combined thermal and sulphuric acid treatment method", *South African J. Sci.*, 100 (2004), pp. 411-414
- [5]C. Conklin, "Potential uses phosphogypsum and associated risks", *US Environmental Protection Agency*, 1992
- [6]Nurhayat Degirmenci, ArzuOkucu, AyselTurabi, "Application of phosphogypsum in soil stabilization", *Building and Environment*, Vol.42, Pages 3393-3398, 2007
- [7]Nguyễn Văn Quang, La Văn Bình, La Thế Vinh, "Quá trình khử gypsum bằng cacbon hoạt tính kết hợp với silic dioxide ở nhiệt độ cao", *Tạp chí hóa học*, 75-78, 2015.
- [8]Quy định 393/QĐ-BXD ban hành ngày 21 tháng 5 năm 2019 về việc Ban hành chỉ dẫn kỹ thuật "Sử dụng thạch cao phospho và thạch cao FGD làm nguyên liệu sản xuất tấm thạch cao".
- [9]Wolfgang Gauster, Linz (Danube), Walter Miller, Leonding, near Linz (Danube), and Ferdinand Weinrotter, Linz (Danube), "Process for removing fluorine and phosphate from gypsum product in the manufacture of phosphoric", *U.S. Patent*, 3,547,581, 1970.
- [10] F. Burat, O. Kokkilic, O. Kangal, V. Gurkan and M.S. Celik. "Quartz-feldspar separation for the glass and ceramics industries", *Mineral and Metallurgical Processing*, Vol. 24 (2), 75-80, 2007.
- [11] TCVN 9807:2013, *Thạch cao dùng để sản xuất xi măng*
- [12] ASTM C471M - 17ae1, Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products
- [13] TCVN 9191: 2012, *Đá vôi - phương pháp phân tích hóa học*
- [14] TCVN 11833:2017, *Thạch cao phospho dùng để sản xuất xi măng.*
- [15] TCVN 9339:2012, *Bê tông và vữa xây dựng - phương pháp xác định pH bằng máy đo pH*

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