

HANOI UNIVERSITY OF MINING AND GEOLOGY (HUMG)



CURRENT STATUS OF RESEARCH AND USE OF PHOSPHOGYPSUM (PG) IN VIETNAM: A PRELIMINARY CASE STUDY TO ORIENT PROCESSING TECHNOLOGY

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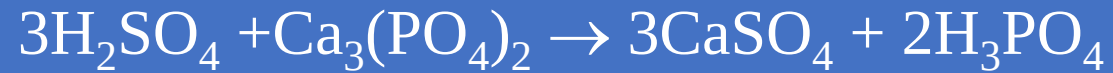
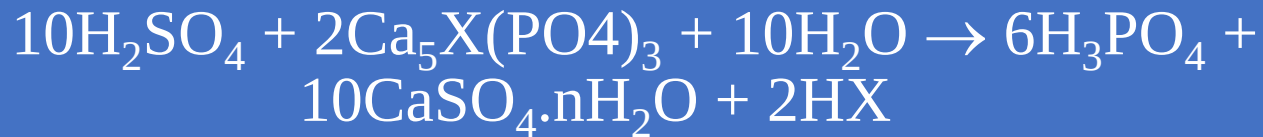
Part IV

❑ Orientation on processing and using phosphogypsum from Mineral processing site



INTRODUCTION

Phosphogypsum (PG) is the main solid waste from the production of ammonium phosphate and phosphoric acid raw materials (*Zhang, 2014*).



X: OH⁻, F⁻, Cl⁻, Br⁻ or other ions of Fe²⁺ /Mg²⁺

The composition of PG: calcium sulphate dihydrate (CaSO₄·2H₂O), phosphoric acid (H₃PO₄), hydrofluoric acid (HF), heavy metals (Sr, Ba, Cu, Cd, etc.), and radioactive-elements (226Ra, 238U).

Phosphogypsum



INTRODUCTION

Normally: 4 – 6 tonnes of PG for every ton of phosphoric acid produced (*Pliaka & Gaidajis, 2022; Saadaoui et al., 2017; Seraya et al., 2023*);

The total amount of PG: around 6 billion tonnes (2006);

The annual produced PG: 160 million tonnes/year and could reach 200–250 million tonnes within the next decade;

PG was disposed of on the Earth's surface, which not only wasted a lot of resources, but also caused serious pollution of the atmosphere, soil, and water near the burial locations (*Saadaoui et al., 2017; Tayibi et al., 2009*);

The effective utilisation of PG as an industrial waste is closely related to the coordinated development of natural resources, environment, and economy.



INTRODUCTION

Only about 15% of PG has been reused in different fields such as soil stabilisation amendments, agricultural fertilisers, as set controller in cement manufacture, and in building materials

Because of the physical and chemical characterisations of PG, strong acidity ($\text{pH} < 3$) and high moisture content

Cemented paste backfill (CPB) for use in underground mine stopes

Cement retarder

Increasing the proportion of ordinary Portland cement (OPC) in mixtures or adding other tailings, such as fly ash, waste lime an zeolite, as the hydration activators



INTRODUCTION

Many researchers tried to remove or at least reduce the impurities in PG to guarantee its safe use in the construction field

PG with aqueous citric acid solution, intending to convert phosphatic and fluoride impurities into water removable citrates, aluminates and ferrates

Neutralisation treatment

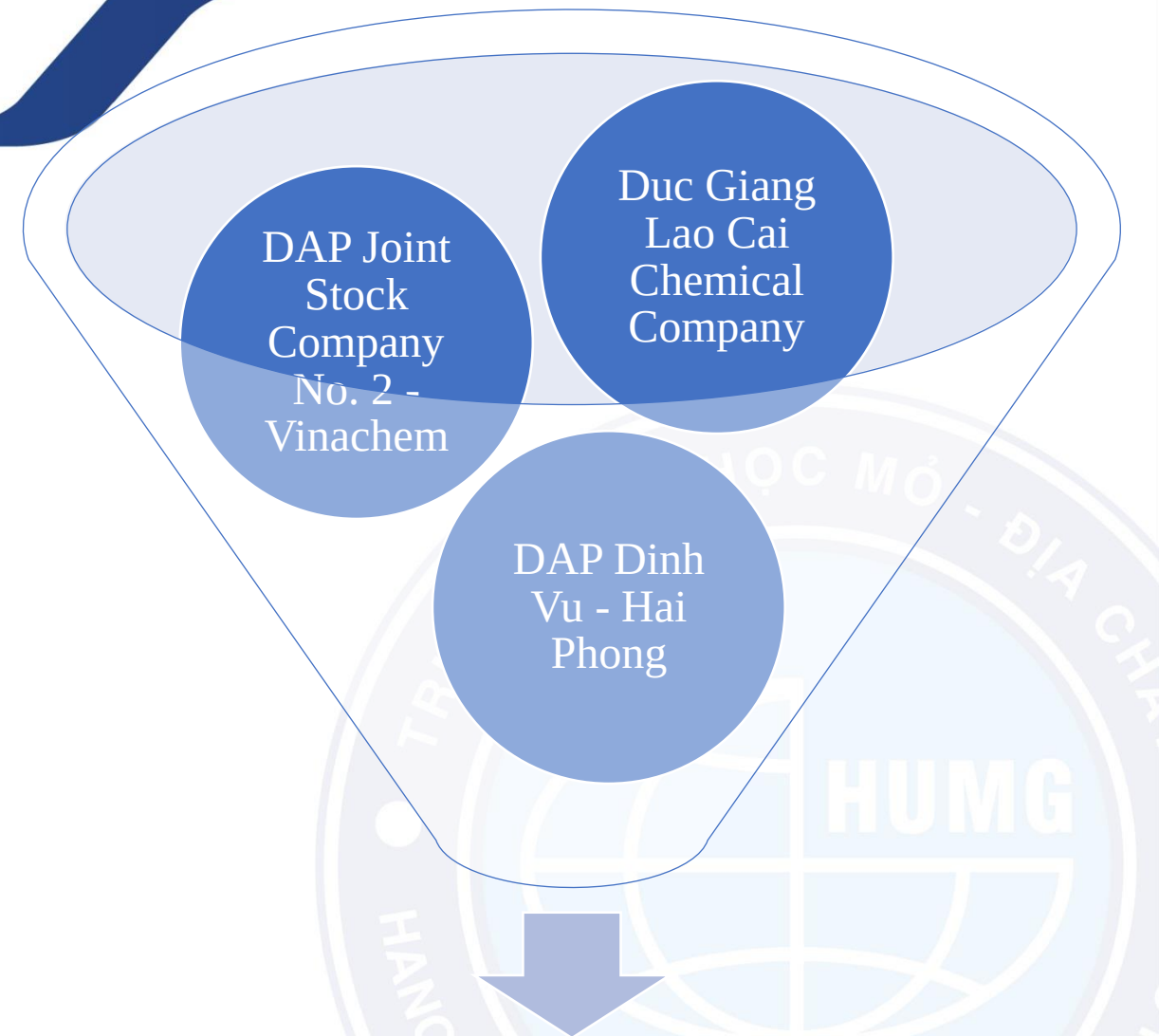
Treatment with ammonium hydroxide or sulphuric acid was effective in reducing set retardation of PG based CPB

⇒⇒ The above pre-treatment methods can remove the impurities in PG to different degrees, but the properties of the prepared mixture are different due to the different mechanisms of the pre-treatment methods



CURRENT SITUATION OF PG IN VIETNAM

In Vietnam, there are currently 03 fertilizer factories with a demand for apatite of about 4.5 million tonnes/year, along with it is the discharge of millions of tonnes of solid PG



PG waste stored from 3 DAP fertilizer factories will be about 12.7 million tonnes/year



CURRENT SITUATION OF PG IN VIETNAM

A PG gypsum processing plant (Dinh Vu Gypsum Joint Stock Company) as a cement additive with a capacity of 600,000 tonnes/year and put into operation since 2017, and has been operating stably

Truong An Hai Phong Joint Stock Company it has now come into operation, processing PG gypsum as a cement additive. The design capacity of 600,000 tonnes/year.

Ngoc Linh Company has the design capacity of the PG waste treatment line up to 750,000 tonnes/year. The company's artificial products are being supplied to more than 30 cement factories.

Song Da Cao Cuong JSC. have conducted research to perfect the technology, design and manufacture a processing line for phosphogypsum (PG) of DAP Dinh Vu as an additive for cement and gypsum boards. with processing capacity of 750,000 tonnes of PG/year



CURRENT SITUATION OF PG IN VIETNAM

Trinh Thi Cham (2010) studied the use of PG from DAP - VINACHEM JSC as an additive to adjust the setting time of cement. $\Rightarrow$ PG can be used as an additive to adjust the setting time, does not have a major impact on cement strength and workability

Trinh Thi Cham et al. (2019) conducted a study on the processing of PG as a building material and gypsum boards: PG used as a raw material for the production of gypsum boards, it is necessary to process: dissolved P_2O_5 , dissolved F^- , SiO_2 , pH, whiteness.

To process PG, use chemical methods + physical methods.

using citric acid $\Rightarrow$ as an additive for cement

using sulfuric acid, PG can meet the requirements for the production of gypsum boards.

Negative: the use of highly concentrated acid, heating for the reaction, it is not economically efficient $\Rightarrow$ Therefore, it is technically possible to process PG for gypsum board production, but it does not guarantee economic and environmental efficiency



CURRENT SITUATION OF PG IN VIETNAM

Dang Ngoc Phuong (2023)

The optimal technological parameters to remove P_2O_5 in phosphorus gypsum waste: sulfuric acid concentration 10%, L/S 3 ml/g, temperature 29°C , the efficiency of obtaining artificial gypsum reached 50%

Tran Duc Trung et al. (2023)

Study on the processing and manufacturing of high-strength, water-resistant gypsum binder from PG

Converted form of $\beta\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O}$: temperature of 160°C for 2 hours

It is completely possible to manufacture a mixed gypsum binder with water resistance and high strength

Nguyen Van Quang (2017)

Studied the use of PG as fertilizer and cement additive

The conversion efficiency into ammonium sulfate: 82.75%; temperature of 30°C ; stirring speed of 500 rpm after 1 hour, mass ratio of $\text{PG}/\text{NH}_4\text{F} = 10:3.2$; with the addition 5ml H_2O / 1g PG.

Author showed the efficiency of calcium sulfate reduction in PG of the DAP plant to SO_2 form after reduction with sulfur and carbon



ORIENTATION ON PROCESSING AND USING PG FROM MINERAL PROCESSING SITE

1. Initial PG - Gypsum: SO_3 24 - 35%; Total P_2O_5 1.5 - 2.6%; Dissolved P_2O_5 0.5%; SiO_2 10 - 14%
2. Quality of required PG products:

No.	Analysis criterias	Unit	Requirement
1	SO_3	%	>40%
2	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	%	>85%
3	Insoluble residue	%	<5%
4	Dissolved P_2O_5	%	<0.05%
5	Total P_2O_5	%	<0.5%
6	SiO_2	%	<3%
7	Whiteness	%	>90%



ORIENTATION ON PROCESSING AND USING PG FROM MINERAL PROCESSING SITE

Particle size distribution

Fraction size, mm	Yield,%	Grade contents P_2O_5 , %	Grade contents SO_3 , %	Grade contents SiO_2 , %
+0.3	2.36	17.62	2.19	69.74
0.02-0.3	50.72	0.81	41.60	7.42
-0.02	46.92	1.82	37.38	14.26
Total	100	1.68	38.69	12.1



ORIENTATION ON PROCESSING AND USING PG FROM MINERAL PROCESSING SITE

No.	Composition (%)	
1	SO ₃ (%)	38.69
2	P ₂ O ₅ (%)	1.68
3	SiO ₂ (%)	12.10
4	Fe ₂ O ₃ (%)	0.32
5	Al ₂ O ₃ (%)	0.099
6	MgO(%)	0.052
7	K ₂ O(%)	0.03
8	TiO ₂ (%)	0.044
9	BaO(%)	0.0216
10	NiO(%)	0.0029
11	CuO(%)	0.0017
12	La ₂ O ₃ (%)	0.0045
13	CeO ₂ (%)	0.003
14	Nd ₂ O ₃ (%)	0.0036



ORIENTATION ON PROCESSING AND USING PG FROM MINERAL PROCESSING SITE

Mineralogy	Range grade content (~%)
$\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$	1 – 2
$\text{CaSO}_4 \cdot 0.5(\text{H}_2\text{O})$	34 – 36
CaSO_4	34 – 36
Quartz – SiO_2	11 – 13
Feldspar – $\text{K}_{0.5}\text{Na}_{0.5}\text{AlSi}_3\text{O}_8$	1 – 3
Illite – $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$	10 – 12
Clorite – $\text{Mg}_2\text{Al}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_8$	≤ 1
Gibbsite – $\text{Al}(\text{OH})_3$	≤ 1



ORIENTATION ON PROCESSING AND USING PG FROM MINERAL PROCESSING SITE

Reagents	Supplier	Role
Armac T (Tallowalkyl amine acetate)	Akzo Nobel	Collector
Berol 8305	Akzo Nobel	Collector
Sodium Hexa methaphosphate (SH)	Merck	Depressant
Sodium Silicate	Scharlau	Depressant
CaO	China	pH adjuster
H ₂ SO ₄	China	pH adjuster
Pine oil	China	Frother



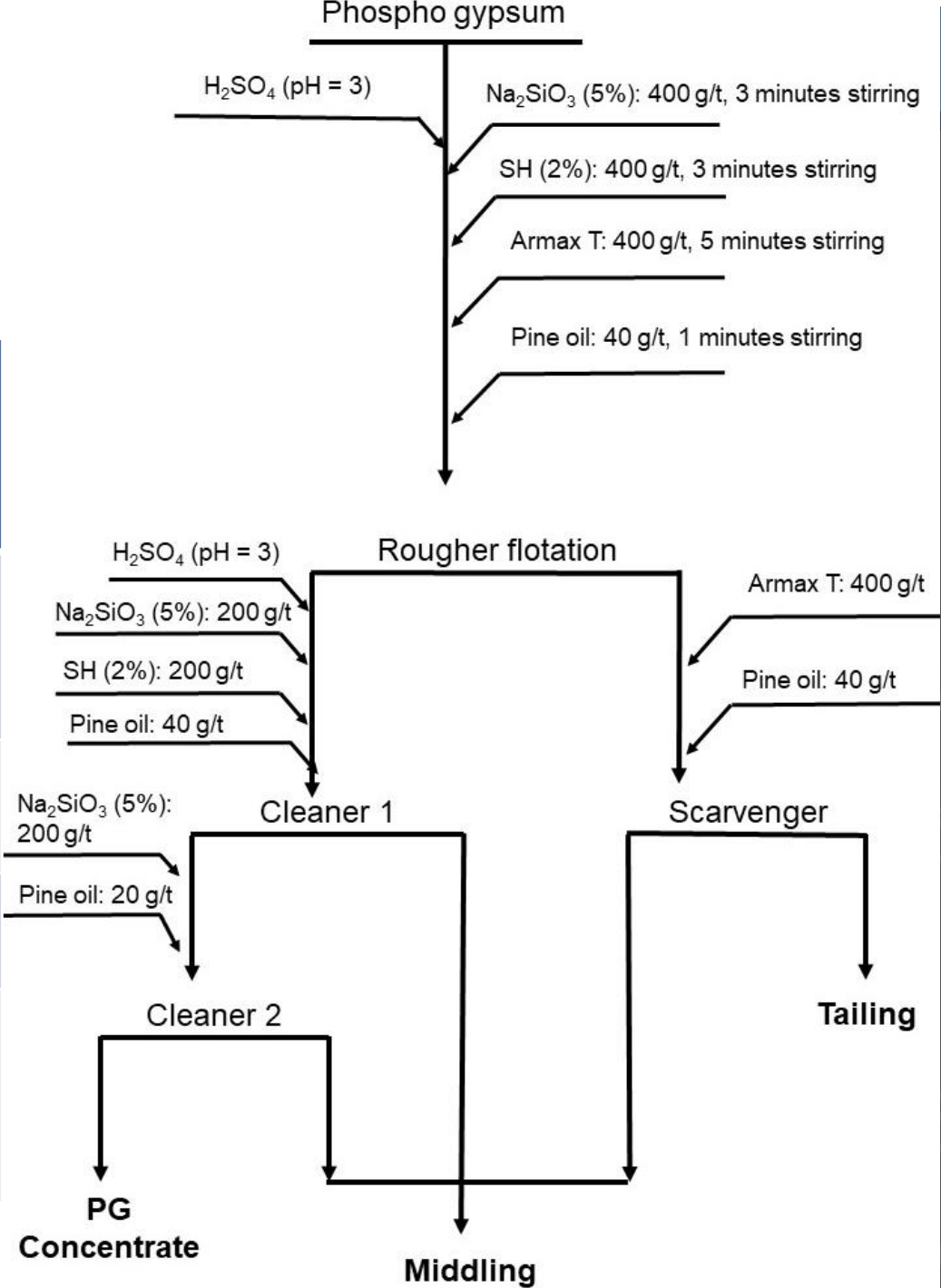
ORIENTATION ON PROCESSING AND USING PG FROM MINERAL PROCESSING SITE





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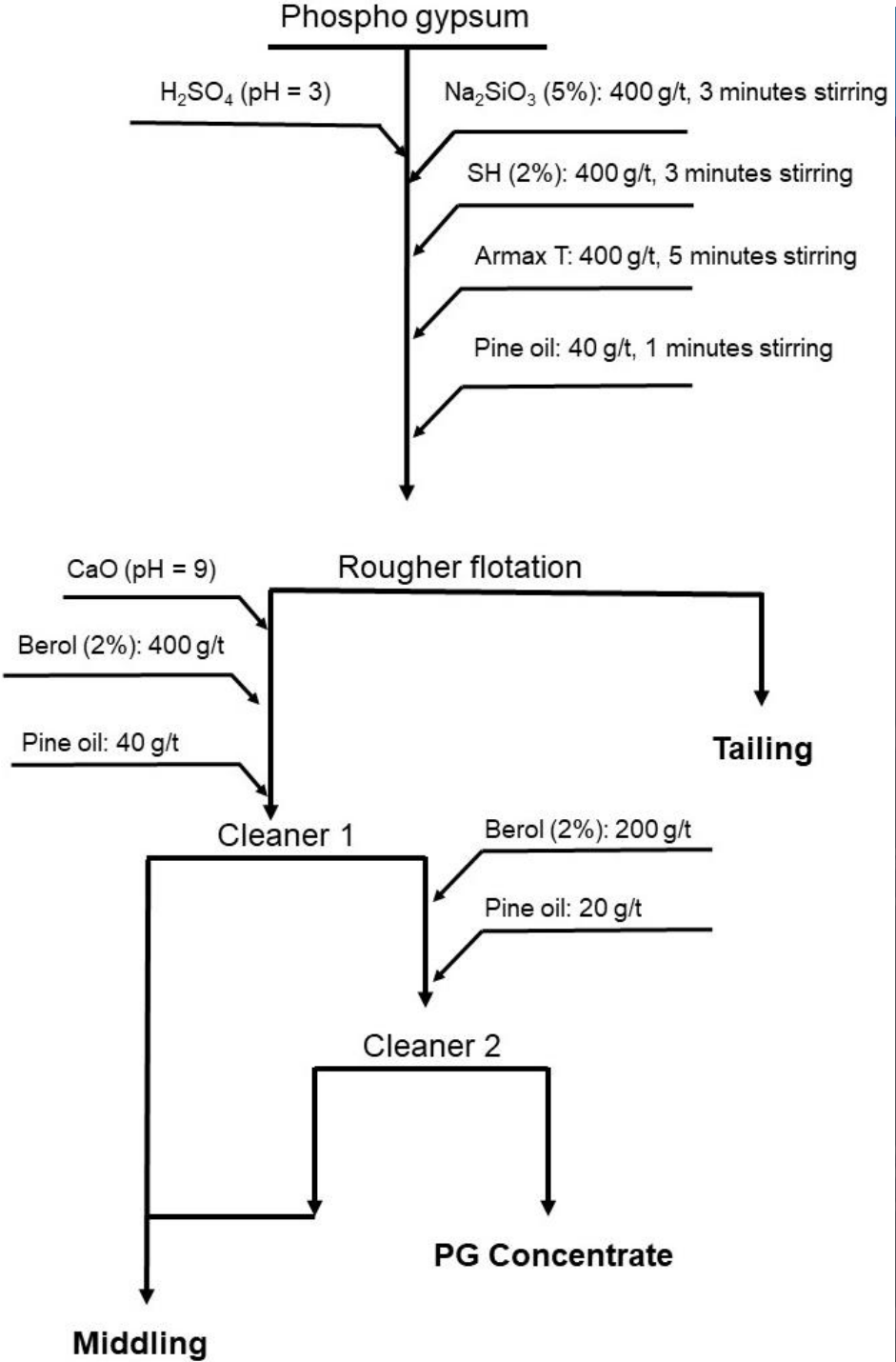
Product	Yield,%	P ₂ O ₅ grade content,%	SO ₃ grade content,%	SiO ₂ grade content,%
PG concentrate	3.8	0.74	40.12	6.20
Middling	33.93	3.34	36.23	21.18
Tailing	62.27	2.22	37.21	27.65
Feed PG	100	1.68	38.69	12.10





ORIENTATION ON PROCESSING AND USING PG FROM MINERAL PROCESSING SITE

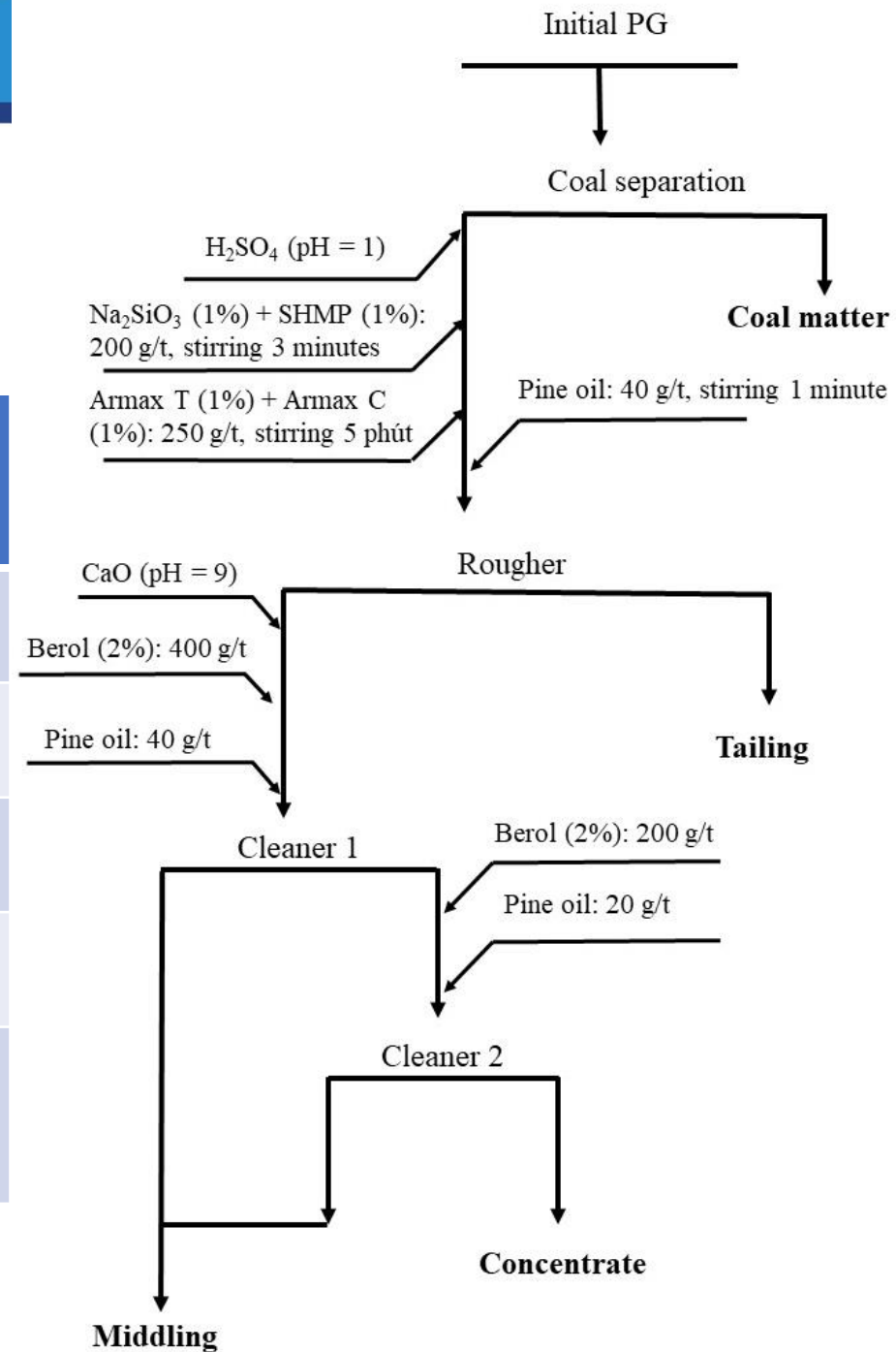
Product	Yield, %	P ₂ O ₅ grade content, %	SO ₃ grade content, %	SiO ₂ grade content, %
PG concentrate	36.52	1.30	42.06	2.50
Middling	10.71	1.90	36.75	17.62
Tailing	52.77			
Feed PG	100	1.68	38.69	12.10





ORIENTATION ON PROCESSING AND USING PG FROM MINERAL PROCESSING SITE

Samples	Yield, %	Content SO ₃ , %	Recovery SO ₃ , %	Content P ₂ O ₅ , %	Content SiO ₂ , %
Concentrate	43.44	51.2	57.52	0.52	2.68
Middling	26.20	40.3	27.3	2.93	2.67
Tailing	14.90	6.35	2.45	2.92	31.8
Coal matter	15.46	31.85	12.73	1.8	24.3
Initial PG	100.0	38.67	100	1.71	12.21





CONCLUSION

PG reserves from three DAP fertilizer factories in Vietnam are very large, if not treated they will cause environmental disasters and waste resources

Studies conducted in Vietnam mainly study the use and treatment of low-quality PG as construction materials and agricultural production

Good quality PG can be used for cement additives, however, this amount is not much while low-quality PG with many impurities needs to be upgraded to meet the demand of construction material manufacturers.

Preliminary research by flotation using a variety of flowsheets and reagents can increase SO_3 grade content, and reduce SiO_2 and P_2O_5 content according to the artificial gypsum standard of Vietnam.



RECOMENDATION

There should be comprehensive studies on the beneficiation flowsheet, reagents, optimization of the dosing regime as well as the pretreatment stages of PG samples.

The waste products of the beneficiation process should be studied for treatment and utilization as well as having an environmental impact assessment

The ICP - MS results showed the existence of rare earths in the PG sample, so solutions are needed to recover and utilize this rare resource

Rare earth elements	Li	Be	La	Ce	Pr	Nd	Sm	Eu
ICP-PG sample	2.0658	N/A	39.3907	29.0696	8.4488	36.4062	6.7324	1.4351
ICP-repeat samples	2.1135	N/A	34.5991	25.4472	7.5006	32.3173	5.8604	1.5522

Rare earth elements	Gd	Tb	Dy	Ho	Er	Tm	Lu	Nb
ICP-PG sample	7.8435	1.1426	7.5544	1.7216	4.8410	0.5212	0.2376	0.4071
ICP-repeat samples	6.9482	1.0086	6.6586	1.5230	4.2643	0.4610	0.2072	0.0257



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