

HANOI UNIVERSITY OF MINING AND GEOLOGY (HUMG)



OVERVIEW OF APATITE-CARBONATE ORE BENEFICIATION STUDIES IN LAO CAI, VIETNAM

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BENEFICIATION OF PHOSPHATES X

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INTRODUCTION



Apatite crystal
(<https://vi.wikipedia.org/wiki/Apatit>)

Phosphate fertilizers: *single superphosphate (SSP), fused phosphate fertilizer, diammonium phosphate fertilizer (DAP)*

Yellow phosphorus

Phosphoric acid (H_3PO_4)





INTRODUCTION

Type I: single mineral, Apatite, in the weathered part with a P_2O_5 content of about 28-40%.

(49.94 million tons)

Type II: an unweathered apatite-carbonate with a P_2O_5 content of 18 - 25%

(243.97 million tons)

Type III: weathered quartz apatite ore with a P_2O_5 content of 12 - 20%, an average of 15%

(244.43 million tons)

Type IV ore is unweathered apatite-quartz-mica ore with P_2O_5 content of 8-10%.

(300.92 million tons)

APATITE IN VIETNAM (*Do&Tran, 2013*)

17 mineral deposits, mines, and ore points are metamorphic sedimentary apatite. The apatite resources (calculated to -900 m): 2.1 billion tons, the reserves around 800 million tons.



INTRODUCTION

Type I ore (mainly)
and type II ore (a
small part with high-
grade content)

- are being mined and sold directly to consumers
- are being depleted

Type III ore is
supplied to
beneficiation plants

- type III ore are being depleted

Type IV ore has not
yet mentioned

- Very low P_2O_5 grade contents
- Complex mineralogy composition

TYPE II ORE (APATITE-CARBONATE) HAVE TO...

mining,
processing,
and using

will be the
primary raw
material for
phosphate
fertilizer
production in
Vietnam



TYPE II ORE

Several minerals, apatite, dolomite and calcite
with similar surface properties that are very difficult to separate by flotation

Type II ore is extensive studied
<-> has not yet been put into commercial production

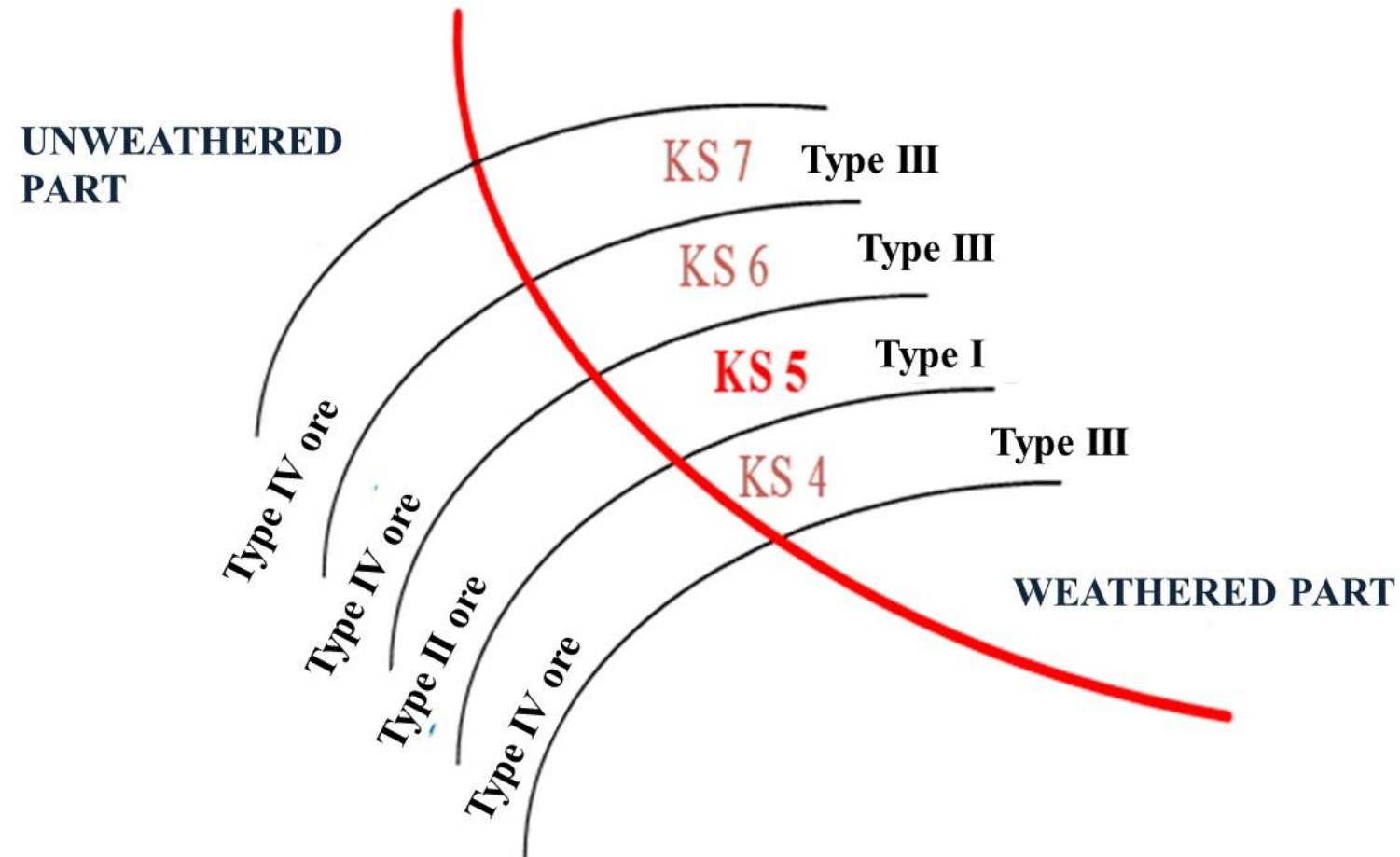
The presence of ions $(\text{CO}_3)^{2-}$ and F^- substituted for $(\text{PO}_4)^{3-}$
along with the cationic substitutions of Mg^{2+} for Ca^{2+} interacting with flotation reagents, reducing their adsorption ability or precipitation them

The formation of fine slimes after grinding, the formation of porous
which increase the dosage of reagents, increase the degree of fine contamination and the low ability of mineral particle - air bubble system forming when separated by conventional flotation machines



GEOLOGICAL CHARACTERISTICS

- ❑ Lao Cai apatite deposits are located along the veins and are affected by the weathering subsidence process in geology layers which called “Diep Koc San” (symbol “KS”).
- *It is divided into nine topographic layers and is characterized by sedimentary composition.*
- *Of the nine layers, 4 contain apatite: KS4, KS5, KS6, and KS7.*





GEOLOGICAL CHARACTERISTICS

❑ Type II apatite ore is located below the chemical weathering boundary KS5

Elements	P ₂ O ₅	SiO ₂	CaO	Fe ₂ O ₃	MgO	Al ₂ O ₃	F	MnO
Content, %	18.1-28.7	3.06-12.36	39.8-48.68	0.96-2.03	3.25-7.13	0.2-1.22	1.78-2.99	0.19-0.85

Mineralogy	Apatite	Quarzt	Mutscovite	Hydroxyt iron	Canxite	Dolomite
Grade contents, %	60-80	2-7	1.5-2	1-3	12-15	25-30



RESEARCH PROJECT

The amount of high-grade ore is no longer abundant, requiring the development of beneficiation technologies to enrich lower content type II ore.

produce
Yellow
phosphorus



Apatite type II
quality requirements:
 P_2O_5 content of 32-34% (28%), moisture <4%, and a particle size of 50-100 mm



extract
Phosphoric
acid

Fused
phosphate
fertilizer

Hệ thống quản lý chất lượng
Quality Management System
ISO 9001 : 2015



CTCP TẬP ĐOÀN HÓA CHẤT ĐỨC GIANG
DUC GIANG CHEMICALS GROUP JSC

Đặc tính kỹ thuật/Specifications



CTCP TẬP ĐOÀN
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**AXIT PHÓT PHORIC
PHOSPHORIC ACID**

H_3PO_4
MW: 97.81

AR HÓA CHẤT TINH KHIẾT

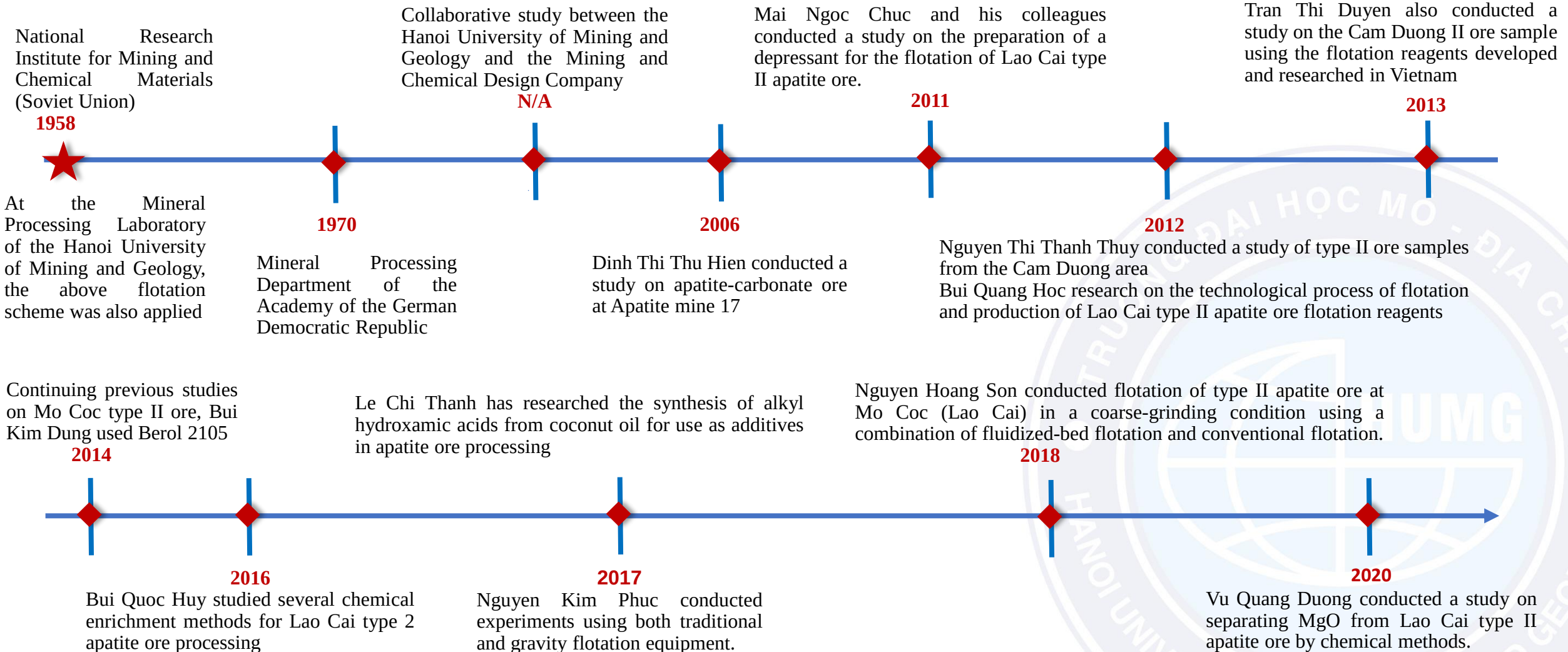
Thể tích/Volume: 500ml
TCCS 01: 2009/HCDG
Hạn sử dụng 3 năm kể từ ngày sản xuất

Hàm lượng/Assay, %..... $\geq$ 85%
Cặn sau nung, %..... $\leq$ 0.2
(Ignition residue)
Clo (Cl)/Chloride, %..... $\leq$ 0.0003
Sunphat(SO_4)/Sulphate, %..... $\leq$ 0.003
Nitrat(NO_3)/Nitrate, %..... $\leq$ 0.0005
Sắt(Fe)/Iron, %..... $\leq$ 0.001
Asen(As)/Arsenic, %..... $\leq$ 0.0001
Kim loại nặng(Pb), %..... $\leq$ 0.001
(Heavy metals(as Pb)
Lot No:

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RESEARCH PROJECT





RESEARCH PROJECT

National Research
Institute for
Mining and
Chemical
Materials (Soviet
Union)
1958

- Mo Coc ore: 24.28% P_2O_5 and 6.01% MgO
- Technology: selective aggregate flotation flowsheet using phosphoric acid
- Concentrate: **34% P_2O_5** at recovery of **75%**
- The dosage of the flotation reagents: 2.0 kg/t of fatty acid, 0.5 kg/t liquid glass, and 10 kg/t of H_3PO_4

- ❑ At the Mineral Processing Laboratory (HUMG), the above flotation scheme was also applied
- *Concentrate: **37.5% P_2O_5** at a recovery of **75%**, from an initial ore with a content of 27% P_2O_5 .*
 - *The dosage of flotation reagents: 1.5 kg/t oleic acid, 1.5 kg/t liquid glass, 5.0 kg/t Na_2CO_3 , ~30 kg/t sulfuric acid*



RESEARCH PROJECT

In 1970, type II ore with surrounding rock was studied at the Mineral Processing Department of the Academy of the German Democratic Republic

Technology: Special beneficiation flowsheet using phosphoric acid
Mo Coc sample: 22.4% P_2O_5 and 5.94% MgO

- Concentrate with **35% P_2O_5** at an actual recovery of **60%**. For recovery up to **80%**, the concentrate content decreased to **32% P_2O_5** , the MgO content around **2% to 3%**
- The dosage of the reagent was 0.5-1 kg/t oleic acid, 1.0 kg/t liquid glass, and 7.0 kg/t phosphoric acid



RESEARCH PROJECT

Calcination and direct flotation of type II ore with various depressants were conducted

Although efforts have been made to diversify types of depressants, the experimental results remain ineffective

(Liquid glass (modulus 2.5; 3.25), activated carbon, taniauh, quebracho, sodium sulfate + ammonium sulfate, liquid glass + copper sulfate, and liquid glass + sodium phosphate dibasic)

A reverse flotation experiment with one rougher and three cleaners

Concentrate (collector 500g/t and 6500g/t H_3PO_4): **29.27% P_2O_5 and 2.33% MgO , P_2O_5 recovery of 80.36%.**

Concentrate (collector 500g/t and 12000g/t H_3PO_4): **30.97% P_2O_5 , 1.62% MgO , with a recovery of P_2O_5 of 87.77%**

Collaborative study between the Hanoi University of Mining and Geology and the Mining and Chemical Design Company



RESEARCH PROJECT

Master thesis

A study on apatite-carbonate ore at Apatite mine 17 (Ngoi Dum area) (Dinh, 2006)

Initial ore: 22.38% P_2O_5 and 5.44% MgO

Technology: The flotation reagents used were Kemira (collector) and liquid glass, starch, and tripolyphosphate (depressant)

Concentrate: 29-29.5% P_2O_5 ; 3.5-4% MgO, P_2O_5 recovery of 60%

A study of type II ore samples from the Cam Duong area (Nguyen, 2012)

Initial ore: 21.9% P_2O_5 , 5.8% MgO, fine disseminated (20-60 μm)

Technology: one rougher + three cleaners. Grinding fineness 93.26% - 0.074 mm, slurry concentration 300 g/l, Na_2CO_3 600 g/t; liquid glass 500 g/t, starch 300 g/t, hydroxamic 175 g/t

Concentrate: content of 31-32% P_2O_5 and 3.0-3.5% MgO, with a recovery of 70-80%

A study on the Cam Duong type II ore sample using the flotation reagents developed and researched in Vietnam (Tran, 2013)

Technology: slurry concentration 30%, grinding fineness 98.72% (- 0.074 mm), acid 10kg/t, VH10 (a type of collector produced in Vietnam) dosage 600g/t

Concentrate: 28.1% P_2O_5 at a recovery of 89.35%.

Closed-flowsheet: 28.57% P_2O_5 at a recovery of 88.3%,



RESEARCH PROJECT

Continuing previous studies on Mo Coc type II ore, Bui (2014) has used

- 2 stages flotation flowsheet with Berol 2105 (600 g/t), starch (300 g/t), liquid glass (500 g/t), Na_2CO_3 (500 g/t)
- concentrate with a content of **30-32% P_2O_5 at a recovery of 70-80%**

The gravity-flotation method for type II ore has also been studied in the Dong Ho area (where type II ore has a high Si content) by expert from Russia

Initial ore: 5.7% P_2O_5 , 9.7% MgO

Concentrate: >30% P_2O_5

- Option 1 is a one-stage gravity separation followed by flotation of high-density products
- Option 2 uses a two-stage suspension beneficiation process, followed by flotation to treat the middling and fine products of the initial sample
- Option 3 is similar to option 2; however, flotation is used to treat the heavy products from gravity separation and the fine products from the initial sample $\Rightarrow$ Option 3 yields relatively good results, with the final concentrate content exceeding 36%.



RESEARCH PROJECT

A research focus on upgrading the coarsest possible ore (Nguyen, 2017) using both traditional and gravity flotation equipment. Obtained concentrate **>32% P_2O_5** at a recovery of nearly **90%**

Open-flowsheet flotation condition (1 rougher, 3 cleaners, 1 scavenger): sludge concentration 30%, Na_2CO_3 600 g/t, starch 500 g/t; Berol + oleic acid 400 + 100 g/t.

Gravity-flotation (1 rougher): Na_2CO_3 600 g/t, berol + diesel 1000 g/t, starch 500 g/t

Nguyen (2018) conducted flotation of type II apatite ore at Mo Coc (Lao Cai) in a coarse-grinding condition using a combination of fluidized-bed flotation and conventional flotation

*Fraction of 0.2 - 0.5 mm (0.5 kg/t of starch, 0.6 kg/t of Na_2CO_3 , 1 kg/t of collector (oleic acid + diesel of 1:1), water for the fluidized bed (18 l/min): **27.65% P_2O_5** at a recovery of **79.06%**.*

*Fraction of 0.2 mm: **33.72% P_2O_5** at a recovery of **91.47%**. Conventional flotation (starch 0.5 kg/t, Na_2CO_3 0.15 kg/t, 0.3 kg/t of collector (oleic acid and Berol in a ratio of 1:1)*



RESEARCH PROJECT

Mai (2011) conducted a study on the preparation of a depressant for the flotation of Lao Cai type II apatite ore

- *the author successfully developed the technology for synthesizing modified CMS*
- *Type 2 ore was preliminarily tested using CMS*

Bui (2012) researched on the technological process of flotation and production of Lao Cai type II apatite ore flotation reagents

- *Synthesis technology for alkyl hydroxamic acids and developed new flotation varying hydrocarbon chain lengths*
- *Concentrate: 30.7÷32.5% P_2O_5 , 0.9÷2.05% MgO , P_2O_5 recovery from 59.48÷62.94%.*
- *Technology:*
 - *2-stages direct-reverse flotation process, grinding finesses $\approx 94.33\%$ (-0.074 mm), sludge concentration $\approx 52.88\%$,*
 - *For direct separation stage: Liquid glass 500 g/ton, Starch 600 g/ton, soda = 150 g/ton, AHA collector 300 g/ton.*
 - *For reverse separation stage: H_3PO_4 9 kg/ton, STTP 400 g/ton, H_2SO_4 3 kg/ton, VH15 0.8 kg/ton*

Flotation reagents



RESEARCH PROJECT

PhD thesis

Le (2017) has researched the synthesis of alkyl hydroxamic acids from coconut oil for use as additives in apatite ore processing

The prepared chemicals meet the quality standards for making apatite type II ore beneficiation in Lao Cai

Bui (2016) studied several chemical enrichment methods for Lao Cai type II apatite ore with a composition of 24.6% P_2O_5 and 12.1% CO_2

The calcination - extraction method using NH_4Cl : 31.9% P_2O_5 ; recovery of 97.5%

The calcination - hydration and decantation method: 29.6% P_2O_5 ; recovery of 97.3%.

Acid leaching with HCl : 31.91% P_2O_5 ; recovery of 97.3%.

Phosphoric acid leaching: 29.49% P_2O_5 ; recovery of 97.82%

Vu (2020) conducted a study on separating MgO from Lao Cai type II apatite ore by chemical methods

MgO in type II apatite ore was separated using a solution of H_3PO_4 and $Mg(H_2PO_4)_2$

Concentrate: 0.9-1.2% MgO ; 33-35% P_2O_5



CONCLUSION

Type II apatite ore of Lao Cai (Vietnam) is an unweathered apatite-carbonate ore of the KS5 ore layer with a P_2O_5 content of about 18-25%, with reserves of over 200 million tons.

This ore has been used only to a limited extent in the production of fused phosphate fertilizer. Other applications, such as fertilizer production, animal feed, and phosphoric acid extraction, remain limited because ore-processing technology has not been perfected.

The types of type II apatite ore in different mining areas (Mo Coc, Dong Ho, Apatit mine 17, Cam Duong, etc.) have different properties and selectivity.



CONCLUSION

The main challenges of type II apatite ore are:

- (1) the similarity in surface properties of apatite with calcite and dolomite;
- (2) the presence of cations and anions in impurities;
- (3) apatite minerals have fine disermiated,;
- (4) The complete release of beneficial minerals



CONCLUSION

Studies use the direct and reverse flotation method with a variety of flotation reagents. Concentration basically of 28 - 35% P_2O_5 , 2-3.5% MgO, at a recovery of 70-80%.

Gravity-flotation method: concentrate (30 - 35% P_2O_5 ; 1.4-3.5% MgO, recovery 63.5 - 81.7%).

Combining fluidized bed flotation and conventional flotation: concentrate (32.21% P_2O_5 , recovery 88.50%).

Flotation reagents: modified starch depressants and alkyl hydroxamic acid (AHA) compound collectors have been studied and tested on a semi-industrial scale

- *This type of reagent responds well to some easily selected type II ores (Mo Coc), but in other mines, the results are not particularly convincing.*

Chemical methods for processing type II ores, such as calcination-extraction, hydration calcination, acid leaching, and MgO leaching, have been studied and implemented. Still, the production costs are high, and there are many potential environmental issues.



RECOMMENDATIONS

Synchronous research on type II ore in Vietnam's mining areas, and to propose an optimal technological scheme and ensure flexibility

The flotation reagents need to be researched to improve their selectivity, ensuring the ability to separate apatite from carbonate minerals and other impurities. The dosage of flotation reagent needs to be reduced while still providing other technological

Developing fine and ultrafine flotation machines due to the minor apatite mineral contamination of this ore.

Optimizing the cominution circuit and equipment, reducing the cost of mineral preparation

Research at a semi-industrial scale to create a solid foundation for commercial-scale implementation



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