MINISTY OF EDUCATION AND TRAINING
HANOI UNIVERSITY OF MINING AND GEOLOGY

TRAN THI HIEN

TECHNOLOGICAL STUDIES ON BENEFICIATION OF GRAPHITE ORES FROM THE BAO HA GRAPHITE MINE - LAO CAI PROVINCE TO MAXIMIZE THE RECOVERY OF FLAKE GRAPHITE

Major: Mining Processing Engineering
Code : 9520607

THESIS OF DOCTOR IN ENGINEERING

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INTRODUCTION

1. IMPERATIVENESS OF THE THESIS

Vietnam has the reserves and resources of graphite ore about 26.327 million tons, of which the reserve reaches 9.774 000 tons, the estimated resource is 16.553 thousand tons, mostly in Yen Bai and Lao Cai province. The reserves and resources graphite ore of Bao Ha mine in Lao Cai province are estimated around 3.171 million tons.

Among the graphite mines and deposits discovered so far, the graphite in Bao Ha mine, Lao Cai province is considered to have the best quality and value, especially, the graphite ore has a flake structure. This has a large percentage accounting for over 90% in the mine. Flake-structured graphite is the product with the highest commercial value.

However, studies to determine the technological process of beneficiate graphite ore from Bao Ha mine, Lao Cai province, to maximize the recovery of flake graphite, have not been fully studied in previous works and have not been tested, on pilot scale. This research work is both scientific because it elucidates the general theoretical issues about the material composition as well as the structure of the graphite ore of Bao Ha mine and the selective grinding problem for this ore. At the same time, it has both practical significance that is to improve the economic value and quality of graphite products, to meet the requirements of raw materials for further processing and to be able to replace imported goods. Therefore, the topic "*Technological studies on beneficiation of graphite ores from the Bao Ha graphite mine in Lao Cai province to maximize the recovery of flake graphite"* was conducted to solve the above problems.

2. OBJECTIVES OF THE THESIS

Building a scientific basis to clarify the issues:

+ Influence of the characteristics of the material composition of graphite minerals and samples of graphite ore from Bao Ha mine - Lao

Cai province on the beneficication process. Determining the existence of flaky graphite minerals in the ore.

+ Influence of beneficiation methods and procedures for graphite ore from Bao Ha mine, Lao Cai province, in order to obtain:

* Technological flowsheet and suitable regime to maximum recovery of flake graphite.

* Combined graphite concentrate with the following quality:

+ Carbon content 80 ÷ 92% C; Total recovery ≥ 90%;

In which: Grade flake graphite +100 mesh (+0.149 mm) with carrbon content up to 94 %

3. OBJECT AND SCOPE

The object of the thesis is a sample of graphite ore from graphite the Bao Ha mine, Lao Cai province.

Research scope:

- Characteristics of material composition of graphite ore at Bao Ha mine, Lao Cai province;
- The influence of technological parameters on the grinding and flotation processes of graphite ore at Bao Ha mine, Lao Cai province;
- Applying the process of attrition milling of the prefloated graphite concentrate;
- Optimized milling and flotation flowsheet and modes for maximum recovery of flake graphite.

4. RESEARCH METHODOLOGY

In the thesis, the following research methods were used:

- Integrated approach;
- Experimental method:

+Mineralogy and petrography analysis; distribution and particle size characteristics of graphite; chemical analysis, material density analysis on centrifuge equipment;

+ Laboratory experiments on ball mill, attritor mill and flotation equipment;

- Inheritance method: The doctoral thesis is inherited from the results of a state-level project: *Research on technology for* *beneficiation and deep processing graphite ore at Bao Ha mine, Lao Cai province*. Code: ĐTL.CN.44/15, chaired by Candidate.

- Methods of analysis and evaluation: Processing by Excel, Word, drawing charts.

5. CONTENT

To achieve the research purpose, the thesis solves the following tasks:

- An overview of domestic and international research on graphite ore beneficiation technology, existing forms, physicochemical properties of graphite, fields of use and product value recently.
- Sampling and analysis of the graphite ore to elucidate structural features, material composition, especially to determine the composition of graphite minerals that exist in the graphite ore formation of Bao Ha mine, Lao Cai province.
- Research on flotation at coarse grinding fineness to separate associated impurities from graphite, in which clarify the influence of a number of conditions parameters such as type and consumption of collectors, depressors, pH regulator,ore slurry concentration...
- Research to propose the optimal attrition milling coefficient, from here, research on optimizing the process of selective attrition milling, separating of graphite flakes.
- Studying the process flowsheet and proposing the technological procedure of beneficiation for Bao Ha graphite ore, Lao Cai province.

6. SCIENTIFIC SIGNIFICANCE

- The thesis has clarified the structural characteristics and determined the composition of graphite minerals that exist in the graphite ore formations of Bao Ha mine, Lao Cai province.
- The topic has proposed a methodology to research, evaluate and optimize the process of attrition milling graphite concentrates to recover the maximum amount of coarse graphite flakes.
- The topic has clarified the scientific basis of the process flowsheet and the technological regime of graphite ore beneficiation with preliminary flotation at coarse grinding fineness combined with

attrition milling of preliminary concentrate to recover the maximum amount of flake graphite in the ore.

- The research methodology for attrition milling as well as the proposed process flowsheet and technological regime can be applied to other graphite ore objects in Vietnam.

7. PRACTICAL SIGNIFICANCE

- The project has proposed a process flowsheet and technological regime to beneficiation of graphite ore from Bao Ha - Lao Cai mine in order to recover the maximum amount of flake graphite, including a significant amount of coarse flake graphite.
- The data of the topic can be used for larger-scale studies as well as as a basis for designing equipment and process flowsheets, as well as adjusting the process of graphite Bao Ha mine, Lao Cai in practice.

8. INNOVATIONS OF THE THESIS

1. The thesis has shown that the existing form of graphite in Bao Ha mine, Lao Cai province is flake graphite, in which flake graphite accounts for 90-95%; amorphous graphite 5-10%.
2. The thesis topic has proposed the methodology and coefficient of optimal attrition milling to evaluate the process of attrition milling of graphite concentrates.
3. For the first time in Vietnam, the process flowsheet including combination of graphite ore flotation at coarse feed and attrition milling to regrinding the graphite concentrate has been proposed.

9. DEFENDED STATEMENTS

Statement 1: Graphite of Bao Ha mine exists in the form of flake graphite with the amount of flake graphite accounting for 90% of which there is a quantity of coarse flake graphite. A small amount of silicate impurities penetrated the graphite matrix.

Statement 2: Clean +0.149mm coarse flake graphite can be recovered by the -0.5mm coarse feed flotation process combined with attrition milling, and re-flotation.

Statement 3: Apply the method of density fractionation in heavy solutions by centrifuge to evaluate the graphite liberation degree in graphite products. From here, the criterion K is proposed to optimize the milling process to ensure both graphite liberation and coarse grain size of flake graphite products.

$$K_O\ (t)= (\gamma_{+0.149mm}(t).\ \gamma_{+0.149mm-2,1}(t))/\ (\lambda_{+0.149mm}\ )$$

Where:

$\gamma_{+0.149mm}$ is the yield of size fraction +0.149 mm in the milled product expressed as a percentage;

$\gamma^{+0.149mm}{}_{-2.1}$ is the weight ratio of the density fraction -2.1 in sink-float test of size fraction +0.149 mm in product, in unit part;
+0.149 mm in product, in units

$\lambda_{+0.149mm}$: is the yield of size fraction +0.149 mm in milling feed expressed as a percentage;

10. THESIS STRUCTURE

Besides the introduction, conclusion, reference and apendix, the thesis structure includes 5 chapters:
Chapter 1: Overview of graphite: resources, processing and uses
Chapter 2: Material composition of ore sample and research orientation
Chapter 3: Research on preliminary flotation of graphite ore
Chapter 4: Research on recovering of coarse flake graphite by attrition milling and flotation
Chapter 5: Research on flotation flowsheet to maximization of the flake graphite recovery

CHAPTER 1.
GRAPHIT OVERVIEW:
RESOURCES, MINING, PROCESSING AND USE

1.1. A brief introduction to graphite

There are two types of graphite: synthetic graphite and natural graphite. In particular, natural graphite is divided into three types of amorphous graphite, flake graphite and vein graphite/crystalline graphite. Flake graphite usually exists in the form of intermittent flakes, sized from 50 ÷ 800 micrometers in diameter and 1 ÷ 150 micrometers in thickness. This graphite ore has a graphite content of 5 ÷ 30% C and 85 ÷ 95% or more after enrichment.

Graphite has many special properties such as high natural inertness and strength, high corrosion and heat resistance, unaffected by weathering conditions, high natural lubricity, high heat resistance up to about 2,500^{o}C; high electrical and thermal conductivity, low thermal expansion, high chemical resistance at normal temperature, flame retardant, low friction, high compressive strength. So flake graphite has many applications in life, some applications of flake graphite are as follows: Natural flake graphite is a cathode material for lithium and vanadium batteries in electric cars, wind and electricity batteries metal crucibles, die casting machine parts need high precision. Graphite is the feedstock material to produce spherical graphite to encapsulate radioactive materials of new generation nuclear power reactors.

1.2. Reserves, distribution, mining, processing and use of graphite ore in the world.

According to statistics of the United States Geological Survey (USGS), the total natural reserves of graphite worldwide according to statistics in 2021 reached 320 million tons. China maintains its position as the world's leading producer of graphite with an estimated 700 thousand tons. Mozambique is the second largest producer of graphite with 100,000 tons, followed by Brazil, Canada, Ukraine and Russia.

The value of graphite products depends mainly on three main factors, which are graphite grain size, purity (high or low carbon content of graphite) and secondary mineral composition (or ash composition). Therefore, in order to satisfy the above 3 factors, it is necessary to study to determine the grinding - beneficiation to do the work reasonable cost. In essence, separating graphite from other minerals is not difficult, but to obtain high-purity graphite is very complicated. The normal graphite flotation process includes 1 rougher stage, 6 ÷ 7 cleaners combined with regrinding of the cleaners concentrates.

1.3. Reserves, distribution, technological studies for the beneficiation and use of graphite ore in Vietnam.

Vietnam has the reserves and resources of graphite ore about 26.327 million tons, of which the reserve reaches 9.774 000 tons, the estimated resource is 16.553 thousand tons, mainly concentrated in two provinces of Yen Bai and Lao Cai and the forecasted resource of graphite ore of Bao Ha mine in Lao Cai province is about 3.171 million tons.

Graphite ore beneficiation technology in Vietnam has been implemented since 1985 with the following research works: *"Study on the beneficiation mode and flowsheet of some graphite ore samples in Mau A mine, Yen Bai"; "Research on beneficiation technology of graphite samples Hung Nhuong - Quang Ngai"; "Research on beneficiation technology of graphite ore at Nam Thi - Lao Cai mine"; "Study to beneficiate graphite ore in Yen Thai area, Yen Thai commune, Van Yen district, Yen Bai province".*

1.4. Research situation of graphite ore in Bao Ha mine, Lao Cai.

There are two types of graphite ore in Bao Ha mine: weathered ore and original ore.

The results of chemical composition analysis of Bao Ha graphite ore have determined the average basic chemical composition in the explored ore bodies as follows:

+ For weathered graphite ores: C 11.79%; Vpt 2.94%; Ak 85.23%; S 0.15%

+ For original graphite ore: C 11.19%; Vpt 0.70%; Ak 86.58%; S 1.75%

The research work *"Study on the beneficiation of original and weathered graphite ore from Bao Ha mine, Lao Cai province"* was carried out by the Institute of Mining Science and Technology - Metallurgy in 2013 to serve the geological exploration report. From the head ore with a content of 10.35 ÷ 14.51% C, the first concentrate has a carbon content of ≥ 88% C; the second fine concentrate has a carbon content of ≥ 80% C, corresponding to the total recovery of 89 ÷ 90%.

1.5. Review, evaluate the chapter overview

- Graphite is an important material used in many modern industries today. Graphite is a source of raw materials for the production of advanced materials in the fields of batteries, aerospace, nuclear power, electrodes, etc. The value of graphite depends on the type and purity (carbon content). and grain size, in which coarse flake graphite products with a content of more than 94%C have a higher selling price.

- In the world high quality graphite products are recovered from the ore through the beneficiation process. The world's traditional graphite flotation technology is applied by multi-stage flotation with regrinding of concentrates to avoid overground concentrates which lead to reduce its quality and recovery.

- Graphite is an important resource in Vietnam with reserves of more than 20 million tons, mainly concentrated in the Lao Cai region, Yen Bai. The graphite ore beneficiation plants in operation all apply fine grinding and flotation technology to produce low quality products (85-86%C concentrate). Studies on graphite ores in Vietnam all apply multi-stage grinding-flotation and receive low grade concentrates (<90% C).

- Graphite from Bao Ha - Lao Cai mine has large reserves and exists in the form of flakes. The study on beneficiation to the maximum recovery of flake graphite is a matter of great scientific and practical significance in Vietnam.

CHAPTER 2.
MATERIAL COMPOSITION OF ORE SAMPLE AND RESEARCH ORIENTATION

2.1 Research purpose.

Material composition analysis will determine the presence and proportion of flake graphite in the ore. The existence form of waste rock minerals in the ore matrix as well as in the graphite mineral also needs to be elucidated.

2.2. Research sample

The research sample has been composed from 6 single samples, with size d ≤300 mm. The sample is crushed, mixed and reduced through many stages to gradually reduce the particle size to d = -2 mm, meeting the requirements of taking samples for chemical analysis and test samples that are representative of the whole mine.

2.3. Research results on material composition of ore samples

Table 2.1. Mineral composition of Bao Ha graphite ore, as determined by XRD study, %

Mineral	Weight (~%)
Quartz - SiO_2	42 ÷ 44
Graphite - C	17 ÷ 19
Feldspar – $K_{0.5}Na_{0.5}[AlSi_3O_8]$	9 ÷ 11
Illite – $KAl_2[AlSi_3O_{10}](OH)_2$	16 ÷ 18
Chlorite – $Mg_2Al_3[AlSi_3O_{10}](OH)_8$	4 ÷ 6
Calcite – $CaCO_3$	1 ÷ 3
Amphibol	≤ 1
Lepidocrocite – FeO.OH	≤ 1

Table 2.2. Chemical composition of combined graphite ore sample

Assays, %						
C	**Al_2O_3**	**Fe_2O_3**	**S**	**SiO_2**	**Ash**	**Volatility**
11.80	10.72	7.50	2.02	57.10	85.20	1.00

The SEM analysis results showed that the interlayer sandwiched between the flake graphite sheets was also contaminated by impurity minerals such as quartz, feldspar, amphibol, biotite, illite, pyrite. In Figure 2.1, it is shown that between the flake graphite sheets are the non-ferrous layers of feldspar K, Na, and Ca, which is the cause of the low carbon content of flake graphite. Therefore, it will be difficult for the separation process to obtain a high concentration of graphite flake ore.

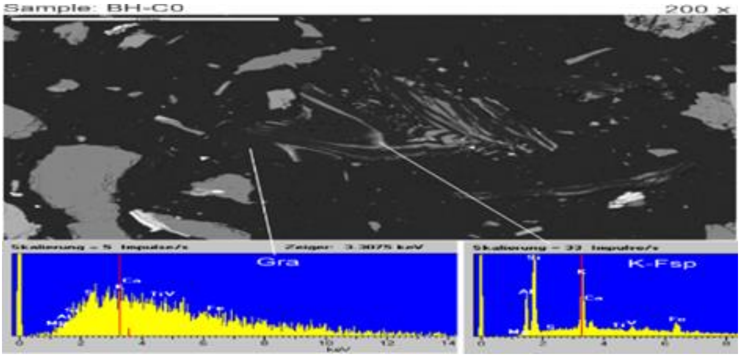

Figure 2.1. SEM-EDX mapping shows graphite flakes associated intimately with other minerals represented by K- felspat (K-Fsp) Si, Al, Fe, and Ti elements

2.4. Conclusion on the characteristics of material composition of Bao Ha graphite ore samples

- Research results show that the average C content of graphite ore in Bao Ha mine, Lao Cai is 11.80%, the content of impurities includes: 10.72% Al_2O_3; 7.50% Fe_2O_3; 57.10% SiO_2. In addition, volatile matter content is 1.00%, ash content is 85.02%, sulfur 2.08%. The main mineral composition in the sample is graphite, quartz, feldspar, illite...
- Graphite ore from Bao Ha mine, Lao Cai contains many graphite with flake structure, accounting for 90÷95%, the rest is 5÷10% amorphous structural graphite. A significant portion of the graphite from Bao Ha mine is coarse in size. Graphite exists in the sample as plates elongated, flaky or fibrous, interspersed between non-ore plates, fairly thickly diffused in the sample matrix, size from (0.05 x 0.2) to (0.15 x 0.5) mm, with some spots arranged in clusters, the fibrous scales often have a winding shape. In addition, in the research sample, graphite-containing minerals were found in amorphous crystalline form, infiltrated with pyrrhotite, pyrite and impurity minerals, mainly quartz, feldspar, illite, garnet and some impurities. other substance. At the same time, the sample also detected some sulfide-containing minerals such as pyrite, pyrrhotite and iron-containing minerals such as hematite, limonite.
- To improve the carbon content in graphite ores Bao Ha mine, Lao Cai, it is necessary to separate accompanying impurities such as quartz, feldspar, illite, biotite, pyrite, pyrrhotite, hematite, limonite... Flotation method is often used to separate these minerals. In addition,

flotation - gravity methods are also considered. With the graphite mineral structure in the form of flakes, interspersed with the impurities mentioned above, it is necessary to pay attention to the selection of processing solutions to both liberate the graphite from the accompanying impurities and keep the maximum size of the graphite flakes. present in the ore.

2.5. Technology research orientation

On the basis of analysis and study on the characteristics of the material composition of the above-mentioned Bao Ha graphite ore, the study will be conducted according to the following steps:

- Research on coarse grinding and use of flotation method to separate graphite and associated impurities.
- Research and investigate the mode of attrition milling and cleaning of preliminary graphite concentrate. Screening of graphite concentrate to obtain coarse flake graphite concentrates that meet quality standards.

The attrition milling method is suitable for the purpose of retaining graphite flakes. Therefore, Candidate will deeply analyze the theoretical basis and practical experiment of this attrition milling process in order to select equipment with technical features suitable to the characteristics of the material composition of the research sample in order to collect the maximum flake graphite.

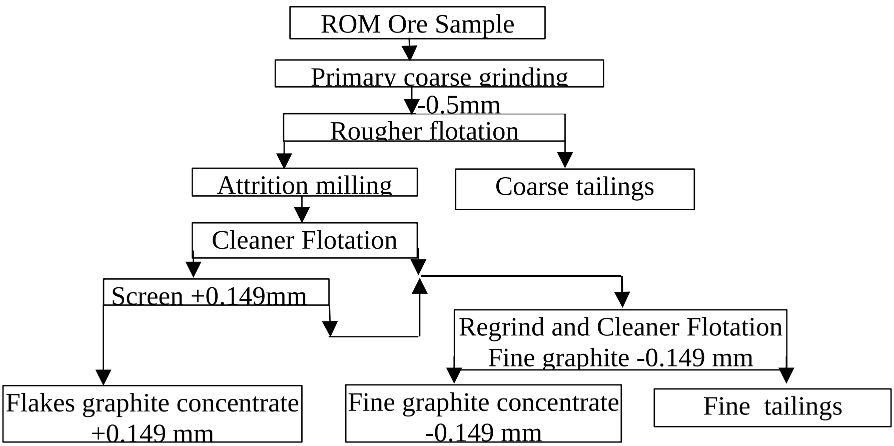

Figure 2.2. Flowchart of technology research orientation for graphite ore beneficiation

In the thesis, a grain size of 0.149 mm was used to separate coarse and fine flake graphite concentrates on the basis of:

- Grade of coarse flake graphite +0.149 mm (corresponding to grain size +100Mesh) is included in the standards of many manufacturers around the world. This grade is easy to mechanically upgraded to 94%C content, is used in high-grade purposes and has prices significantly more than the smaller grade;
- Grain size of graphite in the ore matrix is in the range of 0.01x0.2mm to 0.15x0.5mm. In the process of crushing and releasing minerals, the graphite grain size will be reduced. Selecting a larger coarse flake graphite product size will reduce the yield and the recovery of coarse flake graphite.

CHAPTER 3.
RESEARCH ON PRELIMINARY FLOTATION OF GRAPHITE ORE

3.1 Target and experimental methods.

The target of the preliminary flotation stage is to discharge as much of the waste rock minerals as possible, to recover the coarse-grained graphite to continue to improve the quality in the following stages.

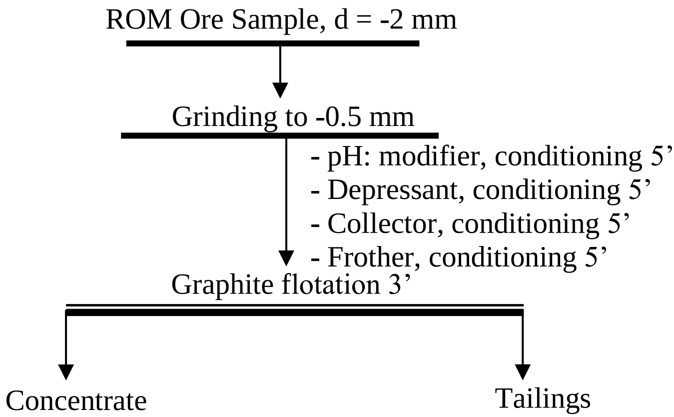

Figure 3.1. Principal flowsheet of condition flotation test

3.2.Grinding characteristics test

The test sample with a mass of 1 kg was ground in a 7 liter laboratory mill. Mass ratio of balls: ore: water = 14.5:1: 0.7. The grinding time varies from 5 minutes to 25 minutes. As the grinding time changed from 0 to 25 min, the +0.074 mm grain grades gradually decreased, the -0.074 mm grain grades increased from 14.39% up to 80.55%.

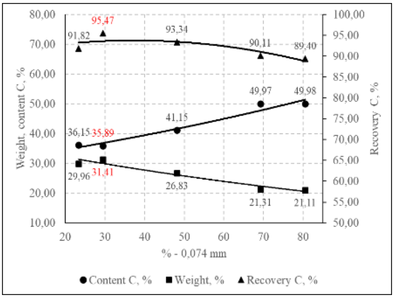

Fig 3.2. Effect of grinding fineness on graphite flotation results

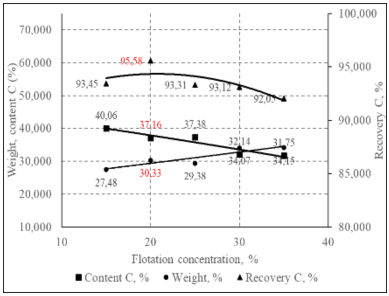

Fig 3.3. Effect of concentration on graphite flotation results

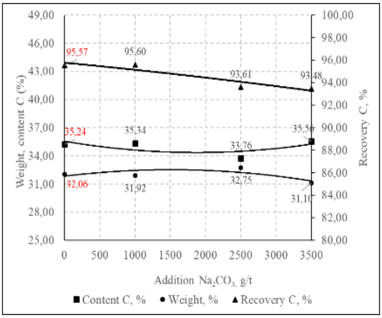

Fig 3.4. Effect of pH on graphite flotation results

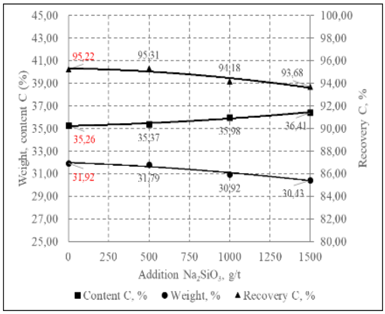

Fig 3.5. Effect of Na_2SiO_3 on the flotation results

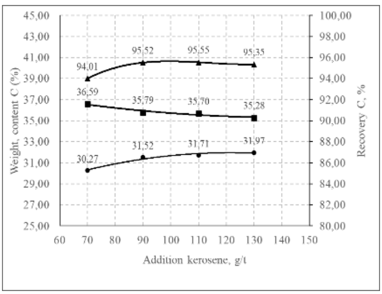

Fig 3.6. Effect of kerosene on graphite flotation results

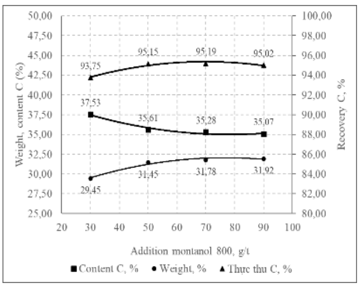

Fig 3.7. Effect of frother on graphite flotation results

3.3. Condition test of rougher flotation

The investigated condition parameters include: grinding fineness, pulp concentration, pulp pH, type and additions of depressors, collectors and frothers. The best parameter values in the previous series of tests were kept for the following. The other main conditions are chosen according to the references.

The test conditions are as follows:

- Weight of test sample: 700g/sample; grinding fineness: 29.47% -0.074 mm (100% -0.5 mm); pulp concentration 20% solid; pH flotation medium 7 ÷ 7.5; addition of liquid glass (Na_2SiO_3) 500 g/t with condition time 5’, addition of kerosene collector 200 g/t with condition time 5’ and addition of Montanol 800 frother 70 g/t with condition time 5’, flotation at 3 minutes.

3.4. Scavenging test

The scavenging operation includes 2 stages: At first scavenger - 40 g/t of kerosene collector and 25 g/t of Montanol 800 frother are added. At second scavenger 20 g/t of kerosene collector and 10 g/t of Montanol 800 frother are added.

3.5. Cleaning test

The cleaning operation includes 5 stages, adding liquid glass at the consumption of: Cleaner 1 : 150 g/t; Cleaner 2: 150 g/t; Cleaner 3: 100 g/t; Cleaner 4: 50 g/t; Cleaner 5: 30 g/t.

3.6. Conclusion of Chapter 3

- Experimental results confirm the possibility of preliminary flotation of Bao Ha graphite ore at coarse grinding fineness. From feeding ore with grinding fineness 29.47% -0.074mm (about 100% -0.5mm) by flotation process, the preflotation graphite concentrate was obtained with 22.17% yield, the 49.40 %C content and the recovery is over 92%. The flotation process allowed a 70% reduction in coarse-grained waste rock with little loss. This allows to reduce the overall cost of the beneficiation and subsequent processing. This is also a new point in graphite ore beneficiation technology in Vietnam because in previous studies the flotation feed ore was often finely ground to 0.1mm.

- Experimental research has determined the flotation flowsheet and the technological parameters suitable for the preliminary flotation process of graphite ore. Specifically, the process flowsheet with 01 Rougher, 01 Scavenger and 01 Cleaner with the following regime: grinding fineness 29.47 % -0.074 mm; pulp concentration of 20% solid; The pH of the pulp medium is neutral 7 ÷ 7.5 (no reagent to adjust the environment); the addition of 150 g/t liquid glass depressor in the stage of cleaning; the addition of kerosene collector 90g/t; the addition of frother Montanol 800 50g/t;

- Preliminary flotation grades of graphite concentrates only reach C content in the range of 45-57%, not reaching commercial content. This shows that in the concentrate there are still many intergrown particles. In order to obtain the final ore concentrates, it is necessary to continue processing and further processing.

CHAPTER 4.
RESEARCH ON RECOVERING OF COARSE FLAKE GRAPHITE BY ATTRITION MILLING AND FLOTATION

4.1. Research purposes

The purpose of the regrinding of the premilinary graphite concentrate by attrition milling is to achieve both a high mineral liberation degree and to avoid crumbling the coarse flake graphite. specifically the +0.149mm grade.

4.2. Overview of attrition milling process and equipment

The attrition milling process also belongs to the category of grinding process with free movement of the grinding media similar to the tumbling grinding processes. However, with the much smaller size of the ball as well as the way it moves the ball, the grinding effect and therefore the field of application are fundamentally different.

4.3. The methodology to evaluate the mineral liberation degree of by density fractionation in heavy solutions

Proposing the coefficients to evaluate the attrition milling process

The coefficient for graphite liberation degree

$$\mathbf{K_L = \gamma_{+0.149mm-2.1},} \qquad (4.1)$$

Where K_L - the coefficient for graphite liberation degree in the product;

$\gamma^{+0.149mm}_{-2.1}$– the weight ratio of the density fraction -2.1 in sink-float test of size fraction +0.149 mm in product, in unit part;

The coefficient of coarse flake graphite preservation during attrition milling

$$\mathbf{K_P = \gamma_{+0.149mm} / \lambda_{+0.149mm}} \qquad (4.2)$$

Where $\gamma_{+0.149mm}$ is the yield of size fraction +0.149 mm in the milled product expressed as a percentage;

$\lambda_{+0.149mm}$: is the yield of size fraction +0.149 mm in milling feed expressed as a percentage;

The coefficient of optimal attrition milling

Optimal attrition milling coefficient is proposed to take into account the influence of the above two objectives

$$\mathbf{K_O\ (t) = (\gamma_{+0.149mm}(t).\ \gamma^{+0.149mm}_{-2.1}(t)) / (\lambda_{+0.149mm})} \qquad (4.3)$$

This K_O coefficient will be used to investigate the influence of parameters on the efficiency of the attrition milling process for preliminary flotation graphite concentrate.

4.4.The evaluation test of mineral liberation degree after attrition milling

The factors that greatly affect the efficiency of attrition milling are investigated, including: Stirring speed, solid-liquid ratio, time of attrition and the influence of ball/ore ratio.

Research sample: Size fraction +0.149mm in the premilinary graphite concentrate with carbon content: 49 ÷ 50% C.

Attrition milling equipment: 1 liter capacity; propeller-type impeller; grinding balls <5mm in size. Bromoform heavy density solution ($HCBr_3$) with density 2.89 g/cm3

4.4.1. Analysis of the density composition of size fraction +0.149mm in prelimitary graphite concentrate

The size fraction +0,149mm was separated from the preliminary concentrate and then was subjected to sink-float density analysis. Fraction -2.1 has a C content of over 94% including most of the liberated graphite particles. The remaining density fractions are intergrown graphite with waste rock particles in different proportions. It is noteworthy that the fraction +2.6 is only about 10% graphite but has also floated into the froth product. It can be said that these are particles with only thin layers of graphite on the surface, the mass ratio is not large, but the surface ratio is high and makes the interstellar particles easy to flotation.

4.4.2 Study on the influence of parameters on the attrition milling process

Experiments to investigate the effects of parameters on the grinding process are shown in Figure 4.1, Figure 4.2, Figure 4.3, Figure 4.4, Figure 4.5, Figure 4.6, respectively.

4.5. Conditions test of attrition milling and flotation to improve the quality of graphite products

The material after attrition milling is subjested to flotation to get the froth, then sieved to receive the fraction +0.149 mm to determine the yield, then analyze the C content and determine the recovery, thereby evaluating the results of attrition milling of the prelimilary concentrate. The test results are shown in the graphs Figure 4.7 to Figure 4.10.

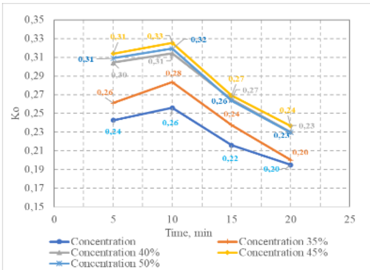

Fig 4. 1. Effect of pulp solid content on Ko

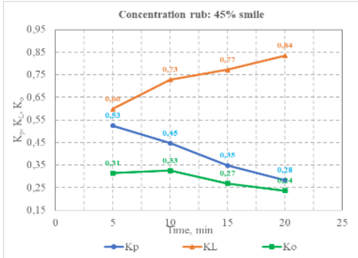

Fig 4.2.. Effect of milling time on coefficients K_P, K_L, K_O

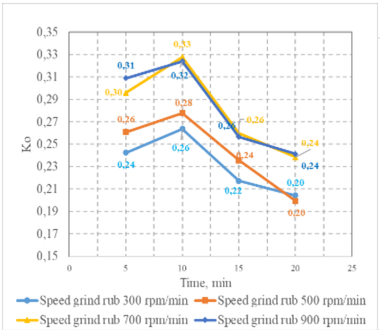

Fig 4.3. Effect of attritor speed on the coefficient Ko

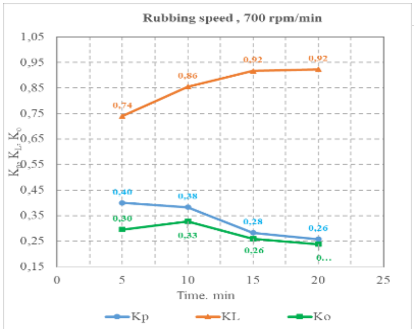

Fig 4.4.. Effect of attritor speed on coefficients K_P, K_L, K_O

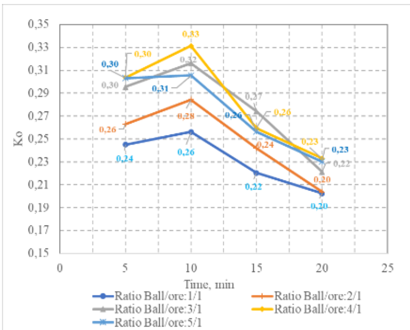

Fig 4.5.. Effect ratio Ball/ore on the coefficient Ko

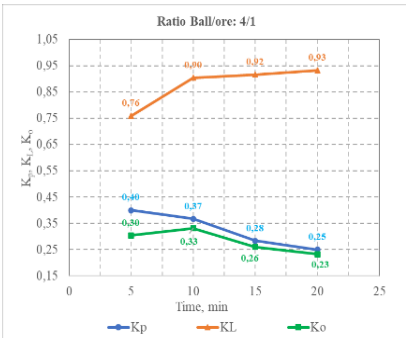

Fig 4.6.. Effect of ratio ball/ore on coefficients K_P, K_L, K_O

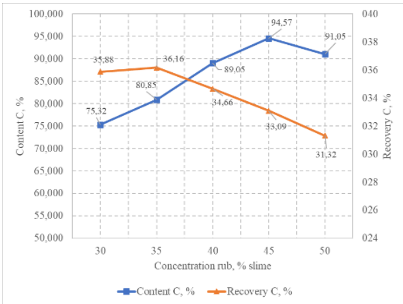

Fig 4.7. Effect of % solid content on flotation efficiency C

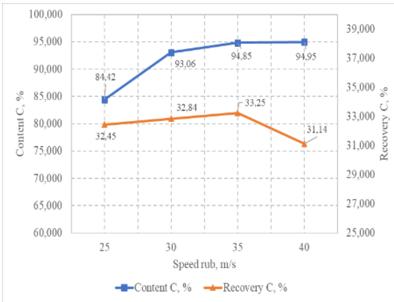

Fig 4.8. Effect of attritor speed on flotation efficiency C

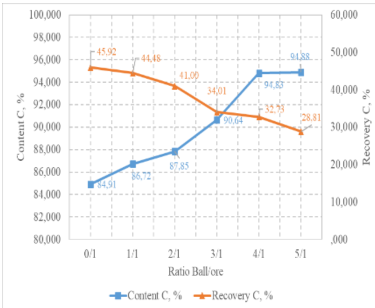

Fig 4.9. Effect of ratio ball/ore on flotation efficiency C

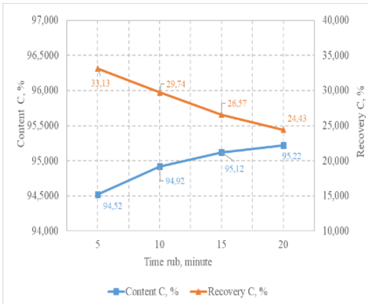

Fig 4.10. Effect of attrittion milling time on flotation efficiency C

4.6 Conclusion of chapter 4

- The method of density fractionation in heavy solutions by centrifuge has been applied to evaluate the graphite liberation degree. From here, we propose K_L - the graphite liberation coefficient, K_P - the coarse flake graphite preservation coefficient in the attrition milling process and K_O - the optimal attrition milling coefficient to evaluate and determine the optimal attrition milling regime of the preflotation concentrate to both ensure the quality of the graphite concentrate and to keep the maximum size of the graphite flakes as well.

- Experimental research on the attrition milling process according to the proposed methodology has clarified the influencing laws of some process parameters and therefore to create the basis and interpret the results of the attrition milling and flotation test. The agreement between the coefficient K_O and the yield of coarse flake graphite concentrates when the graphite quality is above 90% has confirmed the applicability of this coefficient in optimizing the milling process.

- The combined process attrition milling - flotation has allowed to obtain the product of coarse graphite flakes +0.149mm with content >94% C. Research results have established suitable technological parameters for the process of attrition milling of graphite ore samples from Bao Ha mine, Lao Cai province is as follows: grinding and attrition milling speed 35 m/s (700 v/min); ball/ore ratio 4/1; pulp solid content 45%; attrition milling time: 5 minutes + 5 minutes with fractional grinding method.

- In the studied flotation-attrition milling flowsheet, fine graphite products have low C content as well as intermediate products containing graphite. In order to obtain fine graphite concentrate products with higher C content as well as to obtain maximum overall graphite, it is necessary to continue studying closed-circuit flowsheet, optimizing the flowsheet taking into account the reprocessing of intermediate products.

CHAPTER 5.
RESEARCH ON FLOTATION FLOWSHEETS FOR MAXIMIZATION OF THE FLAKE GRAPHITE RECOVERY

5.1 Target and experimental procedure

The cleaning of the -0.149mm fraction separated from the graphite concentrate has been researched to recover fine graphite concentrate ore with high content and recovery. The next step is to study the treatment of intermediate products (the tailings of cleaner oprations) in order to recover more of the graphite contained in these products. Finally, the optional closed – circuit flowsheets were investigated in order to recover the maximum amount of graphite both coarse and fine flakes.

5.2. Cleaning test to recover fine flakes graphite ore

The cleaning operation includes 5 cleaner stages, adding liquid glass at the consumptions of: Cleaner 1: 150 g/t; Cleaner 2: 150 g/t; Cleaner 3: 100 g/t; Cleaner 4: 50 g/t; Cleaner 5: 30 g/t.

5.3. Intermediate products regrinding and reprocessing test

The intermediate reprocessing operation was carried out with the following regime: Attrition milling to size 87% - 0.074 mm; pH: 7 ÷ 7.5; liquid glass addition: 200 g/t; kerosene (collector) addition : 20 g/t; Montanol 800 (frother) addition: 10 g/t.

5.4 Closed-circuit test

Evaluated on the economical and technical aspects, the option of process flowsheet that includes three concentrate regrinding stages and six cleaner stages were chosen as the best to get a graphite flakes concentrate of 94,40 %C; fine graphite concentrate of 82.92 % C, recovery and tailings of 0.86 % C. Test results of Bao Ha graphite ore processing follows Table 5.1

Table 5.1. Chemical composition in wt.% of concentrate graphite ore

Analytical organization	**Assays, %**						
	C	**Al_2O_3**	**Fe_2O_3**	**S**	**SiO_2**	**Ash**	**Volatility**
Coarse Flaky Graphite							
Vietnam Institute of Industrial Chemistry	94.69	-	-	-	-	4.61	0.69
Analysis Center-Vimluki	94.40	1.35	0.89	0.12	1.89	-	-
Fine Graphite							
Vietnam Institute of Industrial Chemistry	82.92	-	-	-	-	15.84	1.24
Analysis Center-Vimluki	83.45	1.61	1.43	0.21	4.11	-	-

5.5. Pilot test of graphite ore beneficiation

The pilot equipment line for the Bao Ha graphite ore beneficiation has been installed according to the process flowsheet that has been researched and established at the laboratory. Before installing the line, it is necessary to calculate the quantitative material and water balances, check the available equipment. After installing the line and the no-load test running, the continuously loaded test has been carried out to get the products.

Coarse flake graphite concentrate has a yield of 4.23%, a carbon (C) content of 94.17%, corresponding to a recovery of 33.52%; fine graphite concentrate has yield of 8.65% with C content of 82.09%, corresponding to recovery of 59.79%. Total concentrates recovery is

93.31%. Combined tailings has a yield of 87.13%, a carbon content of 0.91%, corresponding to a carbon distribution of 6.69%.

5.6. Recommendated flowsheet and expected performance

- Recommendated flowsheet as figure 5.1

Table 5.4. Expected performance of Bao Ha graphite ore processing

Product's name	Weight, %	Content C, %	Recovery C, %
Concentrate 1	≥4	≥ 94.40	≥33
Concentrate 2	8.30	≥ 82	≥60
Tailings	87.70	<1	≈ 6.00

5.7. Conclusion of chapter 5

- With the goal of maximum recovery of flake graphite in which coarse flake graphite product +0.149mnm has C content > 94% and fine graphite product content > 80-82%, has proposed and tested five optional closed-circuit flotation flowsheets. These process flowsheets differ in the number of attrition re-grinding stages as well as the intermediate product treatment options. All process flowsheets show that the grade of coarse flake graphite concentrate is over 94%, of the fine graphite concentrate is over 80% with the total graphite recovery over 90%. Option of flotation flowsheet $N^0$5 was chosen because the total flotation compartment capacity is calculated as the lowest. According to this flowsheet, coarse flake graphite concentrate ore with content of 94.40 % C and recovery of 33.41% was obtained, fine graphite concentrate ore with content of 82.92% C and recovery of 60.07%, total recovery reached 93.48%.
- According to the proposed process flowsheet, a pilot equipment line with capacity of 100 kg/hour has been calculated, designed and tested. The test results on the pilot line confirm the results obtained at the laboratory. From the ROM ore, after the beneficiation process, coarse flake graphite concentrate with the content of 94.17 % C and the recovery of 33.52% was obtained, the fine graphite concentrate with the content of 82.09% C and the recovery was 59.79. %, total recovery reached 93.31%.
- On the basis of laboratory and semi-industrial test results, the proposed flowsheet as Figure 5.1. has been recommendated.

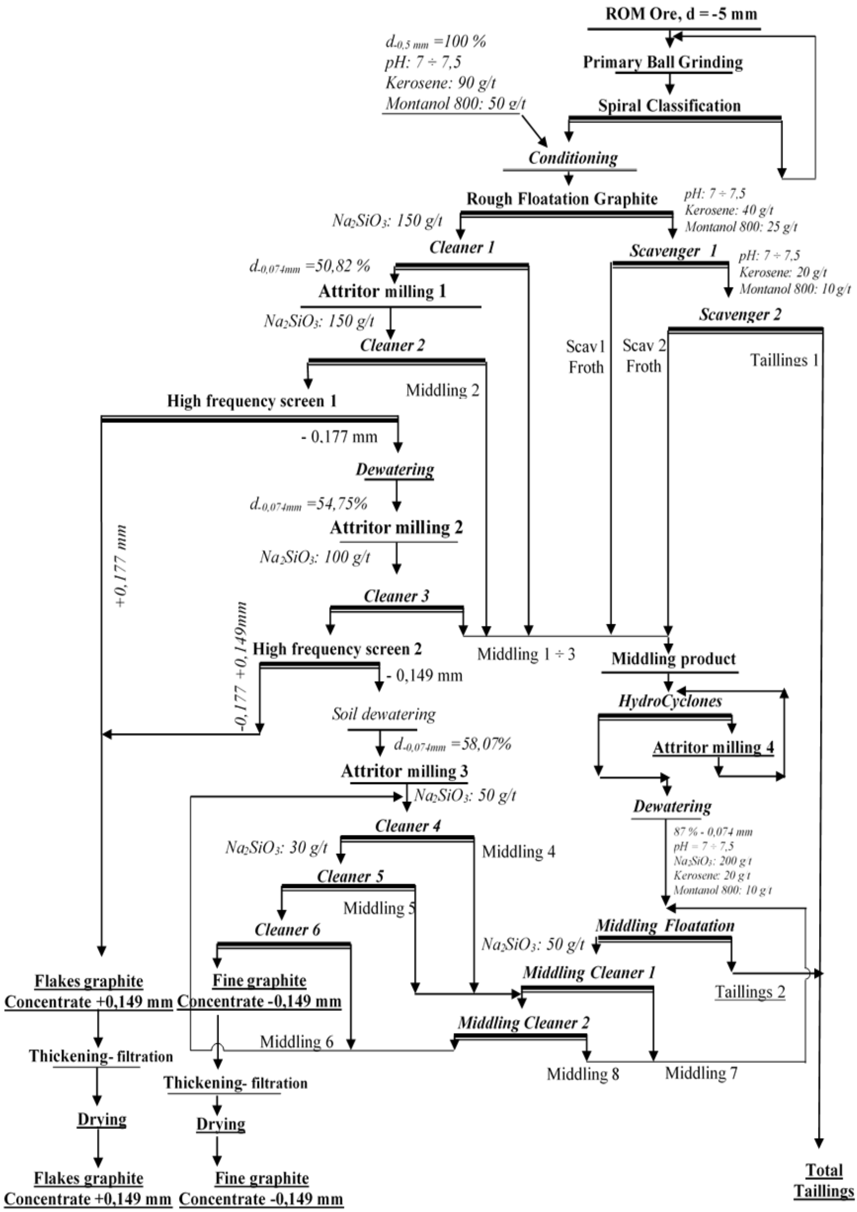

Fig 5.1. Recommendated process flowsheet for recovery of graphite flakes from Bao Ha mine, Lao Cai province

CONCLUSIONS AND RECOMMENDATIONS

I. Conclusions

1. The value of using graphite products depends on crystal type, grain size and C content, in which coarse flake graphite products with C content > 94 % have the most value.

2. Graphite of Bao Ha mine, Lao Cai province mainly exists in the form of graphite flakes and amorphous. Flake graphite accounts for 90-95% of total graphite which there is a quantity of coarse flakes. Amorphous graphite accounts for 5-10%. In the flake graphite, there is a small amount of finely infiltrated silicate mineral impurities that can reduce the quality of the graphite concentrate. The recovery of high-quality coarse flake graphite is a matter of great economic benefit.

3. A considerable amount of high quality +0.149mm coarse flake graphite can be obtained by combination of flotation at -0.5mm coarse feed and attrition milling of the flotation concentrate,. The process of coarse grinding and preliminary flotation not only allows to reduce the cost of grinding energy, but also significantly improves the product value.

4. The method of density fractionation in heavy solutions by centrifuge has been applied to evaluate the mineral liberation degree in graphite products. From here, the optimal grinding coefficient K_O is proposed to evaluate and determine the optimal grinding mode for graphite pre-flotation concentrate to both ensure the quality of the graphite concentrate ore in coarse flakes and ensure the flake size. .

5. The overall process flowsheet has been established and proposed for the beneficication of graphite ore from Bao Ha, Lao Cai mines. The process flowsheet includes 01 coarse grinding stage, 01 rougher flotation stage, 02 scavenger stages, 03 attrition milling stages, 06 cleanering stages; 01 stage of attrition milling and reflotation of intermediate products. The recommended process flowsheet is shown in the Figure 5.1.

6. The optimal technology mode is established: Primary grinding to -0.5mm (29.47% -0.074mm). Reagents used for rougher flotation: kerosene: 90g/t, Montanol 800: 50 g/t; for scavenger 1: 40g/t kerosene and 25 g/t Montanol 800; scavenger stage 2: 20g/t kerosene and 10 g/t Montanol 800. In the cleaning stages, liquid glass should be added.

7. According to the proposed process flowsheet in the above optimal technology regime, coarse flake graphite fine ore +0.149mm content >94% was obtained with the recovery of 33-35%. Fine graphite fine ore with content >82% with a recovery of 60%. Total recovery of graphite is 93-95%.

II. RECOMMENDATIONS

1. It is necessary to further research and optimize the process of attrition milling on equipment on a larger scale.

2. It is necessary to study the flotation of graphite ore in Bao Ha, Lao Cai on some other gravity flotation devices (first of all, the Hydrofloat device) to improve the grain size and the recovery of coarse flake graphite.

3. Study the applicability of the proposed flow sheet and technology regime for other types of graphite ores in Vietnam

LIST OF PUBLICATIONS RELATED TO THE THESIS

Vietnamese

1. Tran Thi Hien (2016), "Geological structure, composition mineral and technological orientation of the selection and high purity processing of graphite ore from Bao Ha mine - Lao Cai ", Processing minerals in Vietnam, p. 104 - 110.
2. Dao Duy Anh, Do Hong Nga, Tran Thi Hien (2016), "Application and situation of graphite mining and processing in the world and in Vietnam", Mining Industry Journal, 30(1), p. 86 - 90.
3. Tran Thi Hien, Dao Duy Anh, Tran Ngoc Anh (2017), "Research on technology for selecting graphite ore from Bao Ha mine, Lao Cai province", Journal of Mining Industry, 31(4), p. 60 - 63.
4. Tran Thi Hien, Dao Duy Anh, Do Hong Nga, Tran Ngoc Anh (2018), "Technology of deep processing and selection of graphite ore in Bao Ha mine, Lao Cai", National Conference on Earth Science and Natural Resources with Sustainable Development, p. 216 - 223.
5. Tran Thi Hien, Nguyen Hoang Son, Tran Ngoc Anh (2018), "Research on technology to select graphite from Bao Ha, Lao Cai mines in order to maximize the recovery of flake graphite", Collection of scientific and technological conference reports. 5th national mineral recruitment, pp.291 - 298
6. Tran Thi Hien (2018), "Synthesis report on scientific and technological results of research on technology for selecting and deep processing graphite ore in Bao Ha mine, Lao Cai province", Hanoi.

English

7. Hien Tran Thi, Nga Do Hong (2017), "Sulfuric Acid Leaching Process for Producing High Purity Graphite from 92,6 % C to 98%C", *World Journal of Research and Review*, 5(1), tr. 23 - 26.
8. Hoang Thi Minh Thao, Tran Thi Hien, Dao Duy Anh, Pham Thi Nga (2017), "Mineralogical characteristics of graphite ore from Bao Ha deposit, Lao cai Province and proposing a wise use", *Vietnam Journal of Earth Sciences*, 39(4), tr 326 - 339.
9. Tran Thi Hien, Dao Duy Anh, Dinh Thi Thu Hien (2018), "Bao Ha'S Graphit Flotation" *XXIX international mineral processing congress 2018.*