

PRE-FEASIBILITY STUDY OF IMPROVING QUALITY OF LOW-GRADE FLUORITE. A CASE
STUDY AT PHANOMTHUAN DEPOSIT, KANCHANABURI, THAILAND



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Georesources and Petroleum Engineering
Department of Mining and Petroleum Engineering
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แร่พนมทวน, จังหวัดกาญจนบุรี.



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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Thesis Title	PRE-FEASIBILITY STUDY OF IMPROVING QUALITY OF LOW-GRADE FLUORITE. A CASE STUDY AT PHANOMTHUAN DEPOSIT, KANCHANABURI, THAILAND
By	Miss Keosaychai Souvannavong
Field of Study	Georesources and Petroleum Engineering
Thesis Advisor	Associate Professor SOMSAK SAISINCHAI
Thesis Co Advisor	APISIT NUMPRASANTHAI, Ph.D.

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in
Partial Fulfillment of the Requirement for the Master of Engineering

----- Dean of the FACULTY OF
ENGINEERING
(Professor Doctor SUPOT TEACHAVORASINSKUN, D.Eng.)

THESIS COMMITTEE

----- Chairman
(Assistant Professor THITISAK BOONPRAMOTE, Ph.D.)

----- Thesis Advisor
(Associate Professor SOMSAK SAISINCHAI)

----- Thesis Co-Advisor
(APISIT NUMPRASANTHAI, Ph.D.)

----- External Examiner
(Associate Professor Pinyo Meechumna, Ph.D.)

แก้วสายใจ สุวันนะวง : การศึกษาความเป็นไปได้เบื้องต้นของการปรับปรุงคุณภาพแร่
ฟลูออไรต์คุณภาพต่ำ กรณีศึกษาแหล่งแร่พนมทวน, จังหวัดกาญจนบุรี.. (PRE-
FEASIBILITY STUDY OF IMPROVING QUALITY OF LOW-GRADE FLUORITE. A
CASE STUDY AT PHANOMTHUAN DEPOSIT, KANCHANABURI, THAILAND) อ.ที่
ปรึกษาหลัก : รศ.สมศักดิ์ สายสินธุ์ชัย, อ.ที่ปรึกษาร่วม : ดร.อภิสิทธิ์ น้ำประสานไทย

ในการศึกษานี้ได้นำเสนอการศึกษาความเป็นไปได้เบื้องต้นของการแปรรูปฟลูออไรต์
จากแหล่งแร่พนมทวน จังหวัดกาญจนบุรีประเทศไทย การศึกษาคั้งนี้มีวัตถุประสงค์เพื่อสำรวจหา
เงื่อนไขที่เหมาะสมในการลอยแร่ฟลูออไรต์เพื่อกำจัดสิ่งเจือปนที่มี SiO_2 สูง CaCO_3 และแร่ธาตุอื่น
ๆ รวมทั้งประเมินโครงการในเชิงของเศรษฐศาสตร์

ดังนั้น การปรับปรุงคุณภาพของฟลูออไรต์โดยใช้เทคนิคการลอยฟองสามาตได้
เกรดเซลามิค ลักษณะของแร่ป้อนในการศึกษานี้ประกอบด้วย $\text{CaF}_2 = 29.4 \text{ Wt.}\%$, $\text{SiO}_2 = 43.9$
 $\text{Wt.}\%$ และ $\text{CaCO}_3 = 6.9 \text{ Wt.}\%$ โดยเฉลี่ย หลังจากกระบวนการลอยแล้วผลลัพธ์ของการอัฟเกรด
ประกอบด้วย $\text{CaF}_2 = 96.46 \text{ Wt.}\%$, $\text{SiO}_2 = 2.1 \text{ Wt.}\%$, และ $\text{CaCO}_3 = 0.7 \text{ Wt.}\%$ นอกจากนี้ผล
การวิเคราะห์ทางการเงินแสดงให้เห็นถึงความเป็นไปได้ในการลงทุน โดย NPV =
377,575,304 บาท, Discount rate = 10%, MIRR = 35% และระยะเวลาคืนทุนส่วนลด 2 ปี

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ปีการศึกษา	2562	ลายมือชื่อ อ.ที่ปรึกษาหลัก
		ลายมือชื่อ อ.ที่ปรึกษาร่วม

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In this study was presented the pre-feasibility study of improving quality of low-grade fluorite from Phanomthuan deposit, Kanchanaburi province, Thailand. The purpose of this study aims to explore the optimal condition in order to remove the impurities which contained high SiO_2 , CaCO_3 and other minerals, also evaluate the project in term of economic.

Therefore, the improvement quality of fluorite by using froth flotation techniques was reach the ceramic grade. The raw material characterization contains $\text{CaF}_2 = 29.4 \text{ Wt.}\%$, $\text{SiO}_2 = 43.9 \text{ Wt.}\%$ and $\text{CaCO}_3 = 6.9 \text{ Wt.}\%$. After flotation process the optimal condition result which contains $\text{CaF}_2 = 96.46 \text{ Wt.}\%$, $\text{SiO}_2 = 2.1 \text{ Wt.}\%$, and $\text{CaCO}_3 = 0.7 \text{ Wt.}\%$. Moreover, the financial analysis indicated that this project possibly to invest due to the Discount cashflow result were NPV = 377,575,304 baht, Discount rate = 10%, MIRR = 35% and Discount payback period 2 Years.

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Student's Signature

Advisor's Signature

Co-advisor's Signature

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CHAPTER 1

INTRODUCTION

1.1. Preamble

Fluorite is an essential mineral composed of calcium and fluorine (CaF_2), also known as fluorspar which is mostly vital mineral supply that apply in many sectors with different specifications product such as hydrofluoric acid, fluorine-based chemicals, ceramic processed, manufacture of glass, and metallurgy, etc. (1) Therefore, fluorite has a wide variety of uses through mineral processing.

The improvement of modern innovation is developing interested for top notch fluorite mineral (with the substance of CaF_2 over 93%). (2). With high usage demand of high-grade fluorite, froth flotation is proven to be the most environment friendly and economically conceivable technique. Flotation is beneficial process to recovery fluorite from ores which contains silicon dioxide and calcite. However, to separate fluorite from calcite are found to be complex because their similarity floatability.

Floatability is due to fluorite and calcite are salt minerals, the similarity of physical and chemical properties such as reagent adsorption behavior, chemical composition, dissolving properties, crystal structure and so on. Principally considered, collector adsorption on fluorite and calcite is affected by the pH of flotation systems because of reagents mechanism with mineral in flotation process is very complex. (3).

Nevertheless, fluorite ore associated with large amount of gangue minerals which contain 29% CaF_2 , 43.9% SiO_2 , 6.9% CaCO_3 and others trace mineral, it is great need to explore the optimal condition of flotation performance to remove the impurities which is meet fluorite grade standard requirement.

1.2. Objective

The aims of this study were to recover fluorite from poorer fluorite ores and to estimate the cost of pre-feasibility study of project. In order to achieve the expected benefits of this study as following objectives were applied.

- Explore the optimal flotation performance by significant parameters such as:
 - pH variation
 - Collector dosage variation
 - Depressant dosage variation
 - Conditioning time variation.
- Estimate the cost of project to determine DCF model.

1.3. Methodology

Experiment conditions were applied to achieve the objectives. X-Ray Diffraction (XRD) and X-ray fluorescence (XRF) were used to investigate the mineral characterization of raw material and after process of fluorite. Froth flotation technique was undertaken to investigate the separation of fluorite from silicon dioxide, calcite and others trace mineral contains through consider the parameters such as pH variation, chemical reagents variations and conditioning times. The methodology was shown in flowchart of study. Figure 1.1.

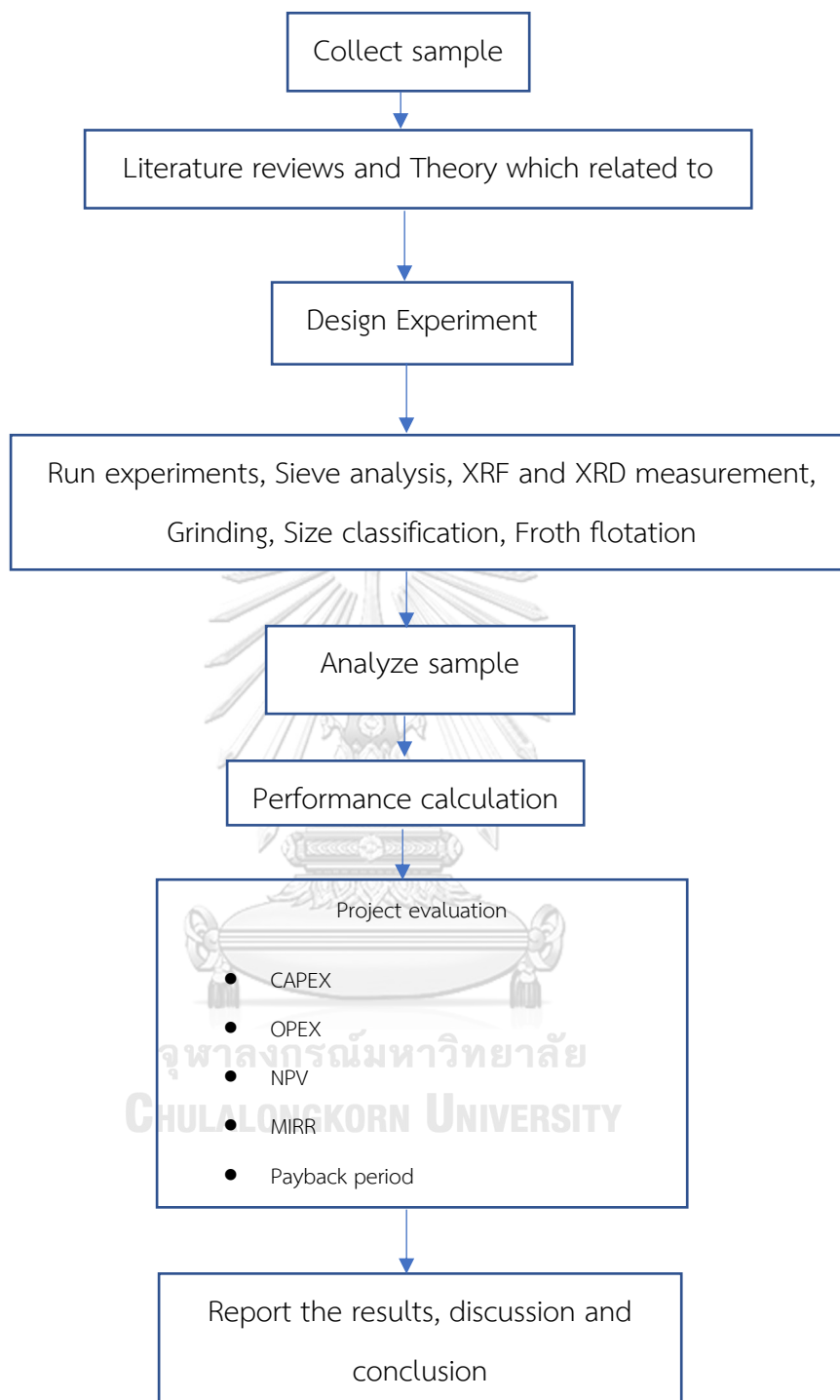


Figure 1.1. Flowchart of study

1.4. Structure of thesis

This thesis contains five chapters including chapter 1-3 provide introduction, theory and experimental methodology and the later chapters 4-5 provide experimental results and discussion followed by conclusions and recommendation for future study.

Chapter 1 provides of an introduction which introduce the background of the strength of this study including aims, objectives and concise of methodology of this research.

Chapter 2 Reviews the theory and literature that related to this study which begins with fluorite properties standard. Subsequently, the reviews of froth flotation principle, collectors, frother and modifiers were presented. A review of fluorite floatation with various significant condition were mentioned. Components of project evaluation such as discount cash flow (DCF) to determine Net present value (NPV), Modified internal rate of return (MIRR), and discount payback period (DPP) are presented.

Chapter 3 Introduces methodology of experimental techniques and instruments used in this. Clarify data analysis by using XRF and XRD to measure mineral characterization.

Chapter 4 Presents results and discussion of fluorite recovery from ores tailing by using froth flotation technique to separate fluorite from quartz and calcite in each condition. Provides results and discussion of project evaluation in term of economics.

Chapter 5 is a last chapter which presents research conclusion and provides recommendations relating to future study.

CHAPTER 2

THEORY AND LITERATURE REVIEW

This chapter is providing of previous research which is relevant to this study it is begins with principle of flotation, the previous studies of fluorite flotation and reagents use for flotation which the beneficial process to recover fluorite from ores. The fluorite properties standard was present in this chapter. Therefore, the theory of project evaluation such as discount cash flow (DCF) to determine Net present value (NPV), Modified internal rate of return (MIRR), and discount payback period (DPP) are presented.

Table 2.1 *Fluorite properties standard (Ministry of Industry, Thailand)*

Chemical composition	Chemical or acid grade (%)	Ceramic grade (%)		Metallurgy grade (%)	
		1	2	1	2
CaF ₂	97	95	98	85	75
SiO ₂	1	3		17	22
CaCO ₃	1	1.5	1.5		

In order to reach the fluorite properties standard grade requirement shown in Table 2.1. it is necessary to explore the optimal condition from significant parameter of fluorite flotation performance which is the main purposed of this study.

2.1 Flotation technology

Flotation is a physical-chemical process where target mineral particles within an aqueous pulp selectively attach to air bubbles, forming particle bubble aggregates, which are subsequently transported out of the pulp into a froth phase. As the air bubbles mainly differentiate between hydrophobic and hydrophilic surface

properties, selectivity is essentially based on differences in wetting properties of the solid particles suspended in the pulp. (4)

2.2 Principles of Flotation

Flotation is a process that multi part minerals and ores are isolated into their constituent components. The process is depending on differences physiochemical surface properties among hydrophobic and hydrophilic surfaces, which either occur normally or are artificially prompt by utilizing substance reagents (Figure 2.1).

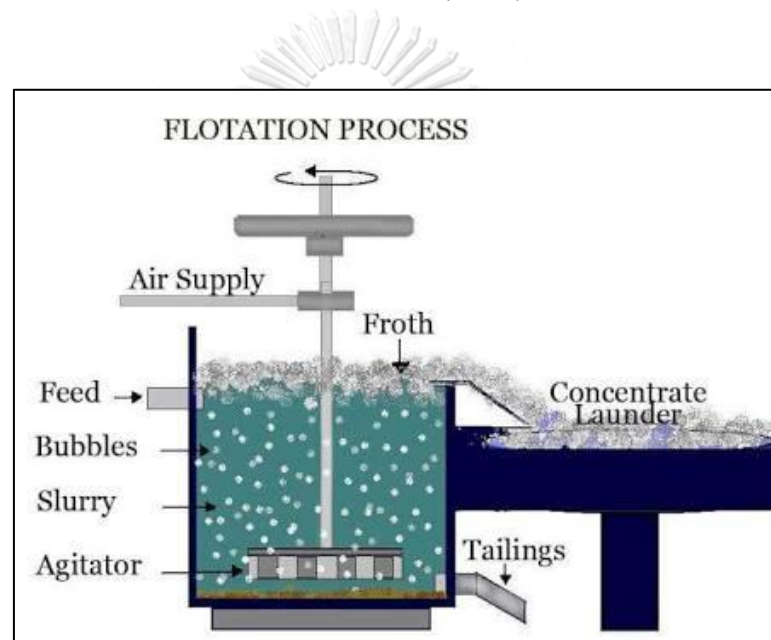


Figure 2.1 Flotation process (5)

Flotation is an incredibly versatile method for physically keeping apart particles based totally on differences in the potential of air bubbles to selectively adhere to unique mineral surfaces in a mineral/water slurry. The particles with attached air bubbles are then carried to the surface and removed, whilst the particles that stay wetted continue to be in the liquid phase. Froth flotation can be adapted to a broad range of mineral separations, as it is viable to use chemical redress to selectively alter mineral surfaces so that they have the necessary properties to separate. Furthermore, It is currently in use for various diverse

applications, it is particularly useful for processing fine-grained ores that are now not amenable to traditional gravity concentration.(6) as shown in Figure 2.2.

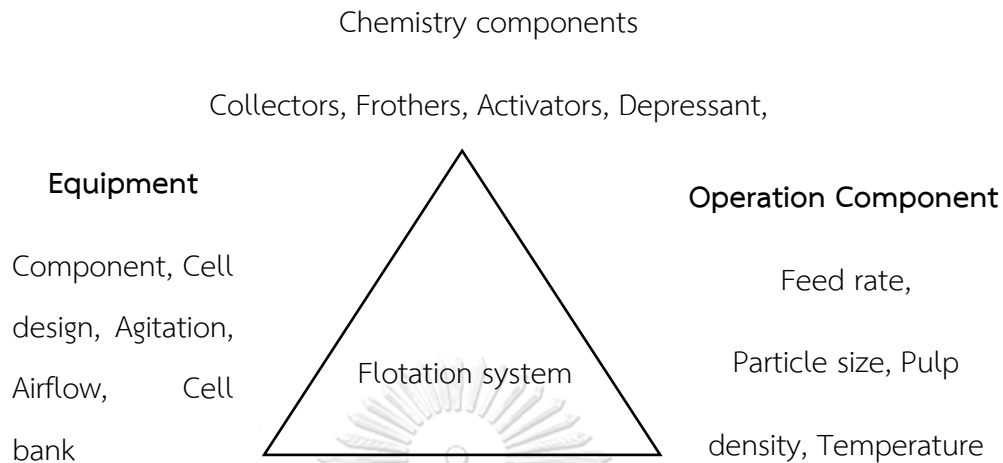


Figure 2.2 The flotation system (Klimpel, 1995).

2.2.1 Hydrophilicity/hydrophobicity

The fundamental of froth flotation is the distinction in wettability of various minerals. Particles extend from those that are effectively wettable by water (hydrophilic) to those that are (hydrophobic). If a mixture of hydrophobic and hydrophilic particles is suspended in water, and air is bubbled through the suspension, at that point the hydrophobic particles will attach to the air bubbles and float to the surface as shown in figure 2.3. The froth layer that structures on the surface will at that point be vigorously stacked with the hydrophobic mineral and can be removed as a separated result. (7) Particles either be normally hydrophobic, or the hydrophobicity motivated by chemical treatments. Normally, hydrophobic materials consist hydrocarbons, and non-polar solids for example, elemental sulfur. Chemical treatments to perform a surface hydrophobic are basically strategies for specifically covering a molecule surface with a monolayer of non-polar oil.

A low contact angle which usually means less than 90° leads to a hydrophilic surface while a higher contact angle than 90° leads to a hydrophobic

surface. The schematic hydrophobic and hydrophilic contact angle indicates in Figure 2.3.

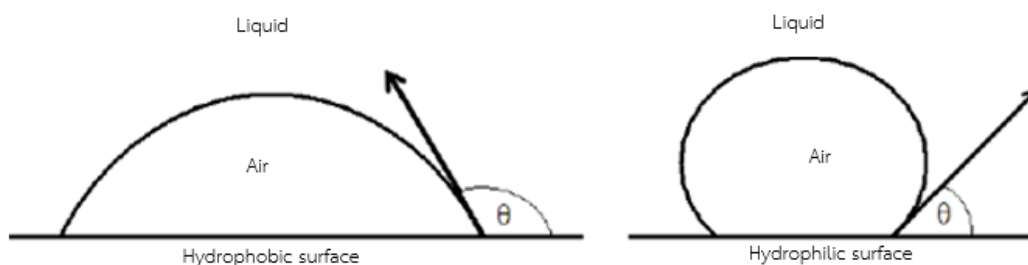


Figure 2.3 Hydrophobic and hydrophilic surface attached to air bubbles which show a difference contact angle.

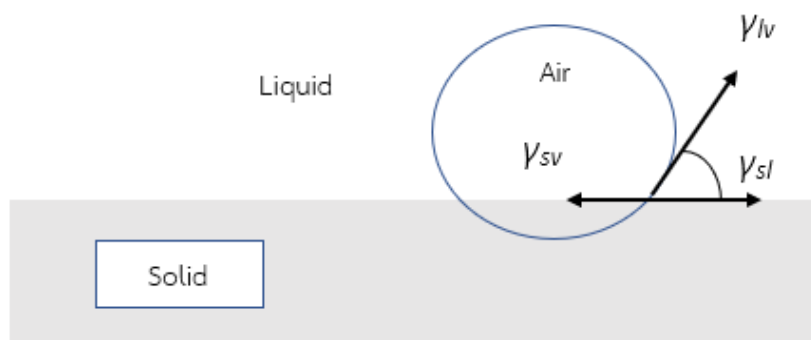


Figure 2.4 Contact angle between and air bubble and a solid surface.

2.2.2 Particle Bubble Contact

Particles are rendered hydrophobic; it should be acquired contact with gas bubbles and attach to the surface. On the other hand, if the air bubble and surfaces does not contact, at that point no flotation occur in Figure 2.5.

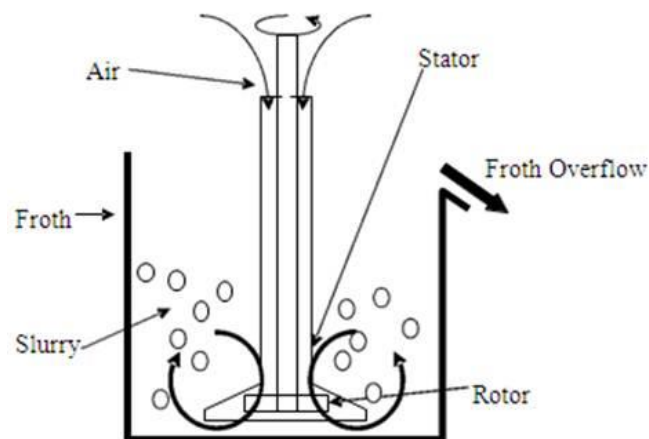


Figure 2.5 Conventional flotation cell.

Particle bubble crash is influenced by the relative sizes of the particles. The large bubbles relative to the particles, fluid flowing around the bubbles can clear the particles past without coming in contact. Consequently, if the particle diameter is comparable to the bubble diameter practically identical to the molecule breadth to guarantee great molecule/bubble contact.

As bubble diameter is reduced, the flotation rate of both the coarser and finer particles is improved. Coarse particles can attach to more than one bubble if the bubbles are small, and therefore the chances of the particle being torn loose and sinking again is reduced. For fine particles, the probability of collision with the bubble is improved if the bubble is small, as then the hydrodynamic forces tending to sweep the particle away from a collision are reduced. The reduction of bubble diameter has the added benefit of increasing the available bubble surface area for the same amount of injected air. It is therefore desirable to produce bubbles as fine as possible.

2.2.3 Collection in the Froth flotation

Particle and bubble have come in contact, the bubble must be suitable for flotation to lift the particle to the surface. The particle and bubble must remain attached while they move up into the froth layer at the top of the cell. The froth

layer must persist long enough to either flow over the discharge lip of the cell gravity, or to be removed by mechanical froth scrapers. If the froth is insufficiently stable, the bubbles will break and drop the hydrophobic particles back into the slurry prematurely. However, the froth should not be so stable as to become persistent foam, as a foam is difficult to convey and pump through the plant.

The surface area of the bubbles in the froth is also important because the particles are carried into the froth by attachment to bubble surfaces, increasing amounts of bubble surface area allows a more rapid flotation rate of particles. Also, increased surface area also carries more water into the froth as the film between the bubbles. Thus, fine particles that are not attached to air bubbles will be unselectively carried into the froth along with the water (entrainment), excessive amounts of water in the froth can result in significant contamination of the product with gangue minerals.

- **Chemical Reagents**

Chemicals are necessary for both to control the relative hydrophobicity of the particles, and to maintain the proper froth characteristics. There are many different reagents involved in the froth flotation process, with the selection of reagents depending on the specific treated mineral mixtures.

- 1). Collectors

Collectors are used to selectively adsorb onto the surfaces of particles. The collectors have ability to increase the contact angle so that bubbles will adhere to the surface. Collectors can be generally classed depending on their ionic charge and the selection of collector is critical for an effective separation by froth flotation. The most commonly used in fluorite flotation is anionic collector.

❖ Anionic Collectors

Anionic collectors are acid salts or weak acids that producing a collector that has a negatively charged end that will attach to the mineral surfaces, and a hydrocarbon chain that extends out into the liquid as shown in Figure 2.6.

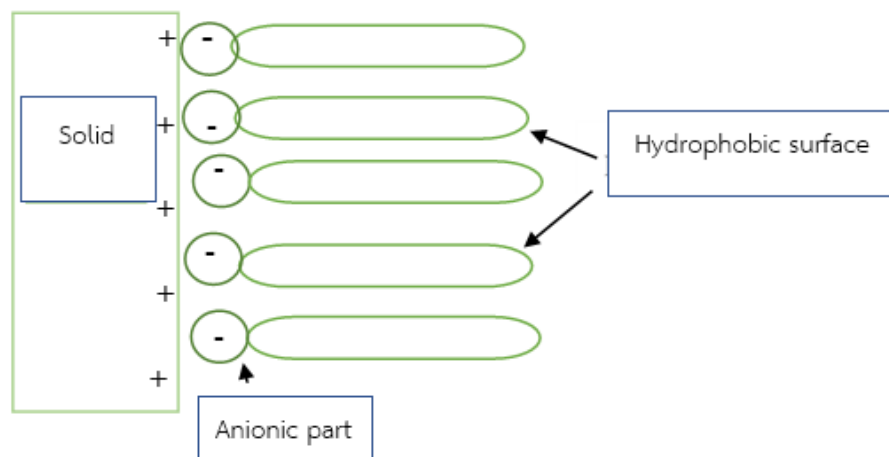


Figure 2.6 Adsorption of anionic collector.

The anionic portion is responsible for the attachment of the collector molecule to the surface, while the hydrophobic part alters the surface hydrophobicity.

A typical anionic collector for fluorite flotation is sodium oleate, the sodium salt of oleic acid, which has the structure shown in Figure 2.7. The anionic group responsible for attach to the mineral surface is the carboxyl group, which dissociates in water to develop a negative charge. The negatively charged group is then attracted to positively charged mineral surfaces.

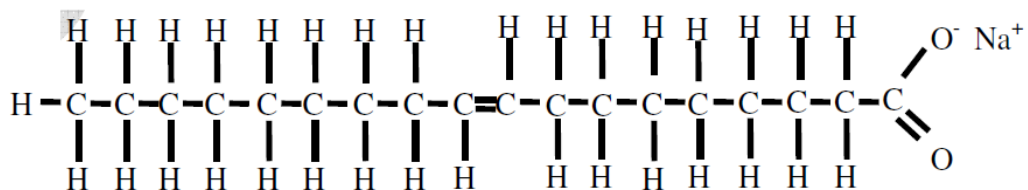


Figure 2.7 The structure of oleic acid.

2) Frother

Frother are usually organic compound surfactants. A typical example is heteropolar compounds such as alcohols or polyglycol ethers. These compounds generally comprise of a polar group (OH, COOH, C=O, OSO₂ and SO₂OH) which is capable to adsorb in the water air interface. (Figure 2.8).

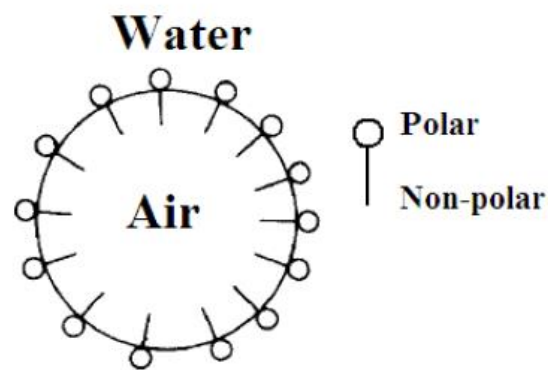


Figure 2.8 Frother adsorb to the air-water interface.

The most commonly used frother are normally water soluble are alcohols, particularly MIBC (Methyl Isobutyl Carbinol, or 4-methyl-2-pentanol, a branched-chain aliphatic alcohol) or any of several water-soluble polymers based on propylene oxide (PO) such as polypropylene glycols in order to spread out evenly in the slurry in the flotation cell otherwise it could not perform fully effective.

Modifiers

Modifiers influence the way that collectors attach to mineral surfaces and increase the adsorption of collector onto a given mineral (activators) or prevent collector from adsorbing onto a mineral (depressants).

Table 2.2 Modifiers for sulfide and non-sulfide mineral flotation

Inorganic	Small Organic and Oligomers	Organic Polymeric
Hydrofluoric acid	triethylenetetramine [TETA], etc.)	Starch
Soda ash	Tannins or quebracho (sporadic in sulfide; more regular in non-sulfide).	Synthetic
Sodium meta silicate		functionalizes polymer

pH regular

The pH control is affected to the surface chemistry in minerals. In general minerals has a positive surface charge under acidic conditions and a negative charge under alkaline conditions. Since each mineral change from negatively charged to positively charged at some pH, it is possible to manipulate the attraction of collectors to their surfaces by pH adjustment but complex effects due to pH that change the way that collectors adsorb on mineral surfaces.

Depressants

Depressants typical use is to increase selectivity by preventing one mineral from floating, while allowing another mineral to float unimpeded effect of activators by preventing collectors from adsorbing onto mineral surfaces.

2.3 Performance calculation

2.3.1 Ratio of Concentration

The weight of the concentrate relative to the weight of the feed, the Ratio of Concentration is F/C , where F is the total weight of the feed and C is the total weight of Concentrate. The limitation of this calculation is that uses the weights of Concentrate and feed. It is used in laboratory experiments, only assays will be available but in the plant is likely that the ore is not weighed. However, it is possible

to express the Ratio of concentration in terms of ore assays. Starting with the mass balance equations, and the definition of the ratio of concentration.

$$F = C + T, Ff = Cc + Tt,$$

$$\text{Ratio of Concentration} = F/C$$

Where F, C, and T are the % weights of the feed, concentrate, and tailings, respectively; and f, c, and t are the assays of the feed, concentrate, and tailings. We now need to eliminate T from these Equations so that we can solve for F/C:

$Ff = Cc + Tt$, and multiplying ($F = C + T$) by t gives us:

$Ft = Ct + Tt$, so subtracting this equation from the previous eliminates T and gives:

$F(f - t) = C(c - t)$, and rearranging produces the equation for the ratio of concentration:

$$F/C = (c - t)/(f - t)$$

2.3.2 % Recovery

Percent recovery or percentage of the metal in the original feed that is recovered in the concentrate this can be calculated using weights and assays, as $(Cc)/(Ff) \cdot 100$. Or, since $C/F = (f - t)/(c - t)$, the % Metal Recovery can be calculated from assays alone using $100(c/f)(f - t)/(c - t)$.

2.3.3 % Loss

Percent loss is the opposite of the % Recovery, and represents the material lost to the tailings. It can be calculated simply by subtracting the % Metal Recovery from 100%.

2.3.4 % Weight Recovery

Percent weight recovery is ratio of concentration and equals $100 \cdot C/F$ or $100 \cdot (f - t)/(c - t)$.

2.3.5 Enrichment Ratio

Enrichment ratio is calculated directly from assays as c/f , weights are not involved in the calculation.

2.3.6 Grade/Recovery Curves

flotation performance for different conditions were calculated values are useful for comparing, it is most useful to consider both grade and recovery simultaneously, using a “Grade/Recovery Curve” is particularly useful for comparing separations where both the grade and the recovery are varying. A set of grade/recovery curves is shown in Figure 2.16.

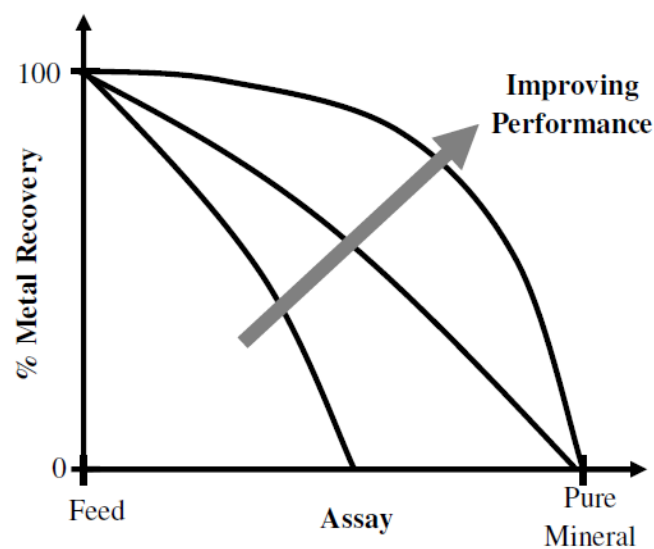


Figure 2.9 Grade/Recovery Curves for froth flotation

2.4 Collector used in fluorite flotation

Floatability influence of sodium oleate and oleic acid on fluorite and calcite in different pH value. As can be seen, collecting capacity of sodium oleate on mineral

greater than oleic acid. Figure 2.10 shows that fluorite was depressed when sodium oleate as collector at pH value less 4, while fluorite flotation was very good on the condition of pH value more 4. Recovery rate is not exceeded 40 percent when oleic acid as the collector at pH value less 10 under laboratory medicine dosage. While with oleic acid as collector, fluorite recovery rate is increase rapidly when pH value more than 10. (3).

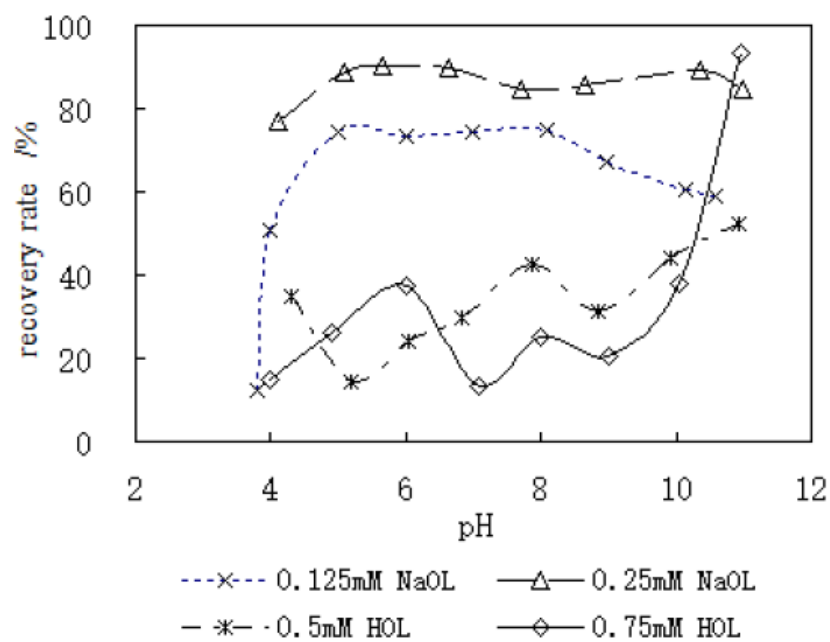


Figure 2.10 Effect of pH on fluorite flotation recovery with various addition of NaOL and HOL

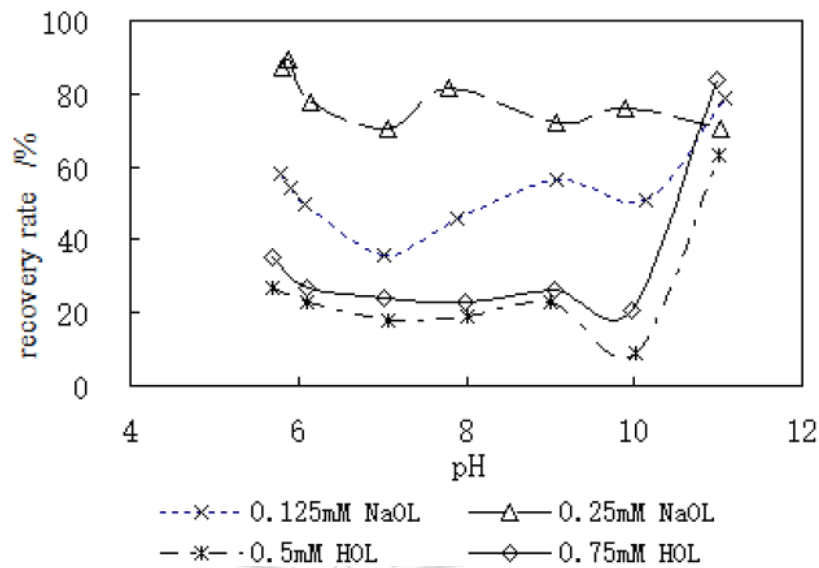


Figure 2.11 Effect of pH on flotation recovery of calcite with various addition of NaOL and HOL.

Collecting capacity of sodium oleate on mineral greater than oleic acid. Calcite recovery rate was lowest by sodium oleic as collector about pH 7, while calcite can float well in other pH condition. Calcite floatability is best by oleic acid as collector above pH 10 and the recovery rate is lowest at pH 10. Shown in Figure 2.12

The collecting ability of sodium oleate is better than oleic acid and fluorite floatability is better than calcite, with sodium oleate collector, calcite recovery rate is low at about pH 7. Collector chemical adsorption on mineral fluorite can obtain good flotation recovery when pH above 10 oleate ions collecting of calcite is also accomplished by chemical adsorption, namely oleate and calcium cations in mineral surface chemically reacted form calcium oleate. (3).

Yu, Wang (8) reported that oleic acid is a widely used anionic collector in the flotation of spodumene. The maximum flotation recovery and adsorption amount of collector was obtained under slightly alkaline pH conditions. Solution chemical analysis illustrates that oleic acid hydrolyzes to form ions (RCOO^-) at strong alkaline pH and molecules (RCOOH) at acid and neutral pH; in the slightly alkaline pH region,

both ions and molecules exist in oleic acid solution, which associate by van der Waals force to form ionic–molecular complexes. (8)

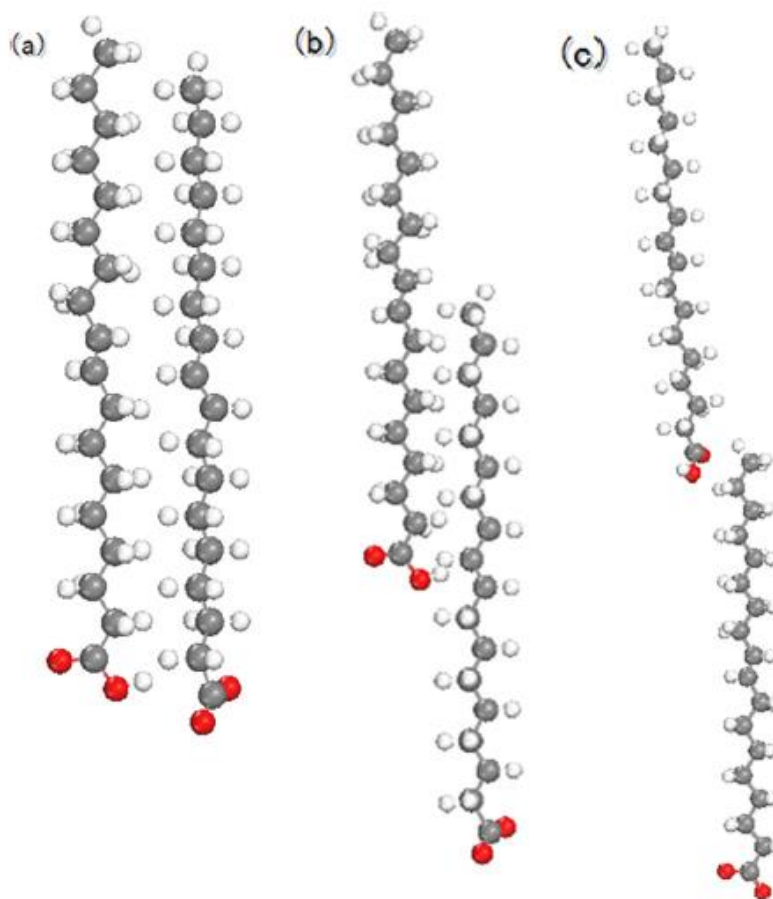


Figure 2.12 Ionic–molecular complexes of oleic acid (a) head–head; (b) head–middle; and (c) head–tail.

The ion and molecule of oleic acid are more likely to be associated by the modality of “head–head”; the modality of “head–middle” could also possibly happen; the formation of “head–tail” will never take place. the more overlapped of the hydrocarbon chains of ion and molecule, the stronger of the van der Waals force formed between them, the more stable of the ionic–molecular complexes.

The ion and molecule of oleic acid associate by van der Waals force in “head–head” modality, and the COO⁻ groups in the complexes combine with the Al sites

on spodumene surface by chemical adsorption, a molecular model of oleic acid adsorbing on spodumene surface can be established.

According to Liu, Zhang (9), Oleic acid is strong collecting ability and a small amount of dosage in cassiterite flotation but it is short selectivity. Oleic acid is sensitive to Fe_{3+} and Ca_{2+} , causing it is easy to be floated with iron minerals, fluorite and calcite. Generally, oleic acid used to concentrate cassiterite-quartz slime in the condition of neutral or alkaline. (9)

Due to the floatability of fluorite from apatite, calcite and other gangue minerals, sodium oleate is most widely used as a collector for fluorite flotation (10).

Collectors used in plant operations for the flotation of alkaline earth semi soluble salt minerals are summarized in Table 2.4.

Table 2.3 Collectors used in plant operations for the flotation of alkaline earth semi soluble salt minerals.

Mineral	Collector	Flotation strategy	Conditions	Reference
Fluorite (CaF_2)	Fatty acid: 0.25-1kg/ton	Use quebracho (0.25-0.5kg/ton) depress carbonates: Use Na_2CO_3 and NH_4CO_3 (0.5-3.5kg/ton) to disperse clay slimes.	pH not mentioned	(Bentzen, 1986)

Sis and Chander (11) found that fatty acids and their soaps are commonly used collectors in the flotation of oxide and sparingly soluble minerals. Nevertheless, their use suffers from sensitivity to slimes and ions, the higher temperature requirement, sensitivity to pH variation, and the relatively high consumption and increasing price.

An oily collector (e.g., fuel oil) is mostly used together as collector or collector extender to reduce the consumption and excess foaming the fatty acids. (11)

2.5 Sodium silicate in the flotation separation

In order to separate fluorite from calcite effectively, extensive documents have concentrated on screening depressants for calcite, such as acidized sodium silicate (SS), valonea extract, quebracho, and tannin and starch. Low-cost SS is a widely used depressant in industry for calcite in fluorite flotation. The obvious weak point of SS, however, lies in its huge dosage (as much as 6–10 kg per ton of run-of-mine), which deteriorates the fluorite recovery and causes a serious problem for wastewater treatment due to a very slow sedimentation rate. For other depressants, the main disadvantages include complicated flotation flow sheets and high operation costs for depressing calcite in practice. In view of the disadvantages of depressing calcite and floating fluorite in the traditional fluorite flotation, it may be a promising alternative to remove calcite from fluorite ore in a reverse way, especially for complex and unmanageable fluorite ores containing high-grade calcite gangue mineral. In this regard, the development of a selective depressant for fluorite as well as the simplification of the reagent scheme is of great significance to the reverse flotation of separating fluorite from calcite. (12)

Zhang, Gao (13) found that using sodium oleate as collector fluorite easily floated but quartz sink down. Sodium silicate depress the hetero-coagulation and improves the separation efficiency in flotation of mixed binary minerals, with high modulus of sodium silicate eliminates the hetero-coagulation more thoroughly through increasing the energy barrier between fine fluorite and quartz. (13)

Sodium silicate is a soluble silicate ($K_2O \cdot nSiO_2$ or $Na_2O \cdot nSiO_2$) that is manufactured by the reaction of alkali metal oxides (K_2O or Na_2O) and silicon dioxide (SiO_2). It commonly used in the mineral processing industries as dispersant or

modifier. The molar ratio (n) of silicon dioxide to alkali metal oxides, termed modulus, is an important parameter for water glass used in flotation process. The modulus has a direct effect on the properties of the water glass, such as solubility, viscosity, dispersion and depressant ability when the modulus increases, the depression effect of water glass on silicate minerals are also increase. Moreover, Water glass has long been the depressant for quartz and other silicate minerals in the flotation of oxide ores and supplied ores, especially for the flotation of fluorite. (14)

However, the flotation separation of fluorite from quartz using water glass is ineffective, there is always a small amount of fine quartz (less than $10\mu\text{m}$) in the fluorite concentrate. The floated fine quartz in fluorite concentrate has been reported to be the result of metal ion activation on the fine quartz that defeats the depressant effect of the sodium silicate. (15-17).

2.6 Effect of pH on fluorite flotation recovery

Influence of pH on fluorite flotation is very important due to the mechanism effect of pH on flotation of fluorite and calcite.

Zhao, Liu (18) studied the effect of floatation on percent recovery of fluorite floatation, and this experiment ran by the pH changing from 4 to 11. The point of zero charge (PZC) of fluorite is $\text{pH}=9.5$ and the PZC of calcite is $\text{pH}=8.5$. The optimum pulp pH of the flotation of fluorite and calcite is determined as 9.5~10 and 8~9 respectively. pH value should be controlled above 9 to depress calcite. Finally, 9.5~10 was determined as the optimum pH to float the fluorite from the calcium-containing fluorite ores. The effect of pH on fluorite flotation was investigated at a basic medium in which the pH value is between 8 and 9.5, because low pH particularly >6 , could not be controlled. The optimum pH value is considered to be 9. (12)

Zhang, Gao (13) studied on the flotation of fluorite, quartz and a weight equivalent mixture (all less than $10\mu\text{m}$) using water glass (with different modulus) as depressants and sodium oleate as collector were conducted. The mechanism of fine quartz entering the fluorite concentrate was investigated through optional observations and rheology measurements on the flotation pulp. The particle interactions between fine fluorite and quartz under flotation-related conditions were analyzed through zeta potential measurements and DLVO calculations. The results revealed that there existed strong hetero coagulation between fluorite and quartz particles in the flotation pulp, which could be the main reason for the quartz entering the fluorite concentrate in the flotation process. Water glass with higher modulus could eliminate the hetero coagulation more totally but inevitably influences the floatability of fluorite. (13)

Zhou, Moreno (14) found that at the grade of 97% CaF_2 (acidic grade of fluorite concentrate), The results shown that acidized water glass was a better depressant for fluorite flotation. It increased the sedimentation rate of fine particles in tailing slurry and thus produced cleaner recycled water and improved fluorite recovery and flotation rate. AWG was more selective between fluorite and gangue minerals (carbonate and silicate minerals) in fluorite flotation. (14)

Song, Lopez, Martinez, Torres (19) proposed that CMC (carboxymethyl cellulose) or water glass in order to improve the beneficiation of the fluorite ore by froth flotation, it has been found that the dispersion processing with CMC as dispersant could effectively improve the fluorite flotation, increased the Fluorite recovery from 72% to 78.5% at the same concentrate grade of 98% CaF_2 . (19)

Ayhan, Bozdogan & Temel (12) studied on Enrichment of fluorite by flotation the optimum conditions obtained from rougher flotation tests were as follows: particle size 0.180 mm, pH 9, depressant amount 160 g/t, depressant conditioning time 5

mins, collector amount 600 g/t and collector conditioning time 16 mins. The rougher concentrate containing 70%CaF₂ with 90.9% recovery was obtained. The optimum amount of reagents used at three cleaning stages was investigated under three different experimental conditions. The best result was obtained under the second experimental conditions in which reagent amounts used were half of that at the rougher flotation stage. It was found that a concentrate containing 92.1%CaF₂ with 82% recovery was obtained from a feed containing 43.3%CaF₂ at 30 °C. The CaF₂ content and recovery of the concentrate obtained at 16 °C were lower than that obtained at 30 °C. (12)

Ucar & Ozdag (20) have been studied on collector adsorption in fluorite flotation the electro kinetic potential measurements, the point of zero charge of fluorite is pH 3.6. Fluorite minerals of different origins has different point of zero charge. Due to calcite has an organic origin it does not affect in isoelectric point in alkali media. CaCl₂ increased the pzc of fluorite while it decreased the zeta potential of calcite and fluorite. Na₂CO₃ and Na₂SiO₃ increased the negative charge on calcite and fluorite surface approximately in similar proportions in alkali media. The measurements showed that oleic acid and sodium oleate as anionic collectors were chemically adsorbed fluorite and calcite surface. Therefore, oleic acid and sodium oleate are chemically adsorbed at various pH and different amount of fluorite and calcite surface. (20)

2.7 X-ray diffraction (XRD) and X-ray fluorescence

X-ray diffraction (XRD) X-rays to obtain information on the structure of crystalline materials. A primary technique is the identification and characterization compounds from diffraction pattern. The dominant effect that occurs when an incident beam of monochromatic X-rays interacts with a target material is scattering of those X-rays from atoms within the target material. In materials with regular structure (i.e. crystalline), the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of X-rays by crystals is

described by Bragg's Law by equation $n\lambda = 2d \sin\theta$, where λ = wavelength (nanometer), d = lattice spacing (nanometer), n = order number.

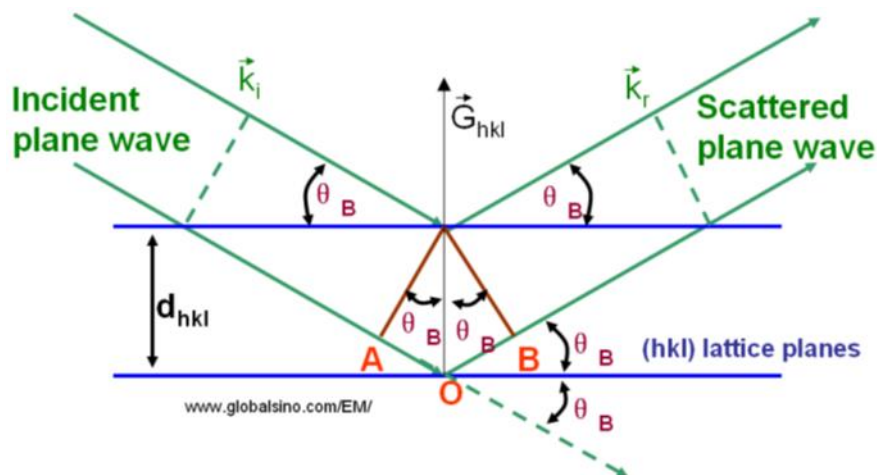


Figure 2.13 Bragg's Law

X-ray fluorescence is a technique to irradiate the sample by the polychromatic radiation from an x-ray tube. Elements in the sample are excited to discharge their characteristic x-ray radiation.

The secondary x-ray radiation from the sample consists of several lines which are diffracted by a crystal plate and separated into the individual wavelengths. X-Ray Fluorescence which is characteristic for the elemental composition of the sample Shown in Figure 2.15

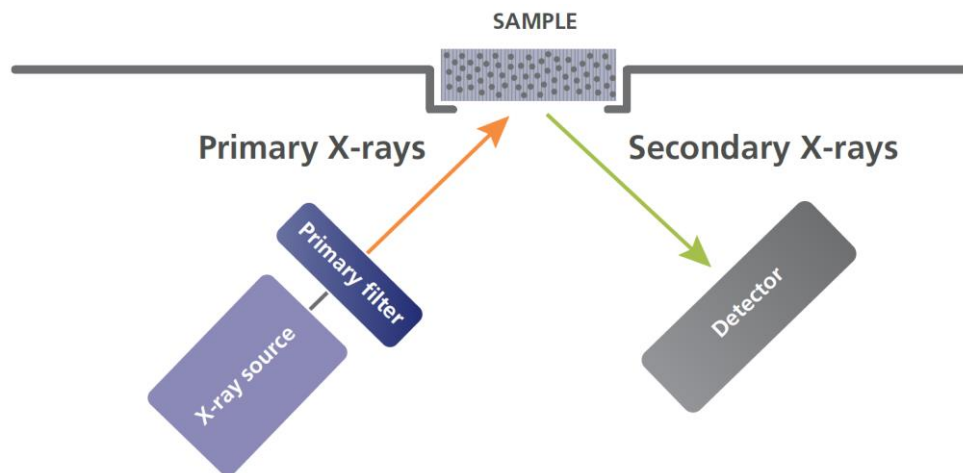


Figure 2.14 X-ray fluorescence (XRF)

2.8 Project evaluation

A pre-feasibility study used in measuring the ability and to complete the project successfully including all relevant factors. It must account for factors that affect it such as economic, technical and legal and scheduling factors. Pre-feasibility studies to determine potential positive and negative outcomes of a mining project before investing a considerable amount of time and money, it is focusing on to evaluate the project which is considering many factors such as: Net present value, internal rate of return, modified internal rate of return and discount payback period.

In this study focus on discount cash flow (DCF) to determine Net present value (NPV), Modified internal rate of return (MIRR), and discount payback period (DPP).

The cash flow is referring to net inflow of money that occurs during a specific period following by some equations are following.

- Gross profit = gross revenues – operation expense – depreciation & depletion
- Net profit = gross profit (taxable income) – tax
- Cash flow = net profit + depreciation and depletion – capital cost

The discounted cash flow method is widely applied in the industry for all types of capital investment evaluations.

2.8.1 Discounted cash flow model (DCF)

Discounted cash flow (DCF) is a method used to estimate the value of an investment based on its future cash flows. DCF analysis finds the present value of expected future cash flows using a discount rate. A present value estimate is then used to evaluate a potential investment. If the value calculated through DCF is higher than the current cost of the investment, the opportunity should be considered (21).

DCF is calculated as follows:

$$DCF = \frac{CF_1}{(1+r)^1} + \frac{CF_2}{(1+r)^2} + \frac{CF_3}{(1+r)^3} + \dots + \frac{CF_n}{(1+r)^n}$$

CF = Cash Flow

r = discount rate (WACC)

2.8.2 Weighted Average Cost of Capital (WACC)

The weighted average cost of capital (WACC) is a calculation of a firm's cost of capital in which each category of capital is proportionately weighted. All sources of capital, including common stock, preferred stock, bonds, and any other long-term debt, are included in a WACC calculation (22).

A firm's WACC increases as the beta and rate of return on equity increase because an increase in WACC denotes a decrease in valuation and an increase in risk

The Formula for WACC is

$$WACC = \frac{E}{V} * Re + \frac{D}{V} * Rd * (1 - Tc)$$

- Re = cost of equity
- Rd = cost of debt
- E = market value of the firm's equity
- D = market value of the firm's debt
- V = E + D = total market value of the firm's financing (equity and debt)
- E/V = percentage of financing that is equity

- D/V = percentage of financing that is debt
- T_c = corporate tax rate

2.8.3 Net Present Value (NPV)

Net present value (NPV) is used in capital budgeting and investment planning to analyze the profitability of a projected investment or project (23).

The following formula is used to calculate NPV:

$$NPV = \sum_{t=0}^n \frac{R_t}{(1+i)^t}$$

In this equation:

R_t = net cash inflow-outflows during a single period t

i = discount rate or return that could be earned in alternative investments

t = number of time periods.

2.8.4 Internal Rate of Return (IRR)

The internal rate of return (IRR) is a discount rate that makes the net present value (NPV) of all cash flows from a particular project equal to zero used to estimate the profitability of potential investments. (24).

The Formula for IRR is

$$IRR = NPV = \sum_{t=1}^T \frac{C_t}{(1+IRR)^t} - C_0 = 0$$

Where:

- C_t = net cash inflow during the period t
- C_0 = total initial investment costs
- IRR = the discount rate
- t = the number of time periods

2.8.5 Modified Internal Rate of Return (MIRR)

The modified internal rate of return (MIRR) assumes that positive cash flows are reinvested at the firm's cost of capital and that initial outlays are financed at the firm's cost of financing cost. The traditional internal rate of return (IRR) assumes the cash flows from a project are reinvested at the IRR itself. The MIRR, therefore, more accurately reflects the cost and profitability of a project.

The Formula for MIRR is

$$\text{MIRR} = \sqrt[n]{\frac{\text{FV (Positive cash flows } \times \text{ Cost of capital)}}{\text{PV (Initial outlays } \times \text{ Financing cost)}}} - 1$$

Where:

FVCF (c) = the future value of positive cash flows at the cost of capital

PVCF (fc) = the present value of negative cash flows at the financing cost of the company.

n = number of periods

2.8.6 Discounted payback period (DPP)

The discount payback period (DPP) is a number of years for which a discounted annual net cash flow must be summed before the sum becomes positive.

The payback period is the amount time during which the initial cash outflow of investment is expected to recover from the cash inflows generated by the investment.

Discounted Payback Period = Cut off Period + Initial / Cash inflow per period.

CHAPTER 3

METHODOLOGY

This chapter presents materials, instruments and experimental conditions used in this study. Ball-mill and cup-mill were used to grind sample for size reduction. Sieve (ASTM Standard Size 325mesh) was used for size classification. X-ray fluorescent (XRF) and X-ray diffraction (XRD) were used for measurement the sample characterization. WEMCO Froth flotation laboratory scale test was ensured to investigate the flotation responses by study of many factors such as pH, collector dosage, the use of frother, depressant dosage and conditioning times.

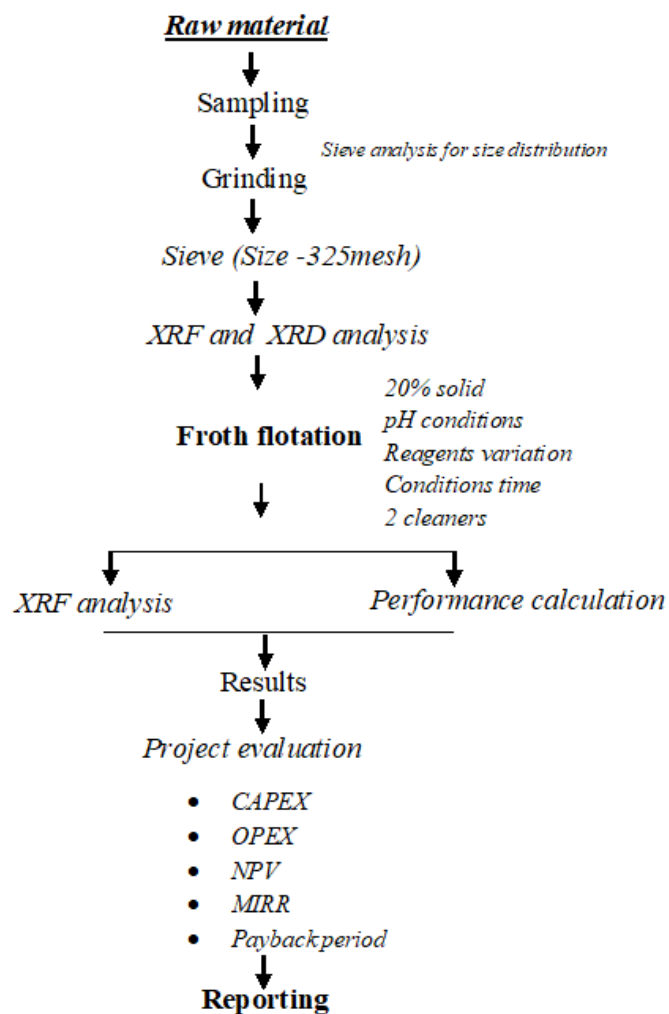


Figure 3.1 Methodology flowchart

3.1 Background and Sample Preparation

The fluorite ore was collected from Phanomthuan deposit, Kanchanaburi province which is from Silurian-Devonian period. Silurian and Devonian sedimentary rocks are widely distributed in Thailand. In the literature generally they have been described together as coherent stratigraphic sequences throughout the country, and they will be so treated here. A lower (metamorphosed) Kanchanaburi Formation and equivalent rocks throughout Thailand are Silurian and Devonian in age. An upper formation (generally unmetamorphosed) was designated as the new Kaeng Krachan Formation consisting of part of the former Phuket Series and its equivalents (some metamorphosed) of Devonian and early Carboniferous ages. The Kanchanaburi Formation is dominantly clastic sediments, metamorphosed to slate, phyllite, and quartzite and is present throughout Thailand except for the Kholat Plateau in the northeast. (Shawe, 1984) The fluorite processing plant produce fluorite for many years and the low-grade ores are remains in that areas, due to the grade of fluorite ore are very low which contained large amount of silicon dioxide, calcium calcite, and other minerals. it is a great need to adapt optimal condition by using froth flotation techniques.

In the first step, take sample into oven for 24hrs with 105° c to remove the moisture content. John's riffle was used to representative sample for further experiment, it is using V-shape of machine to reducing the amount of sample to obtain a reasonable representative. Then, the feed of sample was taking out 250g to investigate by sieve analysis for 20 minutes.

3.2 Particle size distribution

Particle size distribution of raw material was investigated by sieve analysis to determine the particle size of fluorite sample. Firstly, the sample has dried for 24hours then used the john's riffle to representative 200g out of 2000g was

obtained. Furthermore, the 200g of sand was sieved through size including inch 1. ½ inch 1, inch ¾, inch ½, # 3. ½, # 4, #10, #20, #40, #60, #80, #100, #120, #140, #170, #200, #230, #270, #325 within 20 minutes shown in Figure 3.2. Then, weight each of retained to calculate cumulative passing size of all sample by 50% and 80% passing. The consideration of particle size of the raw material is important for mineral processing, which is used for equipment capacity and machine selection for processing plant. After that the sample was ground to proper size -325mesh (40micron) using ball mill and cup mill for the size -40 micron for flotation tests, Figure 3.3 and 3.4.



Figure 3.2 Sieve analysis



(a)



(b)

Figure 3.3 Ball mill laboratory scale (a) and Cup mill ((b)



Figure 3.4 Sieve size -325Mesh

3.2.1 X-ray fluorescence.

In this test using approximately 5grams of samples with combined properly and put in cup before analyze sample the XRF machine was set and warm up for 30 minutes as shows in Figure 3.5 (a) and 3.5 (b).



(a)



(b)

Figure 3.5 X-ray fluorescence (PANalytical, EPSILON4)

3.2.2 X-ray diffraction

. The sample preparation for XRD was compress in plate with carefully, XRD was performed on a PANalytical B.V. Software Licensing activation shown in Figure 3.7 (a) and 3.7 (b).



Figure 3.6 PANalytical B.V. Software Licensing activation.

3.3 Experimental conditions

Table 3.1 Chemical reagents used in this experiment

Reagents	Formula	utility
Oleic Acid	$C_{18}H_{34}O_2$	Collector
Sodium silicate	Na_2SiO_3	Depressant
Sodium carbonate (Soda ash)	Na_2CO_3	Modifier
Hydrofluoric acid	HF	Modifier
Methyl isobutyl carbinol (MIBC)	$C_6H_{14}O$	Frother
Sodium Oleate	$C_{18}H_{33}NaO_2$	Collector

3.3.1 pH Variation

The flotation experiments on pH variation were undertaken which vary the target pH at 7, 9, and 11 for each test. The test conditions for these measurements employed similar collector, depressant amount dosage and the conditioning time. Approximate 29% CaF₂ content of feed in the flotation charge was prepared by 1000gram of sample with 4L of water was added to flotation cell produce 20% solid content. The flotation of fluorite was then stirred at 600rpm to give the condition for 2 minutes. HF and Na₂O₃ was applied to adjust the pH of fluorite flotation. The Oleic acid collector was added at the selected dosage 800gram per ton condition for 10 minutes followed by 500 gram per ton of sodium silicate was added. Then, the rougher concentrate was treated by 2 step cleaners with flotation time of 5 minutes was selected for first concentration, followed by 3 minutes of each the second and third concentration step as shown in Table 3.2.

Table 3.2 1st experiment with differences pH

1st experiment				
%Solid	pH Modifier	Oleic acid (g/ton)	Sodium silicate (g/ton)	Collector Conditioning time (min)
20%	7	800	500	10
	9	800	500	10
	11	800	500	10

3.3.2 Collector variation

The flotation experiments on the fluorite collector was undertaken. The experiments involved 2 main tests including a vary of collector dosage and the use of MIBC frother was added. The test conditions for these measurements employed similar to first experiment but MIBC as frother addition applied. The flotation pH 9 was selected for each test in this experiment. The oleic acid and frother were then

added at the selected dosage 600 gram per ton of oleic with 100 grams of MIBC for the first condition followed by the second condition which used 1000 gram per ton of oleic with 100 gram per ton of MIBC. The flotation condition time and 2 cleaners' step were similar with the first experiment as shown in Table 3.3.

Table 3.3 2nd experiment collector with differences dosage

2nd experiment					
%Solid	pH Modifier	Oleic acid (g/ton)	Sodium silicate (g/ton)	MIBC (g/ton)	Conditioning time (min)
20%	Optimal	600	500	100	10
		1000	500	100	10

3.3.3 Depressant variation

The flotation experiments on depressant amount dosage were undertaken. The investigation involved two amount dosage variation the condition tests were used at 600 gram per ton and 700 gram per ton of sodium silicate. The test conditions such as condition time and 2 cleaners' step for these measurements employed similar to the second experiment the flotation pH 9 was followed by 800gram per ton of oleic with 100 gram per ton of MIBC were selected for each test in this experiment shown in Figure 3.4.

Table 3.4 3rd experiment depressant with differences dosage

3rd experiment					
%Solid	pH Modifier	Oleic acid (g/ton)	Sodium silicate (g/ton)	MIBC (g/ton)	Conditioning time (min)
20%	9	800	600	100	10
			700	100	10

3.3.4 Conditioning time

The flotation conditioning times which important of flotation were undertaken. The floatation conditioning times were compared with 3 variation time included 5 minutes, 10 minutes and 15 minutes. The test conditions such as percent solid content and 2 cleaners' step for these measurements employed similar to the third experiment. The flotation conducted pH 9, 800gram per ton of oleic collector with 100 gram per ton of MIBC and 500 gram per ton of sodium silicate were selected for each test shown in Table 3.5.

Table 3.5 4th experiment conditioning times variation

4 th experiment					
%Solid	pH Modifier	Oleic acid (g/ton)	Sodium silicate (g/ton)	MIBC (g/ton)	Conditioning time (min)
20%	9	800	500	100	5
				100	15

3.3.5 Collector comparison

The flotation tests on collector performance between oleic acid and sodium oleate were compared. The flotation test conducted from the optimal in each experiment from experiment 1 to 4 were used in this experiment. The flotation conditions were selected at pH 9, 800gram per ton of oleic acid with 100 gram per ton of MIBC followed by 500 gram per ton sodium silicate and condition time for 10 minutes. The test conditions for these measurements employed similar by compared collector performance shown in Table 3.6.

Table 3.6 5th experiment using oleate as collector

5 th experiment					
%Solid	pH Modifier	Sodium Oleate (g/ton)	Sodium silicate (g/ton)	MIBC (g/ton)	Conditioning time (min)
20%	9	800	500	100	10

3.4 Froth flotation

In this study flotation tests were carried out using WEMCO froth flotation laboratory scale. Each Tests were conducted at a solid content of 20% in the slurry with 1000g of ore sample and 4l of water was prepared, soda ash and hydrofluoric acid are used add to adjust the pH of slurry which checked by pH meter in each experiment before injected oleic acid as a collector to recover fluorite from quartz and calcite, MIBC as a frother. Then, the slurry was conditioning with depressant with 600 rpm and 1200 rpm to froth bubble out. After that, rougher flotation starts and follow by two step cleaner flotation to upgrade rougher concentrate to remove quartz, calcite and others associated minerals from fluorite ore to figure out the optimal condition in order to obtain high concentrate grade of CaF₂ as shows in Figure 3.8 and Figure 3.9. However, all of experiments condition was investigated in froth flotation test with single time test.



Figure 3.7 WEMCO froth flotation laboratory scale.

In the ending step, opened the inlet of air to allow bubble attached fluorite by the collectors and floated it out. Furthermore, a fluorite concentrate was taken from flotation cell and dry in oven for 24hours after that take the concentrate was measure the chemical composition through XRF.

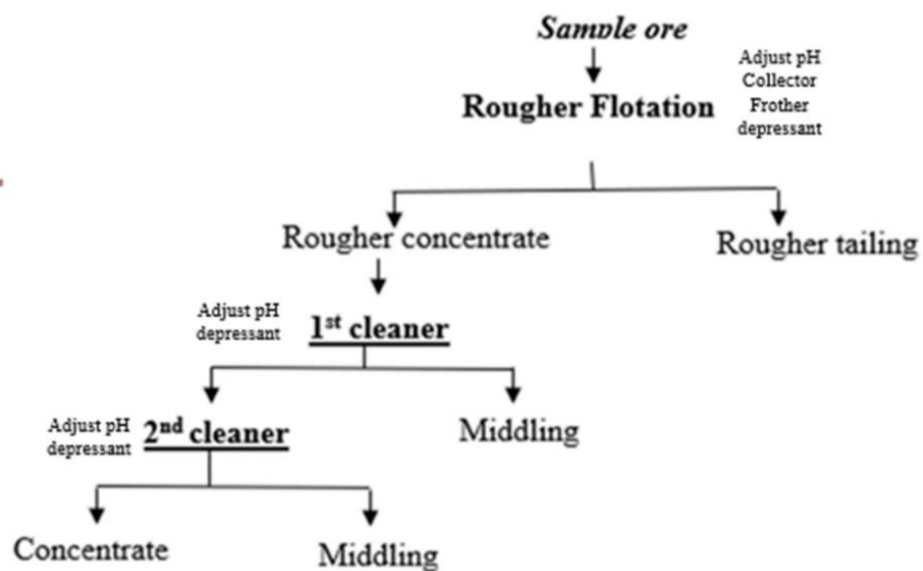


Figure 3.8 Fluorite flotation test flowsheet.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter description the result of all experiments from the investigation of fluorite flotation and discusses the effects in each condition of flotation. Due to the raw material is contained large amount of gangue mineral the optimal condition of fluorite flotation was met the fluorite specification standard of ceramic grade. The result of project evaluation analysis of this study was presented.

4.1 Raw material characterization

4.1.1 Particle size distribution

The result of particle size distribution presented as 200 grams of fluorite ore shown the particle size in fluorite ore 37,500 μ m or 37.5mm and 4,750 μ m or 4.75mm at 80% and 50% passing respectively, Figure 4.1, illustrate that most of sample is mainly retained on #80 (180 μ m) was 3.4% sample has distribution of each size regularly. Particle size can be recovered effectively by flotation range between 10 μ m and 37 μ m, whereas the particle size less than 10 μ m is ineffective in conventional flotation. (9) According to the particle size decreases the specific surface area increases significant the augmentation of reagents dosage when slime coatings are indicated in flotation. (25) & (26).

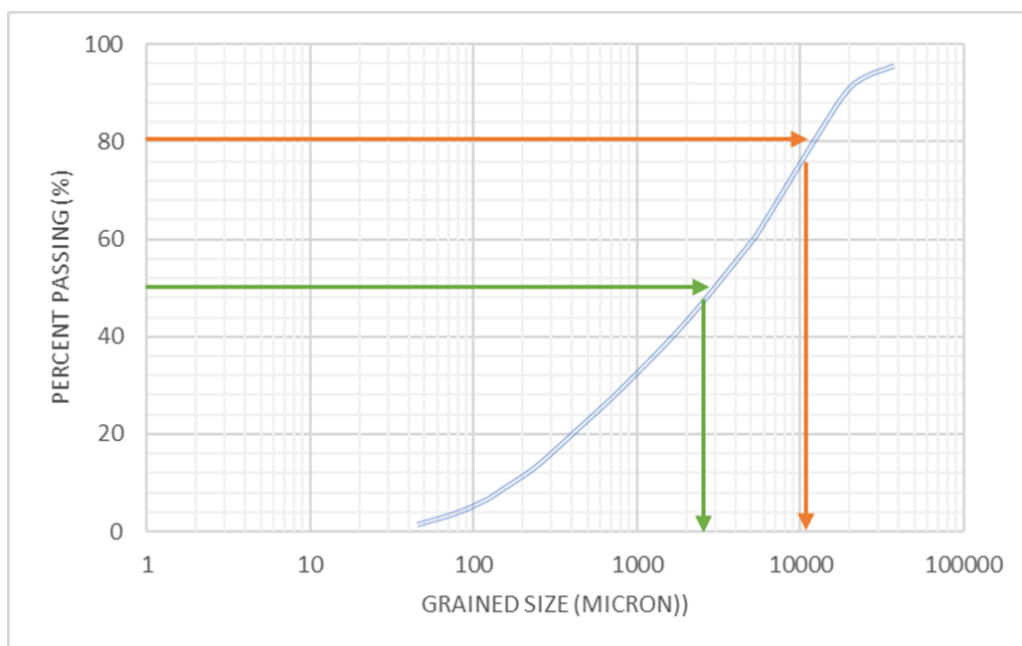


Figure 4.1 Particle size distribution.

4.1.2 The Chemical properties of fluorite ore

The chemical composition of fluorite ore was measured through the x-ray fluorescence (PANalytical, EPSILON4). The raw fluorite ore was taken from the field are come up with others minerals shown in Table 4.1. The result from x-ray fluorescence was illustrate that silicon dioxide and calcite are highly contained, the others minerals conjoining is defined by weight percentage (Wt. %). Figure 4.2, illustrated of raw material there are contains impurities along with CaF_2 such as: quartz, calcite and some unidentifiable minerals which confirmed by XRD result as shown in Figure 4.2.

Table 4.1 Mineral Composition of feed from XRF measurement used in this study.

Compound	% SiO_2	% CaF_2	% CaCO_3	% Al_2O_3	% MgO	K_2O	Fe_2O_3
% by weight	43.94	29.47	6.90	11.46	0.79	2.05	4.24

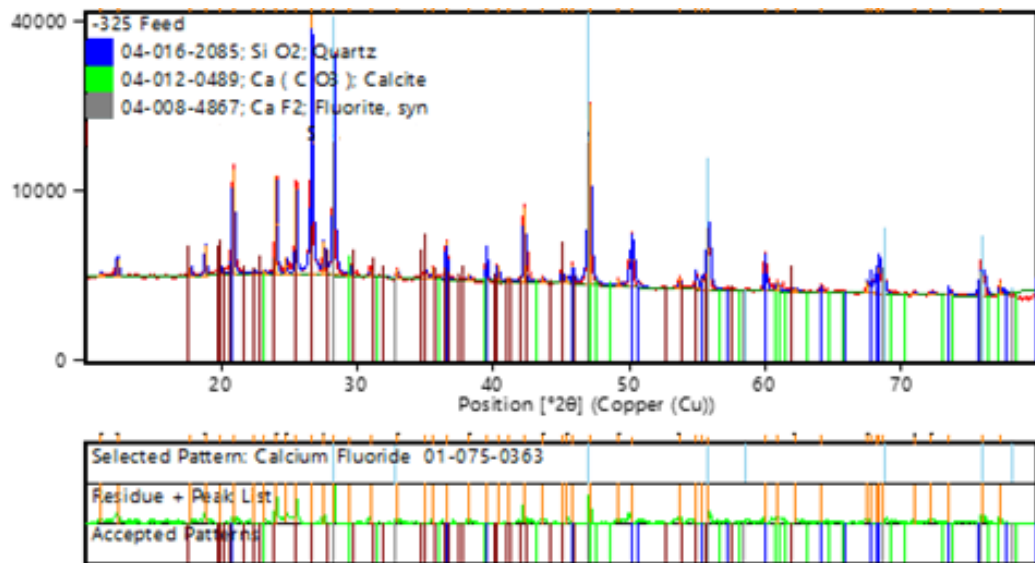


Figure 4.2 XRD pattern of raw material.

4.2 Froth flotation

In WEMCO froth flotation laboratory scale tests were carried out using oleic acid and sodium oleate as collector. The significant parameter of flotation conditions such as: pH, collector, depressant, frother and conditioning times are reported. A various froth flotation conditions were undertaken to optimize the fluorite ore flotation performance. The fluorite concentrate in each test in flotation process were dry in oven at 105°C for 24hours then, XRF was used to measure the components of fluorite concentrate.

4.2.1 Effect of pH in fluorite flotation

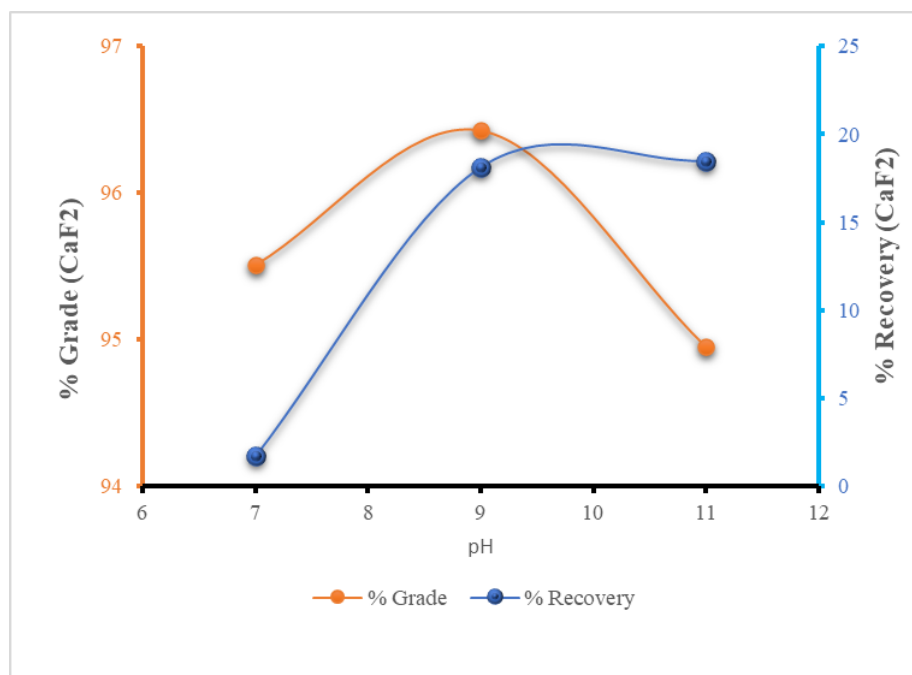


Figure 4.3 Effect of pH slurry in fluorite floatation.

The effect of pH slurry on fluorite grade and recovery of concentrate, using 800 g/ton of oleic as collector and 500 g/ton of sodium silicate as depressant. The grade of fluorite concentrates was 95.5% at pH 7, 96.4% CaF₂ at pH 9 and 94.9% CaF₂ at pH 11 whereas, the recovery was 1.74%, 18.12% and 18.49% respectively. Shown in Figure 4.3 The result shown that the grade of CaF₂ concentrate were very close, whereas recovery of pH 7 was lower than pH 9 and 11. The pH condition indicates that weak alkaline at pH 9 fluorite ore slurry was a strong hypercoagulation.

4.2.2 Effect of collector variation

Fluorite flotation tests were carried out with oleic acid as collector at various dosage included 600 g/ton, 800 g/ton and 1000 g/ton respectively, with 100 g/ton of MIBC as frother and 500 g/ton of sodium silicate as depressant were added. Fig. 4.4 shown the effect of collector at 800 g/ton of oleic acid with 100 g/ton of MIBC addition, the CaF₂ concentrates and recovery were 96.9% and 29.77% whereas, with

600 g/ton and 1000 g/ton the concentrate grade was 95.8% and 95.4% whereas the recovery was 5.52%, and 3.82% respectively. The result shown the grade of CaF_2 in three concentrates were similar whereas fluorite recovery obtained using oleic acid 800 g/ton was higher than 600 g/ton and 1000 g/ton. This comparison indicates that using oleic acid with MIBC as frother could possibly effective increasing recovery in fluorite flotation because frother has influence on fluorite and calcite flotation behaviour. Due to the amount dosage of frother is large, MIBC as frother is more adapted to flotation in order to separate fluorite from calcite. However, MIBC is low the strength than terpineol. (27)

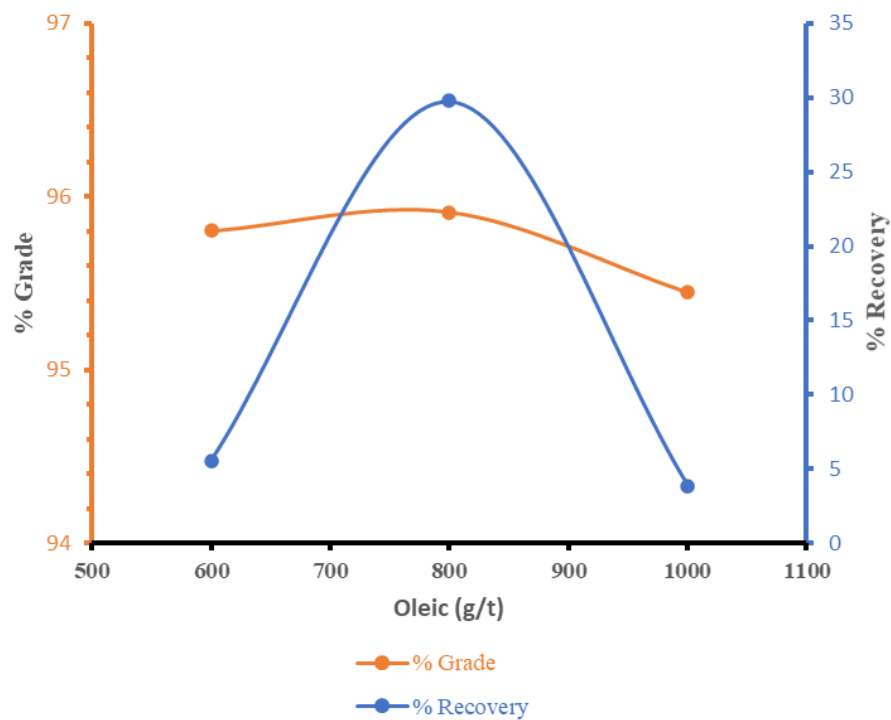


Figure 4.4 Influence of collector dosage (g/t) on the concentrate grade and recovery of CaF_2 .

4.2.3 Effect of depressant variation

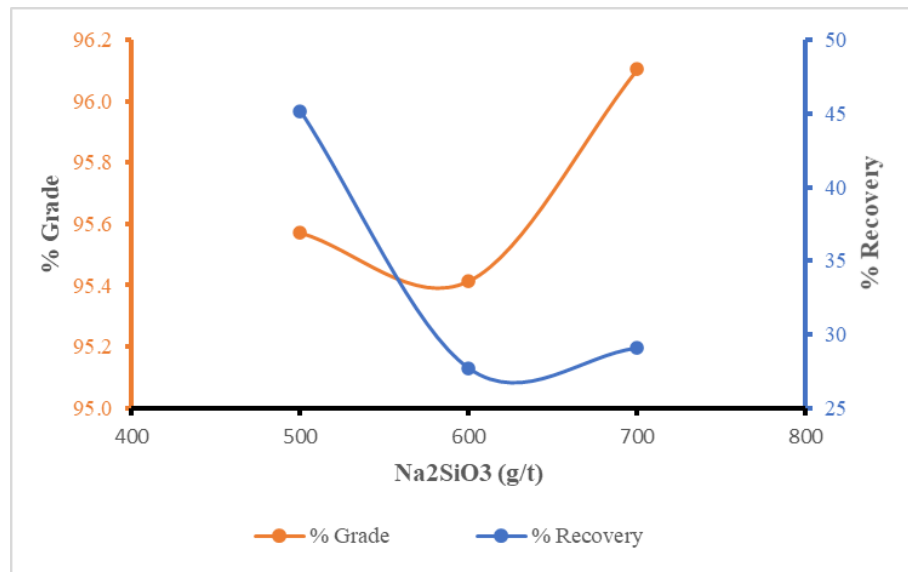


Figure 4.5 Influence of depressant dosage (g/t) on the concentrate grade and recovery of CaF₂.

The comparison at various dosages of sodium silicate as depressant of fluorite grade and recovery of concentrates from the flotation. The results shown that the grade of CaF₂ from concentrates ranged between 95.4% to 96% CaF₂. With 500 g/ton addition, the fluorite recovery was increased about 45%, whereas at 600 g/ton and 700 g/ton addition, the difference in fluorite recovery was about 2% between two various dosage of sodium silicate. It can be observed that when increase of sodium silicate addition, at 700 g/ton the CaF₂ was increased whereas recovery was lower and with 500 g/ton addition, achieved more higher fluorite recovery shown in Figure 4.5. The comparison indicated that sodium silicate could be effective depressant for silicate mineral in fluorite flotation from ores tailing.

4.2.4 Conditioning time

Conditioning time results from fluorite flotation are presented in Figure 4.6. The effect of variation conditioning time on fluorite recovery from the flotation of fluorite ore, using oleic acid as collector, MIBC as frother and sodium silicate as depressant at the same dosage. The grades of all concentrates ranged between

95.5% and 96.5% of CaF_2 . It can be seen that at 10 minutes the fluorite recovery influenced increased. At 5 minutes, the recovery was about 31.55%, compared with that at 10 minutes the grade of CaF_2 was decreased to 95.5% while, the recovery was increased to 45.16%. With an increase in the conditioning time at 15 minutes the recovery was decreased to 22.25% whereas, the grade was 96.5% of CaF_2 . These results suggest that the oleic acid possibly effectively used as collector in fluorite flotation at the conditioning time at 13 minutes due to the recovery and grade of CaF_2 were optimize.

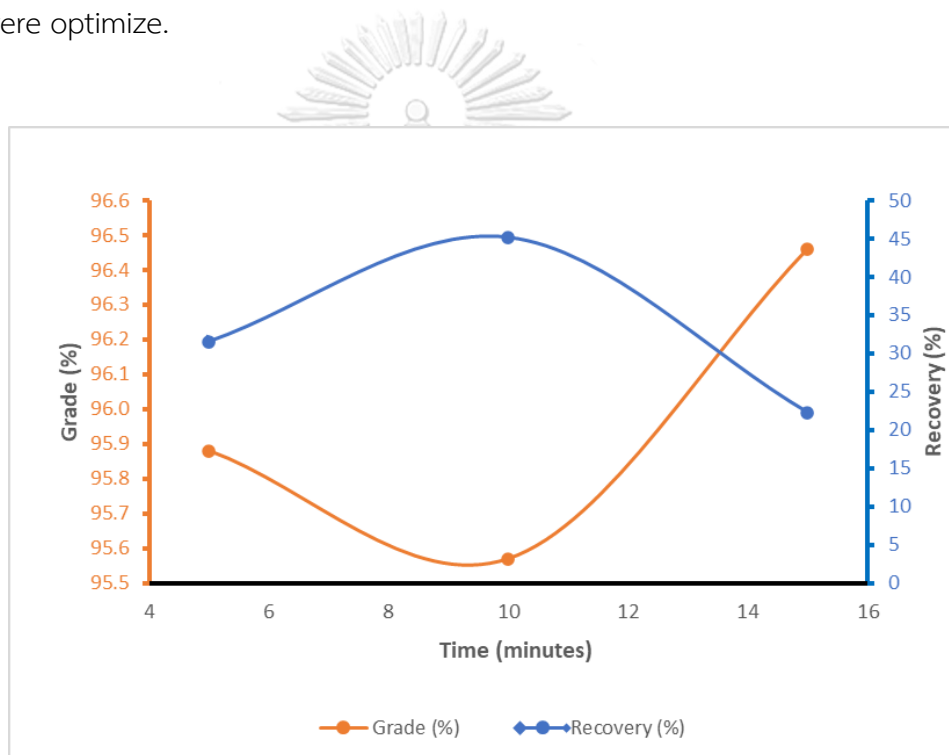


Figure 4.6 Effect of conditioning times on the concentrate grade and recovery of CaF_2 .

4.2.5 Collector comparison

Collector comparison with the same condition and dosage between oleic acid and sodium oleate. The effect of sodium oleate on fluorite flotation was experimentally

studied. The results shown in Figure 4.7, in the form of fluorite recovery as a collector performance.

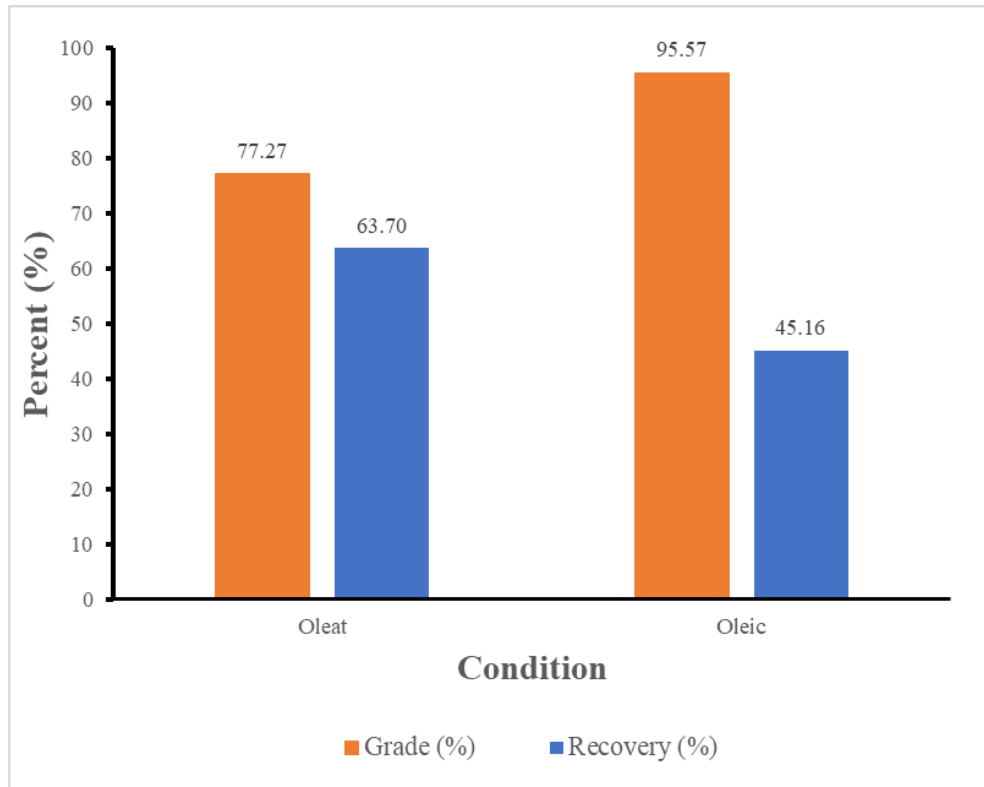


Figure 4.7 Collector comparison between oleic acid and sodium oleate on the concentrate grade and recovery of CaF_2 .

The grade of concentrates used of oleic acid was 95.57% and recovery was 45.16% while the used of sodium oleate was 77.27% and recovery was 63.7%. It can be seen that the collector performance of sodium oleate in recovery higher than oleic acid whereas, the grade of CaF_2 was lower than oleic acid. According to oleic acid and sodium oleate are anionic collectors and their chemically adsorbed on the surface of fluorite and calcite at difference ph. (20) Oleic acid is sensitive to Fe^{3+} and Ca^{2+} , it easy to floated with iron minerals, fluorite and calcite. (9). The collect capability of sodium oleate on minerals is better than oleic acid, the fluorite floatability is better than calcite, due to the strength of oleate ions on fluorite is stronger than water and OH^- , whereas on calcite is opposite. Collecting ability of

sodium oleate ions on fluorite is strong, and less affected by OH^- and water modulus. (3).

Table 4.2 Results of froth flotation

All experiment of fluorite flotation by weight% (Margin error $\pm 5\%$)			
Sample ID	%CaF ₂	%SiO ₂	%CaCO ₃
Con 1A	96.42	0.32	3.12
Con 1B	95.51	1.84	1.21
Con 1C	94.95	1.56	1.14
Con 2A	95.91	1.21	2.45
Con 2B	95.80	1.49	1.78
Con 2C	95.44	1.89	1.52
Con 3A	95.57	1.75	2.03
Con 3B	95.41	1.29	2.66
Con 3C	96.10	1.14	2.19
Con 4A	95.88	2.6	0.68
Con 4B	96.46	2.1	0.73
Con 5	77.27	22.72	
Mean	94.33	3.20	1.79
Median	95.57	1.75	1.91
Min	77.27	0.32	0.68
Max	96.46	22.72	3.12

The overall of % CaF₂ results from fluorite flotation which the target of this study, the grade arranges from 77.27 to 96.46%, and the mean value is 94.33%, whereas the median value is 95.57% with % error ± 5 . Sample 4B is acceptable for the commercial specific grade of fluorite ceramic grade which is contains 96.4% CaF₂, and 2.1% SiO₂ and 0.7% CaCO₃ as shown in Figure 4.8 and **Error! Reference source not found..**

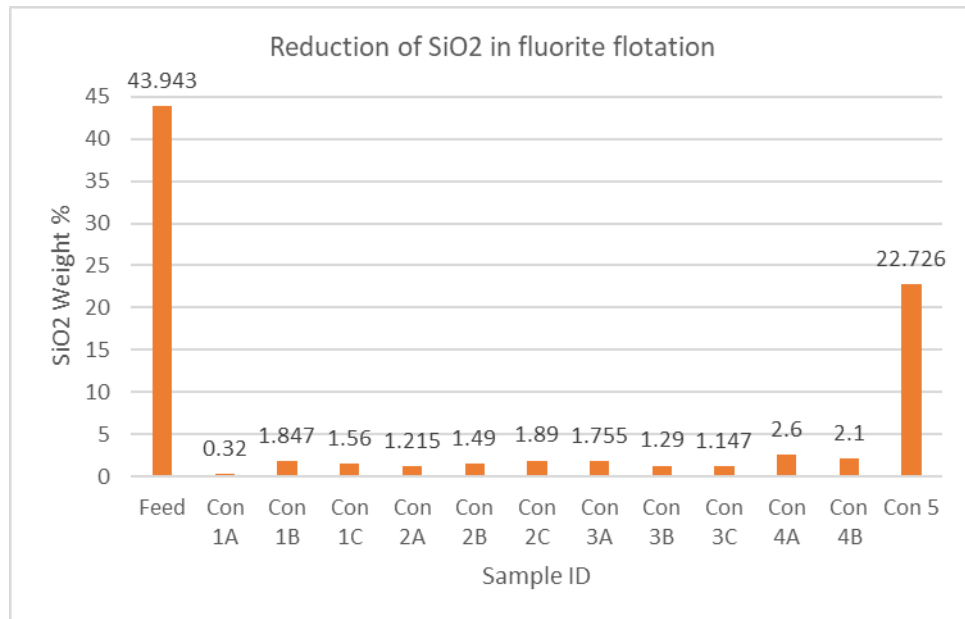


Figure 4.8 Reduction of silicon dioxide in fluorite flotation

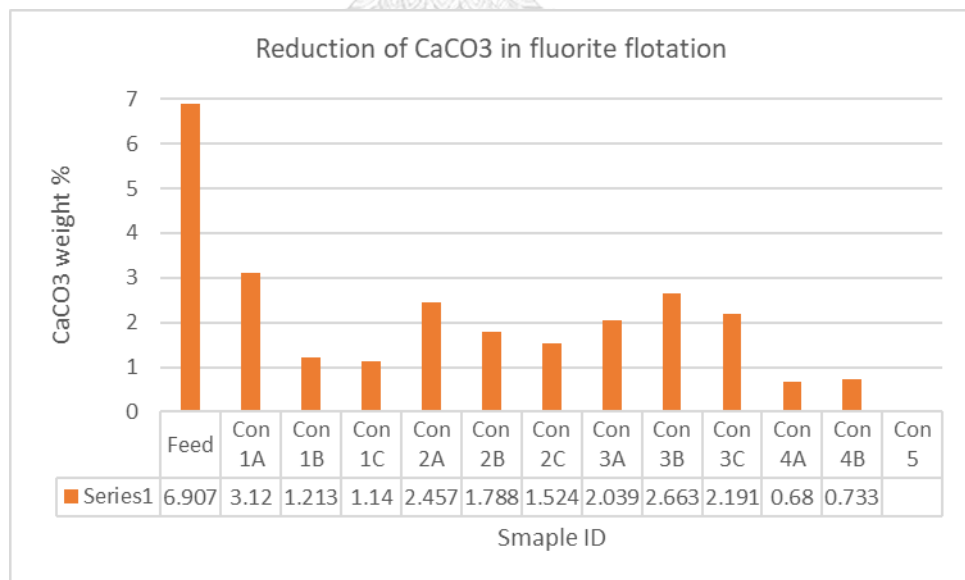


Figure 4.9 Reduction of CaCO₃ in fluorite flotation

Table 4.3 Performance calculations of froth flotation

Sample ID	%Recovery	% Loss	%Yield	Enrichment Ratio
Con 1A	18.12	81.87	5.54	3.27
Con 1B	1.74	98.25	0.54	3.24
Con 1C	18.49	81.50	5.74	3.22
Con 2A	29.77	70.22	2.97	3.25
Con 2B	5.52	94.47	1.7	3.25
Con 2C	3.82	96.17	1.18	3.23
Con 3A	45.16	54.83	13.93	3.24
Con 3B	27.70	72.29	8.56	2.90
Con 3C	29.08	70.91	8.92	3.26
Con 4A	22.11	77.88	6.8	3.25
Con 4B	31.74	68.25	9.7	3.27
Con 5	63.70	36.29	6.37	2.62
Mean	26.32	73.67	6.60	3.17
Median	27.70	72.29	6.37	3.24
Max	63.70	98.25	13.93	3.27
Min	1.74	36.29	0.54	2.62

The raw material sample was contained SiO₂, CaF₂, CaCO₃ were 43.94%, 29.47% and 6.9% respectively. After finished the froth flotation process the concentrate of each concentrate were used to performance calculation to determined the relationship between grade % by weight with performance calculation as shown in Figure 4.10. The ranged of grade were 77.27% to 96.46% of CaF₂ (error ±5%), whereas the recovery were 1.74% to 63.7% respectively.

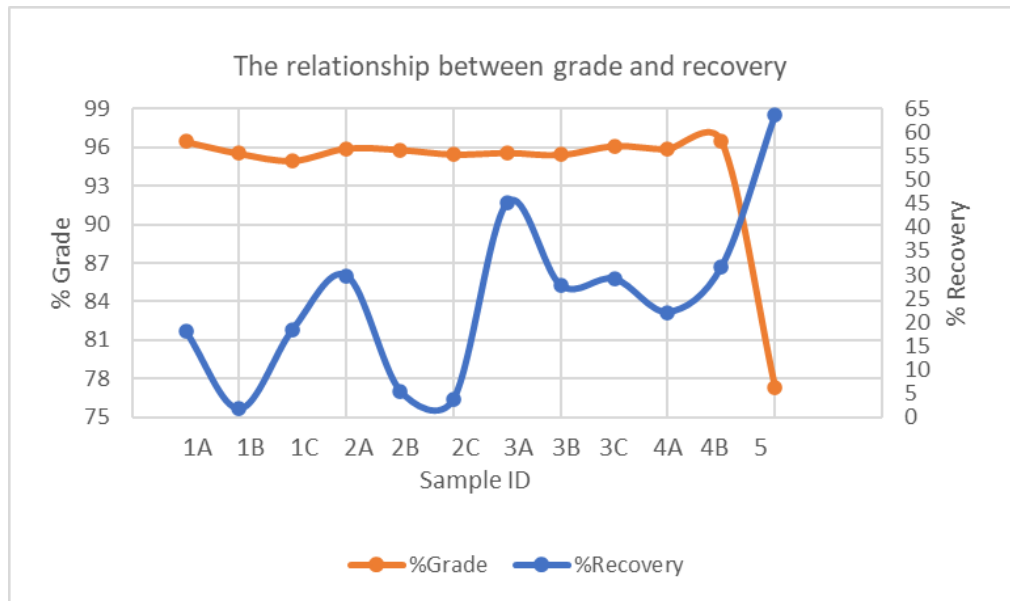


Figure 4.10 The relationship between grade and recovery in fluorite flotation

4.10 illustrate the sample 4B is possibly to meet the marketable specification target which contains silicon dioxide 2.1 Wt.%, 96.46 Wt.% of CaF_2 and 0.7 Wt.% of CaCO_3 .

According to the results indicated that the removing of gangue minerals from fluorite ore can be used these chemical reagents with optimal condition, which is more significant for ceramic grade but it would be less % recovery due to the raw material is contain large amount of gangue minerals conjoining.

Finally, the significantly separate fluorite from gangue minerals by froth flotation technique with 800g/ton of oleic acid with 100 g/ton of MIBC, 500 g/ton of sodium silicate was effective in order to depress silicon dioxide which met the requirement of fluorspar ceramic grade remove SiO_2 from 43.9 to 2.1 Wt.%, reducing CaCO_3 from 6.9 to 0.7 Wt.% and increasing CaF_2 from 29.4% to 96.4% Wt.%.

4.3 Fluorite processing plant design

After the result from experiment conditions in laboratory were undertaken to design as a fluorite processing plant as shown in Figure 4.12. The raw material feeds to hopper by wheel loader, the further fed into ball mill with rate 15 ton per hour with 70% solid then classified size (-325mesh) by spiral classification after that the conveyed to conditioner tank with inject soda ash to adjust pH 9 the oversize will conveyed to conditioner to tank classifier by pumping machine and hydro cyclone for separate organic matter overflow on the top of the plant then feeds in second ball mill to grind again, and the under size further conveyed to rougher flotation cell with 20% solid and infuse 800 gram per ton of oleic acid with 100 gram per ton of MIBC condition for 10 minutes then 500 gram per ton of sodium silicate was infuse for 5 minutes, after that the rougher tailing was treated by scavenger 2 stages before tailing whereas, the rougher concentrate was treated by 7 step cleaners. Finally, the concentrate from flotation cell fed to conditioner tank and pump to thickener tank before conveyed to dump filter to reduce moisture content before conveyed to stockpile which defined as fluorite product.

The procedure for fluorite processing by using froth flotation techniques to improve the quality of CaF_2 from very low grade or as ores tailing. Therefore, the optimal condition when applying to processing plant scale of industrial it would be required more step cleaner due to the big scale and the flotation cell is continuously and to recover mineral wisely than laboratory scale in term of profitable. Shown in Figure 4.11.

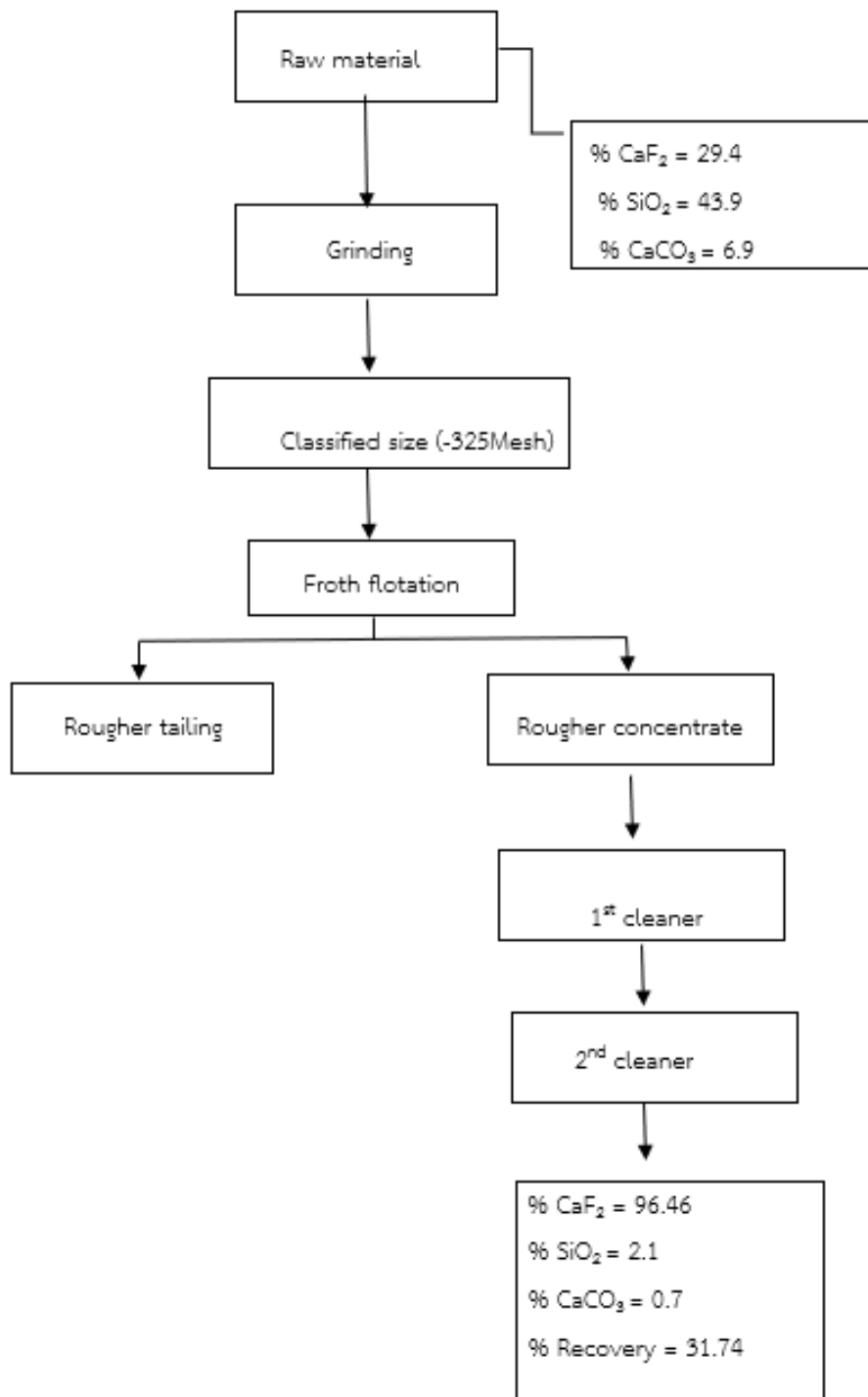


Figure 4.11 Flowsheet of Fluorite flotation in laboratory test

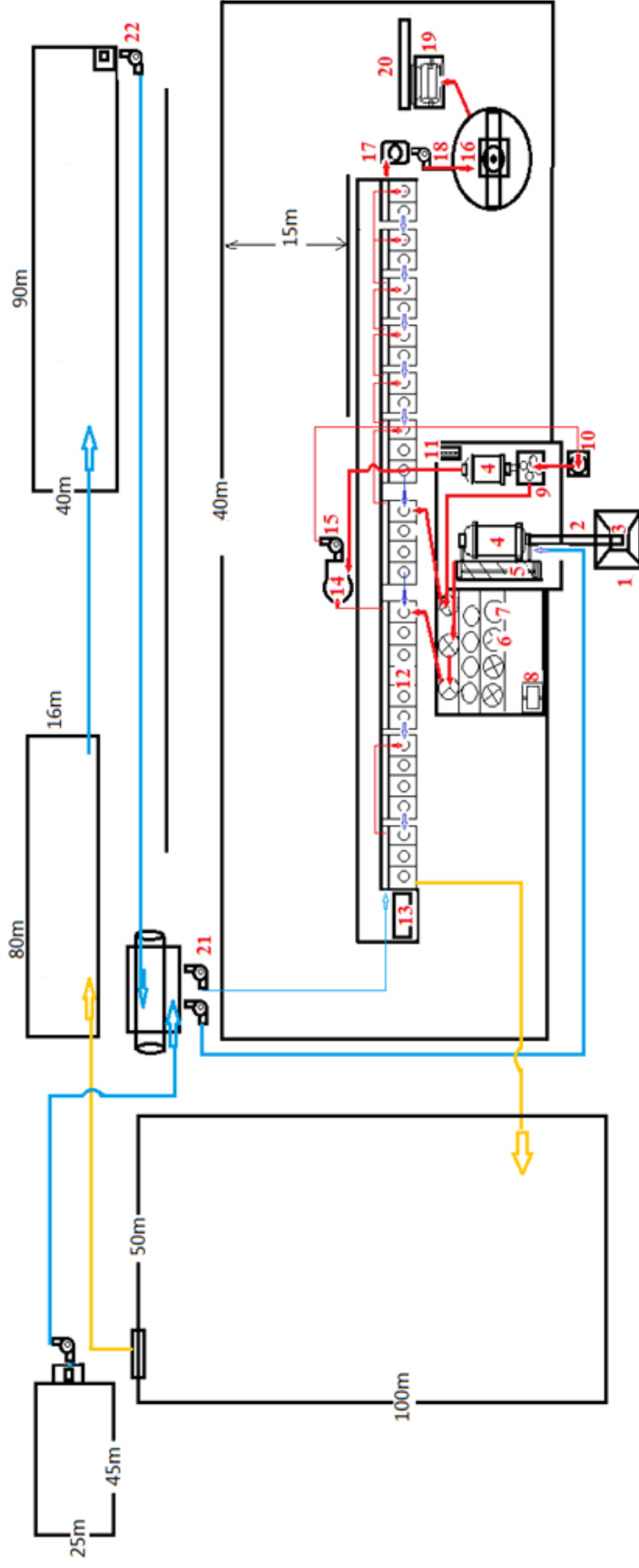


Figure 4.12 Fluorite processing plant arrangement

4.4 Project evaluation

Decision for long-term project investment financial analysis common use discount cash flow DCF model analysis. It provided discount rate of 10% for net present value critical, and the internal rate of return IRR. All investment project needs to consider essential parameters for feasibility study such as: DCF, NPV is the project validated value, IRR to determine the interest of project, MIRR to modified IRR and payback period to estimate the period time to obtain money back.

4.4.1 Discounted cash flow calculation (DCF)

In order to determine the discounted cash flow there are many stages, the parameters input to calculate in this stage are capital cost (CAPEX), operation cost (OPEX), depreciation, tax rate, and royalty rate. In this project was operating one product which contained 96.46% CaF₂.

Table 4.5 illustrate the product design to produced 11,426 ton per year for 15 years with project life. The royalty at 7%, profitable tax rate 30% and discount rate 10%.

Table 4.4 Capital Expenditure

Investment	Baht
Land and License	9,007,661.00
Machinery	39,565,636.00
Plant/ Construction/ Installation	22,000,000.00
excavator	5,390,000.00
Wheel loaders	4,340,000.00
Truck	3,208,332.00
Total	(83,511,629.00)

In this project was invest on capital cost (CAPEX) or initial investment cost approximately 83,511,629.00 baht, whereas the cost of operation (OPEX) was 40,100,303 baht in year 1 and increasing 5% from year 2 to year 5, and 42,811,360 from year 5 to year 15 the time of project life. Table 4.6 was illustrating the total operation cost include all expense, labor cost and 5% increasing per year for 5 years. In addition, this project considers the welfare and management assumed 20% of the investment.

Table 4.5 Total operation cost

Years	Processing cost	Labor Cost 5% /year	Welfare and management (20%)	Total Operation Expense
1	26,545,022	11,296,068	2,259,214	40,100,304
2	26,545,022	11,860,871	2,372,174	40,778,068
3	26,545,022	12,425,675	2,485,135	41,455,832
4	26,545,022	12,990,478	2,598,096	42,133,596
5	26,545,022	13,555,282	2,711,056	42,811,360
6	26,545,022	13,555,282	2,711,056	42,811,360
7	26,545,022	13,555,282	2,711,056	42,811,360
8	26,545,022	13,555,282	2,711,056	42,811,360
9	26,545,022	13,555,282	2,711,056	42,811,360
10	26,545,022	13,555,282	2,711,056	42,811,360
11	26,545,022	13,555,282	2,711,056	42,811,360
12	26,545,022	13,555,282	2,711,056	42,811,360
13	26,545,022	13,555,282	2,711,056	42,811,360
14	26,545,022	13,555,282	2,711,056	42,811,360
15	26,545,022	13,555,282	2,711,056	42,811,360

4.4.2 Net present value (NPV) and WACC

NPV has been determine from summation of discount cash flow and present value. In this project, NPV value is positive, it would be considering of feasibility study. According to the excel calculations NPV is THB 377,575,304 baht which is considers financially feasibility to investment shown in Table 4.7





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Table 4.6 Annual project

Year	Product (ton)	Sale Product (THB)	Gross Revenue	Royalties 7%	Net Revenue	Depreciation	Operation Expense	Income before Tax	Tax 30%	Income after Tax	Cash Flow	Cum Cash Flow
0				39THB							(83,511,629)	(83,511,629)
1	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	40,100,304	82,510,832	24,753,250	57,757,582	61,849,448	(21,662,181)
2	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	40,778,068	82,510,832	24,753,250	57,757,582	61,849,448	39,712,831
3	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	41,455,832	81,833,068	24,549,920	57,283,148	61,375,013	100,613,409
4	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,133,596	81,155,504	24,346,591	56,808,713	60,900,578	161,039,552
5	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	80,477,540	24,143,262	56,334,278	60,426,143	220,991,260
6	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	79,799,776	23,939,933	55,859,843	59,951,708	280,942,968
7	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	79,799,776	23,939,933	55,859,843	59,951,708	340,894,676
8	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	79,799,776	23,939,933	55,859,843	59,951,708	400,846,384
9	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	79,799,776	23,939,933	55,859,843	59,951,708	460,798,092
10	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	79,799,776	23,939,933	55,859,843	59,951,708	520,749,800
11	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	79,799,776	23,939,933	55,859,843	59,951,708	581,489,068
12	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	77,174,577	23,152,373	54,022,204	60,739,268	642,228,336

13	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	77,174,577	23,152,373	54,022,204	60,739,268	702,967,603
14	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	77,174,577	23,152,373	54,022,204	60,739,268	763,706,871
15	11,426	11,129	127,159,954	456,953	126,703,001	4,091,865	42,811,360	77,174,577	23,152,373	54,022,204	60,739,268	824,446,139
NPV@ 10%												377,575,305



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The total capital is 83,511,629.00 baht invested in the year zero, it can be seen that the gross revenue is rising at the first-year operating, it means this project can be recovered the in the short period of time of investment. Shown in Figure 4.13.

Therefore, the budget of investment in this project was borrowed from bank and the owner of the project. Thus, this project was assumed that 20 percent fund from the bank and 80 percent from the owner. WACC was calculate from assuming weight of debt 20%, corporate tax 30%, cost of debt 10%, risk premium 8%, risk free rate 3%, annual inflation rate 10%, and market premium 10% so the WACC value is 10%.

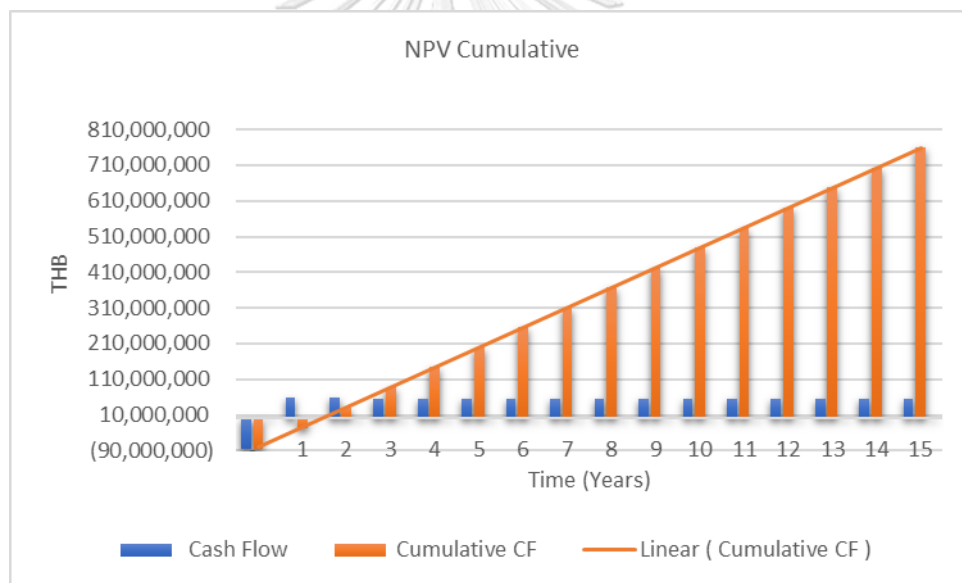


Figure 4.13 Cumulative cash flow

4.5 Modified Internal rate of return (MIRR)

Internal rate of return (IRR) is the rate to measuring the return by an assuming the rate of cash flows reinvestment. IRR is the rate to made NPV = 0, as an essential for investment, also identify the discount payback period of project. The project will not obtain profit when IRR equaled to WACC or discount rate, NPV equaled to zero. In this project NPV was THB 377,575,304 baht, IRR was 73% and MIRR was 35%

respectively. Therefore, IRR was concerned in this project by change the assumption rate of reinvestment growth in the project, MIRR is designed to solve the IRR. Consequently, the payback period was investigated determine the project life in order to recover initial investment by given a number of years. In this project, the payback period was 2 years of recover initial investment.

However, NPV and IRR methods may provide the confliction results in case of mutually exclusive project. Figure 4.14 shown the IRR value gives an over number of potentials of project, whereas the MIRR value gives more realistic of project evaluation.

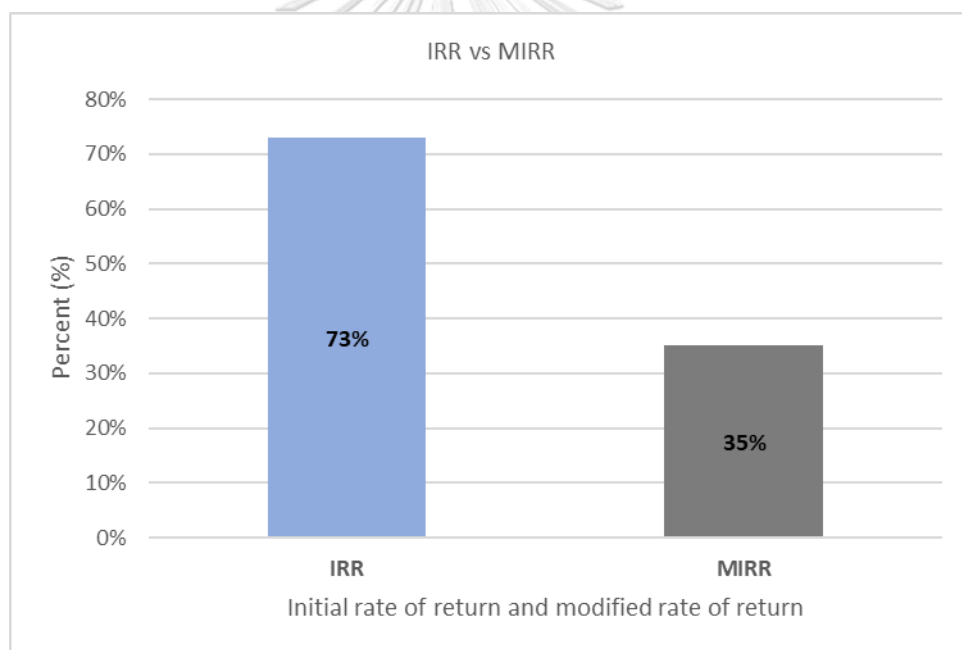


Figure 4.14 Initial rate of return and modified rate of return

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the result in laboratory scale experiment in this study the aim of thesis was conducted with recovery fluorite from ore tailing and project evaluation in term of economic. The beneficiation of fluorite which characterize raw material was following by $\text{CaF}_2 = 29.4 \text{ Wt. } \%$, $\text{SiO}_2 = 43.9 \text{ Wt. } \%$ and, $\text{CaCO}_3 = 6.9\% \text{ Wt.}\%$ which is represented of raw fluorite. Therefore, the laboratory scale froth flotation was investigate using 800 gram per ton of oleic as collector, 100 gram per ton of MIBC to prevent the bubble breaking, modifier 500 gram per ton of sodium silicate to depress silicon dioxide and soda ash to adjust pH 9, which is upgrading fluorite from 29.4 to 96.46 Wt. % whereas the SiO_2 reduced from 43.9 to 2.1 Wt.% and CaCO_3 reduced from 6.9 to 0.7 Wt. % within % recovery = 31.74%. Based on the result of fluorite flotation the optimal condition was undertake to determine the financial analysis including CAPEX was 83,511,629 baht. The raw material price is 300 baht per ton, including the price of transport to processing plant, the operating cost 391 baht per ton, and total processing cost is 691 baht per ton. Whereas the OPEX was 40,100,303 baht in year 1 and increasing 5% from year 2 to year 5, and 42,811,360 from year 5 to year 15 the time of project life. The net revenue was 120,582,886 baht, the depreciation cost was 5,800,256 and decreasing 5% in each year for 15 years, the income before tax 30% was 74,682,325 and income after tax was 52,277,627 in year 1 respectively and increasing 0.21% in every single year within 15 years of operation. Nevertheless, the Net present value was 377,575,304 baht, IRR was 73% MIRR was 35%, and WACC rate was 10% which is possibly to obtain money back from initial investment within 2 years.

5.2 Recommendation

There are some recommendations for further study are: according to the experiment results indicated that the concentrate were highly while the recovery were nominal it may cause from the size classification of wet sieve which should use sieve No. 400 under sieve No. 325 mesh to classified the smaller size over sieve No. 400 mesh out because the fine particle is ineffective in recovery.

Therefore, fluorite flotation used another chemical reagent to compared with oleic acid, MIBC and Sodium silicate with explore the suitable condition to increasing % recovery in order to figure out the optimization between grade % and % Recovery.

Furthermore, the results from experiments in this study focused on various condition variation and the limitation of sample, it is recommended that further study must repeat the experiment at least 3 times.

Final, the financial analysis of this project indicated that this project could be considering to continue estimation in deep detail as a feasibility and reasonable to investment.

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Fluorite flotation results

Sample results Feed			
Feed	%CaF ₂	%SiO ₂	%CaCO ₃
Compound	29.47	49.94	6.9

Sample results Exp.1			
Compound	%CaF ₂	%SiO ₂	%CaCO ₃
1A	96.42	0.92	3.12
Con 1B	95.51	1.84	1.21
Con 1C	94.95	1.56	1.14

Sample results Exp.2			
Compound	%CaF ₂	%SiO ₂	%CaCO ₃
Con 2A	95.91	1.21	2.45
Con 2B	95.8	1.49	1.78
Con 2C	95.44	1.89	1.52

Sample results Exp.3			
Compound	%CaF ₂	%SiO ₂	%CaCO ₃
Con 3A	95.97	1.75	2.03
Con 3B	95.41	1.29	2.66
Con 3C	96.1	1.14	2.19

Sample results Exp.4			
Compound	%CaF ₂	%SiO ₂	%CaCO ₃
Con 4A	95.88	2.6	0.68
Con 4B	96.46	2.1	0.73

Sample results Exp.5			
Compound	%CaF ₂	%SiO ₂	%CaCO ₃
Con 5	77.27	22.72	-

Capital Expenditure

Investment	Baht	Baht/Unit	Investment 2	DA 10 years	DA 5 years
Land	8,100,000.00	8,100,000.00			
License	907,661.00	907,661.00			
Machinery	19,782,818.00	19,782,818.00	19,782,818.00	19,782,818.00	19,782,818.00
Plant/ Construction/ Installation	22,000,000.00	22,000,000.00		14,666,666.67	7,333,333.33
excavator	2,695,000.00	2,695,000.00	2,695,000.00	2,695,000.00	2,695,000.00
Wheel loaders	2,170,000.00	2,170,000.00	2,170,000.00	2,170,000.00	2,170,000.00
Truck	1,604,166.00	1,604,166.00	1,604,166.00	1,604,166.00	1,604,166.00
Total		57,259,645.00	26,251,984.00	40,918,650.67	33,585,317.33
Total		83,511,629.00		4,091,865.07	6,717,063.47

Equipment

			จำนวน	ราคารวม฿
ชุดล้างแร่ ย่อยแร่		kW		
ถัง ป้อนแร่ (Hopper)	3000 X 4800 X 1000		1	170000
ตะแกรงสั่น (Grizzly Screen)	4 ฟุต X 12 ฟุต	40	1	380000
สายพานลาเลียยง (Belt Conveyor)	24 นิ้ว X 13 ม.	15	1	221000
ตะแกรงหมุน (Revolving Screen)	Ø 1500 X 6000 , 1 ชั้น	30	1	500000
สายพานลาเลียยง (Belt Conveyor)	24 นิ้ว X 12 ม.	15	1	221000
สไปรอล (Spiral Classifier)	1000 X 4000	7.5	1	200000
สายพานลาเลียยง (Belt Conveyor)	24 นิ้ว X 12 ม.	15	1	204000
ตะแกรงสั่นคคขนาด (Vibrating Screen)	4 ฟุต X 8 ฟุต , 2 ชั้น	30	1	400000
สายพานลาเลียยง (Belt Conveyor)	20 นิ้ว X 12 ม.	10	3	540000
ปั๊มน้ำ (Water Pump)	6 นิ้ว X 4 นิ้ว	20	1	200000
ชุดคคขนาดแร่				
ถัง ป้อนแร่ (Hopper)	3000 X 4000 X 1000		1	100000
เครื่องบดแร่ (Jaw Crusher)	40 X 8 นิ้ว	40	1	500000
สายพานลาเลียยง (Belt Conveyor)	15 นิ้ว X 12 ม.	5	1	120000

ตะแกรงสั่นคดขนาด (Vibrating Screen)	4 ฟุต X 8 ฟุต , 3 ชั้น	20	1	300000
สายพานลาเลียยง (Belt Conveyor)	400 มม. X 10 ม.	3	1	776968
สายพานลาเลียยง (Belt Conveyor)	15 นิ้ว X 12 ม.	5	1	120000
เครื่องบดแร่ (Impact Crusher)	-	30	1	540000
ย้ง เก็บแร่ (Bin)	5 ม. X 5 ม.		4	800000
ชุดลอยแร่				
ย้ง ป้อนแร่ (Hopper)	4000 X 4000 X 1120		1	100000
สายพานป้อนแร่ (Belt Feeder)	60 ซม. X 4 ม.	3	1	100000
สายพานลาเลียยง (Belt Conveyor)	20000 x 600	15	1	360000
Ball Mill	Ø 1500 x 3000	90	1	1481898
สไปรอล (Spiral classifier)	4 x 4 Spirals	7.5	1	754116
Conditioner	2000 X 2000	5.5	2	646338
Flotation Cell	1000 X 1000	5.5	30	3693690
มู้มสูบแร่	3 นิ้ว x 2 นิ้ว	22	3	416922
ไฮโดรไซโคลน (Hydrocyclone)	Ø 375	22	1	161568
Ball Mill	Ø 1500 x 3000	22	1	1481898
Thickener	Ø 12000	1.5	1	2477772
Drum Filter	GW-3	1.5	1	615648
มู้มน้ำ (Water Pump)	6 นิ้ว X 4 นิ้ว	20	1	200000

Tower Crane และ ไฮโดรไลโคลน	สูง 12 ม. , Ø150 มม. x 1 ม.	22	1	500000
weight mechine				500000
			Total	19,782,818.00
Infrastructure (electricity, water pipe, roadway), Power system facilities Power lines				22,000,000.00
Total consumption				41,782,818

Operation cost

Items	Baht/ton
Raw material	300
Chemical reagent	0.134725
Electricity	391.204
Processing cost	691.338725
Feed/year	36,000.00
	24,888,194.10
Production/year	11,426.40
Plastic bag 145THB/1psc	1,656,828.00
Total Operation expense	26,545,022.10

VITA

NAME	Keosaychai Souvannavong
DATE OF BIRTH	26 June 1996
PLACE OF BIRTH	Khammouan, Lao P.D.R.
INSTITUTIONS ATTENDED	Department of Mining Engineering, National University of Laos, Vientiane, Laos.
HOME ADDRESS	Khammouan, Laos.
PUBLICATION	Fluorite Recovery from Ores Tailing by using Flotation Technique at the International Conference on Metallurgy Technology and Materials (ICMTM) held in Kuala Lumpur, Malaysia on February, 2020.
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