



February 2012 Master Thesis

# Removal of Heavy Metals from Gold Mine Tailing

Graduate School of Chosun University Dept. of Energy & Resources Engineering Davaasuren Jambal

# Removal of Heavy Metals from Gold Mine Tailing 금광산 광미로부터 중금속 제거에 관한 연구

Feb. 24, 2012

Graduate School of Chosun University Dept. of Energy & Resources Engineering Davaasuren Jambal

# Removal of Heavy Metals from Gold Mine Tailing

Advisor Professor: Han, Oh Hyung

A thesis submitted for the degree of Master of Engineering

October 2011

Graduate School of Chosun University Dept. of Energy & Resources Engineering Davaasuren Jambal

# Davaasuren Jambal's Thesis for degree of Master is certified

Chairman: Prof. Park, Cheon-Young (인) Member: Prof. Kang, Seong-Seung (인) Member: Prof. Han, Oh-Hyung (인)

November 2011

Graduate School of Chosun University

# Table of Contents

Abstrac	t
Chapter	1. Introduction
	1.1 Ore beneficiation
	1.2 Mine tailing5
	1.3 Heavy metals in mine tailing7
Chapter	2. Experiment method
	2.1 Flotation principles
	2.2 Reagents
	2.3 Zeta potential
	2.4 Column flotation
Chapter	3. Experiment
	3.1 Experiment purpose 20
	3.2 Sample preparation20
	3.3 Analysis21
	3.4 Batch flotation28
	3.4.1 Collectors
	3.4.2 Frothers
	3.4.3 Depressants
	3.4.4 pH modifiers 33
	3.4.5 Pulp density and RPM

	3.4.6 Calculations
Chapter	4. Results and discussions
	4.1 Effect of Collectors
	4.2 Effect of Frothers
	4.3 Effect of Depressants 41
	4.4 Effect of pH change43
	4.5 Pulp density effect
	4.6 Effect of Impeller speed
Chapter	5. Conclusions 48
Referen	ces52
Acknow	ledgements

# List of Tables

Table	1.1	Priority list of (top 20) most hazardous substances9
Table	3.1	Chemical composition of Kumpoong tailing raw sample21
Table	3.2	Concentrations of target heavy metals in raw sample21
Table	3.3	Result of wet screen analysis on particle size
Table	3.4	Heavy metal concentration by particle size distribution
Table	3.5	Collectors used in batch flotation tests
Table	3.6	Frothers used in batch flotation tests
Table	3.7	Depressants used in batch flotation tests
Table	3.8	pH regulators
Table	3.9	Dp and RPM
Table	4.1	Compared assays and removal rate on target heavy
	met	als in the presence of KAX (potassium amyl xanthate)
Table	4.2	Results of batch flotation40
Table	4.3	Results of batch flotation41
Table	4.4	Batch flotation results in the Dp:20%45

# List of Figures

Figure	1.1	Breaking of larger materials to smaller pieces
Figure	1.2	Primary and Secondary crushers2
Figure	1.3	Vibratory screen with multiple removable and
		replaceable decks. 3
Figure	1.4	Photo of typical tailing disposal and AMD
Figure	1.5	The factors generating heavy metal pollution
Figure	2.1	Photo of particle attachment on bubble11
Figure	2.2	Flotation in the mechanical cell
Figure	2.3	Schematic illustration of froth structure
Figure	2.4	Contact angle between particle and bubble
Figure	2.5	Schematic showing the electrical double layer
Figure	2.6	Schematic illustration of microbubble column
		flotation machine
Figure	3.1	Kumpoong mine tailing storage20
Figure	3.2	A. Illustration of typical size measurement.
		B. Sieve shaker for wet screen analysis24
Figure	3.3	X-ray diffraction pattern of raw sample25
Figur 3	8.4 >	(RD patterns by size range (raw sample)25
Figure	3.5	SEM and X-Ray dot mapping images of raw sample27
Figure	3.6	Laboratory scale Denver Sub-A type flotation machine

Figure	3.7	Flotation products. 29
Figure	4.1	Effects of Collectors on heavy metals removal
Figure	4.2	Effect of various frothers on batch flotation
Figure	4.3	Effect of frother dosage on batch flotation
Figure	4.4	Effect of various depressants on Heavy metal
		removal and recovery
Figure	4.5	Effect of pH on Heavy metal (a) removal and
		(b) recovery ······44
Figure	4.6	Effects of different pulp densities on
		Heavy metal removal
Figure	4.7	Effect of RPM on Heavy metal (a) removal and
		(b) recovery

## 초 록

# 금광산 광미로부터 중금속 제거에 관한 연구

Davaasuren Jambal 지도교수 : 한 오 형 에너지자원공학과 조선대학교 대학원

채광 및 야금 작업으로 인해 발생하는 많은 양의 광미는 오염된 미립자와 함께 중금속을 포함한다. 현존하는 광미의 중금속은 각종 심각한 문제와 환경오염의 주 된 요인으로 많이 발생하고 있다. 광산 광미에서 발생하는 중금속은 많은 심각한 문제들을 유발하고, 환경오염의 주된 요인이 된다. 광산 폐석으로부터 방출되는 중 금속은 용해도와 유동성 때문에 지질학적인 환경뿐만 아니라 지하수와 표층수에서 도 발생 할 수도 있다. 광미는 보통 황화광물을 포함하고 있어, 공기에 노출되는 경우, 산화, 용해, 침전, 흡착과 탈착 등이 발생한다. 또한 황화광물의 산화는 황을 함유한 광물에서 중금속을 방출하므로 주변 토양과 지하수를 오염시킨다. 또한, 광 산 광미의 중금속은 사람의 내장 기관에 쉽게 축적되는 특징 때문에 곡식과 물을 통해 섭취할 경우, 치명적인 질환을 유발할 수 있다. 이러한 문제를 해결하기 위해 서는 광산의 중금속의 제거를 위해 적합하고 경제적인 재활용과 오염 제거 기술을 개발하는 것이 중요하다. 따라서 본 연구의 목적은 다양한 광물처리 공정의 적용과 부유선별을 통해 금광산 광미의 중금속 제거의 실행가능성을 입증하는데 있다.

본 연구에서 사용한 시료는 충청북도에 위치한 금풍광산에서 채취하였다. 약 113 kg의 샘플을 실험대상으로 채취하여 무게비를 확인한 결과, 전체 무게의 78.11 % 가 +270 mesh 구간에 분포함을 알 수 있었고, 10.72 %가 -500 mesh 구간에 분 포함을 확인하였다. 원광을 대상으로 XRF 분석을 한 결과, 불순물의 53 %가 SiO<sub>2</sub> 로 관찰되었으며, CaO 17.67 %, Al<sub>2</sub>O<sub>3</sub> 9.64 %, Fe<sub>2</sub>O<sub>3</sub> 5.41 %로 확인되었다. 또 한, 중금속은 As 78.98 ppm, Cd 14.64 ppm, Cu 227.41 ppm, Pb 244.18 ppm, Zn 594.65 ppm으로 확인되었다. 원 시료를 대상으로 Denver Sub-A type의 일반 부유 선별기를 사용하여 일반부선을 실시하였으며, 광액농도는 10~20 %, pH는 4~12까지 변화를 주어 실험을 실시하였다. 사용된 포수제로는 K.A.X (potassium amyl xanthate), Sodium oleate, Oleic acid, S.D.S (Sodium dodecyl sulfate)였 으며, 기포제로는 DF250, AF65, MIBC, pine oil, 억제제로는 S.S (Sodium silicate), S.M.P (Sodium meta phosphate), Lime, S.S+S.M.P, S.S+Lime, Lime+S.M.P를 사용하여 실험을 진행하였다. 또한, NaOH와 HCI을 사용하여 pH를 변화하였으며, 각각 다른 종류의 시약과 첨가량을 변화하여 부선실험을 진행하였 다. 한 편, 회수된 정광과 광미를 분석하여 중금속 제거율과 회수율을 산출하였다.

# Abstract

## The Removal of Heavy Metals from Gold Mine Tailing

By Davaasuren Jambal Advisor : Prof. Han Oh Hyung, Ph.D. Dept. of Energy & Resources Engineering Graduate School of Chosun University

Mining and metallurgical operations extract large volumes of mine tailings which are invariably contaminated with fine particles, chemical reagents and heavy metals. The presence of toxic heavy metals in mine tailings is causing lots of serious problems and act as a main source of environmental contamination. Heavy metals may be released from the mine wastes to the ground and surface water systems, as well as geological environment due to their solubility and mobility. Furthermore, heavy metals from mine tailing may cause fatal diseases in humans through crops and water due to their characteristic of easy accumulation in internal organs. In order to resolve these problems, it is important to develop a suitable and economical recycling and decontamination technology for removal of heavy metals from mine tailings.

The aim of this work is to demonstrate the feasibility of removing toxic heavy metals from gold mine tailing with the use of froth flotation technology. Mine tailing used in this study were collected from the Kumpoong mine tailing site located in North Chungcheong province, Korea.

Approximately 113 kg of tailing sample were collected for laboratory tests. 78.11% of total weight is +270 mesh particles and 10.72% is -500 mesh particles. Raw sample XRF analysis showed 53% of whole impurities is SiO2, followed with CaO 17.67%, Al2O3 9.64%, Fe2O3 5.41%. Target heavy metals such as As:78.98ppm, Cd:14.64ppm, Cu:227.41ppm, Pb:244.18ppm, Zn:594.65ppm were identified.

Batch flotation experiments were conducted with a Denver Sub-A type laboratory-scale flotation machine on a tailing sample. Mineral and water slurry prepared with Dp 10% and 20%, pH range between 4-12 were adjusted. Flotation Reagents KAX (potassium amyl xanthate) and Sodium oleate, Oleic acid, SDS (Sodium Dodecyl sulfate) as collectors and DF250, AF65, MIBC, Pine oil as frothers, SS (Sodium silicate) and SMP (Sodium meta phosphate). Lime and in their combined forms such as SS + SMP. SS + Lime, Lime + SMP as depressant, NaOH and HCI are as pH modifiers were used in the flotation tests. Every reagent effects were tested in a range of different dosages. Concentrates and tailings were analysed and Heavy metal removal and recoveries were investigated. Overall study results showed that the froth flotation technology is efficient in reducing heavy metal impurities those existing in gold mine tailings and for the removal of heavy metals as As, Cd, Zn with the highest removal rates of As: 87.37%, Cd: 75.48%, Zn: 72.27%. But the removal of Cu: 45.68%, Pb: 38.90 % are showing a relatively lower results and further studies on removal of this heavy metals must be developed

# Chapter 1. Introduction

In this chapter the basics of mineral processing methods, mine tailing and its sources and heavy metals in mine tailings were briefly described.

#### 1.1 Ore beneficiation

Metals and other mineral resources are rarely found in their pure form. In mineral industry the raw ore mined from run of mine should be treated with several mineral processing applications in order to extract valuable minerals from its unwanted host rocks and gangue minerals and to increase valuable minerals concentrate in ores. This process is called ore beneficiation and it can be grouped into two major operations as liberation and separation. Small sized mineral particles are attached and locked in a host rock and this mineral bearing rock is called raw ore. In order to free and unlock these attached and locked particles, mineral ore should decrease in size through a mineral particles liberation processes such as crushing and grinding applications. The separation and concentration of the valuable mineral can take place after the ore is crushed, ground, and classified into the required particle size distribution. There are number of different techniques such as sorting, gravity and dense-medium separation, magnetic separation and froth flotation are employed in concentrating the valuable minerals. These techniques exploit differences in physical or chemical properties of the valuable and gangue minerals.

Particle size and its reduction is one of the most important factors in a mineral processing. In order to separate the minerals from gangue (the waste minerals), it is necessary to crush and grind the rock to unlock ,or liberate, valuable minerals so that they are partially or fully exposed. (Figure 1.1) This process of size reduction is called comminution. The crushing and grinding process will produce a range of particles with varying degrees of liberation.

- 1 -

Any particles that exceed a target size required for physical separation or chemical extraction are returned to the crushing or the grinding circuit.



Figure 1.1. Breaking of larger materials to smaller pieces. Darker regions represent the valuable minerals. (Met-Solve,2010

Within the crushing circuit crushing equipments grouped as primary and secondary crushers, a primary crusher reduces material down to a size that can be conveyed and fed to the secondary crushing circuit including those shown in Figure 1.2. The two of the most common primary crushers used for coarse run-of-mine material are the jaw and gyratory crushers.



Figure 1.2. Primary and Secondary crushers( Met-Solve, 2010)

These primary crushers break rock through compressive forces created by a hard moving surface forcing and squeezing the rocks towards a hard stationary. Products from primary crushers applied on secondary crushers as cone, impact and roll crushers for further size reduction.

Grinding, the final stage used in the comminution process, is usually

conducted in cylindrical tumbling mills where the particle size is reduced through a combination of impact and abrasion. Grinding media can be steel rods, steel balls, hard pebbles or the ore itself. Autogenous (AG) and Semi-Autogenous (SAG) milling has been increased use in recent years, AG mills employ ore as the grinding media. The addition of steel grinding balls activate this situation. This approach is then termed semi-autogenous grinding. The products from AG or SAG mills typically feed secondary grinding mills as Rod, Ball and Pebble mills with particles that range in size from 5 cm to below 100 microns (0.1 mm). The final particle size is determined by downstream processing requirements. Grinding is carried out as a wet process with water content between 50 - 70% by weight.

There are two major methods for separation of particles based on size such as screening and classification. Screening is simply carried out with various types of screens such as grizzly, revolving and moving screens as reciprocating, oscillating, vibratory or shaking screens. The vibratory screen is the most common screening device found in mineral processing applications. Many of these types of screens have multiple decks so different particle size products can be obtained from a single feed. For example: Vibratory screen shown in Figure 1.3,



Figure 1.3. Vibratory screen with multiple removable and replaceable decks.( www.traderscity.com)

Classification techniques takes advantage of the principle that particles of the same density but of different sizes settle in a fluid at different rates. Exploiting the difference in the settling rates allows for separation based on size. Classification is usually carried out at particle sizes that are considered to be too fine for sorting efficiently by screening methods. Sedimentation and hydraulic classifier, Spiral and Rake classifiers are operate based on the differences in the settling rates of particles and Hydro-cyclones are the most important and widely used classifiers in the mineral processing industry. Hydro-cyclones relies on centrifugal force to accelerate the settling of particles. They have important role in closed circuit within grinding circuits and are used to return coarse material back to the ball or rod mill for further grinding.

The separation and concentration of the valuable mineral can take place after the ore is crushed, ground, and classified into the required particle size distribution. There a number of different techniques such as sorting, gravity and dense-medium separation, magnetic separation and froth flotation are employed in concentrating the valuable minerals. These techniques exploit differences in physical or chemical properties of the valuable and gangue minerals.

Gravity concentration methods separate particles based on the differences in their specific gravity (SG) values and their relative movement within a natural or applied gravitation force. The relative rate of settling based on the gravitational forces and the counter viscous forces are exploited for effective separation. Common gravity concentrators are sluices, spiral separators jigs and shaking tables.

Magnetic separations take advantage of the magnetic properties of minerals. All minerals will have one of three magnetic properties: ferromagnetic, paramagnetic, and diamagnetic. Ferromagnetic minerals are magnetic and are easily separated from other minerals, since they will be attracted to the poles of a magnet. Paramagnetic and diamagnetic minerals are not magnetic, but differ in how they interact with magnetic fields.

- 4 -

Magnetic fields of various intensities can be provided by permanent or electromagnets. Generally, magnetic separators are classified as low or high intensity and whether they work in wet or dry applications.

The valuable minerals separation by froth flotation is the most important mineral recovery process. Froth flotation method applies on the separation for mineral ores with finer particle sizes. There is two main type of flotations cells available in processing circuit. Conventional mechanical flotation and Column flotations. Present study used laboratory scale batch flotations for the removal of heavy metals from mine tailing.

#### 1.2 Mine tailing

The valuable mineral is locked in the in-situ uneconomic rock. These valuable minerals (concentrate) extracted with the use of mineral processing applications. The processing plant uses mechanical and chemical techniques to separate the concentrate and the gangue. The most common and widely used concentrate extraction method is a froth flotation technology. The waste ground rock and the spent processing water and reagents from the flotation process are known as tailings and tailings are a waste product that has no financial gain to a mineral operator at that particular point in time. The unrecoverable and uneconomic metals, minerals, chemicals, organics and process water are discharged, normally as slurry, to a final storage area commonly known as a Tailings Management Facility (TMF) or Tailings Storage Facility (TSF).

The properties of tailings are dependent on the ore body being mined, the grinding and processing circuits, the reagent properties and the thickening process prior to disposal. Tailings can be disposed of and stored in a variety of different methods. The most conventional worldwide is a surface impoundment. Tailings are generally stored on the surface in retaining structures but can also be stored underground in mined out voids by a

process commonly referred to as backfill.

(a)

The disposal of tailings is commonly identified as the single most important source of environmental impact for many mining operations. The minerals beneficiation process and subsequent disposal to surface containment facilities exposes elements to accelerated weathering and consequently increases mobilization rates. The addition of reagents used in mineral processing may also change the chemical characteristics of the processed minerals and the properties of the tailings and waste rock. When this weathering and oxidation processes generate toxic levels, related problems will arise. Acid generation and heavy metal mobilization will occur and eventually find their way into the surrounding environment through runoff or seepage. This process finally generates an acid mine drainage( AMD) as shown in Figure 1.4(b).



(b)

Figure 1.4. Photo of typical (a) tailing disposal and (b) acid mine drainage.

The release of acid drainage and heavy metals from mine tailings into the surrounding environment have high possibility to cause a serious problems such as contamination of the surrounding soil and ground water and may cause fatal diseases in humans through crops and drinking water. Therefore, this tailing storages should follow the appropriate managements and a safe storage methods for preventing from possible environmental hazardous

impacts. Therefore a suitable reclamation and prevention technologies for mine tailings are highly requested. Recent years, froth flotation has been proposed for tailings decontamination as a new management technique with a view to reduce rehabilitation cost. Present study used a tailing sample from Kumpoong mine and the mine is using a surface impoundment storage method for its tailings disposal.

#### 1.3 Heavy metals in mine tailing

Mine tailings are considered as an obvious sources of contamination in the surface environment. Due to inefficiencies in the extraction process, large volumes of sulphides often end up going into the tailings. Over time, the sulphides start to oxidize as they're exposed to wind, snow and temperature changes, creating sulphuric acid. The sulphuric acid mixes with rainwater and eventually works its way out of the tailings and into waterways, where it can change the pH of the water and precipitate harmful heavy metals. As a result, elevated levels of heavy metals can be found in and around mine tailings due to discharge and dispersion of mine wastes caused by failed storage and element mobilization and AMD into nearby agricultural soils, food crops and stream systems. Furthermore, heavy metals contamination may pose a potential health risk to the people in the surrounding area.

"Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 (Lide, 1992).

Large amounts of any of heavy metals may cause acute or chronic toxicity (poisoning) to humans. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer (http://www.lef.org).In Figure 1.5 showed the factors that influence for heavy metal generation thus their transportation into the environment.



Figure 1.5 The factors generating heavy metal pollution

Metals associated with Au-Ag mines, including Cd, Cu, Pb and Zn can be dispersed downstream due to the weathering process of tailings. Thus, the extent and degree of heavy metal contamination around the mines vary depending upon geochemical characteristics and mineralization of tailings.

Korea has a long history of metal mining with over 900 abandoned metalliferous mines and the most extensive activities occurred during the early twentieth century. Most of the mines, however, are abandoned due to the increase of labor cost, loss of competitiveness and the exhaustion of ore reserves, and they have become important point sources of trace elements including Cd, Cu, Pb and Zn in the surface environment (Jung et al., 2001).

Purpose of this study is to remove toxic heavy metals such as As (Arsenic), Cd (Cadmium), Cu (Copper), Pb (Lead) and Zn (Zinc) from

Kumpoong gold mine tailing. All of above heavy metals are listed in the priority list of 275 hazardous substances presented by the US Agency for Toxic substances and Disease Registration (ATSDR) in 2007 and As, Pb and Cd are listed in number 1, 2 and 7 in the top 20 most toxic substances and Zn listed in 74 and Cu listed in 128 with their toxicity. The Priority list showed in Table 1.1.

Table 1.1 Priority list of (top 20) most hazardous substances. US Agency for Toxic substances and Disease Registration (ATSDR),2007.

Note: Full list includes 275 hazardous substances.

2007 RANK	SUBSTANCE NAME					
1	ARSENIC	1				
2	LEAD	2				
3	MERCURY	3				
4	VINYL CHLORIDE	4				
5	POLYCHLORINATED BIPHENYLS	5				
6	BENZENE	6				
7	CADMIUM	8				
8	POLYCYCLIC AROMATIC HYDROCARBONS	7				
9	BENZO(A)PYRENE	9				
10	BENZO(B)FLUORANTHENE	10				
11	CHLOROFORM	11				
12	DDT, P,P'-	12				
13	AROCLOR 1254	13				
14	AROCLOR 1260	14				
15	DIBENZO(A,H)ANTHRACENE	15				
16	TRICHLOROETHYLENE	16				
17	DIELDRIN	17				
18	CHROMIUM, HEXAVALENT	18				
19	PHOSPHORUS, WHITE	19				
20	CHLORDANE	21				
74	ZINC	74				
128	COPPER	133				

# Chapter 2. Experiment method

The present study used froth flotation technology for removal of heavy metals from mine tailing.

Froth flotation in mineral beneficiation process is undoubtedly considered as one of the most significant technological developments in the 20th century. In terms of daily tonnages of ore that are treated globally, froth flotation is the single most important mineral recovery process.

#### 2.1 Flotation principles

Froth Flotation is a physico-chemical separation process that utilizes the difference in surface properties of the valuable minerals and the unwanted gangue minerals(Wills, 2006). Ground fine particle mineral and water slurry (pulp) enters to the equipment in the form of mechanically or pneumatically agitated tanks or cells generate air bubbles, which provides the physical aspect. The chemical aspect is provided by the addition of the reagents to the pulp, which are vary the surface properties of wanted minerals in to hydrophobic and unwanted particles into hydrophilic. Hydrophobic (water repellent) mineral particles attached to the bubbles and rise upward to the slurry surface and form a mineralized froth. The froth is collected as concentrate. Hydrophilic particles remain in the pulp and discharged to tailing. The process of material being recovered by froth flotation from the pulp comprises three mechanisms:

-Selective attachment to air bubbles ( true flotation )

-Entrainment in the water which passes through the froth.

-Physical entrapment between particles in the froth attached to air bubbles (Wills, 2006).



Figure 2.1 Attachment of minerals to air bubble (Courtesy of W. R. Speden) As shown in Figure 2.1, the attachment of valuable minerals to air bubbles are the most important mechanism in the flotation (Wills, 2006). Chemically selective true flotation is the main mechanism in the flotation process but both valuable and gangue minerals can be recovered by entrainment and entrapment and the separation efficiency is also dependent on the degree of entrainment and entrapment. Flotation only can be applied for fine particles. If the particles are too large bubble can not hold it's load due to the less adhesion. Therefore particle size must be controlled. The process that valuable minerals float and gangue minerals remain in the pulp is a direct flotation. On the other hand the gangue minerals separated in the froth is the reverse flotation. As shown in Figure 2.2 the basic flotation process is illustrated.



Figure 2.2 Flotation in the mechanical cell

The function of the froth phase is to enhance the overall selectivity of the flotation process. The froth achieves this by reducing the recovery of entrained material to the concentrate stream, while preferentially retaining the attached material (Wills, 2006). In Figure 2.3 has showed the froth structure and the entrainment and entrapment behaviour of hydrophilic particles in the froth.



Figure 2.3 Schematic illustration of froth structure.

The attachment of the bubbles to the surface is determined by the interfacial energies between the solid, liquid, and gas phases. The tensile forces lead to the development of an angle between the mineral and the bubble surface. At equilibrium,

$$\gamma_{s/a} = \gamma_{s/w} + \gamma_{w/a} \cos\theta \tag{1}$$

where  $\gamma_{s/a}$  is the surface energy of the solid and air interface,  $\gamma_{s/w}$  is the surface energy of the solid and water interface,  $\gamma_{w/a}$  is the surface energy of the water and air interface, and  $\theta$  is the contact angle between mineral surface and the bubble. If the contact angle is very small, then the bubble does not attach to the surface, while a very large contact angle (Figure 2.4) results in very strong bubble attachment. The hydrophobicity of a mineral will increase with the contact angle. A contact angle near 90° is sufficient for effective froth flotation in most cases.



Figure 2.4 Contact angle between particle and bubble

#### 2.2 Reagents

The flotation process begins with a modification of the surface properties of the desired mineral. Most minerals are not water repellent in their natural state and the flotation reagents must be added to the pulp. The addition of surfactants renders the mineral surface hydrophobic (water-escaping), so that the valuable mineral will attach to air bubbles and float to the surface. The unwanted minerals remain hydrophilic (water-loving) and do not attach to air bubbles. The surface of the slurry is modified by other reagents that lower surface tension forces. This allows the air bubbles with valuable minerals attachment to form a mineralized froth. The hydrophobic minerals are recovered by skimming the froth of off the surface, while the hydrophilic minerals remain in the slurry. The establishment of a hydrophobic surface on a wanted mineral particles is to prevent them from wetting and increase their floatability. A hydrocarbon layer is established on the surface because the hydrocarbon surface is not water-wetted. There are three main types of reagents used in flotation: collectors, frothers, and modifiers.

Collectors. In order to make minerals hydrophobic collectors are added to the pulp and conditioning time is given for adsorption during agitation. Collectors are organic compounds which render selected minerals water-repellent by adsorption of molecules or ions on to the mineral surface, reducing the stability of hydrated layer separating the mineral from the air bubble to such a level that attachment of the particle to the bubble can be made contact angle (Wills, 2006).

Collectors can be divided into a non-polar and a polar group with their molecular structure. The non-polar portion of the collector molecule is a hydrocarbon radical, which does not react with water and is therefore water-repellent and the polar part can react with water.

Frothers are added to stabilize bubble formation in the pulp. Frothers are heteropolar surface-active compounds containing a polar group and a hydrocarbon radical, capable of adsorbing in the water air interface. The frother molecules are arranged at the air water interface such that the hydrophilic or polar groups are oriented into the water phase, and the hydrophobic or nonpolar hydrocarbon chain in the air phase. In fact, the frother creates conditions for froth formation. The flotation froth is a three-phase system. The frother concentrates at the interface of water and air bubbles, forming an envelope around the bubbles, which prevents them from colliding or touching. Frothers also lower the surface tension of the water. The forces created around the air bubble in the presence of a frother prevent the bubbles from collapsing (Srdjan M. Bulatovic, 2007).

Modifiers, also known as regulators, are used extensively in flotation to modify the action of the collector, either by intensifying or by reducing its water repellent effect on the mineral surface. Regulators can be classed as activators, depressants and pH modifiers. Activators alter the chemical nature of mineral surface so that they become hydrophobic due to the action of the collector. Depressants used to increase the selectivity of flotation by rendering certain (unwanted) minerals hydrophilic, thus preventing their flotation (Wills, 2006).

The surface chemistry of most minerals is affected by pH change. In general, minerals under acidic conditions, a positive surface charge is developed and a negative charge develope under alkaline conditions, Since each mineral changes from negatively-charged to positively-charged at some particular pH, it is possible to manipulate the attraction of collectors to their

- 14 -

surfaces by pH adjustment. Chemicals that change the pH of the slurry are also used as modifiers. pH modifiers include lime, soda ash, sulfuric acid and they can act as activators and/or depressants by controlling the alkalinity and acidity of the slurry which are plays very important role in flotation process.

#### 2.3 Zeta potential

Adsorption of collectors and modifying reagents in the flotation process is controlled by the electrical double layer at the mineral-water interface. In systems where the collector is physically adsorbed, flotation with anionic or cationic collectors depends on the mineral surface being charged oppositely. Adjusting the pH of the system can enhance or prevent the flotation of a mineral. Thus, the point of zero charge (PZC) of the mineral is the most important property of a mineral in such systems.

The electrical double layer at interfaces plays a broad role in many mineral processing operations and is of primary importance in flotation. Some of the surface physico-chemical effects encountered in these systems include the following:

1. The flocculation and dispersion of mineral suspensions is controlled by electrical double layer interactions. Flocculation-dispersion phenomena are of crucial importance not only to flotation but also to such other unit operations as comminution, gravity separation, thickening, filtration and tailings management.

2. The sign and magnitude of the surface charge controls the adsorption of physically adsorbing flotation agents.

3. A high surface charge can inhibit the chemisorption of chemically adsorbing collectors.

4. Slime coatings are controlled by electrical double layer and hydrodynamic phenomena.

5. The double layer on air bubbles has a significant effect on the flotation of naturally floating mineral systems.

6. Flotation kinetics relates directly to the effect of double layers on the rate of film thinning during bubble-particle contact

7. Fine particle/air bubble/oil droplet interactions are dominated by surface charge effects.

In Figure 2.5 showing the electrical double layer that surrounds a particle in an aqueous medium and the position of the slipping plane. The zeta potential is the electrical potential at the slipping plane



Figure 2.5. Schematic illustration of zeta potential ( www.malvern.co.kr).

#### 2.4 Column flotation

The development of Column flotation is the most significant achievement in the mineral processing. The advantages of column flotation include: improvement in separation performance, better performance on fine materials, low capital and operational cost, less plant space demand. adaptability to automatic control, the ability to operate columns with deep froth beds, wash water application to wash the mineralized froth thus decreasing unwanted impurities in the concentrate.

The first countercurrent column flotation device was designed and tested by Town and Flynn in 1919. Cross-current pneumatic flotation machines were widely used in industry in 1920's and 1930's, but were later replaced by the impeller-type flotation devices in mineral processing plants. These substitutions were the result of the absence of effective and reliable air spargers for fine bubble generation and by the lack of automatic control systems on the early columns. Column flotation devices were re-introduced for mineral processing in the late-1960's in Canada by Boutin and Wheeler (1967) at which time wash water addition to the froth was used to eliminate entrainment of hydrophilic materials to the float product. By the late-1980's column flotation had became a proven industrial technology in the mineral industry. These separators are routinely used on their own or in conjunction with other types of devices within separation circuits (Harold E. Wyslouzil, CPT Inc).

The basic principal involved in a flotation column is the counter current flow of air bubbles and solid particles. The bubbles are generated by injecting air in the diffuser placed in the bottom of the column. Bubbles move upward in counter direction to downward flow of slurry. The attachment of hydrophobic mineral particles to the air bubbles take place in the lower enrichment section of the column between the feed point and air inlet known as flotation zone. The froth from flotation zone moves to cleaning zone (between interface and top of the column). The cleaning zone is a mobile packed bubble bed that is contacted counter currently with wash water from the top of the column to remove the entrained gangue particles from the froth and send back to the flotation zone. This rinsing action prevents the physical entrapment of gangue minerals, thus providing a higher degree of separation. Design and operation of flotation column are totally different in comparison with conventional flotation cell. Also, the basic concept of flotation column looks relatively simple, but the fundamental principles related to performance of flotation column are quite complex.

As mentioned above, column flotation application shows the best performance on relatively fine particle materials. Therefore it will be a useful method for tailings treatment for the removal of heavy metals due to the tailings fine particle characteristic. But in the present study entire flotation tests were carried out in the mechanical flotation machine and the results and observations of conducted flotation tests will be the important experimental data for the further column flotation tests on tailing.

In Figure 2.6 schematic of microbubble column flotation machine is shown. As it illustrates that column flotation cell can be divided into three main sections as Aeration zone: generated bubbles and air enters to the cell and floats upward, Collection zone: feed enters to the column and moves down counter currently with rising bubbles, hydrophobic particles attach to the bubbles and float while hydrophilic ones go down not attaching to the air bubbles. and Cleaning zone: wash water given to the column to reduce and wash hydrophilic particles those come out within the floated material caused by the entrainment and entrapment.



Figue 2.6 Schematic illustration of microbubble column flotation machine.

# Chapter 3. Experiment

### 3.1 Experiment purpose

Mine tailings are contaminated with fine particles, chemical reagents and heavy metals. The presence of toxic heavy metals in mine tailings are causing lots of serious environmental problems. This study is purposed to investigate an optimum removal rate of several heavy metals from gold mine tailing sample trough froth flotation technology. The Kumpoong mine tailing's study was supported by the Korea Mine Reclamation Corporation

## 3.2 Sample preparation

The tailing sample was collected from Kumpoong mine's tailing storage. Kumpoong mine is one of the few domestically running gold mines in Korea and it located in North Chungcheong province. The mine uses a surface impoundment storage dam for its discharged tailing as shown in Figure 3.1. Approximately 113 kg of the mine tailings were collected from the surface of the tailing using a shovel. The sample was put into plastic bags in the field. After transferring to the laboratory, the sample was dried in a owen at 110 °C for 24 hours. The sample was then stored in a sample box.



Figure 3.1 Kumpoong mine tailing storage.

### 3.3 Analysis

Several tests were performed to investigate the characteristics of the sample. Chemical composition of mine tailing was analyzed using an X-ray fluorescence analyzer (XRF) and XRD analysis as well. Wet sieve analysis method used to determine particle size distributions in tailing.

XRF analysis results on raw sample showed in Table 3.1 and it is identified that tailing has a large amount of SiO2 with 52.81%, and following with CaO 17.67%, Al2O3 9.64%, Fe2O3 5.41%.

Elements	Average		
Elemento	concentrations (%)		
SiO2	52.81		
CaO	17.67		
A12O3	9.64		
Fe2O3	5.41		
SO3	4.95		
Na2O	4.22		
MgO	2.91		
K2O	1.35		
MnO	0.312		
ZnO	0.202		
TiO2	0.186		
CuO	0.059		
SrO	0.054		
PbO	0.051		

Table 3.1 Chemical composition of Kumpoong tailing raw sample

Total concentrations of target heavy metals As, Cu, Pb, Cd, and Zn in the sample were determined. In Table 3.2 showed the assays of raw sample.

Table	3.2	Concentrations	of	target	heavv	metals	in	the	tailina	raw	sample
1 apro	0.2	001100110110110	0.	laigot	1100409	motalo			cannig	10.11	oumpro

Chemical composition (ppm)						
As	Cd	Cu	Pb	Zn		
78.98	14.64	227.41	244.18	594.65		

#### Particle size analysis

Particle size analysis used wet screen method. 100 gr of tailing samples were mixed throughly with water and poured on a different mesh screens those placed on the mechanical shaker. Sieve shaker (shown in Fig 3.2 b) is settled on the edge of the plastic bucket which is collecting under size particles. Above the top sieve a water added through spray nozzle to support the sieving process additionally to the sieving motion. The rinsing is carried out until the liquid which is discharged through the sieve is clear. The sample residues on the sieves and the last pass particles collected in the bucket were first filtered and dried in a owen in 105°C for 24 hours and were weighed and calculated. In Table 3.3 shown the results of wet screen analysis. Average particle size is the 200 mesh particles. According to mine tailings fine particle behaviour additional size reduction processes did not applied on Kumpoong tailing prior to batch flotation tests.

Table 3.3 Result of wet screen analysis on particle size distribution of raw sample

Sizo mosh	Woight %	Sizo (micron)	Cum under	Cum over
Size mesn	Weight 10		size	size
-500	10.72	-25	10.72	100
400*500	2.82	(500) 25	13.54	89.28
325*400	4.72	(400) 37	18.26	86.46
270*325	3.63	(325) 43	21.89	81.74
200*270	13.38	(270) 53	35.27	78.11
140*200	12.89	(200) 74	48.16	64.73
100*140	13.26	(140) 113	61.42	51.84
60*100	14.77	(100) 147	76.19	38.58
30*60	22.56	(60) 246	98.75	23.81
30	1.25	(30) 600	100	1.25
Total	100			

Heavy metal analysis were carried out on the different particle size materials. As shown in a Table 3.4 it is obvious that the Heavy metal

concentrations are relatively higher in the more finer size particles of the sample, which are -325 mesh to -500 mesh.

Size	Weight	As	Cd	Cu	Pb	Zn
mesh	%	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
-500	10.17	166.847	24.865	391.700	498.300	1047.598
400*500	2.82	114.455	21.256	88.750	177.928	798.433
325*400	4.72	109.980	21.973	98.063	205.200	840.222
270*325	3.63	80.619	17.676	84.149	170.951	686.140
200*270	13.38	78.171	18.086	107.964	171.213	707.821
140*200	12.89	52.072	12.157	145.291	169.518	485.690
100*140	13.26	44.989	10.254	216.860	201.670	430.842
60*100	14.77	14.913	8.992	286.433	229.903	406.379
30*60	22.56	106.610	13.051	295.724	272.610	521.581
30	1.25	28.255	6.374	342.955	231.382	250.866

Table 3.4 Heavy metal concentrations by particle size distribution



3.2 a



Figure 3.2 A. Illustration of typical size measurement. Sieves of different mesh size are kept on one on top to other. Particles are charged on the top sieve then shaking is started. Discharge of different sieve in terms of weight provides result (www.tcrenq.com),2010.

B. Electric sieve vibrator for wet screen analysis ( www.mltest.com)

### XRD analysis

To identify the mineralogical characteristics of tailing sample XRD analysis have been conducted with X'pert PRO MPD X-ray Diffractometer at Chosun University. Analysis showed in Figure 3.3 that the tailing was dominated by Quartz (SiO2), Calcite (CaCO3), and Albite (NaAISi3O8) components.



Figure 3.3 X-ray diffraction pattern of raw sample



Figur 3.4 XRD patterns by size range (raw sample)

### SEM and element mapping

The image analysis method, SEM (scanning electron microscope) and EDS (energy dispersive spectrometry) was applied on Kumpoong tailing raw sample for distribution of target elements and mineralogical characteristics of tailing material. SEM and X-Ray dot mapping images shown in Figure 3.5. Heavy metal distributions and dominant mineralogies are presented.





Figure 3.5 SEM and X-Ray dot mapping images of raw sample

The results of the physical and chemical characterization analysis of Kumpoong mine tailing indicate that the tailings are sand-slit material with particle diameter between 0.025 and 0.25 mm, with varying proportions of heavy metals and other impurities. Conducted analysis showed that the distribution of heavy metals in mine tailing are higher in the relatively finer particles of the sample, which are -325 mesh to -500 mesh, and an average particle size is 270 mesh particles and the raw feed assays were identified as As 78.98 ppm, Cd 14.64 ppm, Cu 227.41 ppm, Pb 244.18 ppm, and Zn 594.85 ppm. These assays from raw sample used for calculations of heavy metal removal and recovery from mine tailing, together with the assays and values of concentrate and tailings from applied flotation tests.

#### 3.4 Batch flotation

Batch flotation experiments were conducted with a Denver Sub-A type laboratory-scale mechanical flotation machine as shown in Figure 3.6, on a tailing sample. Flotation reagents, such as KAX (potassium amyl xanthate) and Sodium oleate, Oleic acid, SDS (Sodium Dodecyl sulfate) as collectors, DF250, AF65, MIBC, Pine oil as frothers, SS (Sodium silicate) and SMP (Sodium meta phosphate),Lime and in combined forms such as SS + SMP, SS + Lime, Lime + SMP as depressants, are used in the experiment. NaOH and HCl were used as pH modifiers. Every reagent's effects were tested in a range of different dosages. Different pH, Pulp density and Impeller speed were also examined.

Batch flotation procedures are as follows:

- Raw sample and water weighted by the given pulp density and poured in the 2L plastic cell and placed on the flotation base.
- Prepared slurry then were mixing and conditioning for 5 minutes
  (During conditioning period pH is measured and adjusted)
- After 5 minutes flotation reagents added to the pulp with order as depressants with 5 min, collectors 3 min, and frother 2 minute of conditioning time.
- When conditioning time is over Denver flotation was started giving air and produced froth layer was skimmed off with hand skimmer. Flotation period was 10-15 minutes.
- Overflow froth materials collected in a glass tray.
- Concentrate and Tailings (Figure 3.7) are filtered and dried.

Flotation experiment products Concentrate and Tailings were sent for chemical composition analysis. Element analysis carried out by ICP-OES ( inductively coupled plasma optical emission spectrometer) at Dong-A University. With the element analysis results, heavy metals removal and recovery rate were calculated.



Figure 3.6 Laboratory scale Denver Sub-A type flotation machine.



Concentrate

Tailing



# 3.4.1 Collectors

In the flotation tests collectors such as KAX (potassium amyl xanthate) and Sodium oleate, Oleic acid, SDS (Sodium Dodecyl sulfate) were used in this study to investigate the most effective collector. Collector dosages and effects on heavy metal removal and recovery were being tested. Applied collector reagents and dosages showed in table 3.5.

Collectore	Molecular	Polo in flotation	Dosages	
Conectors	formula		tested	
KAX		Dondona minorala	50,100,000	
(potassium amyl	C6H11KOS2	Renders minerals	50,100,200, 300g/ton	
xanthate)		surface into		
Sodium oleate	C18H33NaO2	hydrophobic form	100mL/ton	
Oleic acid	C18H34O2		100mL/ton	
SDS (Sodium	$N_{2}C19H95SO4$		100mI /ton	
Dodecyl sulfate)	Nac121120504		100mL/tom	

Table 3.5 Collectors used in batch flotation tests.

Flotation process::

Dp 10%	Raw sample 200g + water 1800 mL,
Slurry mixing	5 minutes
Collectors	KAX (potassium amyl xanthate) and Sodium oleate,
	Oleic acid, SDS (Sodium Dodecyl sulfate), Cond time
	3 minutes
Frother	DF250 200ml/ton, Cond time : 2 minutes
Depressant	None
Flotation time	10 minute
Impeller RPM	1200

# 3.4.2 Frothers

In order to provide a froth stability in flotation tests thus supporting the effective separation process and to select an appropriate reagent, frother reagents as DF250, AF65, MIBC and Pine oil were applied on conducted experiments.

Frothers	Molecular formula	Role in flotation	Dosages tested
DF250			100 200 mI /ton
(Dow Froth)	Сп3(ГО)40П		100, 200 IIIL/1011
ADGE	Ligh male suley weight	Improve bubble	100, 200, 300,
AF03	nign molecular weight	stability	400, 500 mL/ton
MIBC	СНЗСНСНЗСН(ОН)СНЗ		200 mL/ton
Pine oil	С10Н17ОН		200, 400 mL/ton

Table 3.6 Frothers used in batch flotation tests.

Flotation process::

Dp 10%	Raw sample 200g + water 1800 ml,
Slurry mixing	5 minutes
Collectors	KAX (potassium amyl xanthate) Cond time
	3 minutes
Frother	DF250, AF65, MIBC and Pine oil
	Cond time: 2 minutes
Depressant	None
Flotation time	10 minute
Impeller RPM	1200

### 3.4.3 Depressants

For depressing unwanted materials and to increase selectivity in flotation, reagents S.S (Sodium silicate), SMP (Sodium meta phosphate), and Lime used individual and combined forms as SS + SMP, SS + Lime, Lime + SMP. Sodium silicate were diluted in the hot water for better solubility. Depressants listed in table 3.7 were weighted and added to the pulp, and the conditioning time was 5 minutes.

Depressants	Role in flotation	Dosages tested
S.S (Sodium silicate)		100g/ton
SMP (Sodium meta		100 g/ton
phosphate)	Depressing gangue	1009/1011
Lime	minerals	50, 100, 200, 300, 400, 500 g/ton
SS + SMP		100g/ton
SS + Lime		100g/ton
Lime + SMP		100g/ton

Table 3.7 Depressants used in batch flotation tests.

Flotation process::

Raw sar	nple 200gr+water 1800 ml
5 minute	S
S.S (Soc	dium silicate), SMP (Sodium meta phosphate),
and Lim	e ,SS + SMP, SS + Lime, Lime + SMP.
Conditic	oning time 5 minutes
KAX (po	tassium amyl xanthate) Cond time 3 minutes
AF65	Cond time : 2 minutes
10 minut	e
1200	
	Raw san 5 minute S.S (Soc and Lim Conditio KAX (po AF65 10 minut 1200

# 3.4.4 pH modifiers

For establishing a supportive slurry condition for reagents activity thus providing an efficiency in the flotation process, a pH regulators as NaOH (Sodium hydroxide) and HCI (Hydrochloric acid) applied in flotation. Regulators are added to the slurry until given pH degree is adjusted, while measuring pH degree in slurry with pH meter.

	Role in	Decerce
pH regulators	flotation	Dosages
NaOH ( Sodium hydroxide)	pH increase	until given pH is adjusted
HCl (Hydrochloric acid)	pH decrease	until given pH is adjusted



Flotation process:

Dp 10%	Raw sample 200gr + water 1800 ml
pH adjusting	During slurry mixing period pH of slurry were
	measured by pH meter and have been adjusted to
	the given pH degree by the addition of pH
	regulating agents as NaOH ( Sodium hydroxide)
	and HCI (Hydrochloric acid)

## 3.4.5 Pulp density and RPM

The effects of solids percentage in slurry (Dp) and the Impeller speed (RPM) in the flotation were also examined. Mineral and water slurry were prepared by the given Dp and applied in the flotations.

Batch flotation conditioning period were completed with a lower impeller speed (900RPM) and when reagents conditioning time is over, flotation period starts by giving an air to the conditioned pulp. In this flotation period the impeller speed RPM were adjusted by given rate and the effects on froth formation, froth stability and depth etc., were examined.

Factors	Test aimed at	(%) and RPM
Pulp density (Dp)	effects on flotation	10, 20, 30%
Impeller speed	effects on flotation	900, 1200, 1500, 1800, 2100 RPM

Table 3.9 Dp and RPM

#### 3.4.6 Calculations

Heavy metals removal and recovery rates calculated on each flotation tests. Basic mass balance method calculations used in this study to determine the recovery and the removal rate of heavy metals. Equations used in this study as follows:

$$\frac{Cc}{Ff} \times 100 = R \tag{2}$$

$$\frac{Ff - Tt}{Ff} \times 100 = HmR \tag{3}$$

$$\frac{Cmw \times 100}{Fmw} = Cmd \tag{4}$$

Where: C - Concentrate weight

c - Concentrate assay

 ${\cal F}$  - Feed weight

$$f$$
 - Feed assay

- T -Tailing weight
- $t\,$  -Tailings assay
- R Recovery (%)
- HmR Heavy metal removal (%)

Cmw - Metal weight in Concentrate

Fmw - Metal weight in Feed.

Cmd - Metal distribution in Concentrate (%)

# Chapter 4. Results and Discussions

## 4.1 Effect of collectors

In the flotation tests collectors such as KAX (potassium amyl xanthate) and Sodium oleate. Oleic acid, SDS (Sodium Dodecyl sulfate) were used in this study to investigate the most effective collector. Collector dosages and effects on heavy metal removal and recovery were being tested. Conducted tests and assays showed that the collector KAX is the highly efficient reagent for the removal of heavy metals with the removal rate of As 75.79%, Cd 68.16%, Cu 37.1%, Pb 28.67%, and Zn 66.37%. Therefore collector KAX were selected for the flotation tests. Based on dosage tests results KAX collector dosage of 100gr/ton is selected as an optimum dosage for conducted flotations. Collector test flotations were carried out in the presence of DF 250 frother with the dosage of 200mL/ton. The removal performance of collector K.A.X can be seen from Table 4.1 by comparing the feed and flotation tailing's assays.

Table 4.1 Compared assays and removal rate on target heavy metal in the presence of KAX (potassium amyl xanthate) (Dp: 10%, Collector: (100g/ton), Frother: DF 250 (200mL/ton))

	Feed assay	Concentrate	Tailing	Removal
Heavy metals	(ppm)	Wt% 3.17	Wt% 96.83	(%)
		(ppm)	(ppm)	
Arsenic. As	78.98	1678.618	19.121	75.79
Cadmium. Cd	14.64	376.818	4.662	68.16
Copper. Cu	227.41	3207.028	143.036	37.10
Lead. Pb	244.18	3198.893	174.165	26.67
Zinc. Zn	594.65	17052.821	199.953	66.37



Figure 4.1 Effects of Collectors on heavy metals removal (Dp : 10%, Collector : 100 g/ton, Frother : DF250 (200 mL/ton))

As shown in the Figure 4.1 Collector K.A.X's activity on heavy metal removal is notably higher among other applied collectors as Sodium oleate, Oleic acid, SDS (Sodium Dodecyl sulfate) which are showed relatively weak effects on the removal of heavy metals. Therefore K.A.X is proved to be an efficient collector reagent for the flotation applications in the treatment of heavy metal contaminated mine tailings.

#### 4.2 Effect of frothers

In order to provide a froth stability in flotation tests thus supporting the effective separation process and to select an appropriate reagent, frother reagents as DF250, AF65, MIBC and Pine oil were applied on conducted experiments. DF 250 and AF65 both showed good effects in the flotation. It can be seen from Figure 4.2 that, in the presence of frother DF 250 the Cu removal was higher but As was lower. When AF 65 is applied on the flotation, the result was opposite; the removal of As was higher and Cu removal was lower. In this study, we focused on the removal of As due to its toxicity. Therefore AF 65 was selected as the frother agent in the flotation tests.



Figure 4.2 Effect of various frothers on batch flotation. (Dp: 10 %, Collector : S.D.S (100 g/ton), Frother : 200 mL/ton)



Figure 4.3 Effect of frother dosage on batch flotation. (Dp: 10 %, Collector: K.A.X (100 g/ton), Frother: AF 65)

The dosages of AF 65 has been examined in the flotations to investigate a proper dosage. Collector KAX was used in the flotation and its dosage was 100gr/ton. As shown in Figure 4.3 Heavy metal removal is increasing together with AF 65 frother's increased dosages. It shows that AF 65's increased frother dosage have a positive influence in a removal process. Therefore AF 65 frother dosage 500mL/ton is selected as a proper dosage for the further flotations. The result of presence of frother AF 65 on the removal of heavy metals can be seen from Table 4.2 by comparing the feed and flotation assays.

		Feed assay	Concentrate	Tailing	Removal
Heavy m	etals	(ppm)	Wt% 13.75	Wt% 86.25	(%)
			(ppm)	(ppm)	
Arsenic.	As	78.98	390.963	16.269	79.37
Cadmium.	Cd	14.64	65.304	3.810	73.97
Copper.	Cu	227.41	710.449	126.632	44.31
Lead.	Pb	244.18	696.658	145.151	40.55
Zinc.	Zn	594.65	2880.193	180.220	69.70

#### Table 4.2 Results of batch flotation.

(Dp: 10%, Collector : KAX (100g/ton), Frother : AF65 (500 mL/ton))

#### 4.3 Effect of depressants

For depressing unwanted materials and to increase selectivity in flotation, reagents S.S (Sodium silicate), SMP (Sodium meta phosphate), and Lime used individual and combined forms as SS + SMP, SS + Lime, Lime + SMP. Depressants applied in the Batch flotation tests used the same 100gr/ton dosage. Test results showed that the Depressant Lime and its combined form with S.M.P (Lime+SMP) are have a best effects on the heavy metal removal and the Lime is selected as main depressant agent by comparing the results of these two agent's applications on the flotation tests. Results of depressant Lime showed in the Table 4.3. The removal of heavy metals were relatively high.

#### Table 4.3 Results of batch flotation

(Dp: 10%, Collector : KAX (100g/ton), Frother : AF65 (400 mL/ton), Depressant Lime : (100gr/ton))

	Feed assay	Concentrate	Tailing	Removal
Heavy metals	(ppm)	Wt% 9.36	Wt% 90.44	(%)
		(ppm)	(ppm)	
Arsenic. As	78.98	750.629	12.05	84.8
Cadmium. Cd	14.64	103.427	3.494	76.13
Copper. Cu	227.41	1082.444	120.422	47.05
Lead. Pb	244.18	1091.618	133.049	45.51
Zinc. Zn	594.65	4627.332	191.457	67.80

Results of the presence of various depressant reagents in the flotation process are presented in the Figure 4.4. In a presence of combined depressant Lime+SMP heavy metals removal is quite good but the recovery rate is very low. Application of Lime in the flotation tests shoved higher results on the both removal and recovery of heavy metals.



Figure 4.4 Effects of various depressants

#### 4.4 Effect of pH change

For establishing a supportive slurry condition for reagents activity thus providing an efficiency in flotation, pH regulators as NaOH (Sodium hydroxide) and HCI (Hydrochloric acid) applied in flotation tests. Regulators added in the slurry until the given pH is adjusted, while measuring pH degree in slurry with pH meter. pH ranges 4–12 were given and adjusted in the flotations. Kumpoong tailing natural pH was 8. From the heavy metal removal curve as shown in the Figure 4.5(a) it is clear that overall heavy metals removal is observed higher in the flotation at pH 6, and over pH 10 the curves starting to fall down except As. Therefore pH ranges between 6–8 believed to be a moderate conditions for heavy metal removal flotation.



Figure 4.5 (a) Effect of pH on Heavy metal removal (Dp: 10 %, K.A.X (100 g/ton), AF65 (400 mL/ton), Lime (100 g/ton)



Figure 4.5 (b) Effect of pH on Heavy metal recovery (Dp: 10 %, K.A.X (100 g/ton), AF65 (400 mL/ton), Lime (100 g/ton)

#### 4.5 Pulp density effects

The effect of solids percentage in slurry (Dp) were also examined. Pulp densities as 5% (Raw feed 100gr + water 1900 ml) 10% (Rf 200gr+W1800 ml), 20% (Rf 400gr+W1600ml), and 30% (Rf 600gr+W1400 ml) were tested. Flotation reagents were KAX 100gr/ton and AF 65 400mL/ton. As shown in Figure 4.6 Heavy metal removal is increased until Dp 20%.



Figure 4.6 Effects of different pulp densities on Heavy metal removal

		Feed assay	Concentrate	Tailing	Removal
Heavy m	etals	(ppm)	Wt% 9.53	Wt% 90.47	(%)
			(ppm)	(ppm)	
Arsenic.	As	78.98	672.95	9.97	87.37
Cadmium.	Cd	14.64	99.20	3.59	75.48
Copper.	Cu	227.41	1351.86	123.51	45.68
Lead.	Pb	244.18	1117.58	149.20	38.90
Zinc.	Zn	594.65	5011.77	164.90	72.27

Table 4.4 Batch flotation results in the Dp 20%

As shown in Table 4.4 batch flotation in the 20% pulp density gives quite higher heavy metal removal rates.

#### 4.6 Effect of Impeller speed

Flotation tests carried out to determine the different RPM effects on the flotation reagents activity thus the influences to the batch flotation's results. Flotation reagents were Collector: KAX (100gr/ton), Frother: AF 65 (400mL/ton) and pulp density (Dp) 20%. Impeller speed were adjusted to the given RPM ranges 900, 1200, 1500, 1800 and 2100. In the RPM 900 the froth formation was weak and in the RPM over 1800 the impeller speed was too fast thus causing a unwanted materials overflow. In the 1200–1500 RPM the froth formation was stable thus it is providing an efficient flotation process. As shown in Figure 4.7 (a,b) in the RPM rates between 1200–1500 the heavy metals removal is higher and stable, highest recoveries were recorded at RPM 1500.



Figure 4.7 (a) Effect of RPM on Heavy metal removal



Figure 4.7 (b) Effect of RPM on Heavy metal recovery

# Chapter 5. Conclusions

Mineral processing is a key sector in the Minerals industry. Through mineral processing study on the existing ore, it is investigated that whether is it economically efficient or not to start extraction. In the processing stage extracted ores treated with various processing methods and became valuable minerals concentration. So mineral processing has an enormous role. But it also has a disadvantages such as high energy consumption and large amount of tailings discharge. Tailings contain unrecoverable, unwanted waste materials, due to the grinding process and the chemical additives in the separation phase. These tailings are very fine in size and rich with various chemicals and heavy metals. Heavy metals existing in a mine tailings are considered the most toxic substances and in case of their loss and dispersion to surrounding area, soil, surface and ground water it is extremely harmful to environment and human health. Precautions need to be developed for this possible threat. One of the solutions is a decontamination process as removing toxic heavy metals from mine tailings thus decreasing its hazardous level.

In this work the removal of heavy metals from Kumpoong gold mine tailing with the use of primary batch flotation technology, has been studied. 113 kg of tailing sample were collected for laboratory tests. Mineralogical and element analysis (XRF, XRD, SEM) on raw sample showed that SiO2 52.81%, CaO 17.67%, Al2O3 9.64%, Fe2O3 5.41% are the dominant components and the target heavy metals and their quantity in the tailings were identified : As 78.98ppm, Cd 14.64ppm, Cu 227.41ppm, Pb 244.18ppm, Zn 594.65ppm. Tailings are generally consists of fine particles. Kumpoong tailing particle size analysis showed that the particles in 270 mesh size consists 78.11% of total weight ratio and element analysis on each particle size material showed that the heavy metal distribution is higher in the

particles under -325 mesh size.

Batch flotation experiments were conducted with a Denver Sub-A type laboratory-scale mechanically agitated flotation machine. Flotation experiments were aimed to investigate the optimum flotation reagents and their dosages and to study flotation factors as pH, pulp density and RPM in batch flotation thus finding the suitable flotation conditions for the removal of heavy metals from tailing.

In the flotation tests collectors such as KAX (potassium amyl xanthate) and Sodium oleate, Oleic acid, SDS (Sodium Dodecyl sulfate) were used. Conducted tests and analysis assays showed that the collector KAX is the highly efficient reagent among all applied collectors for the removal of heavy metals with the removal rate of As 75.79%, Cd 68.16%, Cu 37.1%, Pb 28.67%, and Zn 66.37%. Therefore KAX were selected as a main collector for the tailings heavy metal removal flotation. Based on dosage tests results KAX collector dosage of 100gr/ton is selected as an optimum dosage for conducted flotations.

In order to provide a froth stability in flotation tests thus supporting the effective separation process and to select an appropriate reagent, frother reagents as DF250, AF65, MIBC and Pine oil were applied on conducted experiments. DF 250 and AF65 both showed good effects in the flotation. In the presence of frother DF 250 the Cu removal was higher but As was lower and when AF65 applied on the flotation it was opposite, the removal of As is higher and Cu removal was lower. In this study we focused more on the removal of As due to its toxicity. Therefore AF65 has selected as frother agent in the flotation tests. Frother dosage tests showed that heavy metal removal is increasing together with AF65 frother's increased dosages. Therefore dosage of 500mL/ton is considered as proper dosage for AF65 frother. But further studies required.

Depressing reagents as S.S (Sodium silicate), SMP (Sodium meta phosphate), and Lime used individually and as well as combined forms as SS + SMP, SS + Lime, Lime + SMP. were applied in the batch flotation tests and were given the same 100gr/ton dosage. Test results showed that the Depressant Lime and its combined form with S.M.P (Lime+SMP) are have a best effects on the heavy metal removal and the Lime is selected as main depressant agent by comparing the results of these two agent's applications on the flotation tests.

For regulating pH condition of the flotation slurry, pH regulators as NaOH ( Sodium hydroxide) and HCI (Hydrochloric acid) applied on the flotation tests. Regulators are added to the slurry until given pH is adjusted, while measuring pH degree in slurry with pH meter. pH ranges 4–12 were given and adjusted in the flotations. Kumpoong tailing natural pH was 8. Overall heavy metals removal is observed higher in the flotation at the pH ranges between 6–8 and they considered as moderate pH degrees to adjust in the flotations.

The effect of solids percentage in a slurry (Dp) were also examined. Pulp densities as 5% ,10% , 20% , and 30% were tested. Flotation reagents were KAX 100g/ton and AF 65 400mL/ton. Results showed that heavy metal removal is increased in the Dp 20%.

Flotation tests carried out to determine the different RPM effects on the flotation reagents activity thus the influences to the batch flotation's results. Impeller speed were adjusted to the given RPM ranges as 900, 1200, 1500, 1800 and 2100. In the RPM 900 the froth formation was weak and in the RPM over 1800 the impeller speed was too fast thus causing a unwanted materials overflow. In the 1200–1500 RPM the froth formation was stable thus it is providing an efficient flotation process.

Overall study results showed that the froth flotation technology is efficient

in reducing heavy metal impurities those existing in gold mine tailings and for the removal of heavy metals as As, Cd, Zn with the highest removal rates of As: 87.37%, Cd: 75.48%, Zn: 72.27%. But the removal of Cu: 45.68%, Pb: 38.90 % are showing a relatively lower results and further studies on removal of this heavy metals must be developed. Further test works need to focus on the pre-treatment of tailing material such as size reduction in order to increase liberation of heavy metals prior to column flotation application for upgrading the heavy metals removal degree from a more finer particle tailing and the optimum reagents and flotation conditions for the column flotation need to be investigated.

#### References

1. P. Cauwenberg and F. Verdonckt, A. Maes, 1998, "Flotation as a remediation technique for heavily polluted dredged material. I. A feasibility study", The Science of the Total Environment, No. 209, pp. 113-119.

2. Choe Woo Jin, 2004, "Mine waste recycling technology trends and prospects" Resources and Environmental Geology, Vol. 37, No. 1, pp 113-119.

3. Environmental remediation and renewable technologies-Mine waste restore technical report. 1999. Korea Institute of Science and Technology

4. D.W. Fuerstenau, T, Pradip, 2005. "Zeta potentials in the flotation of oxide and silicate minerals" Advances in Colloid and Interface Science. No 114-115, pp 9-26.

5. Gordon M. Ritcey, 2005. "Tailings management in gold plants", Hydrometallurgy No 78. pp. 3-20

6. Harold E. Wyslouzil, President, Canadian Process Technologies Inc. "Mineral producers improve plant performance using column flotation technology" (cpt.eriez.com)

Henrik K. Hansen, Alexandra B. Ribeiro, Eduardo P. Mateus, Lisbeth M. Ottosen. "Diagnostic analysis of electrodialysis in mine tailing materials", 2007. Electrochimica Acta No.52, pp. 3406-3411

8. Heavy metal toxicity, Introduction. (http://www.lef.org)

9. B. A. Klinck, M. P. Hawkins, Y Moore, C Ngorima, U Kelm, B Palumbo, Jin Soo Lee, "The Environmental impact of metalliferous mining: Korea, Chile and Zimbabwe case studies",2002.British Geological Survey.

10. Lide.D 1992. CRC Handbook of Chemistry and Physics. 73rd Edition. Boca Raton, FL: CRC Press

11. Mathias Vanthuyne, Andre' Maes. 2002, "The removal of heavy metals from contaminated soil by a combination of sulfidisation and flotation", The Science of the Total Environment, No 290, pp. 69-80

12. Mineral processing introduction, Met-Solve,2010. (http://www.met-solvelabs.com)

13. Myung Chae Jung, 2001." Heavy metal contamination of soils and waters in and around the Imcheon Au-Ag mine, Korea" Applied Geochemistry No.16, pp. 1369-137

14. Myung Chae Jung, Joo Sung Ahn, Hyo-Taek Chon, 2001. "Environmental Contamination and Sequential Extraction of Trace Elements from Mine Wastes Around Various Metalliferous Mines in Korea", Geosystem Eng., 4(2), 50-60,

15. Srdjan M. Bulatovic, "Handbook of flotation reagents", Volume 1. 2007

16. M. Vanthuyne, A. Maes, P. Cauwenberg, 2003. "The use of flotation techniques in the remediation of heavy metal contaminated sediments and soils: an overview of controlling factors", Minerals Engineering No 16. pp. 1131-1141

17. Wills. B. A, Napier-Munn. T. J, "Wills Mineral processing technology".

Seventh edition. 2006

Figure references

- Breaking of larger materials to smaller pieces.
  Darker regions represent the valuable minerals. (Met-Solve,2010)
- 2. Primary and Secondary crushers( Met-Solve, 2010)
- 3. Vibratory screen with multiple removable and replaceable decks.( www.traderscity.com)
- Attachment of valuable minerals to air bubble (Courtesy of W. R. Speden)
- 5. Schematic illustration of zeta potential ( www.malvern.co.kr).
- 6. Illustration of typical size measurement (www.tcrenq.com), 2010.
- 7. Electric sieve vibrator for wet screen analysis ( www.mltest.com)

## - Acknowledgements -

First of all I would like to thank Professor. Han, Oh Hyung for accepting me in his mineral processing team of Energy and Resource's engineering Department of Chosun University, and giving me a great opportunity to do Master of Science (MS) study. I am deeply appreciated for his kind assistance and support provided over the past two years.

My sincere gratitude should also go to Doctor. Jeon, Hu Seok for his direct support and help for starting my MS study in Korea and for his care.

Many thanks and warm respects to all my lab mates for their great help and friendship. I am pleased to thank Kang, Hyun Ho, Shin, Seung Han, Hong, Jong Won, Park, Sin Woong, Kim, Jun Hee, Kim, Min Gyu and to everyone who helped and supported me during my study.

I want to express my deep appreciation for the scholarship and financial supports granted from the Chosun University and research projects. Without these generous supports it would have been impossible for me to complete this course.

Finally, I would like to thank my family for their love and supports, especially my uncle Dr. Mangalam Sovd for all his grateful efforts and contributions for my life.