DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE INVESTIGATION EFFECT OF SULFIDE COLLECTORS ON FLOTATION OF AŞIKÖY COPPER ORE

by
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September, 2016
İZMİR

THE INVESTIGATION EFFECT OF SULFIDE COLLECTORS ON FLOTATION OF AŞIKÖY COPPER ORE

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in Mining Engineering, Mineral Processing Program

by
Orkun YAVUZKAN

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İZMİR

M.Sc THESIS EXAMINATION RESULT FORM

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THE INVESTIGATION EFFECT OF SULFIDE COLLECTORS ON FLOTATION OF AŞIKÖY COPPER ORE

ABSTRACT

The main objective of this study is to investigate the effectiveness of different types of froth flotation collectors on copper recovery of Asikoy copper ore from Kure Copper Flotation Plant to see if difference in collector type would effect the metallurgical improvement in terms of copper recovey or grade.. In order to determine the functions and effect of individual collector type including the incumber collector, a full factorial Desing of Experiment is prepared to determine the individual factor effects along with the factor interactions.

As the mining market experiencing a major decrease on commodity prices, any improvement in metallurgical performance of plant is welcome. In order to achieve meaningful results, Design of Experiment (DOE) implemented to the work in order to evaluate effect of different variables and those variables analyzed by using Six Sigma techniques.

Chapter 1 presents the background information on history of copper, its physcal and chemical characteristic, important features of copper, its utulization, types and characteristic of copper ore deposits, brief information about copper market and various benecification processes of copper ore in mineral processing industry.

Chapter 2 provides an overview of local geology, ore deposits and their relationships.

Chapter 3 presents the details of experimental study including sampling and size reduction related to this work, sampling precedure, size reduction steps and the representative subsample preparation methods. Characterization of the sample is also presented in this chapter along with froth flotation studies.

Chapter 4 and Chapter 5 provide result and discussion section along with conclusions and findings from the test work conducted on Asikoy Copper ore in details.

Keywords: Chalcopyrite flotation, froth flotation, copper, collector.

AŞİKOY BAKIR CEVHERİNİN ÜZERİNDE SÜLFÜRLÜ KOLLEKTORLERİN ETKİSİNİN ARAŞTIRILMASI

ÖZ

Bu çalışamanın amacı farklı türdeki köpük flotasyonu kollektörlerinin Küre Bakır Flotasyonu tesisinden alınınan bakır cevheri numunesinin üzerinde etkisinin araştırılması ve bu farkli kollektör türlerinin metalurjik olarak verim ve tenöre . etkisinin incelenmesidir. Kollektör türünün etkisini belirleyebilmek içinde tesiste hali hazırda kullanılan kollektöründe yer aldığı geniş çaplı bir deney planı hazırlanıp bu faktörler arasındakı ilişkilerde incelenmiştir.

Birinci bölümde, bakırın tarihçesi, bakırın fiziksel ve kimyasal nitelikleri, önemli özellikleri, bakırın kullanımı, türleri ve bakır yatakları ve özellikleri, bakır piyasası ve cevher zenginleştirme endüstrisinde kullanılan diğer zenginleştirme metodlarıyla ile ilgili bilgiler sunulmuştur.

İkinci bölümde bölgesel jeoloji, cevher türleri ve bunların ilişkileri hakkında bilgiler verilmistir.

Üçüncü bölümde, deneysel çalışmalar ve bu çalışmalar dahilinde numune hazırlama ve boyut küçültme ile ilgili detaylar paylaşılmıştır. Numune hazırlama prosedürü, boyut küçültme adımları ve temsili numunenin hazırlanış yöntemleri paylaşılmıştır. Üzerinde çalışılan numunenin karakterizasyonu köpük flotatasyonu çalısmalari ile birlikte sunulmuştur.

Dördüncü ve beşinci bölümde çalısmalar neticesinde elde edilen sonuçlar tartışılmıştır.

Anahtar Kelimeler: Kalkopirit flotasyonu, flotasyon, köpük flotasyonu, bakır, kollektor

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CHAPTER ONE
INTRODUCTION

1.1 About Copper

Copper is one of the most widely used metal by mankind for thousands of years after iron and aluminum. Copper, as a metal, has a characteristic of reddish brown color, with metallic luster on fresh surfaces. However, as a common feature of all base metals, it quickly oxidizes in air. Copper is relatively soft (2.5-3.0 on Mohr's scale of hardness) which makes the copper more attractive due to its natural malleability and ductility. Copper is widely distributed in nature, and, in the earth crust, it takes the following forms: sulfide ores (as chalcopyrite, bornite, chalcocite, and covellite), oxide ores (as cuprite and tenorite), saline minerals (as malachite, azurite, chrysocolla) and native copper (Davenport et al., 2002).

There are only a small number of copper minerals found to be commercially attractive in mineral processing business or industries, however, there is more than 150 copper minerals have been identified as copper mineral (Bulatovic, 2007). The list of commercially common copper minerals can be found as below in Table 1.1

Table 1.1 Common copper minerals found in economic deposits (Bektas, 1970)

Mineral Name	Chemical Formula	Max Cu Content (wt%)
Chalcopyrite	$CuFe_2$	34.6
Chalcocite	Cu_2S	79.8
Bornite	Cu_5FeS_4	63.3
Covellite	CuS	66.5
Cuprite	Cu_2O	88.8
Malachite	$CuCO_3$-$Cu(OH)_2$	57.5
Native	Cu	100
Tennantite	$Cu_8As_2S_7$	57.7
Tetrahedrite	$4Cu_2S \cdot Sb_2S_3$	52.1
Azurite	$2CuCO_3 \cdot Cu(OH)_2$	55
Enargite	$Cu_3A_5S_4$	48.4
Chrysocolla	$Cu2Alx(H_2xSi_2O_5)$	36.2

1.1.1 History of Copper

Based on archaeological findings it is demonstrated that copper is one of the first and most common metal used by humankind and has been used since the beginning of the time. The various items such as coins and ornaments found in western Asia where people used these items at least 10,000 years ago. Humankind developed various exctaction method during the prehistoric Chalcolithic Period (i.e derived from the Greek word “chalkos”, means copper). Mankind developed different extraction processes for copper in order to produce their daily needs such as coins, ornaments and implements. Based on available literature, copper extraction from earth’s crust started as early as the 4th to 3rd millennium BC. (International Copper Study Group, 2014).

The finding of bronze, by alloying copper with tin, led to the Bronze Age, 2,500 BC. The historical records show that Egyptians used the copper to heal infections and to disinfect water sources. Copper supplied mainly from Cyprus during this period of time for the needs of Greek. "Copper", as a word, is taken from the Latin word of Cyprium. As a valued copper alloy, brass is well known by the Ancient Greeks. Not only ancient Greeks but also Maya’s , Inca civilization in Peru and Aztecs extracted copper along with silver and gold as by product (International Copper Study Group, 2014).

Electricity and magnetism related findings and inventions during late 18th and early 19th centuries has shown the ability of copper to improve the performance of the materials, the products produced by using copper assist launcing the revolution of industry. Today, its use and contributions to our life still continue by delivering needs of humankind beyond our imagination. Even though, mankind is quite familiar with copper and its usage for centuries, there have been always new technologies and applications, unique ideas and developments for copper (The World Copper Factbook, 2014).

1.1.2 Physical and Chemical Characteristics of Copper

Copper is an amazing element that has been used by society since the ancient days of the Romans as explained above. Due to its unique physical and chemical features like malleability, ductility, heat and electricity conductivity, ability to withstand corrosion, and its esthetic characteristics, copper has established crucial importance in virtually all areas of developed and newly developing economies most notably in the areas of construction, transport, and all kinds of electrical and electronic applications. Copper makes a huge contributions to mankind to sustain and improve our quality of life for hundreds of years (Breedis & Caron, 1993).

The copper is the material of choice due to its chemical, physical features. Copper has been used in broad range applications. It can be alloyed with other metals based on desired application. For instance, it can be alloyed with zinc in order to produce brass, tin or aluminum to produce bronzes, or also nickel. It can form as a different material for use in highly specialized applications (The World Copper Factbook, 2014).

Copper is a heavy metal with atomic number 29 and atomic mass 63.54. It belongs in the 11 group of the periodic table along with silver and gold. The electron configuration of the copper in ground state is $[Ar]3d^{10}4s^{1}$. Copper occurs in three oxidation states in the nature; as a solid metal with a charge of zero (Cu^{0}), as the cuprous ion with a plus one charge Cu^{I} ($[Ar]3d^{10}$), and as the cupric ion with a plus two charge Cu^{II} ($[Ar]3d^{9}$). Cu^{II} is defined as a transition Lewis acid, it means that it is highly reactive with both hard and soft Lewis bases, while Cu^{I} is a soft Lewis acid which reacts with soft Lewis bases (Sparks, 2003). Cu^{II} can exhibit an ionic radius of 0.057 nm or 0.073 enabling it to form coordination numbers of 4, a tetrahedral configuration and 6, an octahedral configuration, respectively (Sposito, 2008).

In the environment, copper is partitioned into the aqueous phase, including soluble species and free ions, the solid phase, including sorption to soil constituents and precipitates, and the biological phase, including sorption and incorporation in

organic matter (Flemming and Trevors, 1989). Cu^{II} is the most common copper oxidation state in the environment and is classically thought to exist as the free cupric cation in solution, however, recent observation have concluded Cu^{II} can also exhibit five fold coordination as a result of the Jahn - Teller effect (Pasquarello et al., 2001). The hydrolysis products of $Cu(H_2O)_6$ 2^+ are CuOH+ (pK1=7.93) and $Cu(OH)_2$ 0 (pK2=8.37) (Paulson and Kester, 1980). It can also be complexed with carbonates forming $CuCO_3$ and $Cu(CO_3)_2$ 2- (Sylva, 1976). In the soil, processes that control fixation of Cu include adsorption, precipitation, and biological fixation.

Table 1.2 Physical and atomic properties of Copper (Bektas, 1970).

Chemical Symbol	**Cu**
Atomic Number	29
Atomic Weight	63.54
Density	8960 kgm^3
Melting point	1356 K
Specific Heat cp (at 293 K)	0.383 kJkg-1 K-1
Thermal conductivity	394 W m-1 K-1
Coefficient of linear expansion	16.5 x 10-6 K-1
Young's Modulus of Elasticity	110 x 109 N m-2
Electrical Cond. (% IACS)	1.673 x 10-8 ohm-m
Crystal Structure	Face-Centered Cubic

1.1.3 Utilization of Copper

Copper and copper alloys are used in a variety of application during thousands of years to keep our standard of living at reasonable levels. The continued production of copper from resources and use of it is very crucial and essential for the development of humankind (Mendenhall, 1986).

In order to ensure that sustainable development of community is in place, it is very important to make sure that needs of future are not compromised while controling exploitation and usage of resources. Copper is a one of the major contributor of devoloping economies and developing countries in the world. Mining

industry, mineral processing, recycling and the transformation of metal into a large numbers of products creates jobs and brings wealth. These activities play important role to building and sustaining a country's infrastructure, and generate trade and investment opportunities. Copper will continue to play crucial role to society's development well into the future (American Society for Metals, 1990).

Copper is one of the most recycled and reused metal comparing other metals. As humankind, it is our capability to recycle metals over and over again that makes them a material of choice. Recycling copper increase the efficiency of use of the metals, results in saving energy, and gives oppurtunity to ensure that we have a continuous source of metal for future generations (Joralemon, 1973).

Copper was one of the first metals in history of mankind that ever extracted and used by humans, and it has made essential contributions to sustaining and improving society since the beginning of the history. Copper was first used in coins and ornaments starting about 8000 B.C., and at about 5500 B.C., copper tools helped civilization to move out and develop from the Stone Age. The invention of copper alloyed with tin produces bronze marked the beginning of the Bronze Age at about 3000 B.C. It is easy to stretch, mold, and shape the copper; it is outstanding resistant to corrosion and fatigue; effeciely conducts heat and electricity. As a result, copper was important to humunkind in the beginning of history and continues to be a material of choice even today for a various domestic, industrial, and high-technology applications. (Doebrich, 2009).

Copper is the best commodity metal conductor of electricity as it encounters much less resistance comparing to other metals. Copper is commonly used in power cables, either insulated or uninsulated, for high, medium and low voltage applications. In addition to that, copper's unique strength, ductility and resistance to corrosion makes it the preferred and safest conductor for commercial and residential usage. Copper is a vital component of energy efficient generators, motors, transformers and renewable energy production systems. Renewable energy sources like solar, wind, geothermal, fuel cells and other technologies are all heavily reliant on copper due to its excellent

conductivity (Mendenhall,1986).

Copper plays a very important role in worldwide communications and information technologies including internet service, through the existing copper infrastructure of ordinary telephone wire. Copper and copper-based alloy products are used in domestic lines, wide area networks, phones and personal computers. (American Society for Metals, 1990).

Copper and brass are the one of the best choice for plumbing, taps, valves and fittings. In the event of a fire, copper tubes do not burn like plastic tubing and do not release noxious or toxic fumes, or do not melt. Due to its antibacterial properties, it helps protect water systems from potentially lethal bacteria csuch as legionella (Doebrich, 2009).

Copper's biostatic properties help preventing the transfer of various diseases and microbes when it is used as doorknobs and plates. All major forms of transportation nowaydas depend on copper to perform critical functions. Copper-nickel alloys are used on the hulls of boats and ships to reduce marine biofouling, thereby reducing drag and improving fuel consumption. Automobiles and trucks rely on copper as their important parts produced from copper. Today, the average size automobile contains appoximetly 22.5 kg of copper (American Society for Metals, 1990).

1.1.4 Copper Production and Prices

Internationally, the market for copper is one of the largest of all metals after iron and aluminum. The size of the global market estimation for refined copper is over US$150 billion, annually. As explained in utilization of copper section, Copper has been a material of choise since from the evolution of human civilizations for thousands of years, and the contribution and impact of the copper to our lifes is unquestionable. Copper is easy to work with, a perfect conductor of heat and electricity, corrosion resistant, and abundant. In fact, the US Geological Survey (US Geological Survey [USGS], 2016) estimates that global land based copper resources

of over 3.1 billion tonnes of which 690 million tonnes are listed as reserves. These estimates have more than doubled since 1970 as annual world mined copper production has increased. As an added benefit, recycling contributes substantially to the amount refined copper available, with estimates ranging from 20-30% of annual refined copper production (USGS, 2016).

Except for a brief spike in price in 1994/95, Copper has been consistently sold for a nominal price below US$1 from 1980 to 2003, copper has been sold for a nominal price below US$1 per pound. In fact, the annual price through this time period had a mean of U$0.90 and a median of US$0.82 per pound. The prices of metal have been significantly impacted after the emergence of Brazil, Russia, India, and China from economic depression. The metal most effected has been Iron but copper, lead, and tin prices all increased over 300% between 2003 and 2012. There has been a swift and staggering advance over the last 20 years in mineral processing as industrial production has shifted from developed countries to China. China has become the largest consumer of many base and industrial metals, representing approximately 43% of global copper demand in 2012 according to International Copper Study Group (ICSG) and International Monetory Fond (IMF) (The World Copper Factbook, 2013).

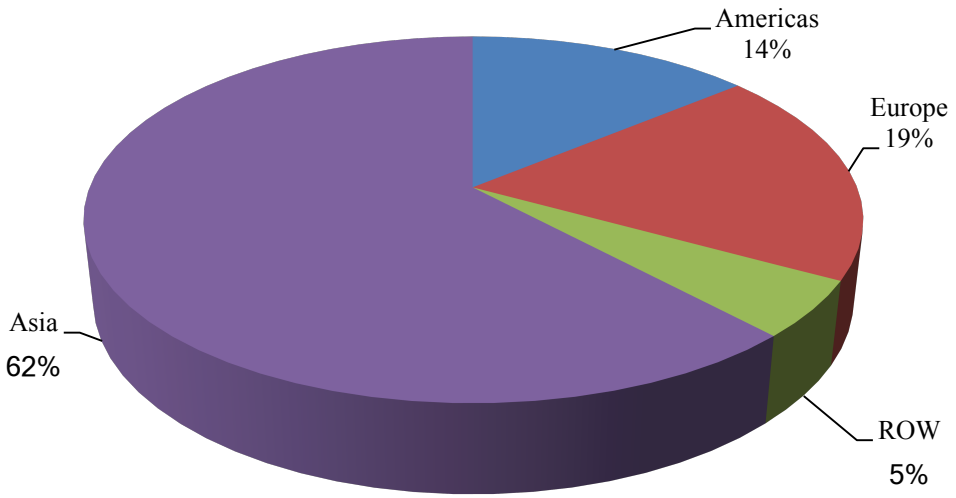

Figure 1.1 Major uses of Copper: Usage by region (ICSG, 2013).

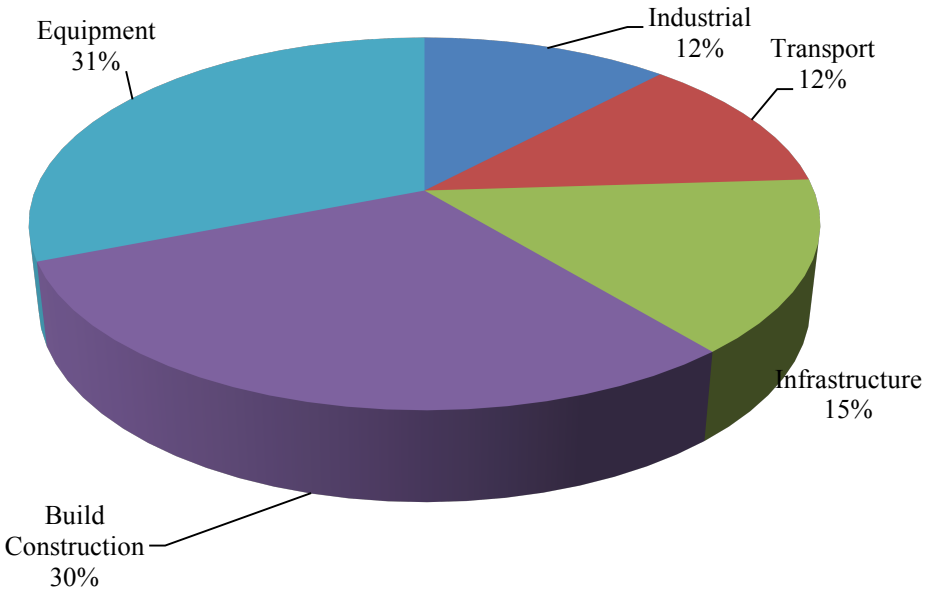

Figure 1.2 Major uses of Copper: by end user sector (ICSG, 2013).

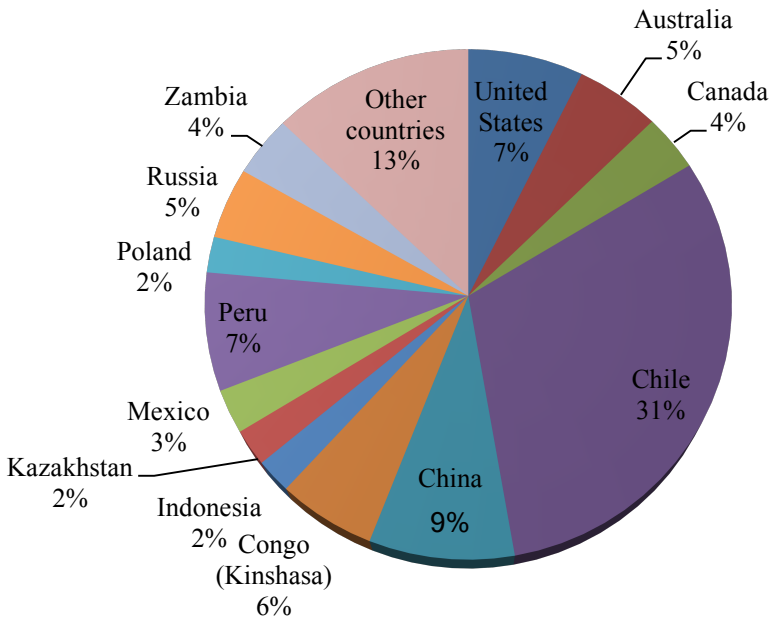

Figure 1.3 Copper Prodcution during the year 2014 (ICSG, 2013).

1.2 Copper and Copper Alloys

As mentioned in utilization of copper section, copper and copper alloys are extensively used in a variety of products and improved our daily lives. Due to its exceptional electrical and thermal conductivitiy, outstanding resistance to corrosion, its strength and formability and many more features make copper material of choise for mankind. Copper and its alloys are so adaptable that they can be used in a variety of different applications in almost all industry groups, from regular copper wires to automotive radiators (Doebrich, 2009).

1.2.1 Copper Alloy Families

Copper alloys are identified by the Unified Numbering System (UNS) which categorizes families of alloys based on their elemental composition and make-up. Wrought products range from Unified Numbering System (UNS) C10000 through UNS C79999; cast products are given numbers between UNS C80000 and UNS C99999 (American Society for Metals, 1990).

Table 1.3 The unified numbering system (UNS) copper alloy designations (Copper Development Association, 2016)

ALLOY	WROUGHT	CAST
Copper	**C10100 to C13000**	**C80100 to C81200**
Brass	**C20500 to C28580**	**C83300 to C85800**
Tin Brass	**C40400 to C48600**	**C83300 to C84800**
Phosphor Bronze	**C50100 to C52400**	**C90200 to C91700**
Aluminum Bronze	**C60800 to C64210**	**C95200 to C95900**
Silicon Bronze	**C64700 to C66100**	**C87000 to C87999**
Silicon Red Bras	**C69400 to C69710**	**C87300 to C87900**
Copper Nickel	**C70100 to C72950**	**C96200 to C96900**
Nickel Silver	**C73500 to C79900**	**C97300 to C97800**

Brasses are alloys that consist of copper and zinc, they show good strength and ductility and grat cold formability properties which improves with increased zinc content up to 35%. Brass coloration ranges from red to golden yellow, depending on

the amount of zinc the alloy contains.

Tin Brasses are mainly an alloy that consist of copper, zinc (2% to 40%) and tin (0.2% to 3%). This type of alloys includes admiralty brasses, naval brasses and free-machining tin brasses. These alloys provide increased corrosion resistance and are often used to make high-strength electrical connector, fasteners, springs, corrosionresistant mechanical products (American Society for Testing Metals).

Silicon Bronzes are part of the subgroup of high-strength brasses. They contain less than 20% zinc and up to 6% silicon and are solid solution strengthened. They are used in order to make bearings, gears and intricately shaped pump and valve components (Mendenhall, 1986).

Nickel-silvers, also called nickel brasses, are alloys containing copper, nickel, and zinc. Though they do not contain silver, they have an attractive silver luster, moderately high strength and good corrosion resistance. They are used to make food and beverage handling equipment, decorative hardware, electroplated tableware, optical and photographic equipment and musical instruments (Mendenhall, 1986).

Copper Nickel alloys contain anywhere from 2% to 30% nickel, are highly corrosion-resistant and thermally stable. The addition of iron, chromium, niobium and/or manganese can improve their strength and corrosion resistance (Breedis & Caron, 1993).

Phosphor bronzes, or tin bronzes as they are sometimes called, contain between 0.5% and 11% tin and 0.01% to 0.35% phosphorus. Tin increases their corrosion resistance and tensile strength; phosphorus increases wear resistance and stiffness (R.F. Schmidt & D.G. Schmidt, 1997).

Table 1.4 Compositions & properties of the more common copper alloys (Copper Development Association, 2016)

ALLOY UNS No:	COMMON NAME	NOMINAL COMPOSITION Wt%	ELECTIRICAL CONDUCTIVITY %IACS	TENSILE STRENGHT Ksi (Mpa)
C11000	Copper	99 min Cu	101	42 (290)
C12200	Phospor Copper	0.025 P	85	42 (290)
C17200	Beryllium Copper	1.90 Be	22	128 (882)
C23000	Red Brass	15 Zn	37	56 (386)
C26000	Cartridge Brass	30 Zn	28	62 (427)
C28000	Muntz Metal	40 Zn	28	70 (483)
C42500	Tin Brass	10 Zn – 2 Sn	28	63 (434)
C51000	Phosphor Bronze A	5 Sn – 0.2 P	15	68 (469)
C52400	Phosphor Bronze D	10 Sn – 0.2 P	11	83 (572)
C65500	High Silicon Bronze	3.3 Si – 1.0 Mn	7	78 (537)
C70600	Copper Nickel, 10%	10 Ni - 1.4 Fe	9	65 (448)
C71500	Copper Nickel, 30%	30 Ni – 0.7 Fe	4.6	73 (503)
C74500	Nickel Silver, 65-10	25 Zn – 10 Ni	9	73 (503)
C75200	Nickel Silver, 65-18	17 Zn – 18 Ni	6	74 (510

1.3 Types and Characteristics of Copper Deposits

The Earth's crust contains greater than hundred naturally occurring elements. The crust, which ranges from 6 to 30 miles or 10 to 50 km thick, can be subdivided into two distinctly disparate parts as the oceanic crust and the continental crust which is different in terms of composition. Some of the common elements that make up the crust are in order of abundance oxygen (O), silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), sodium (Na), potassium (K), and magnesium (Mg) (table 1). Although the same elements are present in both types of crusts, their concentrations are slightly different. The first eight elements listed above constitute more than 98 percent of all crustal material. Thus, one can refer to the distribution of elements in terms of their average crustal abundance. Many useful mineral commodities in the crust are present in very low abundances. The mining industry cannot use most rocks in the Earth's crust as sources of metals or other elements just simply because concentrations are

too low to extraction. Instead, the mining geologist looks for rocks where the desired mineral has been concentrated by some other natural process (Wills et al., 2006).

In nature, mineral deposits occur in various tectonic and geologic settings. Some mineral deposits may be formed in one place but can be transported to another geographic location as a result of tectonic forces or other geologic processes. Therefore, the research on tectonic processes and regional settings and geology is important in order to understand the distribution of mineral deposits in that particular location (Frank, Weathers & Galloway, 2001).

1.3.1 Porphyry Copper Deposits

Porphyry copper deposits comprise from the complex interactions and feedbacks of many processes. Because of intricate features of porphyry deposits, a concise definition that covers the essential attributes of this deposit class is elusive. A porphyry copper deposit can be defined as follows: copper-bearing sulfides are concentrated in a network of fracture-controlled stockwork veinlets and as disseminated grains in the adjacent altered rock matrix; Alteration and ore mineralization at depth of 1-4 km are often related to magma reservoirs emplaced into the shallow crust (6–8+ km), predominantly intermediate to silicic in composition, in magmatic arcs above subduction zones; intrusive rock complexes that are emplaced immediately before porphyry deposit formation and that host the deposits are predominantly in the form of upright-vertical cylindrical stocks and(or) complexes of dikes; Zones of phyllic-argillic and marginal propylitic alteration overlap or surround a potassic alteration assemblage; and, Copper may also be introduced during overprinting phyllic-argillic alteration events (Berger et al., 2008).

1.3.2 Sediment-Hosted Copper Deposits

Sediment-hosted copper deposits are defined as stratabound type deposits. It means that they are restricted to a narrow range of layers between a sedimentary sequence but do not necessarily follow sedimentary bedding. They are epigenetic and

diagenetic, that is, they are materialized after the host sediment is deposited, but in of most the cases, prior to lithification of the host. They form seperately from igneous processes (Cox, D.P., 1986).

Sediment-hosted copper deposits are a large and vey diverse deposit group that includes some of the richest and largest copper deposits in the world (Gustafson and Williams, 1981). The one of the example of this copper deposits are the Zambian Copper Belt, which have produced in excess amount of one billion metric tons of copper at an average grade of approximately 2.7 weight percent copper, as well as high quantities of cobalt and silver (Kirkham, 1989)

Sediment-hosted copper deposits are accured by fluid mixing in permeable sedimentary and volcanic rocks. For a sediment-hosted copper deposit to be formed, four conditions are necessary: (1) an oxidized source of rock, (2) a brine to mobilize copper, (3) a reduced fluid to precipitate copper, and (4) conditions favorable for fluid mixing (Haynes, 1986).

Sediment-hosted copper deposits are restricted to a narrow range of layers within a sedimentary sequence but do not necessarily follow sedimentary bedding. They formed after the host sediment is deposited, but in most cases, prior to lithification of the host. Mineralization is independent of igneous processes. Host rocks comprise two types: calcareous or dolomitic siltstone, shale, and carbonate rocks of marine or lacustrine origin; and non marine sandstone, arkose, and conglomerate. In addition, the iron oxide copper-gold and basaltic copper deposit sub models may be applicable within some of the areas studied (Kirkham, 1989).

Sediment-hosted stratabound copper deposits are bodies of disseminated, cementing, and lesser veinlet-hosted copper minerals with their sedimentary or metasedimentary host rocks. These SSC deposits are characterized by strong zoning of the ore minerals laterally along and across the bedding, from pyrite, to chalcopyrite, to bornite, to chalcocite, and to hematite. Chalcocite and bornite zones are typically the ore zones (Davidson, 1965).

They divided into three subgroups, their typical host lithologies, and their relative reductants are (1) reduced-facies type (2) sandstone-type: gray and (3) red-bed type (Kirkham, 1994)

Reduced-facies and sandstone Copper deposits can be quite large, where red-bed-type deposits hardly have as much as 10 million tonnes of ore. Outside of the Central African Copperbelt, typical Cu grades of reduced-facies-type deposits average around 1.4% Cu; sandstone-type deposits average 1.1% Cu; and red-bed-type deposits average 2.1% Cu (Parks et al, 2012). Average grades of deposits in the Central African Copperbelt are higher: 2.6 % Cu for reduced-facies-type deposits and 2.2% for sandstone deposits. SSC deposits are an crucial source of other metals, ranking first among all deposit types in world cobalt (Co) production and fourth among all deposit types in silver (Ag) production. Twenty five percent of SSC deposits contain Ag, their grades ranging between 2 and 200 g/t, and 14% of SSC deposits contain Co, grading between 0.05 and 0.5 percent in primary ores (Parks et al, 2012). If the deposit contains by product Ag, it does not contain by product Co and vice versa; only exception for this is that the Kupferschiefer, which contains both by product metals (Kirkham, 1994).

1.3.3 Skarn Type Copper Deposits

Skarn type ore deposits can be defined as coarse-grained metamorphic rocks composed of, iron, calcium, magnesium, manganese and aluminum silicate minerals (as known as "calcsilicate" minerals) that form by replacement of carbonate-bearing rocks during contact or regional metamorphism and metasomatism. Even though, skarn deposits are thought to be similar to hydrothermal systems by the majority of the world. These deposits consist of base and precious metal minerals in calcsilicate rocks. Copper skarn generally consists of chalcopyrite in contact metasomatic rocks (Cox & Theodore, 1986).

In generally, metamorphic rock that rich in terms of silica can defined as skarn. Tungsten can be given as an example of Skarn deposits. However, these deposits can

contain other valuable metal such as copper, gold, lead, iron, zinc and molybdenum.

It might be stated that one of the largest skarn type deposit is copper skarns. It is especially ordinary in subduction zones and found in both oceanic and continental settings. The largest copper skarns are associated with mineralized porphyry copper plutons. These deposits can exceed 1 billion tonnes of combined porphyry and skarn ore, with more than 5 million tonnes of copper recoverable from skarn. Generally, skarns are smaller than many other deposit types such as porphyries, however, skarns may occur in association with porphyry copper deposits. For example, the Twin Buttes in Arizona and Bingham Canyon in Utah host both porphyry and skarn deposits (Evans, 1993).

As stated, skarn deposits are found in a variety of tectonic settings and can be defined by their mineralogy. This mineralogy includes a wide variety of calcite and calcium bearing silicate and associated minerals but gnerally is dominated by garnet and pyroxene. Skarn deposits are mostly described based on the dominant economic metal or mineral present in the deposit. It can be copper, iron, tungsten, zinc-lead, molybdenum, or gold (Hastings & Harrold, 1987).

1.3.4 Volcanogenic massive sulphide (VMS) ore deposits

Volcanic-associated massive sulfide deposits can be divided into three general categories as Cyprus type deposits, Kuruko-type deposits and Besshi-type deposits. Cyprus-type deposits generally occur to be small, its head grade is generally in medium level and rich in terms of copper and zinc (Singer, 1986).

Kuroko deposits are most of the time occured in intermediate to felsic volcanic rock. This deposit type often interpreted to have formed in extensional environments associated with arc volcanism. They are mostly high grade and can be very large. Relative to Cyprus-type deposits, they generally contains more zinc, lead, silver, and antimony, which basically describes the composition of felsic volcanic host rocks (Slack, 1993).

Besshi-type deposits are present in mixed volcanic-sedimentary environments. Besshi-type deposits are typically copper-rich and contains small amount of lead and other lithophile elements. Comparing to other volcanic-hosted deposits, most of Besshi-type deposits form thin, laterally extensive sheets of pyrrhotite- and (or) pyrite-rich massive sulfide rock; however, the characteristics of Besshi-type deposits vary considerably (Slack, 1993).

1.3.5 Vein Type Copper Deposits

Vein type copper deposits are mainly hosted by sedimentary rocks (limestone, dolomite, sandstone, and shale) that have been intruded by intermediate to felsic composition igneous stocks, dikes, and sills surrounding geologic terrace. These deposits are in sedimentary rock sequences that host local igneous intrusions (Singer, 1986).

A vein-type deposit is a fairly well defined zone of mineralization, usually inclined and discordant, compared to its length and depth it is generally narrow. Fault or fissure openings are very common in most vein deposits or in shear zones within country rock. They may also reffered as a lode deposit (metalliferous). In vein deposits, a many of minerals such as native gold or silver or metal sulphides are deposited mainly with quartz and/or calcite (Singer, 1986).

1.4 Copper Ore Processing Methods

Copper is most of the time present on the earth's crust as copper-sulphide and copper-iron sulphide minerals such as Chalcopyrite($CuFeS_2$), Bornite($CusFeS_4$) or Chalcocite(Cu_2S). Copper may also occurs as oxidized mineral, as Malachite ($Cu_2CO_3(OH)_2$ or Azurite $Cu3(CO_3)_2(OH)_2$.

More than 80 percent of the world's producton of copper comes from copper-iron-sulphide ore deposits. As Cu-Fe-S minerals minerals are not easily dissolved by aqueous solutions (Davenport et al., 2002), main extraction of copper occurs by using pyrometallurgical method. Remaining copper production from the other 20%

of ores (mainly oxidized ores) is obtained hydrometallurgically, using various solvent extraction methods (Davenport et al., 2002).

1.4.1 Pyrometallurgy

The pyrometallurgical processes which are mainly used for the copper-sulphide minerals mostly involve the following main processes: comminution, beneficiation, smelting and converting, pyrorefining and electro-refining (Davenport et al., 2002; Wills et al., 2006). A flow diagram of a generic pyrometallurgical extraction process contains the main processes of, inputs, outputs and interflows. It is important to note that the process system configuration largely varies from operation to operation; the objective of the generic system illustration is to provide a first understanding of the main process.

The pyrometallurgical extraction of copper from sulfide minerals traditionally consists of the following basic steps (Villarroel, 1998).

- Roasting of sulfide concentrate
- Matte smelting
- Converting
- Fire-refining

The copper is almsot 99.5% pure after fire-refining stage, and is treated further by electrolytic refining to produce extremely high purity copper. There are number of different processes to produce final grade copper and in some cases several different steps are carried out at the same time (Davenport et al., 2002).

1.4.2 Hydrometallurgy

Chalcopyrite ($CuFeS_2$) concentrates are processed traditionally by smelting, which results in sulfur dioxide emissions. The development of a hydrometallurgical process for recovery of metals from concentrates of copper ores offers industry a

low-cost, low-pollution alternative to the traditional pyrometallurgical practices. The hydrometallurgical leaching of chalcopyrite with acid ferric sulfate solution as an alternative process to smelting has been studied extensively (Hayes, 1993).

Hydrometallurgical processing of complicated ores and concentrates is becoming more and more important as the mining and metallurgical industry are looking ways to improve beneficiation of mineral deposits that are hard to treat using traditional mineral processing and pyrometallurgical techniques or processes. Mineral processing is all the time challenged by efficient separation of valuable minerals from their gangues in order to produce saleable or marketable concentrates. Pyrometallurgical treatment of base metal concentrates is requires capital investment and subject to even more strict regulations for environmental control. On the contrary, Hydrometallurgical processing is generally has a lower cost in terms of capital investment for an equivalent metal production rate and more envirometnly friendly as it avoids the gas and dust issues that pyrometallurgical processes have. By product recovery may also make hydrometallurgical processes more profitable (Dreisinger, 2009)

The main difference of hydrometallurgical processes from pyrometallurgy is that parameters such as low operating temperatures, low reaction rates, more environmental friendly, larger production yield for a given throughput of material, low production costs and selective chemical reactions (Hayes, 1993).

1.4.3 Froth Flotation

Flotation defines by most literature resource as a physico-chemical separation process. As can understand from this statement that both physical and chemical factors involve for the separation method and both are equally important in froth flotation. There is a three phase model that exist in a flotation systems, those are; solid, liquid and gas. Interfacial chemistry is controled by all the flotation reagents or chemicals such as collectors, depressants, frothers, activators, and pH modifiers used in the process, water chemistry and the chemistry of the minerals. Physical (or more

precisely, physical-mechanical and operational) factors consist of equipment components like cell design, hydrodynamics, bank configuration, and bank control and operational components such as feed rate, mineralogy, particle size, and pulp density. Even though froth flotation might be classified as simple separation method or concept, due to variables at factors stated as above, it is an extremely complex process in practice as it involves many scientific and engineering practices (Klimpel & Hansen, 1988).

In most froth flotation systems, physical and chemical factors are not independent, that means there are significant interactions between the many variables. Theoretically, when all physical factors are controled or optimized and kept same without changing anything, the effect of the change in a chemical factor should clearly make a measurable difference in flotation efficiency. This mesasurable difference may be defined as recovery or grade. In practice, however, this change may not be resulted immediate difference in recovery, grade or any other performance parameter due to certain operational limitations and plant metallurgists have to anayze the data set with statistical tools to demonstrate significant differences (Mining Chemical Handbook, 2002).

Froth flotation is a separation method that extensively used in order to separate and recover valuable minerals from their ore or in the beneficiation of other materials. The main goal is to attach valuable solid particles to bubbles and form a stable bubble-particle cluster and separate the minerals from their gangue. This is the process where collectors or reagents plays important role. By adding the reagents to the slurry, mineral surface properties will be manipulated or modified as desired. These reagents can be divided into several different groups namely; collectors, activators, depressors, frothers and regulators. Each reagent will play different and very important role on separation process and will promote particular behavior of a contained mineral or change the slurry properties to make separation possible. These reagents and their brief functions explained below and most information obtained from literature (Bulatovic, 2007).

Froth flotation is the most common, important and adaptable concentration methods since it can be applied to many different ores at different particle size range by choosing the right flotation reagents or chemicals. The mineral separation or benecification by flotation uses differences on surface chemistry properties of the valuable and gangue mineras particles. Prior the separation stage, mineral slurry (or pulp) is ground to finer particle size by grinding the ore with water. The pulp is then treated with flotation reagents specific to the processed ore. The flotation chemicals can be divided into three major classes (Crozier, 1992);

a) Collectors
b) Frothers
c) Modifiers (activators and depressants)

Collectors can be simply defined as reagents that attach to mineral particles and make them hydrophobic. Frothers, stabilize the froth layer by changing surface tension in order to have proper frtoh to carry valuable minerals. Modifiers, activators and depressants are used to mak the flotation environment favorable to increase the floatability of specific minerals (Bulatovic, 2007).

1.4.3.1 Classification of Flotation Reagents

Reagents are the crucial for successful flotation as they create favorable environment to separate the desired mineral particles from the gangue or other minerals, by attaching selectively to the valuable minerals and then transportation of minerals will occur with help of frother as bubbles will carry the minerals to froth phase. However, reagents can also be used to keep certain type minerals in the slurry if it is a better option for separation and its efficiency. The overall pH of the slurry is controlled with chemicals at a desired range, where the floatability of mineral occurs most effectively. Also, the froth structure can be enhenced by using the correct chemicals. The right selection of reagent combination may make huge difference in metal recovery. Based on metal market prices this difference makes it worth making the right choose (Bulatovic, 2007).

1.4.3.1.1 Collectors . The one of the most important aspects of froth flotation is that hydrophobization of mineral surface in order to float the valuable mineral selectively. In order to achieve that, collectors are being used and dosed to the slurry to make the valuable minerals water repellent by covering mineral surface. Then, hydrophobic mineral particles will be floated via froth phase and separation will occur (Wills, 2006).

In many of resource and literature, classification of the flotation reagents is made by ability of reagents to dissociate in water and based on the function of a particular reagent. In this case, they can be divided into two distinct groups (Bulatovic, 2007).

Based on their resulting charge, the collectors can be categorized basically as cationic or anionic collector. Anionic collectors can be further classified as oxhydryl and sulfhydryl collectors depending on the basis of their solidophilic properties. Collectors that classified as cationic collectors are chemical compounds in which the hydrocarbon radical is protonized. These reagents are amines and they are the one of the most crucial flotation collectors (Riggs, 1986).

Several thousands of different flotation chemicals were tested in laboratories, in plants as froth flotation reagents. Today, only a few of them found chance in flotation applications. Collectors are a quite large group of organic chemical compounds. Collectors might be different from each other in terms of chemical composition and function. Simply, the main purpose of the collector is to selectively cover the mineral surface and create hydrophobic layer on mineral particle surface in the flotation slurry in order to prepare favorable conditions for mineral to attach hydrophobic particles to air bubbles, to recover of the valuable mineral particles as the froth product (Bulatovic, 2007).

The basic idea of collector system is that selectively form a hydrophobic layer on a surface of the mineral particle in the slurry so that the valuable mineral can be recovered while the gangue remains in the bottom of pulp as hydrophilic (Wills, 2006).

Collectors can be divided into two main groups and these groups categorized as non-ionizing and ionizing groups in many literature resource. Non-ionizing collectors are hydrophobic, mostly liquid and they are not water soluable as they do not dissociate in water due to their non-polar hydrocarbons. However, ionizing compounds are water soluable and they are able to dissociate in water. Ionizing group can be further divided in anionic and cationic collectors (Bulatovic, 2007).

Anionic collector is hydrolyzed in water so that it forms negative collector ion and positive metallic ion, ammonium ion or hydrogen ion. The polar group is anion which might be composed of various species. Anion collector can be based on bivalent sulfur, as an example in the case of dithiophosphates and xanthates. In addition, anionic collector can be based on the carboxyl group or sulfuric acid anions (Bulatovic, 2007). Thiol type collectors such as dithiophosphates, xanthates, thiocarbamates and mercaptans are chemicals, which are regularly used in froth flotation of sulfide ores. These chemicals are heteropolar and contain a polar part, where at least one sulfur atom is not bonded to oxygen. Sulfur group enters reaction with water and it is hydrophilic (Fuerstenau & Urbina, 1988).

Cationic collectors are reagents, in which the main element is the nitrogen group and the polar group is cation. The most crucial chemicals in this group are amines, which are organic derivatives of ammonia. The main characteristics of amine collectors can be determined based on the number of hydrocarbon radicals connected to nitrogen. Cationic collectors are natural collectors and they have a negative surface charge (Bulatovic, 2007; Hukki, 1964).

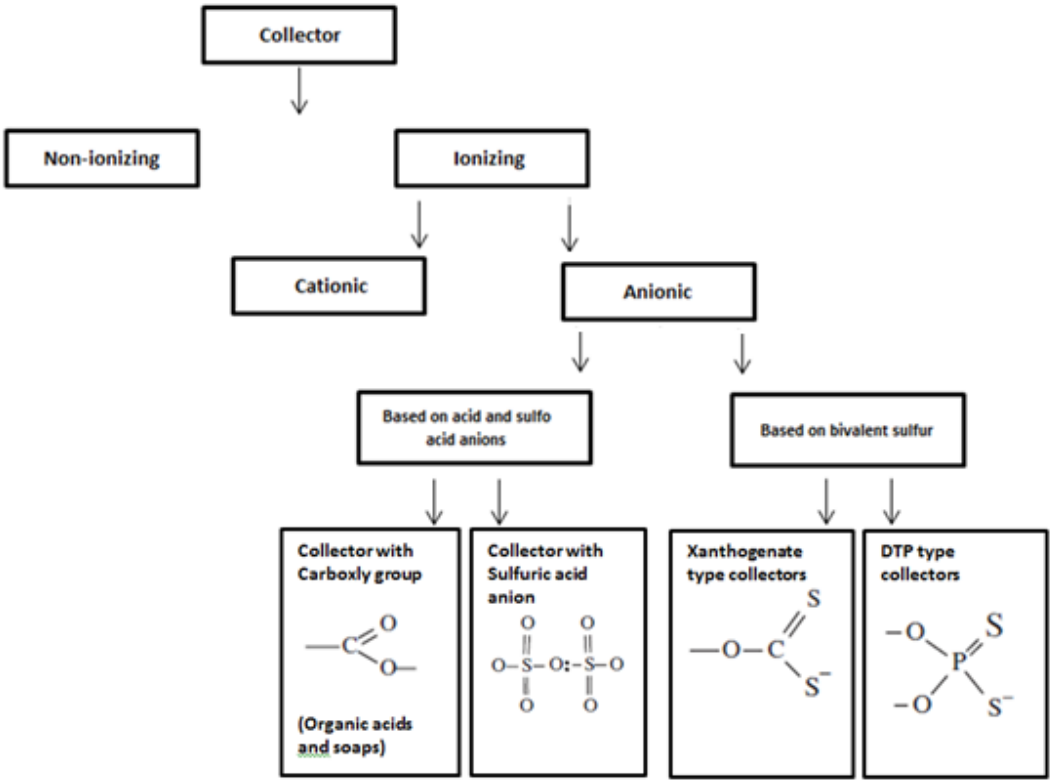

Figure 1.4 Classification of flotation collectors (adopted from Bulatovic (2007))

1.4.3.1.2 Xanthates. Xanthates are one of the most common flotation reagents that used in froth flotation process widely as a collector for concentration and separation of valuable minerals from their host rock (Woods, 1997). Xanthates are one of the eldest and key members of collector family tree. Due to its inexpensive price, long shelf life (when kept cool and dry), high water solubility, and its ability to achieve good recovery, it has been using in mining industry for a long time, predominantly (Bulatovic, 2007).

Xanthates still did not lose their popularity in mining industry. However, their usage is limited when selectivity is needed. In addition, there are various safety concerns related to environment and handling of xanthates. Decompositional features of xanthates, disulfide gas generation with its usage makes operations to look other collector options (Nagaraj, 2006).

When carbon chain length increases, strength of xanthates as collector also increases. However, there is an opposite relationship between increase in carbon

chain length and selectivity, therefore, they become less selectivity decreases. During flotation of base metals, due to high the iron sulfide content in the ore, xanthate is not able to produce desirable selectivity as a result of its unselective nature (Parekh, 1999).

As explain above, the effectiveness, strength and selectivety depends on structure of the carbon chain and affects significantly the performance of the collector (Cytec Aero Xanthate Handbook, American Cyanamid Company, 1972)

Xanthate decomposition in solutions occurs mainly by hydrolysis and it is temperature dependent (Cytec Aero Xanthate Handbook, American Cyanamid Company, 1972). In solution, decomposition of xanthates increases with a decrease in the pH (Lotter, 2009).

Molecular form of xanthate is shown below in Figure 1.5, where "R" represents the hydrocarbon chain (Bulatovic, 2007).

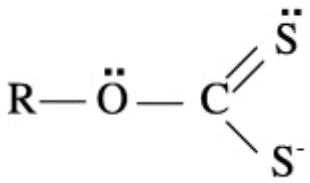

Figure 1.5 The molecular form of xanthate (Lotter, 2009).

1.4.3.1.3 Dithiophosphates. In terms of usage in mineral industrty, the dithiophiospates cover the second major class of sulfide mineral collectors, after xanthates. The dithiophosphates developed in late 1920's and accepted by mining industry as a froth flotation collector right away. They are still extensively used by minig industry under different trade mark names (Nagaraj, 1988).

Depending on minerology, gangue composition, ore type and some other various important parameters in flotation, great performances can be achieved when the ditiophosphates are used as sulfide collectors in froth flotation. Unlike xanthates, the

dithiophosphates are in liquid form, not in pallet form as most xanthates are. Dithiophosphates are slightly weaker collectors than xanthates. Therefore, the dosages requirements are generally higher with dithiophosphates. On the other hand, dithiophosphates have better iron sulfide selectivity comparing to xanthates. They can be used as a secondary collector with xanthates, or alone, and higher pH is required to achieve selectivity against iron sulfides. Depending on producer, dithiophosphates might be slightly expensive comparing to xanthates; however, they are much cheaper than many of the other froth flotation reagents (Parekh, 1999).

Dithiophosphates are derivatives from phosphoric acid. In Figure 1.6, "R" and "R'" presents the alkyl chains of dithiophosphate. As might be uessed, length and structure affects the collector properties. Ditiophosphates are used in globe in sulfide minerals flotation such as copper, lead, and zinc minerals and also in selective flotation of metallic gold (Hukki, 1964; Bulatovic, 2007; Lotter, 2009).

Dithiophosphates are synthesised from a single or from two different alcohols, with sodium hydroxide and phosphorus disulphide. As mentioned before, the length and structure affect the collector features (Bulatovic, 2007).

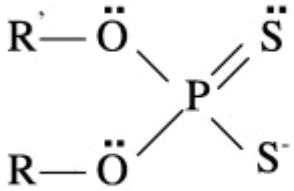

Figure 1.6 The molecular form of dithiophosphate (Lotter, 2009)

1.4.3.1.4 Thionocarbamates. The thionocarbamate collector family is the third largest collector group in terms of usage and consumption in mineral processing industry (Parekh, 1999). Thionocarbamates have longer shelf life comparing to xanthate, they are water soluble and have oily liquid form. They are selective towards iron sulfides than the previously described collectors. . Thionocarbamates strong copper sulphide collectors and can work well in alkaline conditions, where the pH is in the range between 7-12. In addition, they are not very vigorous to water

chemistry variations. The one of the disadvantage of using thionocarbamates is that they have slightly higher price compared to xanthates and dithiophosphates. Basic thionocarbamate collector is isopropyl ethyl thionocarbamate, which molecular form is shown in Figure 1.7 (Parekh, 1999).

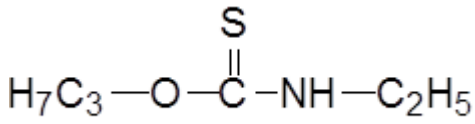

Figure 1.7 The chemical structure of Isopropyl Ethyl Thionocarbamate (Lotter, 2009)

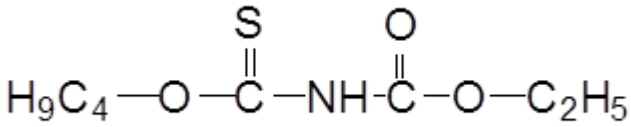

Figure 1.8 The chemical structure of ısobutyl ethoxycarbonyl thionocarbamate (Lotter, 2009)

1.4.3.1.5 Mercaptobenzothiazoles. The mercaptobenzothiazoles has along history and have been used for a long time in the chemical industry even before it was tested in froth flotation as a flotation collector. As a flotation collector, mercaptobenzothiazoles first used in flotation of lead carbonates and than for flotation of tarnished and oxidized copper minerals (Bulatovic,2007). Mercaptobenzothiazoles are used mainly in the acid circuits or close to neutral pH (Parekh, 1999). Mercaptobenzothiazole has a yellowish color and they are insoluble in water, but readily soluble in alkaline solutions (Bulatovic, 2007). They are often used as a mixture collector with dithiophosphates. Mercaptobenzothiazole consist of a benzene ring fused with a thiazole ring, as can be seen in the Figure 1.9.

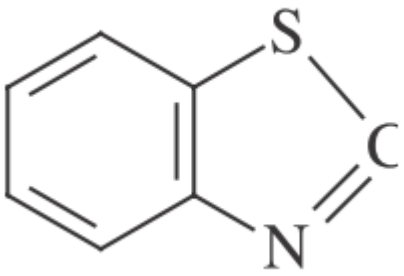

Figure 1.9 The chemical structure of mercaptobenzothiazole (Bulatovic, 2007).

1.4.3.1.6 Modified Thiocarbamates. The o-isopropyl and n-ethyl thionocarbamates can be modified by substitution of an alkoxy carbonyl group on the N donors as per the following structure (Bulatovic, 2007).

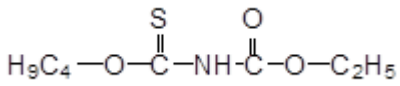

Figure 1.10 The chemical structure of modified thiocarbamate (Bulatovic, 2007)

1.4.3.2 Modifying Reagents

Modifying reagents or modifiers are used to assist adsorbtion of collectors to the certain mineral surfaces by adjusting pulp environment in favor of collectors. With the use of modifiers or regulators, adsorption rate can be adjusted in either way by accelerating the adsorption of collector or preventing adsorption of collector from mineral particle. Modifying reagents makes it possible to separate individual mineral sulfides apart from each other e.g. lead, zinc and copper from complex sulfides ores (Bulatovic, 2007*)*.

Modifying reagents can be divided into two main groups as activators and depressants. Activator is an inorganic chemical that makes the surface of spesific minerals attractive for collector adsorbtion. Depressants have the opposite effect, as they make the minerals hydrophilic, hence preventing their flotation (Bulatovic 2007).

1.4.3.3 Frothers

Frothers are one the first reagents that developed for mineral concentration by froth flotation. Frothers still remained as a key factor in the flotation. Frothers are responsible from various important parameter such as preventing the air bubbles coalescing, keeping the air bubbles dispersed, correct the forth film properties so that the valuable minerals can be carried to the surface,

provide strong and stable bubbles to carry minerals to the lip of the cell, however, it shoud be able break down in the launders (Wills, 2006).

Frothers are heteropolar, organic and surface-active compounds, which have the tendency to concentrate at the interface of water and air bubbles. The aim of using frother is to lower the surface tension of the water, which leads to the formation of a stable froth by increasing the film strength of the air bubbles. Frothers affect to the size of the air bubbles and help hydrophobic minerals to attach them more easily (Hukki, 1964; Bulatovic, 2007).

CHAPTER TWO
GEOLOGY, MINEROLOGY AND CHARACTERIZATION OF ASIKOY COPPER DEPOSIT

2.1 Introduction

Asikoy underground copper mine is located in Küre County, some 60 km north of Kastamonu province and 25 km from Black Sea cost. Underground mining method is longhole stoping with post backfill. Ore production is 420.000 ton/year with an average of %2 copper grade (Gönen, 2010).

2.1.1 Local Geology

The Kure Asikoy deposit are located in the central part of the Pontides zone. The Kure massive sulphide deposit can be characterized as Kieslager type ore deposits are the ore deposits between Cyprus type and Kuruko type. It is located within the basalts forming the upper unit of the Küre ophiolite. The Küre ophiolite is formed by harzburgite and dunite tectonite, intrusive gabbro-diorite and Iherzolite, basaltic volcanics and detritic sedimentary rocks (Çakır, 1995).

There has been important tectonic movements occurred within the Kure formation. The units are intercepted with an N-S oriented fault. The mineralization takes place in the weak zone induced by this fault and also within the toleitic basalts and along the borders of the plagical sediments. The overall geologic map of the study area is demonstrated in Figure 2.1. The ore mass occurs within the altered basalt series that are a part of the Küre ophiolites and is overlain with black shale. The ore mass consists of coarse lenses broken with faults and thrusted. The ore, which is composed of pyrite and chalcopyrite, is in the form of massif lenses with high grades under the hanging wall black shale and in the form of stock work pyrite and chalcopyrite veins with low grades within the altered footwall formation. Pyrites and chalcopyrites occasionally show colloform textures (Gönen, 2010).

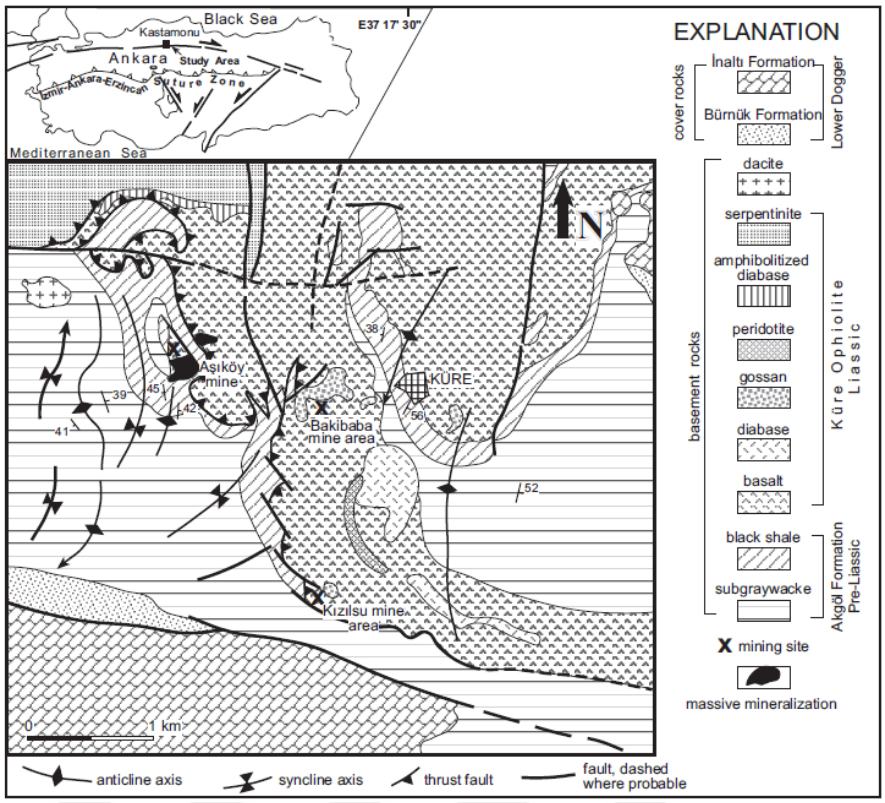

Figure 2.1 Simplified geological map of the Küre mining district (Kuşçu & Erler, 2002)

CHAPTER THREE
EXPERIMENTAL STUDIES

3.1 Sampling and Size Reduction

Sampling is an increadbly crucial step in obtaining plant and lab samples for testing. Sampling can be briefly described as an art of gathering a small portion of representative material from a larger lot. It is well known fact that about 80% of total variances and errors come from during sampling process and ore preparation stages. In order to guarantee success of sample collection stage, modern sampling techniques that combines both technical and statistical parts of sampling, are implemented, thoughtfully.

3.1.1 Sampling from the Kastamonu Kure Flotation plant

The general overview of sample collection procedure from Kastamonu Kure Flotation plant is shown as below in Figure 3.1.

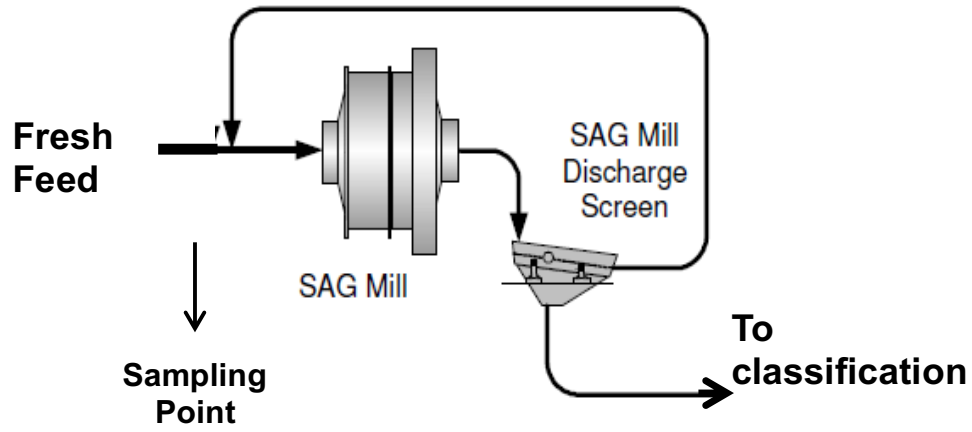

Figure 3.1 Simplified overview of sampling point for the work

A representative ore sample is collected from the plant feed belt, about 300 Kg. The representative sample collected from the SAG mill feed belt by stopping the belt

and collecting half a meter cross section every hour for 48 hour period, until the required amount is collected. In order to diminish further oxidation of ore, the sample shipment completed at the original size to laboratory of Dokuz Eylul University.

3.1.2 Size Reduction - Crushing

In the environment, mineral of interest exists along with other minerals or gangue in host rock. In order to separate mineral of interst from the host rock both physical and chemical separation methods need to be employed. However, without separation of mineral of interest from its host rock, this separation wouldn't be possible. Therefore, in order to access the desired minerals in host rock, the size reduction is required so that the liberation of the mineral from the host rock is possible.

Briefly, one of the first step in mineral processing can be explained as a series of physical processes where valuable minerals are firstly liberated from their host rock or from the gangue, then concentrated to produce an saleable product containing the majority of desired mineral which is the concentrate (Wills, 2006).

During size reduction stage, valuable minerals are separated from surrounding gangue by crushing and grinding the mined ore to fine particles. This process of size reduction is defined as comminution (see Figure 3.2).

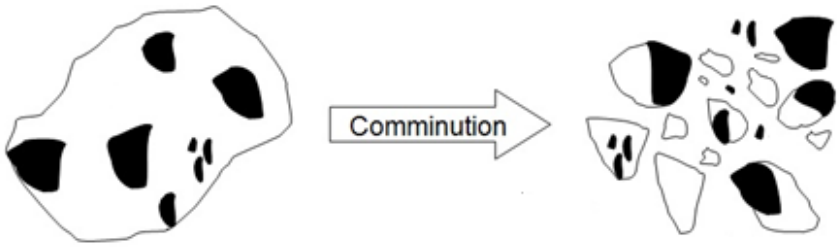

Figure 3.2 Breaking of ore to smaller size results in particles with varying degrees of liberation

The further concentration of minerals is carried out by using the differences in physical properties between minerals and gangue, such as density, electrical conductivity, magnetic and surface properties. In this work, froth flotation is

employed as separation method where differences in surface properties of mineral and gangue species are in consideration.

A representative ore sample is collected from the plant feed belt, about 300 Kg. The ore sample stage crushed below 3.35mm as shown in Figure 3.3. The remaining sample is stored in freezer for further development work.

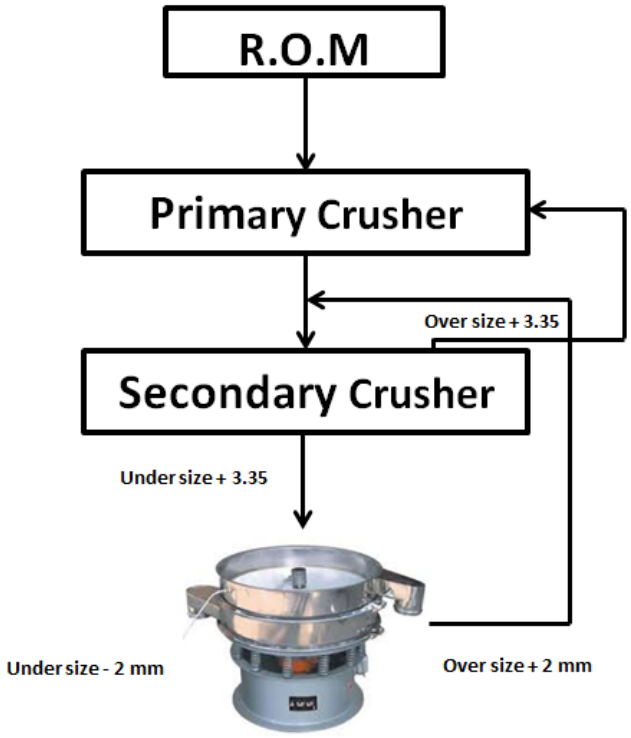

Figure 3.3 The flowsheet representing the crushing procedure of the sample

Initially, the representative sample collected from belt conveyour prior SAG Mill, were crushed in a jaw crusher to achieve size of 100% passing a 6.35 mm. After jaw crusher, the ore was crushed down again in roll crusher to achieve targeted particle size of 3.35mm. In all stages, the material sieved, and then coarser particles on the top of sieve is collected and recrushed in the same crusher as shown in Figure 3.3.

3.1.3 Subsample Preparation

The crushed samples of approxiametly 300 kg of ore is mixed by Gilson riffle (Figure 3.4) cone and quartered and subsamples of 75 kg are formed. In this method, the material fed to sample collection pans. Then, the chute bars equally arranged on both sides in order to creat V- shaped chutes. The gap between bars also arranged as desired so that optimum width of bar opening set as 3 times of the largest particle size in the pile. Once the bars are set, lever released slowly in order to make the material flow freely across the entire width of chute opening. By using Gilson riffle splitter, the ore sample well mixed and quartered to generate homogenize samples.

75 kg of sumsample then fed to hoppers of rotary splitter in order to homogonise the samples and receive 500 gr charges for the study. Please see below for general view and process of preparation of representative 500 gr charges.

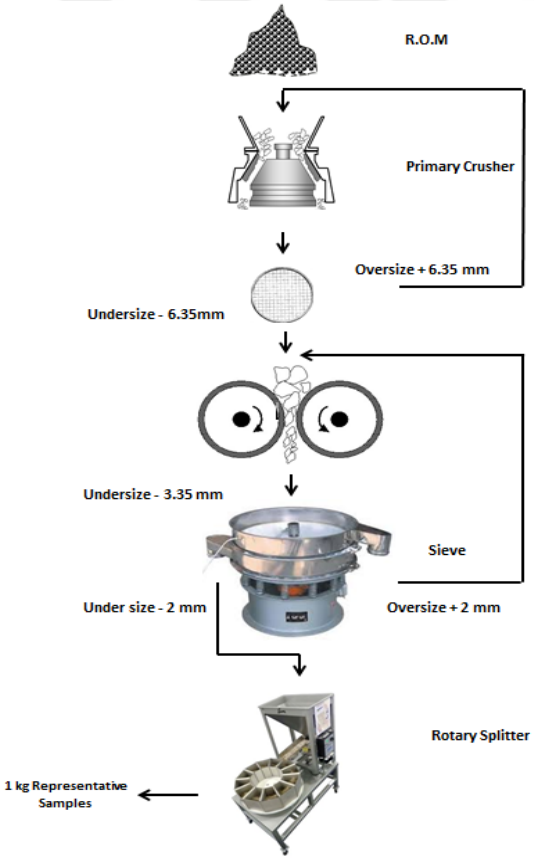

Figure 3.4 Simplified flowsheet of subsample preparation procedure

3.2 Characterization of the Sample

Kure Copper Flotation plant is located in Küre county, some 60 km north of Kastamonu province and 25 km from Black Sea cost, is an example of massive sulfide copper deposit related the Kieslager type deposits, which is between Cyprus type and Kuroko type deposits.

Chalcopyrite, pyrite are the main minerals in the ore with pyrrhotite, gold occurring as accessories. Pyrolusite, limonite (goethite, lepidocrocite) covellite-chalcocite are of secondary origin. The chemical characterization studies completed by ALS using atomic adsorption spectrum (AAS). A 1 gram sample is subjected to a 10% NaCN/1% NaOH leach to dissolve all cyanide soluble copper present. The sample is filtered and the filtrate is sent to Flame AAS for analysis of cyanide soluble copper. The residue is then digested using aqua regia, HF, and saturated potassium perchlorate solution to dissolve any residual copper remaining. The sample is refluxed in HCl and submitted to AAS for analysis of Cu. In order to make sure that representative ore charges are prepared, three random charge has selected and sumitted for elemental analysis. The assay results shown that the representative ore sample contained on the average of 1.06 g/t Au, 6.6 g/t Ag and 3.44% Cu, 167 ppm Pb, 4320 ppm Zn. The results are shown in the table 3.1 below..In this study, characterization of ore minerals on polished sections has been done using the polarizing reflected light microscope which is the standard and widely used for the identification of the ore minerals.

Table 3.1 The chemical characterization of the Kure ore sample by AAS.

Sample No	**Cu**	**Fe**	**Zn**	**Pb**	**Au**	**Ag**
	%	%	ppm	ppm	ppm	ppm
1	3.44	28.1	4320	167	1.06	6.6
2	3.42	28.3	4293	166	1.02	6.7
3	3.44	28.3	4312	168	1.06	6.7

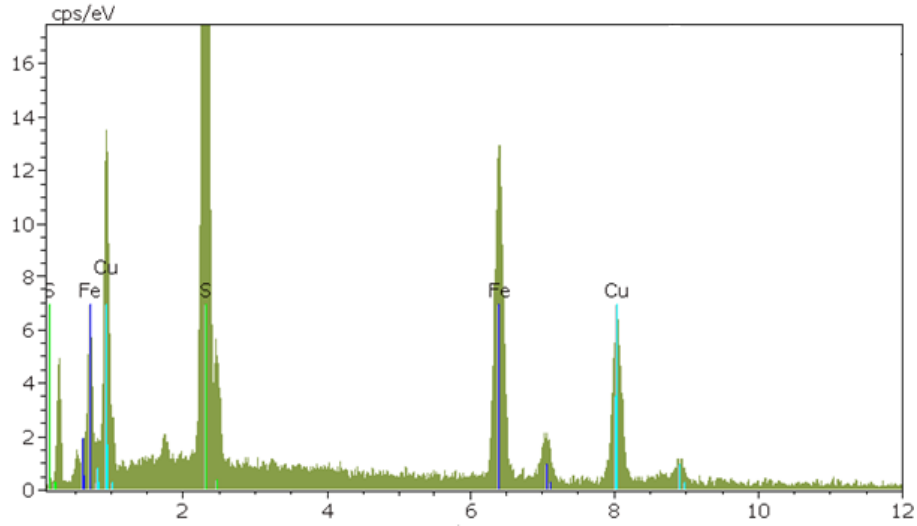

Figure 3.5 XRD analysis result

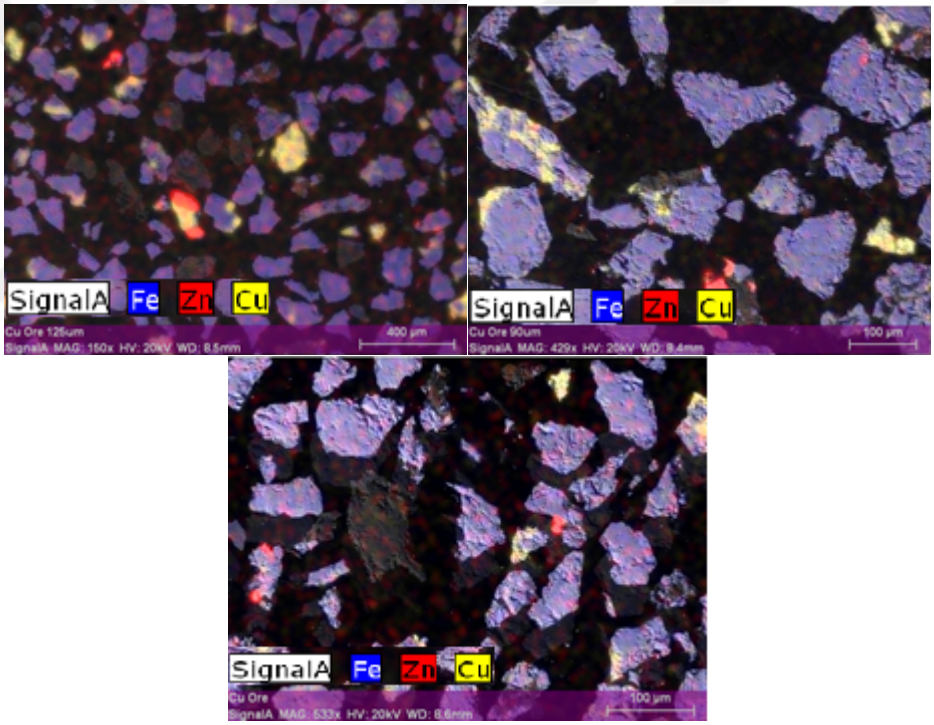

Figure 3.6 Secondary electron microscobe (SEM) images of Kure ore

500 g representative sample were wet sieved using a 45, 53, 75 and 90 micron screens to remove some of the fines prior to preparing polished grain mount. Samples were mounted into 24 hours set epoxy and polished using a Buehler automated polisher. Samples were analyzed using a Zeiss Sigma VP FEG-SEM

equipped with a Bruker EDX detector. All EDX spectra were collected at 20 KeV under variable pressure.

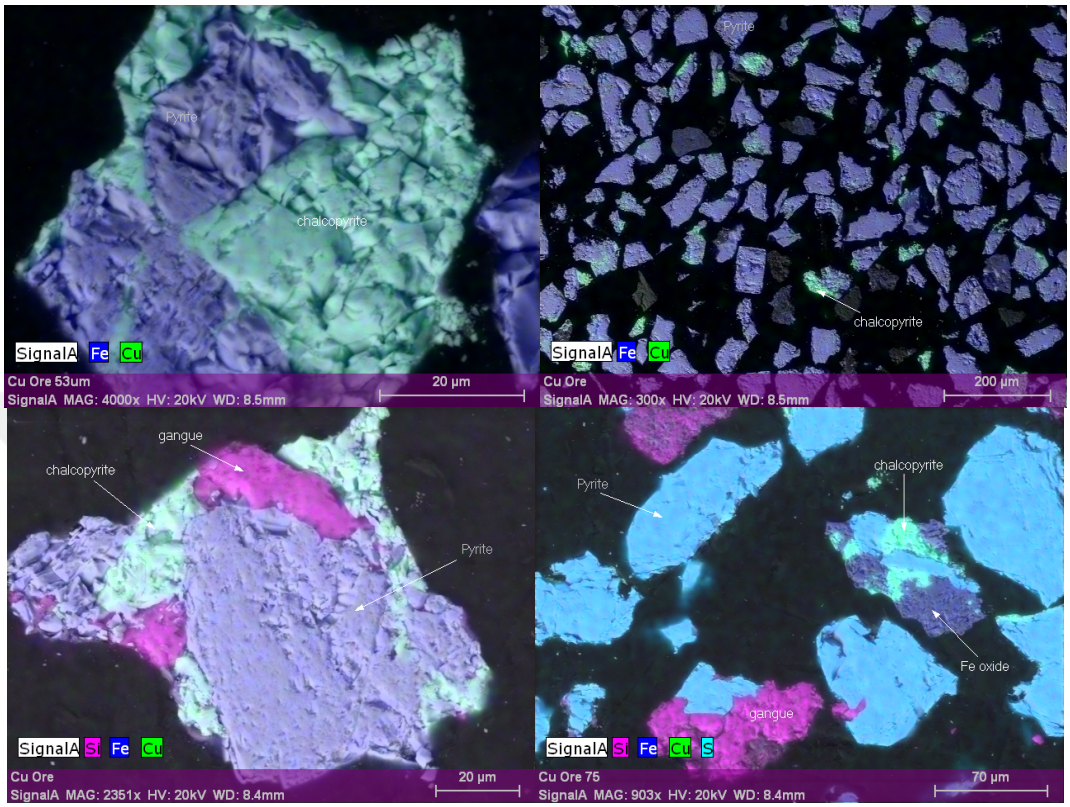

Figure 3.7 Secondary electron microscobe (SEM) images of Kure ore

3.2.1 Grinding Tests Studies

Grinding tests were performed by using a laboratory type rod mill (Figure 3.8). In order to achieve the targeted pulp density at 60%, 500 g of representative ore charge fed to the mill and ground with 325gr water addition. To determine grind time, grinding duration kept as 5, 10 and 15 minutes, respectively.



Figure 3.8 The laboratory type rod mill used for grinding

The cumulative size distributions of the grinding tests are shown as above in Figure 3.8. After 5 minutes of grinding, only 37.51% of material passed 45 micron. 64.34% of material passed 45 micron grind time of 10 minutes. After 15 minutes of grinding, 86.99% of material passed 45 micron. Based on ore characterization and recovery/grade data generated after diagnostic tests resulsts, this particular ore was 80% particles passing 45 micron so that grinding time established as explained below.

Wet grinding was carried out in a grinding mill consisted of a stainless steel mill, 264 mm long by 180 mm diameter, giving a volume of 6.77 litres. The mill was driven by rollers at 83 rpm (60 per cent of critical speed). The grinding media consisted of 25 mm diameter stainless steel rods weight of 8.5 kg (ie 14 rods).

Table 3.2 Sieve weight balance

Mesh vs Micron		5 Minutes			
Mesh	Micron	Weight g	% Retained	Cummulative % Retained	Cummulative % Passing
100	150	0	0%	0%	100%
140	105	70.6	14.22%	14.22%	85.78%
200	74	94.6	19.06%	33.28%	66.72%
270	53	80.2	16.16%	49.44%	50.56%
325	45	64.8	13.05%	62.49%	37.31%
400	38	83.8	16.88%	79.37%	20.63%
pan	-38	102.4	20.63%	100.00%	0.00%
total		496.4	100.00%		
Mesh vs Micron		10 Minutes			
Mesh	Micron	Weight	% Retained	Cummulative % Retained	Cummulative % Passing
100	150	0	0	0%	100%
140	105	24.5	4.92%	4.92%	95.08%
200	74	48.1	9.66%	14.58%	85.42%
270	53	55.6	11.16%	25.74%	74.26%
325	45	49.4	9.92%	62.49%	64.34%
400	38	117.1	23.51%	79.37%	40.84%
pan	-38	203.4	40.84%	100.00%	0.00%
total		496.4	100.00%		
Mesh vs Micron		10 Minutes			
Mesh	Micron	Weight	% Retained	Cummulative % Retained	Cummulative % Passing
100	150	0	0%	0%	100%
140	105	2.5	0.55%	0.55%	99.45%
200	74	5.8	1.19%	1.75%	98.25%
270	53	12.3	2.53%	4.28%	95.72%
325	45	42.5	8.74%	13.01%	86.99%
400	38	77.2	15.87%	28.88%	71.12%
pan	-38	346	71.12%	100.00%	0.00%
total		486.5	100.00%		

In order to establish grinding time, the graph of particle size (mesh) and cumulative %passing is plotted as below in Figure 3.9. The similar graph is generated by using micron as a measurement system in logarithmic plot as shown in Figure 3.10. Based on slope of the each grind plots, an equation is generated in the form of y= x+ k.

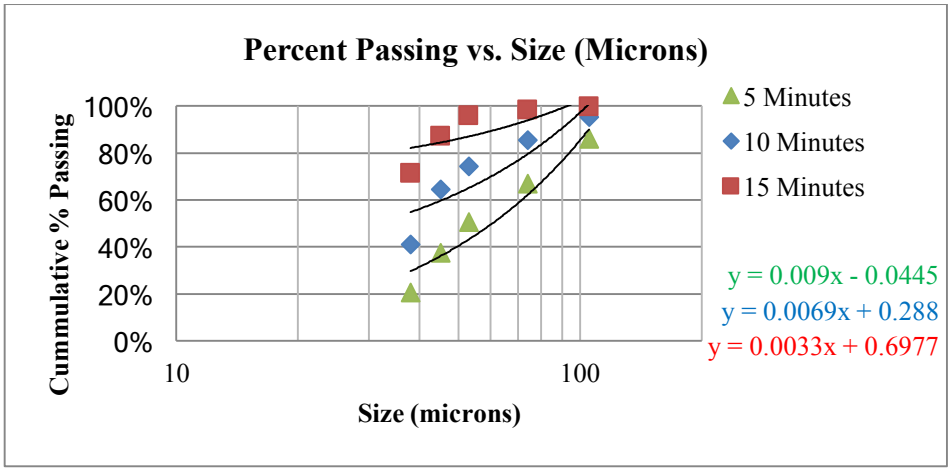

Figure 3.9 The cumulative size distribution of undersize after different periods of grinding (in Micron)

Based on calculated slope of each grinding time, the actual cumulative % passing value is calculated as below in Table 3.3.

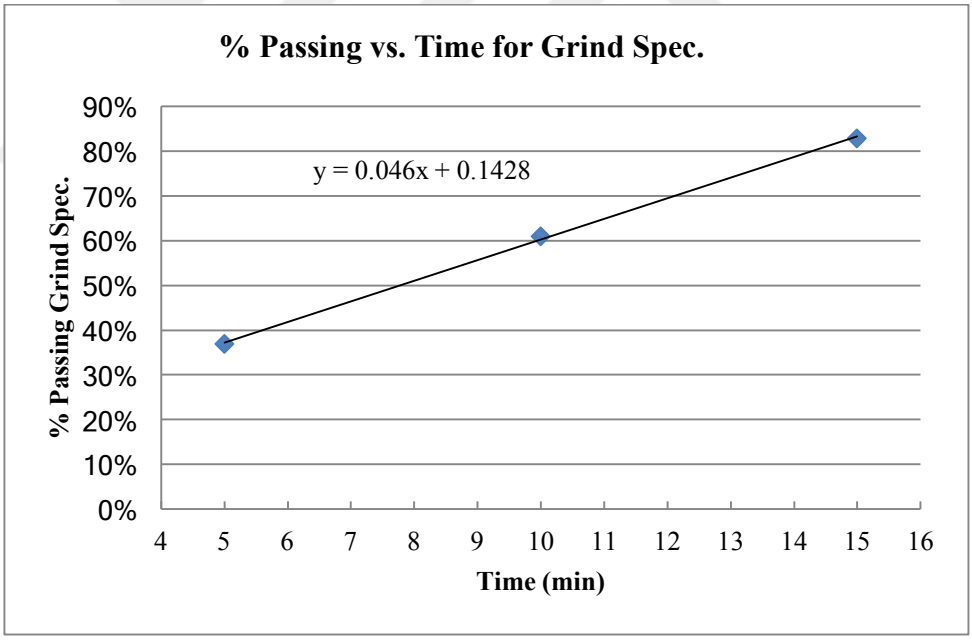

Figure 3.10 The cumulative passing size distribution slope as of grinding time

After all calculations completed, the % passing versus Time for Grind Specification graph is generated and the slope of y=0.046x + 0.1428 is found. Based on this equation, the grind time of 14.01 minute is found to achieve 80% passing 45 micron.

Table 3.3 The grinding time calculation to achieve required grind size

Mesh	Grind Spec.	Cumulative % Passing		
		5 min	10min	15min
	325	36.93%	60.88%	82.88%
% Passing	80.00%		Required time =	14.01

3.3 Froth Flotation Studies

The main goal of the flotation tests were to investigate the effect of different sulphide collector groups on Cu recovery and grade, as well as iron selectivity at different flotation parameters such as collector type, collector dosage, different pH, different frothers were also tests. In order to achieve this objective, design of experiment generated by using Plackett-Burman statiscical design method and the results were evaluated by using JMP 12 statistical software. A summary of the experimental design parameters are presented in table 3.4 below.

Table 3.4 Desing of experiment on Kure Copper ore

Collector Group	Collector Type	Collector Dosage (g/t)	Ph	Test No
Monothiophosphate Formulation	AERO 5688,AERO 6697 ,AERO 8761	25 40 55	10.5 vs 11.8	
Modified dithiocarbamate	AERO 900,AERO 945, AERO 915, AERO XD 702, AERO 7310			
Dithiophosphosphate formulation	Aerofroth 238, AERO 7249,AERO 9810			
Xanthate	PAX,PEX,SIBX,SIPX			
Dithiophosphinate	AEROPHINE 3410,AEROPHINE 3418,AEROPHINE 3420,AEROPHINE 3404			
Modified thionocarbamate	AERO5100,AERO XD 5002,AERO MX 5149,AERo 3894			
Mercaptobenzothiozole formulation	AERO 400,AERO 407,AERO 404			
7 variable	4 variable	3 variable	2 variable	162 TEST

The Equipment Used

Flotation is a quite complex separation process in practice as many scientific and engineering involves due to the utilization of surface properties of the minerals and gangue. There are numerous differenty types of flotation machine and equipment available in market. However, briefly, flotation equipment can be classified as mechanical and non-mechanical cells (Wills, 2006).

While mechanical cells use impellers (rotor and stator) in order to circulate the pulp and keep the solid suspended in the solution, non-mechanical cells do not have the impeller so they rely on compressed air to agitate the pulp. For instance, Denver and Wemco cells for mechanical cells, Jameson and column celss for non mechanical cells. Column cells use air sparger. But, the Jameson cell do not use both impeller or spargers (Wills, 2006).

In the flotation experiments, a Denver-12 mechanical flotation machine (Figure 3.11) with a 2 liter stainless steel flotation cell was used. The speed of impeller was adjusted to 1200 rpm held constant and the air flow rate was adjusted at 3.5 liter per minute on the air flow meter. The froths were manually skimmed every 15 second with n plastic blade and collected in a container. The flotation products were vacuum filtered, dried in an oven at 80ºC, weighted and then analyzed for Cu and Fe in order to calculate metallurgical balance.

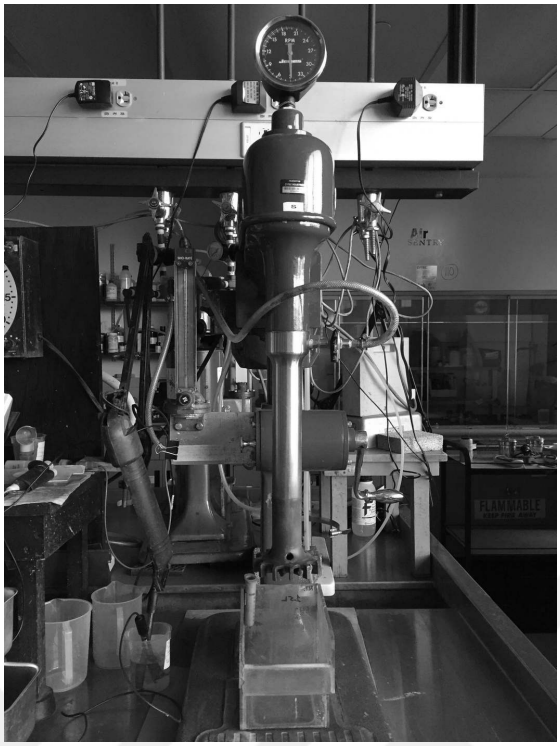

Figure 3.11 The Denver D12 flotation machine used in this study



Figure 3.12 Orion Star A111 pH Benchtop Meter from ThermoScientific

The pH adjustments were done by using Orion Star A111 pH meter as shown in Figure 3.12.

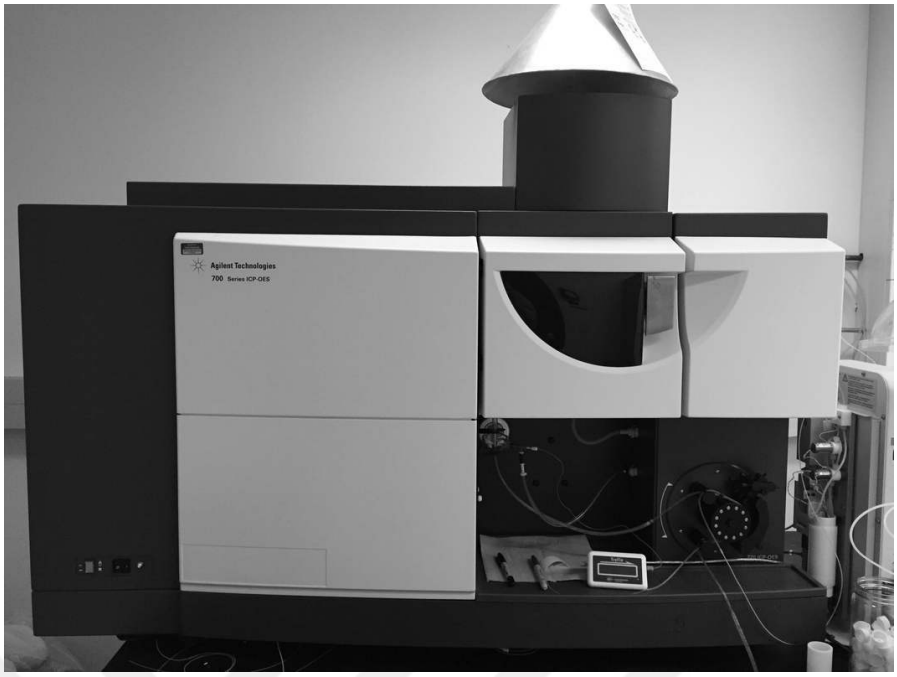

Figure 3.13 Agilent Technologies 700 Series ICP-OES

The chemicall anaysis of flotation products (feed, concentrate,tailing) are conducted by Agilent Technologies company's 700 Series ICP-OES device.

3.3.1 Pre-Diagnostic Study

A pre-diagnostic study of the flotation properties of Asikoy Kure Copper ore was conducted. The main objective of pre-diagnostic tests using multi-variate screening designs were to better understand the response of the ore, quickly screen ideas and products for feasibility, determine main effects, define meaningful ranges for treatment levels and provide direction for next stages. The main conclusion derived from this study was that the ore exhibited a strong natural floatability and fast kinetics.

Pre-diagnostic tests were completed with Hastafloat X-231 as a collector and DowFroth 250 as frother. Flotation tests were accomplished with the Denver flotation cell at 1200 rpm impeller speed and 3.5 psi air pressure. After grinding to the desired particle size, the pulp, with 500 g of sample weight and 30% solids, was transferred directly to the flotation cell with 2 liters volume. The conditioning time

was 10 minutes for the collectors and 2 minutes for the frother. Flotation time was 4+4+6 minutes after kinetic tests were run.

3.3.1.1 Particle Size and its Relation with Copper Recoveries

A number of ore charges were ground in a laboratory rod mill (shown in Figure 3.8). The size distribution for each grind time is determined and the time required to achieve the desired ore target grind 80% of material passing through 45 micron is determined by interpolation and by direct measurement. The size fractions generated during the grind test closest to the target grind to determine the distribution of the copper values as a function of size. The purpose of this determination is to target collector and frother selection not only in terms of mineralogy but also in terms of particle size distribution of minerals. It means that if the copper values are concentrated in coarse fraction one would select a collector and frother capable of floating coarse material, conversely, if the copper values concentrate in the fine fraction then collector and frother selection should take it into consideration this information.

Table 3.5 The copper recoveries and grades for three different grinding periods

Grinding	Concentrate			Tailing		
Time (min)	Cum % weight	Cum. Cu Grade.%	Cum. Cu Rec. %	Cum % weight	Cum. Cu Grade.%	Cum. Cu Rec. %
5	16.66	13.92	74.01	83.44	0.92	25.99
10	25.08	12.30	86.55	74.92	0.59	13.45
15	32.51	9.65	91.35	67.49	0.42	8.65

As can be seen in Table 3.5, depending on grinding time, size distribution will be affected and outcome of the test will be differenciated accordingly. Since grinding time of 5 minutes generated coarser particle distribution, 80% of material passing 90 micron, low cumulative copper recoveries obtain at 74.01% Cu. However, the same test condition was run by grinding time of 15 minutes please note that this number quite close to targeted grinding time which was calculated as 14.04 minutes of grinding – and reasonable recovery of 91.35% Cu achieved. This finding demonstated importance of liberation and the findings agree with reported literature

where the works conducted with similar ore body, minerolgy and gangue composition.

3.3.1.2 Flotation Kinetics Study

The kinetic study was conducted by employing the standart tests. In this test, reagent additions were made at the beginning of flotation and then five separate concentrates were collected in stagesoft 0.5, 1.5, 3.5, 7.5 and 15 minute intervals without any further reagent addition in each stage.

The purpose of flotation kinetic test is to determine the optimum batch flotation time and to determine the nature and association of the gangue components diluting the concentrates. Figure 3.14 illustrates that recovery increases until end of the circuit, the gangue componets is diluting the concentrate so that concentrate final grade will be decreased. Therefore, optimum flotation time needs to be determined depending on our recovery and grade objective.

Based on the flotation kinetic test conducted, flotation time of 12 minutes determined and three separate concentrates are collected during the rest of the test work with flotation times of 3+3+6 minutes, the remaining pulp material in the float cell is taken as tailing sample and filtered. Then, the samples allowed to dry in the oven for weighing. All three concentrates and tailing samples analyzed individually for Cu and total Fe.

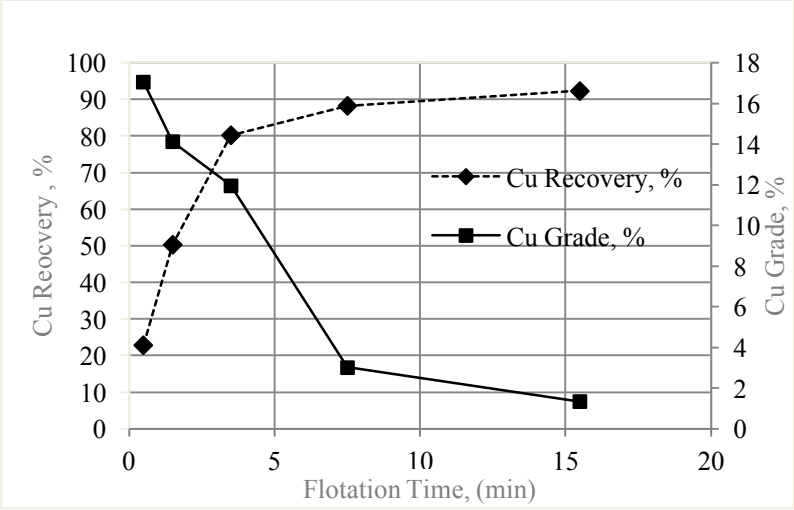

Figure 3.14 The flotation kinetic test Flotation time vs Cum Cu recovery plot

3.3.2 Effect of pH

Three different pH levels were studied while other parameters were held constant. The pH of the pulp was adjusted to the desired level by addition of slake lime to the grind. Finer pH adjustments were made after putting the ground pulp in the float cell. After pH adjustment, desired amounts of collector HOSTAFLOAT X-231 (42 g/t), DOWFROTH 250 (15 g/t) frother additions were made in stages as shown in the proceeding table below and pulp was conditioned for one minute after each addition of reagents.

Table 3.6 The Cu and Fe recoveries and grades for three different pH levels.

pH	Cu Recovery, %			Fe Recovery, %			Cum. Grade, %	
	C1	C2	C3	C1	C2	C3	Cu	Fe
9	83.95	90.00	92.54	24.71	32.88	40.68	8.91	34
10.5	82.33	89.11	92.85	21.89	29.18	36.24	8.78	32.4
11.8	83.06	89.11	92.22	19.30	25.90	31.84	9.35	31.14

The general test procedure of flotation test work can be seen in Figure 3.15.

Project:	Asikoy Cu Ore											Test #:	
Account:													
Operator:	Orkun Yavuzkan											Date:	
Equipment & Constants		Product		Weight (g)									
Ore	AsikoyBlend	Initial			%	Cum%	Frother:	DOW250					
Rolls	b	Conc.1											
Rod Mill:	A	Conc.2					STD Cu Collector						
Solids		Conc.3											
Rod charge	8.5 Kg.	Tails					Coll Addn	Cell					
QZNE spec.		Total		0.00			Fro Addn	Cell Only					
Our Grind:	14.04												
Ore charge	500 gr								Collector	Frother			
Water	325 Mls.	Stage	Time	pH		lime						Con wt	Dry wt
Denver machine			(min.)	target	actual	gms.			HOSTAFLOAT X-231	DOWFROTH 250		(gr)	
Rpm:	1100	Grind	14.04	11.8		1.25							
Cell:	1.5 (L)	Cond.1	1.0						21 g/t				
Pulp Level:	1"	Cond.2	1.0							15 g/t			
		Flot.1	4.0								C-1+W		
		Cond.3							10.5 g/t				
		Cond.4	1.0							7.5 g/t			
		Flot.2	4.0								C-2+W		
(from lip)		Cond.5	1.0						10.5 g/t				
AIR (LPM)	3.5	Cond.6	1.0							(as required)			
Head Assay:		Flot.3	6.0								C-3+W		
Total Cu=	3.41%	Observations:											
Mo=													
Fe=	28.10%	C1											
Natural pH	~7.8	C2											

Figure 3.15 The general test procedures of flotation test work

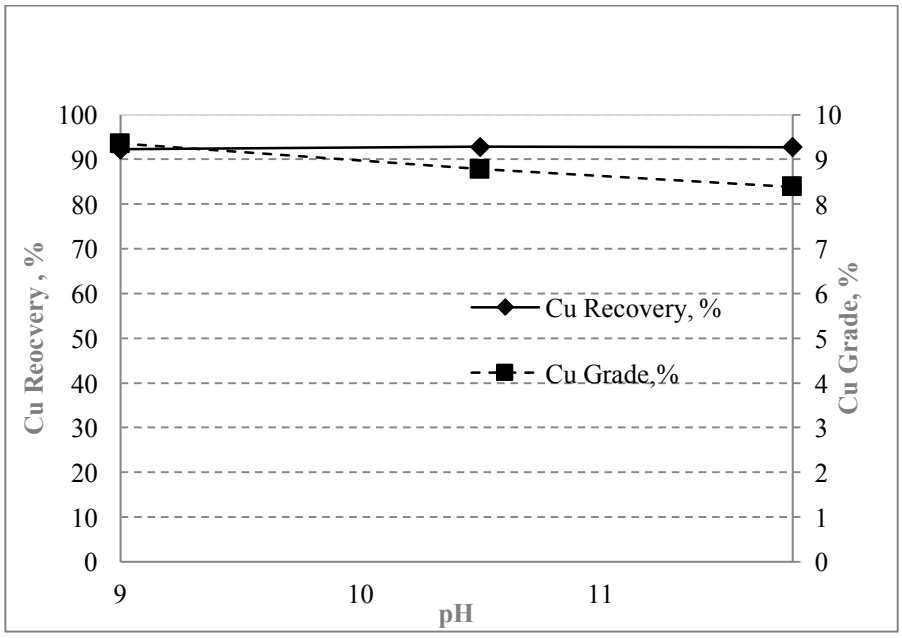

Figure 3.16 The cumulative Cu recoveries and grades for different pH levels

As shown in figures above and below, the iron recovery affected by pH changes as expected. At pH 9, Fe recovery was 40.68% while Cu recovery is 92.54%. At pH 11.8, similar performance obtained in terms of Cu recovery and Cu recoveries remained almost the same. However, significant changes observed on the iron recovery. The recovery of iron was 31.84%. The copper final concentrate grade was also slightly restored with higher pH at 11.8.

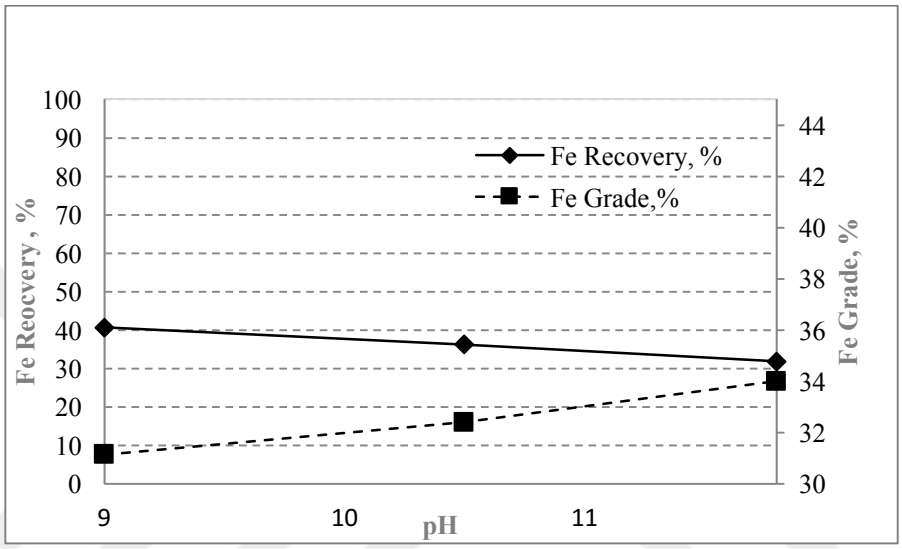

Figure 3.17 The cumulative Fe recovery and grades for different pH levels

3.3.3 Effect of Collector Type

As discussed in Chapter 1, the impact of collector/reagent type to the froth flotain is very tremendous. Reagent dosage and type of collector are very curicial factors that affect performance of separation. The recovery and grade of the final concentrate, overall metallurgical performance depends on various parameters such as pH, dosage of collector, type of collector, adsorbtion capabilities of collector on particles.

The main objective of this section is to analyze the generated data during flotation tests by statistical software in order to differenciate the effect of reagent type. In this section, all collector groups discussed and its data analyzed individually.

Based on pre-diagnostic test conducted prior flotation tests, responsiveness of the ore to the various parametetes evaluated, main effects were determined, and meaningful ranges fpr levels defined. Based on the pre-diagnostic tests, more focused experimental design generated and Laboratory flotation tests were conducted in accordance with the procedure prescribed as shown below.

Ores used:	Asikoy Cu Ore
Charge:	Approximately 500 gr
Grinding:	60% solids
Grinding Time:	14.04 minutes
Particle Size:	20% + 325 mesh (45μm)
Machine:	Denver D-12 flotation machine set at 1200 RPM
pH:	10.5 vs 11.8
Std Collector:	Hostaflot X-231 (42 g/t) + PAX (5 g/t)
Frother:	Dowfroth 250
Activator:	None
Flotation Time:	Rougher I :4 min Rougher II: 4 min Rougher III: 6 min

3.3.3.1 Effect of Monothiophosphate Formulations

Effect of monothiophosphate type collectors were investigated on Asikoy Cu ore. A number of Cytec collectors namely AERO 5688, AERO 6697, AERO 8761 promoters are tested as Cu collectors. The Reagent screening tests have been conducted with these reagents at the standard conditions described earlier and performances are compared to the standard. The list of reagents along with dosage and pH information are in Table 3.7.

Table 3.7 Tabulated version of test design for Monothiophosphate formulations

	COLLECTOR															
	AERO 5688				AERO 6697				AERO 8761				STD			
	Dosage (g/t)		pH		Dosage (g/t)		pH		Dosage (g/t)		pH		Dosage(g/t)		pH	
Coil Type	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max
Monothiophosphate formulation	25	55	10.5	11.8	25	55	10.5	11.8	25	40	10.5	11.8				
Thiocarbamate formulation													42	42	11.8	11.8

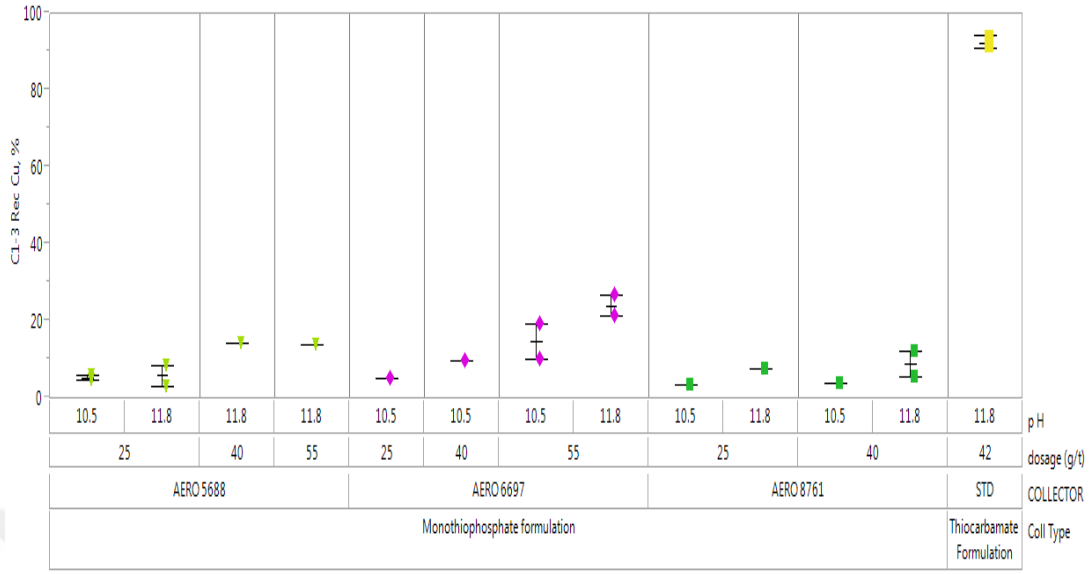

Figure 3.18 The variability chart for Cu recovery of each Monothiophosphate type collector

This series allowed thirteen different test comparison (pH and Dosage) combinations between the tests AERO 5688, AERO 6697, AERO 8761 and standard (Hostafloat X-231 (42 g/t) + PAX (5 g/t)) as shown in figure 3.19. Taking the all available results into consideration, Hostafloat X-231 + PAX combination produced better performance than other three reagents in direct comparison. The best results obtained at 94.71% Cu recovery with standard while the grade of final concentrate was 10.27% Cu. As expected, the monothiophosphate type of collector did not give promising metallurgical results. The plotted data in figure 3.19, agrees with the information available in literature as the monothiophosphate type collectors derived from dithiophosphate by replacing one of the sulfur atom with oxygen. This replacement results changes in electon distribution on the donors. Therefore, the complexation and absortion properties of monothiophosphates are affected. As a result of that, the monothiophosphates are true acid-circuit collectors for sulfide minerals. The results generated with AERO 6697 at ph 11.8 and at dosage of 55 g/t. was the Cu recovery and grade of 26.89% Cu and 14.82% Cu, respectively.

In this series, replicate tests were run as well in order to see reproducibily and good reproducible data is generated.

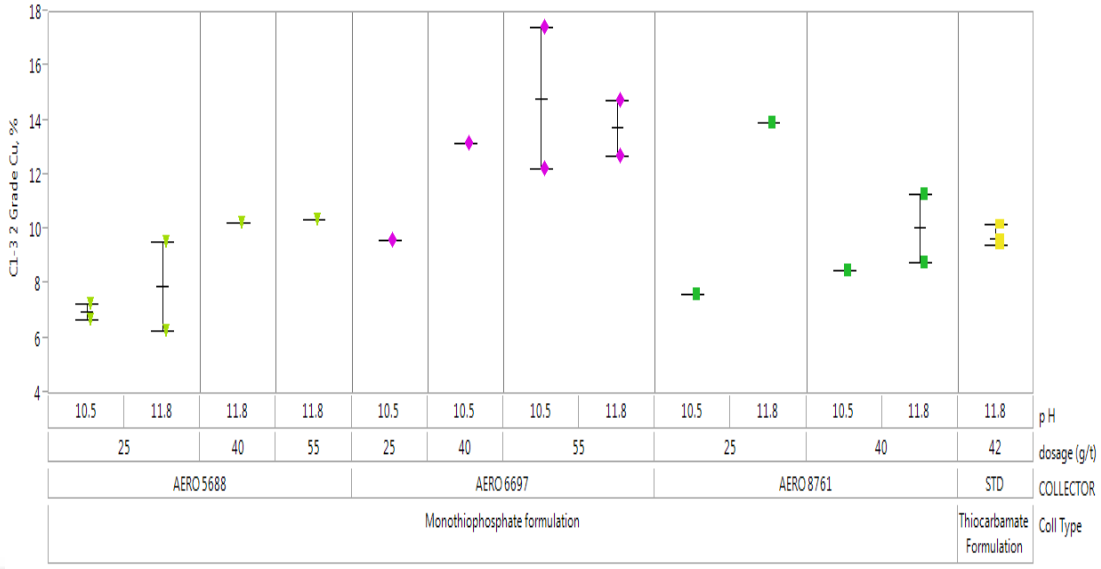

Figure 3.19 The variability chart for Cu grade of each Monothiophosphate type collector

3.3.3.2 Effect of Modified Dithiocarbamate Formulations

In this series, effect of modified dithiocarbamate formulation group of collectors were investigated. A number of Cytec collectors namely AERO MX 900, AERO 915, AERO 945 promoters are tested as Cu collectors and metallurgical test results from these tests compared with thionocarbamate based collector (Hostaflot X-231 (42 g/t) + PAX (5 g/t)).

The test results were analyzed using JMP statistical software and variability charts for Cu recovery & grade are shown in Figure 3.20 and 3.21. A cursory glance at these charts seems to indicate the following:

Total Cu recovery is limited to 79.17-92.75% when AERO MX 900 is used. (see Figure 3.21). Using a higher collector dosage (55 g/t AERO MX 900) yielded 92.76% total Cu recovery. When comparing with the other modified dithiocarbamate collector, AERO MX-900 achieved promising results at this level of recoveries. As noted earlier, standard collector Hostaflot X-232 + PAX combinations achieved average Cu recovery of 92.61% while the overall average Cu grade was 9.73%.

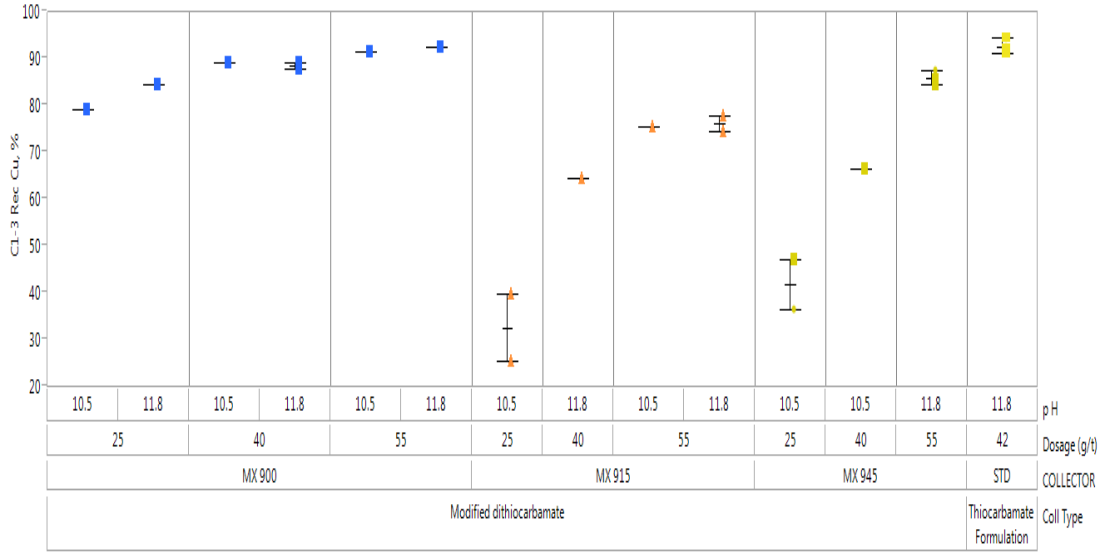

Figure 3.20 The variability chart for Cu recovery of each modified dithiocarbamate collector

The use of AERO MX-915 did not give better metallurgical performance comparing to STD and AERO MX 900 at any dosage or pH level. Based on variability chart in figure xx, the best recovery performance obtained at 55 g/t of AERO MX 915 and the recovery of Cu was 77.87% while the grade is 16.00% Cu. This test run in duplicates and it clearly indicates that tests were highly reproducible. The duplicate test generated similar performance and the copper recovery was 75.8% for Cu and the final concentrate grade was 15.6% of Cu.

AERO MX 945 Promoter, as the last reagent tested from modified dithiocarbamate formulation group of collector evaluated in duplicates. AERO MX 945 Promoter alone produced 87.64% 23 and 84.82% copper recoveries with 12.54% Cu in Con1 and 13.12 % Cu, respectively at ph 11.8 and at the dosage of 55 g/t. AERO MX 945 generated slightly higher final contcenrate grade comparing to STD. This is further supported by visual observations during testing where the froth phase appeared to be relatively clean when AERO MX 945 is used.

The overall Cu final concentrate grades are provided in variability chart below in figure 3.22. As can be seen from these results, AERO MX 900 singly produce quite acceptable results comparing to the standard collector combination.

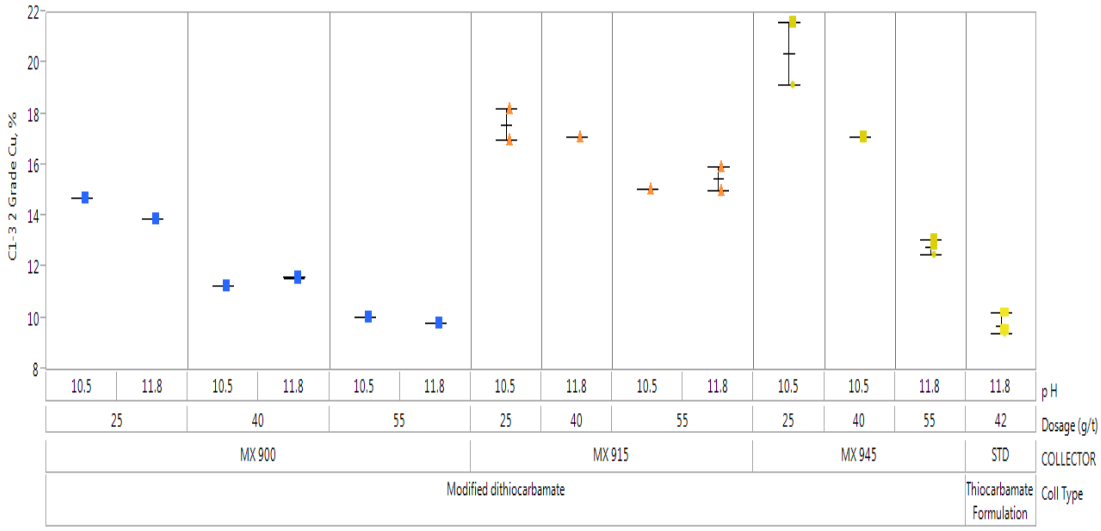

Figure 3.21 The variability chart for Cu grade of each modified dithiocarbamate collector

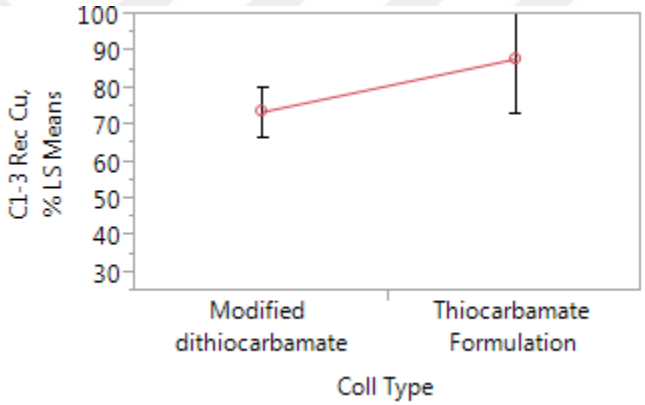

Figure 3.22 The comparison chart for Cu recovery of each modified dithiocarbamate and Thionocarbamate formulation

3.3.3.3 Effect of Xanthate Formulations

The effect of xanthate group collectors were investigated with two different level of pH (at 10.5 and 11.8) and three dosage level (25 g/t – 40 g/t – 55 g/t). The other variables held constant. Based on metallurgical balance, the variability chart for Cu recovery and grade is plotted as Figure 3.23 and 3.24.

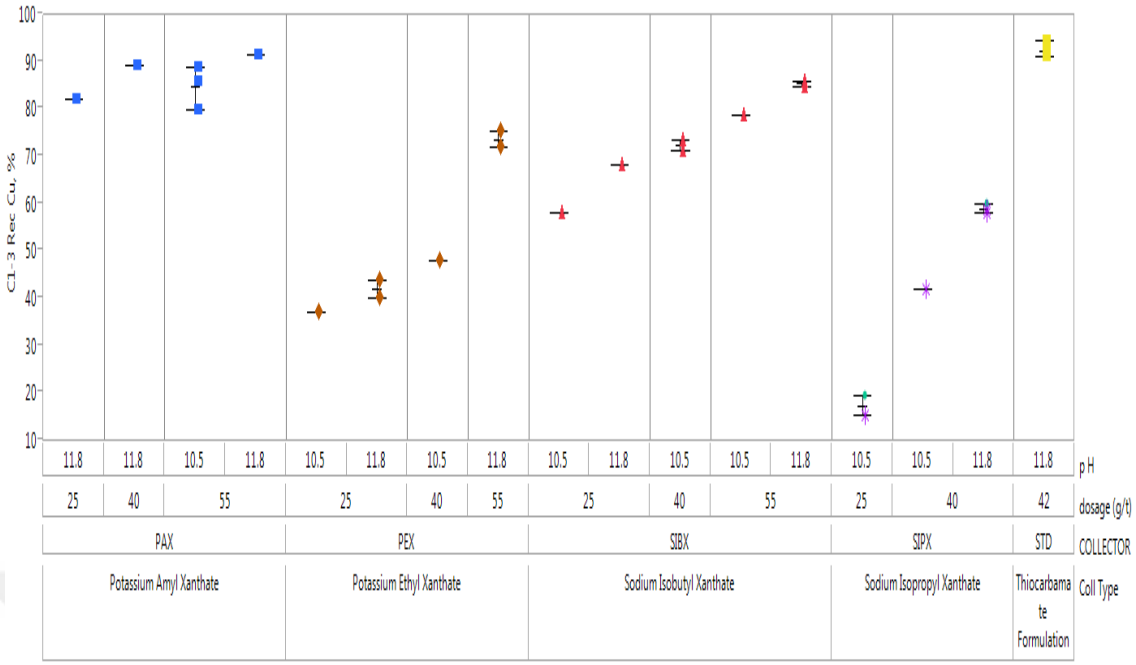

Figure 3.23 The variability chart for Cu recovery of each Xanthate type collector

The plotted variability chart above shows that Potasium Amly Xanthate generated notiable Cu recoveries ranging from 80.31-91.63% while final concetrade grades ranging between 10.23 – 15.27% for Cu. These results accepted as a reasonable metallurgical performance. On the other hand, this performance fits well with literature findings as Potassium Amly Xanthate is strongest but the least selevtive type of xanthate collector due to its chain length comparing to other types.

Sodium Isobutly Xanthate - SIBX, alone produced 85.1% and 86.26% copper recoveries with 21.91% Cu in Con1 and 18.72% Cu in Con2, 13.92% Cu in Con3 and 22.69% Cu in Con1, 17.94% Cu in Con2 and 13.28% Cu in Con3, respectively at pH 11.8, at dosage of 55 g/t.

Sodium Isoproply Xanthate – SIPX, did not generate competive results as expected. SIPX is not a strong xanthate due to its short chain length which makes it less strong but slighlt more selective. Based on variability chart below for overall final Cu concentrade grade, SIBX produced final Cu concetrade grades varied from

16.92% - 22.28%. The overall copper recoveries averaged around 60% (+/- 1%) with exceptional rougher grades ranging from 17.2% to 20.63%.

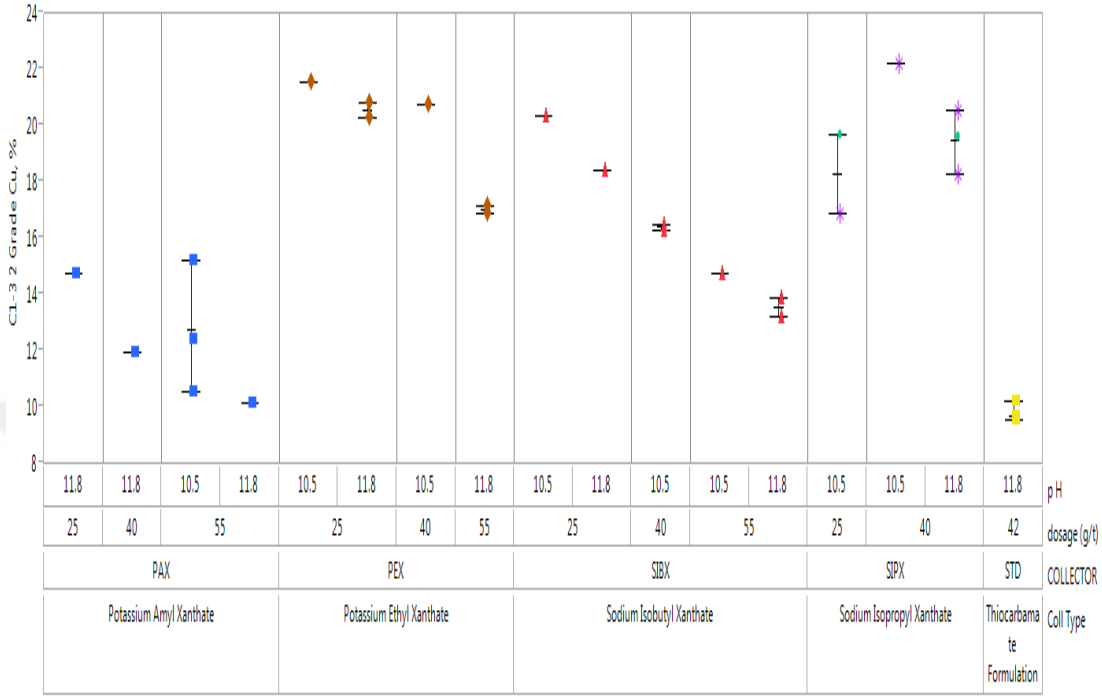

Figure 3.24 The variability chart for grade of each Xanthate type collector

The overall recovery grade profiles for all Potassium Ethly Xanthate – PEX tests are provided in figure 3.24, which shows relatively poor performance with PEX at dosage of 25 g/t and 40 g/t, both high/low pH as compared to that of PAX (91.63% Cu)

3.3.3.4 Effect of Dithiophosphinate formulations

The effect of Dithiophosphinate group collectors were investigated. AEROPHINE 3404, AEROPHINE 3410, AERPHINE 3416, AEROPHINE 3418 and AEROPHINE 3420 were evaluated and compared with thionocarbamate based collector (Hostaflot X-231 (42 g/t) + PAX (5 g/t)) combination.

The overall grade recovery profiles for all collectors plotted in Figure 3.25 and 3.26. As can be seen easily, a high collector dose gave high Cu recovery but.

Total Cu recovery is limited to 35.28-41.96% (see Figure 3.25) when AEROPHINE 3404 used at dosage of 25g/t and 40 g/t, respectively. Using a higher collector dosage (55 g/t) AEROPHINE 3404 still yielded only 53.46% total Cu recovery.

The Cu recovery of 50.48% and 48.76% achieved when 25 g/t AEROPHINE 3410 tested at ph 10.5. Relatively higher Cu final concentrade grade obtained 19.57% Cu and 20.24%, respectively. Please remember that these two tests were run in duplicate so again, reproducibility is quite high. The best results achieved with high dosage at 55 g/t and 91.36% Cu recovery achieved. This value is quite acceptable when we consider average recovery value with STD.

The duplicate tests were run with AEROPHINE 3416 to compare its performance with STD in terms of Cu metallurgy. At the dosage of 55g/t, average Cu recovery of 85.34% obtained at grade of 13.65%.

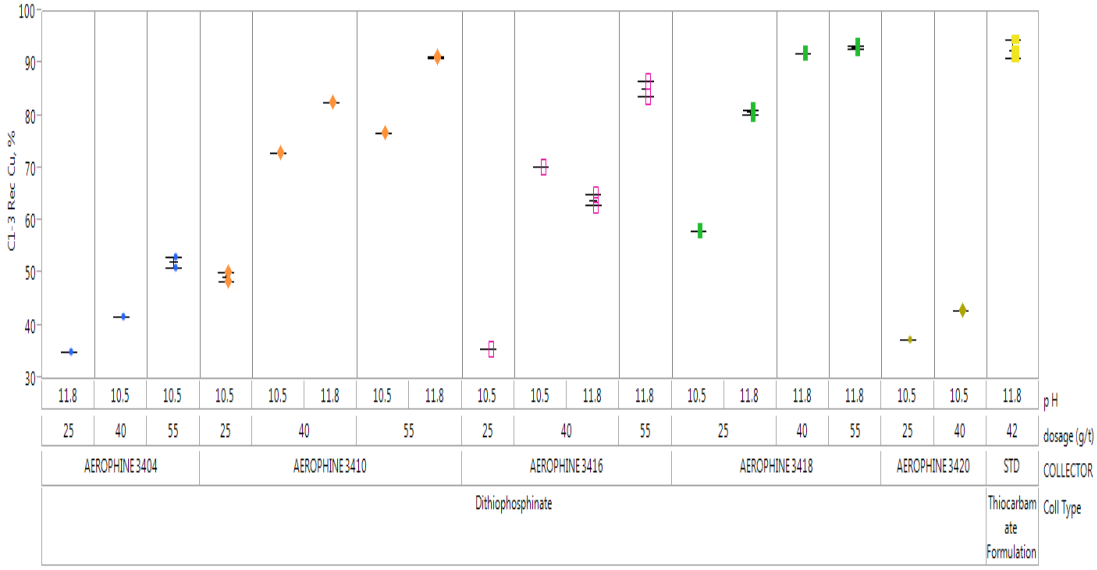

Figure 3.25 The variability chart for Cu recovery of each Dithiophosphinate collector

The overall best performance in terms of Cu recovery and grade achieved by AEROPHINE 3418A at the dosage of 55 g/t with Cu recovery of 93.03% and final concetrade grade of 9.52%. the effect of ph was quite clear when AEROPHINE 3418A tested at low dosage (25 g/t). the recovery of Cu was only 58.18 when ph kept

at 10.5. however, with increase in Ph resulted dramatic change and Cu recovery of 81.45% achieved and grade of 15.13%.

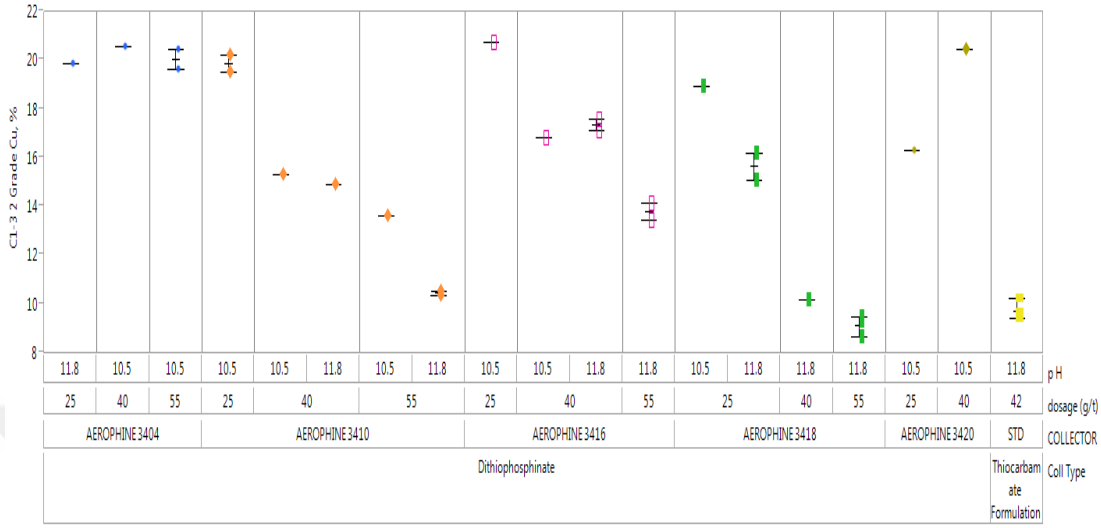

Figure 3.26 The variability chart for Cu grade of each Dithiophosphinate collector

3.3.3.5 Effect of Thionocarbamate Formulations

The effect of thionocarbamate group collectors was investigated. A collector of chooise, namely, AERO 3894, AERO 5100, AERO MX 5149 and AERO XD 5002 were tested at three level of dosage (25 g/t – 40 g/t – 50 g/t) and two level of pH (10 and 11.8).

Based on tests conducted with AERO 3894, the Cu recovery of 73.27% and final Cu concentrate grade of 15.58% obtained at dosage of 25 g/t at pH 10. This performance is expected based on visual observation during the testing showed that froth phase is appeared to be relavitely week due to low dosage of collector. In general, high ph (i.e 11.8) and high dosage (i.e 55 g/t) normally yielded higher Cu recovery which is expexted. The recovery of 89.44% for Cu obtained when pH is 11.8 at dosage of 25g/t. The concentrade grade was 11.97% for this test.

AERO 3894 produced a final copper concentrate containing 10.22% of total copper at 89.12% Cu recovery AERO 5100 gave quite good flotation kinetic during the test work. As can be seen in figure 3.27, AERO 5100 consistently showed high

recoveries (or at least similar) over other tested reagents in almost all treatment conditions. AERO 5100 produced a Cu recovery of 94.11% and 94.14% and concentrate containing 8.56% and 8.62% of Cu, respectively.

The performance of AERO MX 5002 was slightly lower comparing to AERO 5100 and STD. The best result produced with the Cu recovery of 88.69% at concentrate grade of 10.96%.

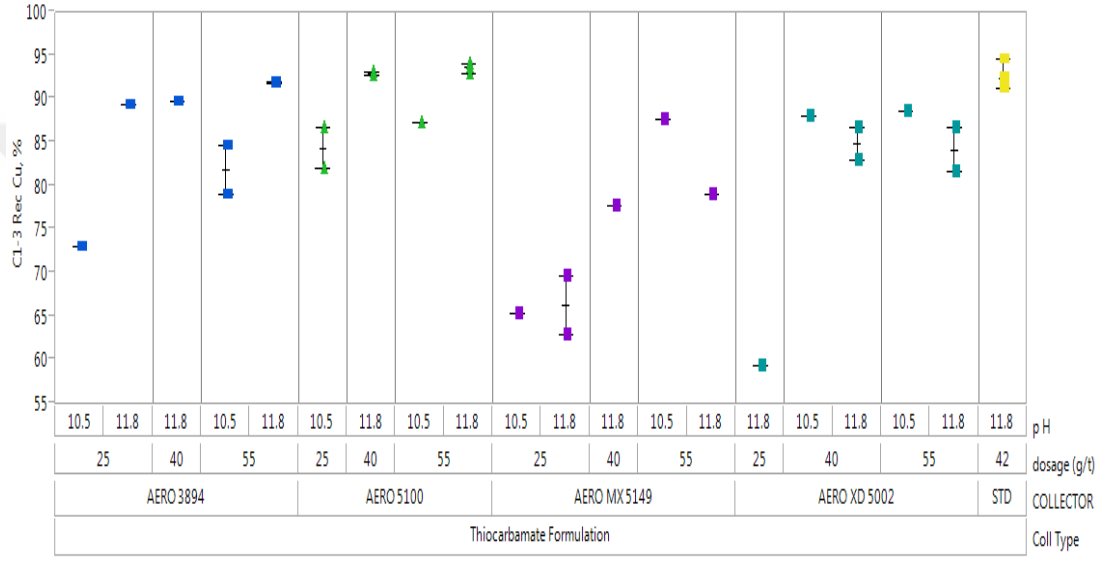

Figure 3.27 The variability chart for Cu recovery of each Thionocarbamate formulated collector

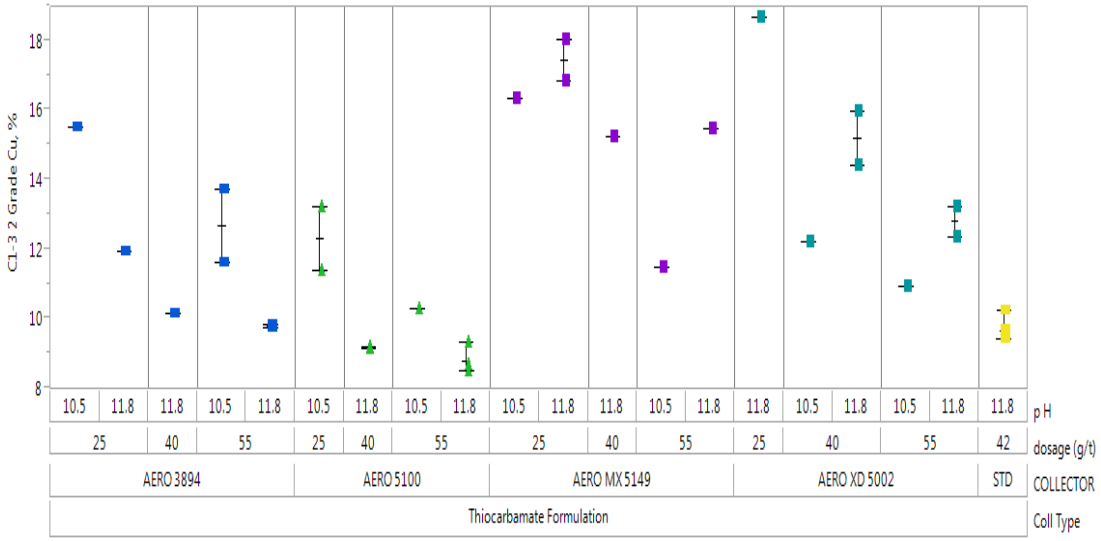

Figure 3.28 The variability chart for Cu grade of each Thionocarbamate formulated collector

3.3.3.6 Effect of Dithiophosphate Formulations

The effect of thionocarbamate group collectors was investigated with a number of collectors of chooise namely, AERI 7249, AERO 9810, AEROFROTH 238 and AERO 7310. Numerous tests conducted with these collectors, metallurgical balance calculated and the variability chart for recovery and grade plotted as shown in figure 3.28.

AERO 7249 gave superior Cu recovery performance at 55g/t and pH 10.5 over other CYTEC collectors. The overall Cu recovery was 80.85% and 81.07%. This results show that reporudcibity was also very good for this tests. When we compare the results with Thionacarbamate formulation (HASTAFLOAT X-231), STD condition showed better performance over all reagants.

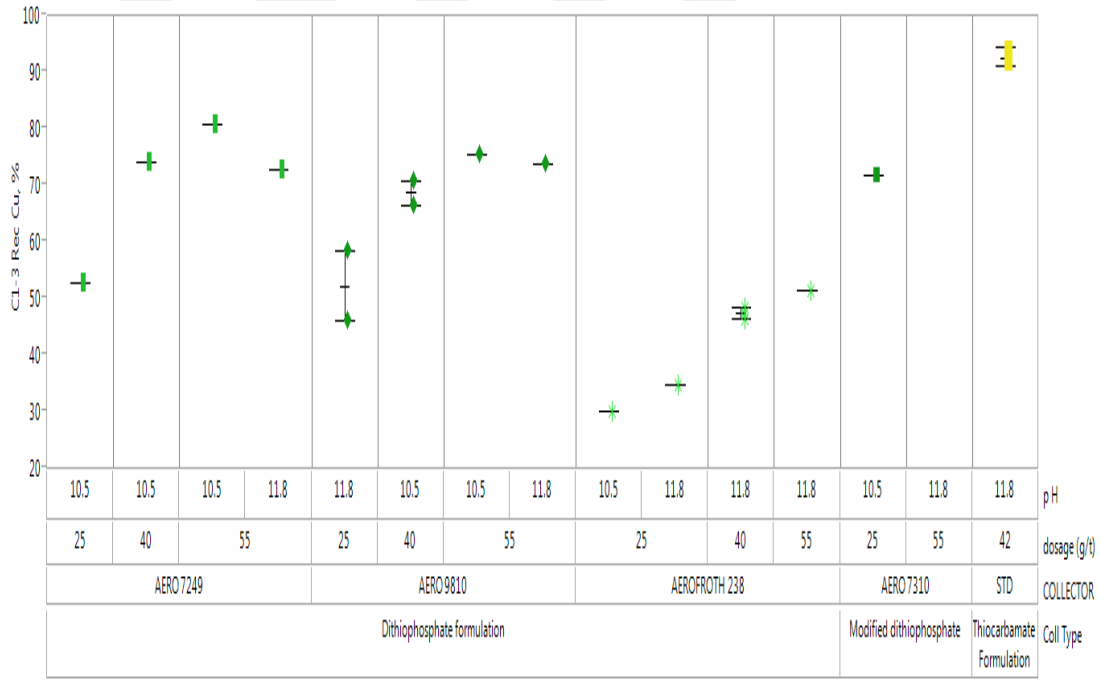

Figure 3.29 The variability chart for Cu recovery of each Dithiophosphate formulated collector

The cumulative Cu grade with AERO 7240 (55 g/t – at pH 10.5) was 16.0%. The cumulative Cu grade when STD conditions employed was 9.64%. As shown in the variability chart as below, the data suggested that AERO 7249 is more selective than HASTAFLOAT X-231 and generated cleaner concentrate.

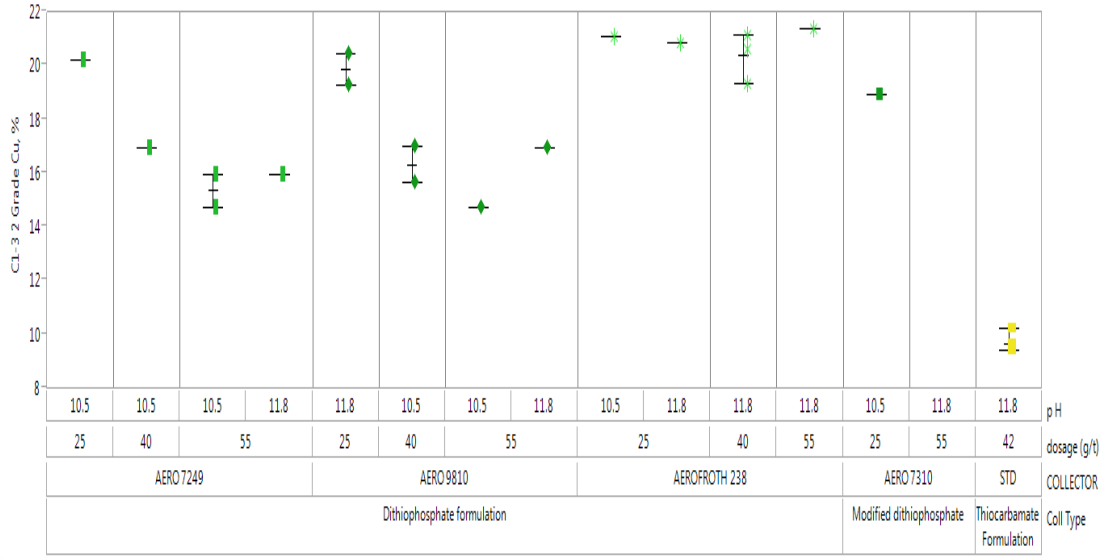

Figure 3.30 The variability chart for Cu grade of each Dithiophosphate formulated collector

3.3.3.7 Effect of Mercaptobenzothiozole Formulations

The effect of Mercaptobenzothiozole group collectors on Kure Cu ore was investigated. A collector of chooise, namely, AERO 400, AERO 404, AERO 407 and AERO 412 were tested at three level of dosage (25 g/t – 40 g/t – 55 g/t) and two level of pH (10 and 11.8).

As can be seen from the variability charts below; effect of dosage and pH is easly noticeable. The cumulative Cu recovery was 68.19% at 55 g/t and pH 11.8 when AERO 400 tested while the recovery of Cu dropped to 46.99% at pH 10.5. Similar trends have seen with all mercaptobenzothiozole group collectors. When pH is at 10.5, cumulative Cu recovery was lover comparing to pH 11.8.

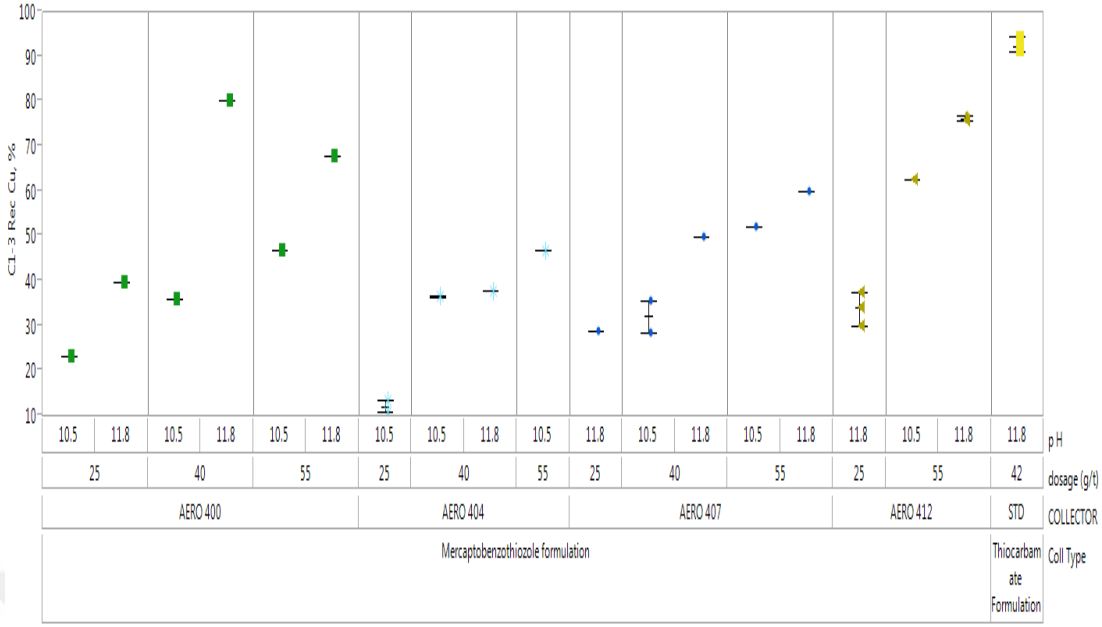

Figure 3.31 The variability chart for Cu recovery of each Mercaptobenzothiozole type collector

The cumulative Cu grades were nit affected as much as recoveries did. The dosage of collector and pH did not show any dramatic effect on Cu grade values.

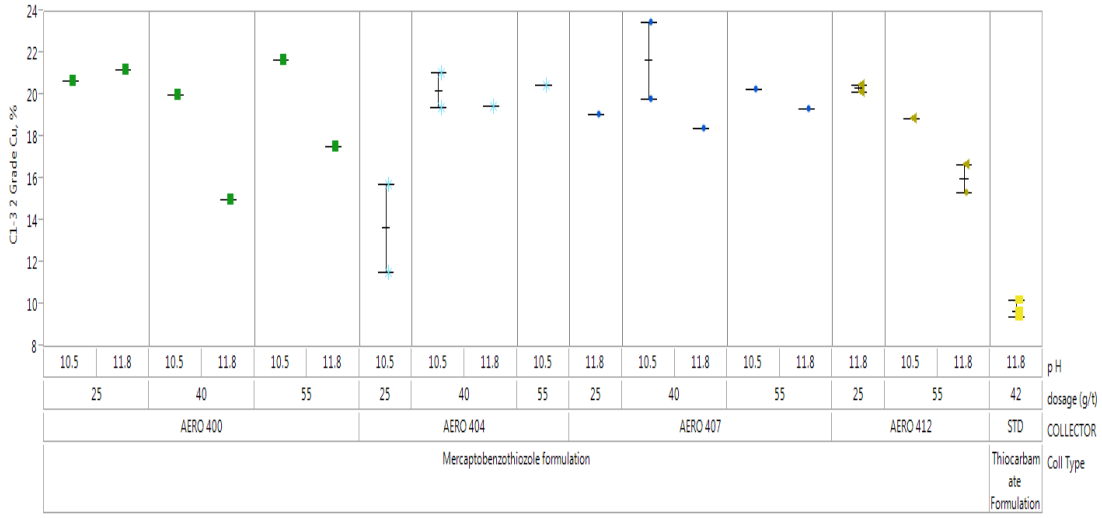

Figure 3.32 The variability chart for Cu grade of each Mercaptobenzothiozole type collector

CHAPTER FOUR
RESULTS AND DISCUSSION

In this study, comprehensive laboratory test work program was undertaken. The main objective of this work was to evaluate effect of different flotation collectors based on their chemistry class. A number of Cytec collectors (24) are selected as potential collectors and have been evaluated to determine if these collectors could provide improved metallurgy in comparison to the operation standard HASTAFLOAT X-231. In order to evaluate the performance and effect of collectors, the design of experiment is generated and test work is conducted.

Before starting the test work, diagnostic tests were conducted using multi-variate screening designs to better understand the response of the ore, quickly screen ideas and products for feasibility, determine main effects, define meaningful ranges for treatment levels and provide direction for next stage test work. The pH of 9, 10.5 and 11.8 is investigated to see effect of Ph on Cu and Fe recovery. The screening tests showed that higher pH did not show any effect on cumulative Cu recovery while Fe recovery effected slightly. Therefore, it is decided to contunie the test work by running the remaining tests at pH 10.5 and 11.8.

As a variable, the effect of particle size to see Cu and Fe recovery performance is studied. The size fractions generated during the grind test closest to the target grind to determine the distribution of the copper values as a function of size. The purpose of this determination is to target collector and frother selection not only in terms of mineralogy but also in terms of particle size distribution of minerals. It means that if the copper values are concentrated in coarse fraction one would select a collector and frother capable of floating coarse material, conversely, if the copper values concentrate in the fine fraction then collector and frother selection should take it into consideration this information. The best cumulative Cu recovery achieved with 15 min grind at 91.35% Cu recovery. The cumulative Cu grade was 9.65% for the test.

The kinetic tests were run to determine the batch flotation time and to see the

nature and asassociation of the gangue components diluting the concentrates. The optimum flotation time determined as 12 min. The concentrate was diluting by gangue components in expense of little improvement of Cu recovery. Therefore, the floatation time did not extended in order to keep the cumulative concentrate grade at reasonable level.

In experiment design, collector dosage (g/t), pH (10.5 vs 11.8) and collector types are taken into consideration. Monothiophosphate formulations, Modified dithiocarbamate formulations, Xanthates, Dithiophosphinates, Thionocarbamate formulations, Dithiophosphate and Mercaptobenzothiozole formulations evaluated. Based on results, AEROPHINE 3418A from Dithiophosphinate formulations, AERO 5100 from Thionocarbamate formulations achived good metallurgical results comparing to HASTAFLOAT X-231 and Cu recovery of 93.03% and 94.11% achieved while concentrate grade was 9.52% and 8.56% of Cu, respectively. The effect of collector choise depending on collector type, particle size, pH differences and dosage plays important role on achieving targeted metallurgical results. Monthiophosphate formulations did not show any promising results at high pH and Dithiophosphinate formulations achieved similar or higher Cu recovery.

CHAPTER FIVE
CONCLUSION

In conclusion, a comprehensive test work is conducted to investigate effect of different sulphide collectors to improve recovery of Kastamonu Kure Cu ore.

A series of experimental designs were completed. Collector type, collector dosage, pH, the effect of particle size included to the work and kinetic work were complete to see natural floability of the Kure Cu ore.

The optimum flotation test parameters for target recovery and grade were as of particle size (p80) -45 micron, Ph (11.5-11.8), 12 minute of flotation time, AEROPHINE 3418A and AERO 5100 as flotation collector at 55 g/t, DowFroth 250 as frother. The cumulative Cu recovery of 93.03% and the cumulative Cu grade of 9.52% is achieved when AEROPHINE 3418A is used as a collector. Overall the average for the company standard, HASTAFLOAT X-231 was 92.58% for cumulative Cu recovery and 9.72% cumulative Cu grade.

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APPENDICES

APPENDIX-1: Metallurgical balanca calculation of Monothiophosphate formulation test work

Collector	Coll Type	Dosage (g/t)		Cum. Wt.%					Calc.	Cum. Cu Rec.%			Cum. Grades		
			p H	C1	C2	C3	T	Total	Head	C1	C1-2	C1-3	C1	C1-2	C1-3
AERO 5688	Monothiophosphate formulation	25	10.5	1.2	2.3	3.1	96.9	100.0	3.43	2.66	4.48	6.21	7.39	6.80	6.77
AERO 5688	Monothiophosphate formulation	25	11.8	0.6	1.2	1.8	98.2	100.0	3.38	1.34	2.34	3.46	8.01	6.82	6.32
AERO 6697	Monothiophosphate formulation	55	11.8	3.2	4.6	5.8	94.2	100.0	3.37	12.66	17.59	21.80	13.54	12.93	12.75
AERO 8761	Monothiophosphate formulation	40	10.5	0.5	0.9	1.7	98.3	100.0	3.36	1.64	2.71	4.29	11.22	9.64	8.57
AERO 6697	Monothiophosphate formulation	55	10.5	0.7	1.6	3.0	97.0	100.0	3.47	2.10	5.49	10.45	10.78	11.57	12.27
AERO 8761	Monothiophosphate formulation	40	11.8	1.0	1.7	2.3	97.7	100.0	3.36	2.89	4.41	5.98	9.57	8.90	8.86
AERO 6697	Monothiophosphate formulation	25	10.5	0.8	1.3	1.8	98.2	100.0	3.37	2.10	3.31	5.23	9.03	8.75	9.67
AERO 5688	Monothiophosphate formulation	55	11.8	2.1	3.4	4.7	95.3	100.0	3.45	5.98	9.69	14.22	9.79	9.89	10.40
AERO 5688	Monothiophosphate formulation	25	10.5	0.8	1.5	2.2	97.8	100.0	3.41	1.51	3.27	4.82	6.59	7.50	7.31
AERO 5688	Monothiophosphate formulation	40	11.8	2.6	4.0	5.0	95.0	100.0	3.47	7.07	11.15	14.75	9.29	9.77	10.31
AERO 6697	Monothiophosphate formulation	55	10.5	1.4	2.6	3.9	96.1	100.0	3.47	6.11	12.28	19.46	15.45	16.69	17.46
AERO 8761	Monothiophosphate formulation	40	11.8	2.0	2.8	3.8	96.2	100.0	3.48	5.97	8.49	12.48	10.16	10.53	11.34
AERO 6697	Monothiophosphate formulation	55	11.8	3.5	4.8	6.2	93.8	100.0	3.44	12.52	19.23	26.89	12.22	13.65	14.82
AERO 5688	Monothiophosphate formulation	25	11.8	1.2	2.2	3.0	97.0	100.0	3.38	3.49	5.92	8.65	9.47	9.13	9.61
AERO 6697	Monothiophosphate formulation	40	10.5	1.0	1.8	2.5	97.5	100.0	3.38	3.27	6.30	9.86	11.50	12.10	13.24
AERO 8761	Monothiophosphate formulation	25	10.5	0.6	1.1	1.6	98.4	100.0	3.39	1.46	2.43	3.60	7.94	7.56	7.69
AERO 8761	Monothiophosphate formulation	25	11.8	1.0	1.6	2.0	98.0	100.0	3.44	3.42	5.53	8.03	11.57	12.02	13.95

APPENDIX-2: Metallurgical balanca calculation of Modified dithiocarbamate test work

Collector	Coll Type	Dosage (g/t)	p H	Cum. Wt.%					Calc.	Cum. Cu Rec.%			Cum. Grades		
				C1	C2	C3	T	Total	Head	C1	C1-2	C1-3	C1	C1-2	C1-3
AERO MX 945	Modified dithiocarbamate	25	11	4.0	6.3	7.8	92.2	100.0	3.55	28.04	41.09	47.34	24.67	23.02	21.64
AERO MX 945	Modified dithiocarbamate	55	12	11.8	16.5	22.9	77.1	100.0	3.46	67.88	77.86	85.51	19.98	16.37	12.94
AERO MX 915	Modified dithiocarbamate	25	11	2.5	5.4	7.5	92.5	100.0	3.44	13.41	29.24	39.98	18.20	18.53	18.24
AERO MX 915	Modified dithiocarbamate	40	12	5.5	8.9	13.2	86.8	100.0	3.52	32.72	50.09	64.51	21.06	19.85	17.17
AERO MX 900	Modified dithiocarbamate	40	11	11.7	19.8	26.9	73.1	100.0	3.39	68.95	83.74	89.44	20.06	14.36	11.31
AERO MX 900	Modified dithiocarbamate	55	11	13.5	22.4	31.4	68.6	100.0	3.47	72.27	85.55	91.50	18.62	13.24	10.12
AERO MX 900	Modified dithiocarbamate	25	12	6.9	12.6	20.9	79.1	100.0	3.44	44.90	67.41	84.82	22.35	18.44	13.93
AERO MX 900	Modified dithiocarbamate	40	12	11.1	18.7	26.1	73.9	100.0	3.38	65.06	82.58	89.29	19.77	14.91	11.59
AERO MX 915	Modified dithiocarbamate	55	11	7.7	12.8	17.8	82.2	100.0	3.56	46.86	65.31	75.75	21.57	18.13	15.11
AERO MX 945	Modified dithiocarbamate	55	12	12.2	18.1	24.4	75.6	100.0	3.49	67.49	80.72	87.64	19.35	15.54	12.54
AERO MX 945	Modified dithiocarbamate	25	11	2.3	4.6	6.6	93.4	100.0	3.47	12.80	26.26	36.54	19.74	19.77	19.21
AERO MX 915	Modified dithiocarbamate	55	12	7.4	11.7	16.1	83.9	100.0	3.30	47.24	65.92	77.87	20.98	18.64	16.00
AERO MX 915	Modified dithiocarbamate	25	11	1.6	3.3	5.2	94.8	100.0	3.44	7.76	16.05	25.63	16.33	16.61	17.04
AERO MX 900	Modified dithiocarbamate	25	11	4.8	11.0	17.8	82.2	100.0	3.32	32.94	63.90	79.17	22.60	19.25	14.75
AERO MX 945	Modified dithiocarbamate	55	12	10.3	16.3	22.7	77.3	100.0	3.51	59.01	75.06	84.82	20.20	16.18	13.12
AERO MX 945	Modified dithiocarbamate	40	11	6.3	9.3	13.7	86.3	100.0	3.53	39.09	51.87	66.73	21.78	19.63	17.15
AERO MX 900	Modified dithiocarbamate	40	12	11.0	18.6	24.9	75.1	100.0	3.30	64.05	81.61	88.16	19.12	14.47	11.67
AERO MX 915	Modified dithiocarbamate	55	12	8.8	12.2	16.0	84.0	100.0	3.42	48.28	60.73	70.48	18.66	17.01	15.08
AERO MX 900	Modified dithiocarbamate	55	12	15.9	24.8	32.5	67.5	100.0	3.45	76.87	88.49	92.76	16.68	12.29	9.84

APPENDIX-3: Metallurgical balanca calculation of Xanthate formulations test work

Collector	Coll Type	Dosage (g/t)		Cum. Wt.%					Calc.	Cum. Cu Rec.%			Cum. Grades		
			pH	C1	C2	C3	T	Total	Head	C1	C1-2	C1-3	C1	C1-2	C1-3
PEX	Potassium Ethyl Xanthate	55	11.8	5.3	8.6	15.1	84.9	100.0	3.39	39.49	53.48	75.45	25.07	21.03	16.91
SIPX	Sodium Isopropyl Xanthate	40	11.8	3.1	6.9	11.1	88.9	100.0	3.44	18.93	40.68	59.22	21.11	20.21	18.35
PAX	Potassium Amyl Xanthate	55	11.8	9.9	21.0	29.4	70.6	100.0	3.29	59.49	85.00	91.63	19.74	13.32	10.23
SIBX	Sodium Isobutyl Xanthate	40	10.5	5.5	10.8	15.3	84.7	100.0	3.51	35.86	59.86	71.51	22.68	19.52	16.34
PEX	Potassium Ethyl Xanthate	25	10.5	1.7	3.3	6.0	94.0	100.0	3.46	10.82	21.13	37.43	22.08	22.11	21.59
PAX	Potassium Amyl Xanthate	55	10.5	1.5	8.5	18.7	81.3	100.0	3.55	8.17	50.00	80.31	19.64	20.92	15.27
PEX	Potassium Ethyl Xanthate	40	10.5	1.6	4.9	8.2	91.8	100.0	3.55	10.13	31.17	48.24	21.93	22.57	20.79
SIBX	Sodium Isobutyl Xanthate	55	11.8	5.6	12.6	21.6	78.4	100.0	3.53	34.84	66.87	85.10	21.91	18.72	13.92
PAX	Potassium Amyl Xanthate	40	11.8	8.6	18.8	26.5	73.5	100.0	3.54	52.01	82.17	89.62	21.54	15.52	11.98
PEX	Potassium Ethyl Xanthate	25	11.8	1.5	3.5	7.0	93.0	100.0	3.55	7.65	20.33	40.21	18.60	20.31	20.33
SIPX	Sodium Isopropyl Xanthate	25	10.5	0.8	1.9	3.2	96.8	100.0	3.49	3.12	8.15	15.74	13.85	15.20	16.92
SIPX	Sodium Isopropyl Xanthate	25	10.5	0.6	1.6	3.4	96.6	100.0	3.47	2.47	8.16	19.61	13.38	17.39	19.74
SIPX	Sodium Isopropyl Xanthate	40	11.8	2.8	6.2	10.1	89.9	100.0	3.57	19.77	40.46	58.43	24.83	23.45	20.63
PAX	Potassium Amyl Xanthate	55	10.5	6.8	15.9	24.2	75.8	100.0	3.49	44.70	75.68	86.11	22.86	16.67	12.44
SIPX	Sodium Isopropyl Xanthate	40	11.8	2.3	5.9	10.7	89.3	100.0	3.51	14.73	38.14	60.28	22.08	22.50	19.70
PEX	Potassium Ethyl Xanthate	55	11.8	4.2	9.4	14.7	85.3	100.0	3.52	27.99	54.26	72.10	23.63	20.31	17.20
SIBX	Sodium Isobutyl Xanthate	25	10.5	2.2	5.7	10.0	90.0	100.0	3.48	15.13	38.09	58.31	23.60	23.23	20.37
SIBX	Sodium Isobutyl Xanthate	25	11.8	3.2	7.4	13.1	86.9	100.0	3.54	21.78	45.79	68.32	24.04	21.99	18.45
SIBX	Sodium Isobutyl Xanthate	40	10.5	4.4	10.1	15.6	84.4	100.0	3.49	29.87	59.09	73.66	23.60	20.44	16.53
SIBX	Sodium Isobutyl Xanthate	55	10.5	6.8	12.8	18.6	81.4	100.0	3.48	44.00	67.51	78.97	22.38	18.31	14.77
SIPX	Sodium Isopropyl Xanthate	40	10.5	1.0	3.9	6.7	93.3	100.0	3.52	5.95	26.24	42.41	20.75	23.36	22.28
PAX	Potassium Amyl Xanthate	25	11.8	4.5	10.6	19.4	80.6	100.0	3.49	27.97	58.76	82.21	21.87	19.34	14.77
PEX	Potassium Ethyl Xanthate	25	11.8	1.6	4.0	7.4	92.6	100.0	3.49	9.15	24.46	44.30	20.26	21.48	20.88
PAX	Potassium Amyl Xanthate	55	10.5	9.6	19.3	28.6	71.4	100.0	3.40	56.36	80.86	89.07	19.90	14.27	10.60

APPENDIX-4: Metallurgical balance calculation of Dithiophosphinate formulations test work

Collector	Coll Type	Dosage (g/t)		Cum. Wt.%					Calc.	Cum. Cu Rec.%			Cum. Grades		
			pH	C1	C2	C3	T	Total	Head	C1	C1-2	C1-3	C1	C1-2	C1-3
AEROPHINE 3410	Dithiophosphinate	40	11.8	6.5	12.5	19.3	80.7	100.0	3.47	46.40	71.42	82.80	24.69	19.90	14.93
AEROPHINE 3410	Dithiophosphinate	55	10.5	7.9	13.1	20.5	79.5	100.0	3.64	49.90	66.67	77.09	22.99	18.57	13.67
AEROPHINE 3416	Dithiophosphinate	25	10.5	0.9	2.3	5.8	94.2	100.0	3.38	4.88	12.53	35.83	18.71	18.13	20.79
AEROPHINE 3416	Dithiophosphinate	40	11.8	2.5	6.0	13.0	87.0	100.0	3.52	16.35	36.36	63.21	22.61	21.45	17.14
AEROPHINE 3420	Dithiophosphinate	25	10.5	2.1	5.2	7.8	92.2	100.0	3.40	5.03	22.64	37.56	8.27	14.89	16.37
AEROPHINE 3418	Dithiophosphinate	25	11.8	4.9	11.1	18.3	81.7	100.0	3.39	34.11	65.61	81.45	23.52	20.06	15.13
AEROPHINE 3410	Dithiophosphinate	55	11.8	8.1	18.6	29.6	70.4	100.0	3.42	54.10	82.40	91.36	22.96	15.21	10.59
AEROPHINE 3418	Dithiophosphinate	25	10.5	1.2	5.1	10.9	89.1	100.0	3.56	6.63	30.07	58.18	19.38	21.16	18.97
AEROPHINE 3404	Dithiophosphinate	55	10.5	1.3	4.6	9.3	90.7	100.0	3.55	7.73	29.76	53.46	20.62	22.71	20.46
AEROPHINE 3418	Dithiophosphinate	55	11.8	7.8	20.6	33.5	66.5	100.0	3.43	50.51	83.93	93.03	22.15	13.98	9.52
AEROPHINE 3416	Dithiophosphinate	40	10.5	3.0	7.2	14.6	85.4	100.0	3.48	20.66	45.11	70.52	24.21	21.93	16.85
AEROPHINE 3418	Dithiophosphinate	40	11.8	8.0	18.6	31.0	69.0	100.0	3.45	50.42	81.52	92.00	21.82	15.10	10.22
AEROPHINE 3410	Dithiophosphinate	40	10.5	4.1	10.7	16.4	83.6	100.0	3.43	29.36	60.21	73.20	24.59	19.36	15.35
AEROPHINE 3404	Dithiophosphinate	25	11.8	1.2	2.9	6.1	93.9	100.0	3.47	5.63	15.39	35.28	16.00	18.63	19.91
AEROPHINE 3416	Dithiophosphinate	55	11.8	5.5	12.3	22.7	77.3	100.0	3.52	36.94	68.17	86.83	23.49	19.55	13.46
AEROPHINE 3416	Dithiophosphinate	40	11.8	2.2	6.2	13.4	86.6	100.0	3.63	11.74	35.74	65.19	19.69	20.81	17.64
AEROPHINE 3410	Dithiophosphinate	25	10.5	1.5	4.4	8.9	91.1	100.0	3.57	8.60	26.26	48.76	20.88	21.31	19.57
AEROPHINE 3404	Dithiophosphinate	40	10.5	1.1	3.4	7.1	92.9	100.0	3.49	5.69	19.67	41.96	17.94	20.48	20.58
AEROPHINE 3418	Dithiophosphinate	25	11.8	1.9	7.2	16.9	83.1	100.0	3.40	12.72	47.71	80.45	22.66	22.61	16.23
AEROPHINE 3404	Dithiophosphinate	55	10.5	1.2	4.7	9.2	90.8	100.0	3.52	6.12	27.43	51.23	18.13	20.72	19.67
AEROPHINE 3416	Dithiophosphinate	55	11.8	3.5	9.8	21.3	78.7	100.0	3.61	22.77	57.07	83.85	23.40	20.90	14.19
AEROPHINE 3410	Dithiophosphinate	25	10.5	1.2	3.9	8.9	91.1	100.0	3.55	5.69	22.94	50.48	17.49	20.92	20.24
AEROPHINE 3418	Dithiophosphinate	55	11.8	11.6	22.6	34.5	65.5	100.0	3.22	65.70	85.23	93.07	18.27	12.16	8.69
AEROPHINE 3420	Dithiophosphinate	40	10.5	1.3	3.8	7.3	92.7	100.0	3.43	6.31	21.92	43.27	17.19	20.07	20.49
AEROPHINE 3410	Dithiophosphinate	55	11.8	7.2	18.0	29.8	70.2	100.0	3.39	46.89	81.31	91.51	22.17	15.34	10.40
AEROPHINE 3418	Dithiophosphinate	55	11.8	11.1	22.9	34.4	65.6	100.0	3.43	65.36	87.01	93.69	20.19	13.01	9.33

APPENDIX-5: Metallurgical balanca calculation of Thionocarbamate formulations test work

Collector	Coll Type	Dosage (g/t)		Cum. Wt.%				Calc.	Cum. Cu Rec.%			Cum. Grades		
			pH	C1	C2	C3	T	Total	Head	C1	C1-2	C1-3	C1	C1-2	C1-3
AERO 5100	Thionocarbamate formulation	25	10.5	7.7	14.8	21.8	78.2	100.0	3.52	47.73	71.70	82.21	21.87	16.98	13.26
AERO XD 5002	Thionocarbamate formulation	40	10.5	12.5	17.4	24.7	75.3	100.0	3.44	72.41	81.13	88.18	19.86	16.02	12.26
AERO XD 5002	Thionocarbamate formulation	40	11.8	9.7	16.2	24.3	75.7	100.0	3.47	61.02	77.85	86.91	21.78	16.73	12.44
AERO 3894	Thionocarbamate formulation	25	10.5	6.6	11.4	16.5	83.5	100.0	3.50	42.20	61.27	73.27	22.37	18.80	15.58
AERO MX 5002	Thionocarbamate formulation	40	11.8	7.7	10.4	15.4	84.6	100.0	3.45	48.53	57.25	71.54	21.64	19.02	16.04
AERO 5100	Thionocarbamate formulation	25	10.5	7.8	19.7	27.2	72.8	100.0	3.59	48.29	80.93	86.81	22.35	14.73	11.44
AERO MX 5149	Thionocarbamate formulation	40	11.8	10.7	14.5	18.2	81.8	100.0	3.58	61.59	71.71	77.84	20.62	17.72	15.28
AERO 3894	Thionocarbamate formulation	55	10.5	6.5	13.8	19.9	80.1	100.0	3.46	41.27	69.29	79.18	22.15	17.39	13.78
AERO MX 5149	Thionocarbamate formulation	25	11.8	7.2	10.0	12.5	87.5	100.0	3.58	45.24	56.21	63.14	22.58	20.10	18.09
AERO MX 5002	Thionocarbamate formulation	55	11.8	12.7	17.2	21.8	78.2	100.0	3.53	65.23	75.43	81.85	18.12	15.51	13.29
AERO 3894	Thionocarbamate formulation	25	11.8	12.1	19.8	25.7	74.3	100.0	3.44	65.53	83.66	89.44	18.61	14.58	11.97
AERO MX 5002	Thionocarbamate formulation	25	11.8	4.1	7.3	11.3	88.7	100.0	3.55	27.82	45.12	59.53	24.29	21.91	18.73
AERO 3894	Thionocarbamate formulation	55	10.5	15.2	20.2	24.7	75.3	100.0	3.40	72.93	80.90	84.74	16.30	13.64	11.66
AERO MX 5002	Thionocarbamate formulation	55	10.5	12.5	17.3	27.1	72.9	100.0	3.35	66.87	76.85	88.69	17.95	14.90	10.96
AERO MX 5149	Thionocarbamate formulation	55	10.5	17.4	23.0	26.1	73.9	100.0	3.44	78.10	85.26	87.77	15.43	12.75	11.55
AERO 5100	Thionocarbamate formulation	40	11.8	18.7	28.2	34.7	65.3	100.0	3.41	80.89	89.90	93.30	14.75	10.88	9.18
AERO 5100	Thionocarbamate formulation	40	11.8	16.5	26.4	33.8	66.2	100.0	3.36	76.68	88.65	92.91	15.59	11.29	9.26
AERO 5149	Thionocarbamate formulation	25	10.5	7.3	10.7	14.1	85.9	100.0	3.53	44.70	57.47	65.50	21.71	19.04	16.39
AERO 3894	Thionocarbamate formulation	40	11.8	17.0	23.0	28.3	71.7	100.0	3.21	77.43	85.50	89.94	14.58	11.96	10.22
AERO MX 5149	Thionocarbamate formulation	25	11.8	7.5	11.0	14.5	85.5	100.0	3.50	46.01	60.45	69.75	21.50	19.26	16.87
AERO 5100	Thionocarbamate formulation	55	11.8	23.6	31.6	37.4	62.6	100.0	3.40	85.08	91.59	94.11	12.28	9.85	8.56
AERO 3894	Thionocarbamate formulation	55	11.8	21.0	26.6	32.0	68.0	100.0	3.44	82.15	88.26	92.10	13.47	11.41	9.89
AERO 5100	Thionocarbamate formulation	55	11.8	25.1	33.0	38.1	61.9	100.0	3.49	85.63	91.91	94.14	11.88	9.73	8.62
AERO MX 5149	Thionocarbamate formulation	55	11.8	11.0	14.4	18.0	82.0	100.0	3.52	64.33	73.15	79.25	20.50	17.83	15.52
AERO 5100	Thionocarbamate formulation	55	10.5	16.9	23.1	29.0	71.0	100.0	3.44	76.47	83.50	87.41	15.57	12.44	10.35
AERO XD 5002	Thionocarbamate formulation	55	11.8	13.5	19.2	24.2	75.8	100.0	3.45	68.38	81.14	86.82	17.51	14.61	12.39
AERO 5100	Thionocarbamate formulation	55	11.8	22.7	30.4	36.7	63.3	100.0	3.41	83.99	91.05	93.88	12.65	10.21	8.74
AERO 5100	Thionocarbamate formulation	55	11.8	18.9	27.5	34.3	65.7	100.0	3.45	79.85	89.49	93.13	14.58	11.21	9.36
AERO 3894	Thionocarbamate formulation	55	11.8	20.3	27.2	32.4	67.6	100.0	3.45	79.22	88.41	91.95	13.45	11.19	9.80

APPENDIX-6: Metallurgical balanca calculation of Dithiophosphate formulations test work

Collector	Coll Type	Dosage (g/t)		Cum. Wt.%					Calc.	Cum. Cu Rec.%			Cum. Grades		
			p H	C1	C2	C3	T	Total	Head	C1	C1-2	C1-3	C1	C1-2	C1-3
AERO 9810	Dithiophosphate formulation	55	11.8	5.7	10.2	15.3	84.7	100.0	3.51	36.96	58.94	73.91	22.73	20.23	16.99
AERO 7249	Dithiophosphate formulation	55	10.5	6.6	11.9	18.8	81.2	100.0	3.43	43.53	67.08	80.85	22.67	19.32	14.75
AEROFROTH 238	Dithiophosphate formulation	40	11.8	2.5	5.1	8.2	91.8	100.0	3.43	16.15	31.49	46.52	22.03	21.03	19.40
AEROFROTH 238	Dithiophosphate formulation	40	11.8	2.1	4.8	8.2	91.8	100.0	3.46	12.41	30.35	48.80	20.91	21.92	20.65
AERO 9810	Dithiophosphate formulation	25	11.8	2.5	4.6	7.9	92.1	100.0	3.49	16.29	29.61	46.22	23.01	22.53	20.51
AERO 7249	Dithiophosphate formulation	40	10.5	4.8	9.8	15.7	84.3	100.0	3.60	31.76	56.96	74.22	23.91	20.91	16.96
AERO 7249	Dithiophosphate formulation	55	10.5	5.2	11.2	18.7	81.3	100.0	3.69	34.78	63.90	81.07	24.54	21.00	16.01
AERO 7249	Dithiophosphate formulation	55	11.8	6.3	11.9	16.6	83.4	100.0	3.63	37.72	61.62	73.14	21.82	18.81	16.00
AERO 7249	Dithiophosphate formulation	25	10.5	1.4	4.6	9.1	90.9	100.0	3.49	7.90	28.46	52.87	19.68	21.40	20.25
AEROFROTH 238	Dithiophosphate formulation	40	11.8	2.1	4.7	7.9	92.1	100.0	3.51	14.03	31.03	47.83	23.42	23.08	21.20
AERO 9810	Dithiophosphate formulation	40	10.5	5.3	10.2	15.8	84.2	100.0	3.48	33.35	56.33	70.98	22.03	19.15	15.69
AERO 7310	Dithiophosphate formulation	25	10.5	3.2	7.7	13.3	86.7	100.0	3.49	23.65	52.61	72.16	25.85	23.83	18.98
AEROFROTH 238	Dithiophosphate formulation	25	10.5	0.9	2.2	4.9	95.1	100.0	3.41	4.95	12.68	30.47	19.72	19.43	21.12
AEROFROTH 238	Dithiophosphate formulation	25	11.8	1.3	3.3	5.8	94.2	100.0	3.45	7.42	19.67	35.04	19.24	20.54	20.92
AERO 9810	Dithiophosphate formulation	55	10.5	5.6	11.5	18.2	81.8	100.0	3.55	36.86	61.47	75.58	23.21	18.94	14.75
AERO 9810	Dithiophosphate formulation	25	11.8	3.3	6.9	10.9	89.1	100.0	3.59	20.53	41.52	58.76	22.59	21.51	19.33
AEROFROTH 238	Dithiophosphate formulation	55	11.8	2.6	6.0	8.6	91.4	100.0	3.56	17.73	39.16	51.71	24.07	23.35	21.43
AERO 9810	Dithiophosphate formulation	40	10.5	3.8	8.2	13.9	86.1	100.0	3.55	22.92	46.80	66.82	21.18	20.39	17.05

APPENDIX-7: Metallurgical balanca calculation of Mercaptobenzothiozole formulations test work

Collector	Coll Type	Dosage (g/t)		Cum. Wt.%					Calc.	Cum. Cu Rec.%			Cum. Grades		
			p H	C1	C2	C3	T	Total	Head	C1	C1-2	C1-3	C1	C1-2	C1-3
AERO 400	Mercaptobenzothiozole formulation	55	10.5	2.3	5.5	7.6	92.4	100.0	3.49	16.67	37.63	46.99	25.13	23.98	21.71
AERO 400	Mercaptobenzothiozole formulation	55	11.8	3.9	8.0	13.7	86.3	100.0	3.53	27.77	49.06	68.19	24.91	21.56	17.61
AERO 412	Mercaptobenzothiozole formulation	25	11.8	0.8	2.5	5.1	94.9	100.0	3.47	5.06	15.05	30.35	21.23	20.81	20.51
AERO 412	Mercaptobenzothiozole formulation	25	11.8	0.8	3.0	5.8	94.2	100.0	3.46	4.38	17.35	34.47	18.37	19.95	20.50
AERO 407	Mercaptobenzothiozole formulation	55	10.5	2.0	4.9	9.1	90.9	100.0	3.54	13.28	31.87	52.29	23.53	23.07	20.36
AERO 404	Mercaptobenzothiozole formulation	55	10.5	1.7	4.6	8.1	91.9	100.0	3.54	10.82	28.47	47.27	22.10	21.95	20.54
AERO 407	Mercaptobenzothiozole formulation	40	10.5	0.9	2.5	5.0	95.0	100.0	3.46	3.76	13.49	28.64	14.11	18.42	19.87
AERO 404	Mercaptobenzothiozole formulation	40	11.8	0.9	3.0	6.5	93.5	100.0	3.32	4.79	16.65	38.05	17.48	18.58	19.51
AERO 400	Mercaptobenzothiozole formulation	40	11.8	6.6	12.4	18.9	81.1	100.0	3.54	40.18	66.08	80.50	21.60	18.79	15.05
AERO 404	Mercaptobenzothiozole formulation	25	10.5	0.6	1.5	3.0	97.0	100.0	3.45	1.73	5.26	13.73	10.03	12.26	15.81
AERO 407	Mercaptobenzothiozole formulation	40	10.5	1.1	3.1	5.8	94.2	100.0	3.76	5.05	15.22	36.02	17.12	18.39	23.53
AERO 407	Mercaptobenzothiozole formulation	25	11.8	1.2	2.9	4.9	95.1	100.0	3.21	5.80	16.59	29.06	15.38	18.17	19.16
AERO 407	Mercaptobenzothiozole formulation	55	11.8	2.2	6.0	10.9	89.1	100.0	3.50	14.07	37.62	60.33	21.94	21.95	19.39
AERO 412	Mercaptobenzothiozole formulation	55	11.8	3.4	8.8	15.9	84.1	100.0	3.50	23.31	53.07	75.97	23.71	21.16	16.71
AERO 400	Mercaptobenzothiozole formulation	25	10.5	0.6	1.8	3.9	96.1	100.0	3.45	2.56	9.79	23.51	14.78	19.08	20.71
AERO 404	Mercaptobenzothiozole formulation	40	10.5	1.4	3.3	6.3	93.7	100.0	3.59	7.86	19.62	36.85	20.65	21.12	21.10
AERO 412	Mercaptobenzothiozole formulation	25	11.8	1.6	3.7	6.6	93.4	100.0	3.54	8.97	21.57	37.78	20.25	20.60	20.18
AERO 400	Mercaptobenzothiozole formulation	40	10.5	0.7	2.7	6.9	93.1	100.0	3.82	2.61	13.90	36.36	13.43	19.34	20.07
AERO 412	Mercaptobenzothiozole formulation	55	10.5	1.8	5.5	11.5	88.5	100.0	3.45	10.75	35.87	62.99	20.97	22.33	18.93
AERO 412	Mercaptobenzothiozole formulation	55	11.8	4.7	10.3	17.8	82.2	100.0	3.56	29.42	56.92	77.14	22.09	19.76	15.43
AERO 404	Mercaptobenzothiozole formulation	25	10.5	0.6	1.3	3.1	96.9	100.0	3.23	2.14	5.70	10.99	11.14	13.85	11.63
AERO 407	Mercaptobenzothiozole formulation	40	11.8	2.7	5.6	9.4	90.6	100.0	3.48	13.49	31.01	49.95	17.69	19.08	18.48
AERO 404	Mercaptobenzothiozole formulation	40	10.5	1.4	3.5	6.7	93.3	100.0	3.54	6.51	17.70	36.69	16.76	18.13	19.49
AERO 400	Mercaptobenzothiozole formulation	25	11.8	1.1	3.1	6.6	93.4	100.0	3.48	5.99	18.36	40.06	18.19	20.80	21.24