INVESTIGATION OF CONCENTRATION POSSIBILITY OF ARTVIN-DEREICI COMPLEX SULFIDE ORE BY FLOTATION

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ABSTRACT

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This study was aimed at investigating the amenability of Artvin-Dereiçi ore to concentration by flotation method. Initially, mineralogical characterization study of run-of-mine Artvin-Dereiçi ore was conducted using both optical microscope and XRD technique. Optical microscope images of samples, prepared as polished sections, and XRD analysis revealed that the ore consisted of minerals with potential economic value, chalcopyrite ($CuFeS_2$), galena (PbS), and sphalerite (ZnS), together with gangue minerals, mainly pyrite (FeS_2), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and quartz (SiO_2). In addition to mineralogical analysis, the elemental analysis of the ore was carried out and the mean metal grades were determined as 1.43% copper (Cu), 1.05% lead (Pb), and 6.32% zinc (Zn). Both mineralogical and elemental characterization studies showed Artvin-Dereiçi ore was a complex sulfide ore. Prior to selective flotation tests, conducted to obtain separate concentrates of copper, lead, and zinc metals with marketable grade and recovery values, the ore was subjected to a series of laboratory scale batch-flotation tests to determine the optimum flotation conditions for obtaining bulk concentrates. In the selective flotation tests, two main methods were applied that in the first method, a bulk copper-lead-zinc concentrate was obtained, while the second one was designed to obtain a bulk copper-lead concentrate. Following the both test methods, the selective flotation studies were conducted. In the flowsheet applied for the first method, two different copper concentrates assaying 23.25% Cu at 88.43% recovery and 9.05% Cu at 6.20% recovery were obtained. In addition, the first method yielded a zinc concentrate, assaying 50% Zn at 90.35% recovery and a lead concentrate having 16.75% Pb grade at 89.32% recovery. As compared to the first method, metallurgical values of copper, lead, and zinc concentrates increased remarkably in the second method. This method yielded a copper concentrate assaying 19.1% Cu at 98.79% recovery and a zinc concentrate assaying 54.52% Zn at 80.0% recovery. Lead grade of the run-of-mine ore was upgraded from 1% to 45.6% Pb with 96.81% recovery utilizing the second method.

Keywords: Flotation, Complex Sulfide Ore, Copper, Lead, Zinc, Chalcopyrite, Galena, Sphalerite

ÖZ

ARTVİN-DEREİÇİ KOMPLEKS SÜLFÜRLÜ CEVHERİNİN FLOTASYON İLE ZENGİNLEŞTİRİLEBİLME OLANAĞININ BELİRLENMESİ

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Bu çalışmada Artvin-Dereiçi cevherinin flotasyon yöntemi ile konsantrasyona uygunluğunun araştırılması amaçlanmıştır. Başlangıçta, tüvenan Artvin-Dereiçi cevherinin mineralojik karakterizasyon çalışması hem optik mikroskop hem de XRD tekniği kullanılarak gerçekleştirilmiştir. Parlak-kesit yöntemi ile hazırlanan cevher numunelerinin optik mikroskop görüntüleri ve XRD analizleri, cevherin kalkopirit ($CuFeS_2$), galen (PbS) ve sfalerit (ZnS) gibi potansiyel ekonomik değere sahip olan minerallerle birlikte başlıca pirit (FeS_2), kalsit ($CaCO_3$), dolomit ($CaMg(CO_3)_2$) ve kuvars (SiO_2) gibi gang minerallerinden oluştuğunu göstermiştir. Mineralojik analize ek olarak cevherin elementsel analizi gerçekleştirilmiş ve ortalama metal tenörleri %1.43 bakır (Cu), %1.05 kurşun (Pb) ve %6.32 çinko (Zn) olarak belirlenmiştir. Hem mineralojik hem de elementsel karakterizasyon çalışmaları Artvin-Dereiçi cevherinin kompleks sülfürlü bir cevher olduğunu göstermiştir. Bakır, kurşun ve çinko metallerinden satılabilir tenör ve randıman değerlerine sahip ayrı konsantreler elde etme amacı ile yapılan seçimli flotasyon testlerinden önce, cevher yığın konsantre elde etmek için optimum flotasyon koşullarını belirleme amacı ile laboratuvar ölçeklerinde kesikli flotasyon testlerine tabi tutulmuştur. Seçimli flotasyon deneylerinde iki ana yöntem uygulanmış olup, ilk yöntemde toplu bakır-kurşun-çinko konsantresi elde edilirken, ikinci yöntem toplu bakır-kurşun konsantresi elde etmek için tasarlanmıştır. Seçimli flotasyon testleri her iki yöntemi de takip edecek şekilde yapılmıştır. İlk yöntem için uygulanan akım şemasında, % 88.43 randıman ile %23.25 Cu tenörlü ve %6.20 randıman ile %9.05 Cu tenörlü iki farklı bakır konsantresi elde edilmiştir. Buna ek olarak, birinci yöntemle %90.35 randıman ile %50 Zn tenörlü çinko, %89.32 randıman ile %16.75 Pb tenörlü kurşun konsantreleri elde edilmiştir. İlk yönteme kıyasla, bakır, kurşun ve çinko konsantrelerinin metalurjik değerleri ikinci yöntemde dikkate değer bir şekilde artmıştır. Bu yöntem ile %98.79 randıman ile %19.1 Cu tenörlü bakır ve %80.0 randıman ile %54.52 Zn tenörlü çinko konsantreleri elde edilmiştir. Tüvenan cevherin kurşun tenörü ikinci yöntemin uygulanmasıyla %1’den %45.56 Pb değerine %96.81 randıman ile yükseltilmiştir.

Anahtar Kelimeler: Flotasyon, Kompleks Sülfürlü Cevher, Bakır, Kurşun, Çinko, Kalkopirit, Galen, Sfalerit

To My Family

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INTRODUCTION

Discovery, development, and exploitation of minerals have played a major role in the advancement of civilization. Starting from the prehistoric ages, metals, and other materials, such as mineral fuels (petroleum, coal, and natural gas), and non-metals (stone, sand, salt, and clays), have been heavily used by humankind in numerous areas that helped to build today's modern society. From houseware to warfare and from agriculture to technology, people have excessively relied on metals to continue their progress. Considering the evolution of our civilization, as long as the existence of human beings continues on the planet, its commitment to metals will continue to persist.

Copper, lead, and zinc are regarded as three of eight metals (others are iron, gold, silver, tin, and mercury) employed since antiquity. Copper was the earliest metal to be used in about 8000 B.C. in the form of small objects such as beads, pins, and awls, which gave start to Copper Age, or alternatively Chalcolithic Age (Murr, 2015). Similar to gold and meteoric iron nickel alloys, copper was found in nature by hunter-gatherer societies in native state. At about 5500 B.C., accidental smelting of copper and tin was resulted in alloy bronze and the invention gave rise to the Bronze Age (Laznicka, 2010). Due to its nature, copper possesses many advantages involving ease of stretching, molding, and shaping, corrosion resistance, heat and electricity conductivity, and therefore, today it is being utilized in industries such as power generation, electronic product industry, construction of buildings, transportation vehicles and machinery industry (Doebrich, 2009).

History of lead dates back to 7000 B.C. that it was used by different cultures in the form of a variety of products including ceramics, cosmetics, and pipes. Lead features similarities with copper regarding its corrosion-resistant nature and molding and shaping simplicity. The major usage of lead in today's technology is in lead-acid batteries, supplied mainly for automobiles, mobile phones and energy storage systems (Rich, 1994).

Before its identification as a distinct element, zinc was utilized to produce alloy brass, made up of copper and zinc. Between the 11th and the 14th centuries and in the 17th century, zinc was produced in Asia in the form of metallic zinc and zinc oxide. Due to its anticorrosive property and capability of bonding with other metals, zinc is the fourth most widely used metal in the industry behind iron, aluminum and copper. Almost half of the zinc produced is used in zinc galvanizing process, which provides protection to iron or steel against rusting. The second leading usage of zinc is in alloy industry to produce brass and other forms of alloy to be used in automobiles, electrical components, fixtures. Production of zinc oxide is another major utilization area of zinc that zinc oxide is employed in manufacture of rubber and protective skin ointment (Kropschot and Doebrich, 2011).

Metal supplies in the world are classified into two groups as primary (new) and secondary (recycled) metals. Primary metals are extracted from the earth crust through mining operations, while secondary metals are recovered from any kind of metal containing objects independent of their age (Laznicka, 2010). In general, metals exist in the earth crust in the combined form as minerals, only a few of them occur in native state. Sulfides, oxides, hydroxides, carbonates, and silicates are some of the mineral group examples that may contain one or more metal in their structure.

Copper minerals are grouped into three types as sulfide, carbonate and silicate copper minerals that latter two are often termed as copper oxide ores. Bornite (Cu_5FeS_4), chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), and covellite (CuS) are the sulfide type copper minerals, in which copper is linked with sulfur. Azurite ($Cu_3(CO_3)_2(OH)_2$) and malachite ($Cu_2(CO_3)(OH)_2$) are the examples of carbonate type copper minerals, formed by copper, carbon, and oxygen. Chrysocolla ($Cu_{2-x}Al_x(H_{2-x}Si_2O_5)(OH)_4 \cdot nH_2O$) is a silicate type copper mineral, which is majorly constituted by copper, silicon, and oxygen (Klein, 2002). Among all mineralogical forms of copper, chalcopyrite is the most abundant form and the most significant source for copper production (Doebrich, 2009). Economically recoverable reserves of copper are approximately 720 M tons and around 19.5 M tons of copper was produced in 2016 in the world. Chile, country having the biggest copper reserves, was responsible for the 28% of the production in 2016. Australia, Peru, Mexico, and the United States followed Chile in terms of copper production in the same year (Brininstool, 2017).

Sulfide and oxide group minerals are dominating examples for lead minerals that galena (PbS), a sulfide type ore, is practically the main source of lead production. Cerussite ($PbCO_3$) and anglesite ($PbSO_4$) are the oxidized forms of galena that cerussite is formed by the action of carbonated waters on galena, whereas anglesite occurs at the oxidized portion of galena. Other important oxidized lead minerals are crocoite ($PbCrO_4$), pyromorphite ($Pb_5(PO_4)_3Cl$), and wulfenite ($PbMoO_4$) (Klein, 2002). In the world, around 88 M tons of economically recoverable lead reserves have been investigated that the total lead production of the world was approximately 4.82 M tons in 2016. China was the leader producer as the country held 49.8% of production in 2016, despite the fact that Australia has the largest lead reserves. In terms of production, Australia, the United States, Peru, and Mexico were the countries in the top four lead-producing countries following China in 2016 (Guberman, 2017).

The most common and important ore mineral of zinc is sphalerite (ZnS), which displays similarities with galena in terms of its mode of origin and occurrence. Therefore, sphalerite, a sulfide mineral, generally occur along with galena in lead-zinc deposits. Smithsonite ($ZnCO_3$), an oxidized ore mineral of zinc, is occasionally occur in zinc deposits with limestone that the associate minerals in such deposits are sphalerite, galena, hemimorphite, cerussite, calcite, and limonite. Hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) is a silicate zinc mineral, occurring at oxidized parts of zinc deposits. Franklinite ($ZnFe_2O_4$), willemite (Zn_2SiO_4), and zincite (ZnO) are the other types of zinc minerals found in certain deposits in associated form (Klein, 2002). After recent investigations, the world's recoverable zinc reserves were estimated as 220 M tons that China was the leading producer, holding approximately 38% of the production in 2016. Peru, Australia, the United States, and Mexico were in the top five zinc-producing countries list following China in the same year (Tolcin, 2017).

Among sulfide minerals, pyrite (FeS_2) is the most abundant and widespread one found in numerous locations. In general, pyrite is regarded as a gangue mineral, particularly in gold and copper mining. Due to its sulfur content, pyrite is mined as an iron source only in limited locations in which oxidized forms of iron are not available. Major utilization area of pyrite, being used as a sulfur source, is the production of sulfuric acid. On the other hand, hematite (Fe_2O_3), magnetite (Fe_3O_4), and goethite (FeO(OH)) are the main oxide ores used for the production of iron and consequently for the steelmaking industry. Siderite ($FeCO_3$) and ilmenite ($FeTiO_3$) are the other important forms of iron ore minerals (Klein, 2002).

After the mining operations, metal or any other valuable mineral bearing ore is subjected to processing, or alternatively beneficiation, to concentrate the valuable ones by removing the gangue minerals. The operation is called mineral processing, aiming at producing commercially valuable concentrates to be utilized in a variety of industries or to undergo further purification. Froth flotation is regarded as the most important and sophisticated mineral processing technique and has allowed the concentration of complex and/or low grade metallic ores (or other types of minerals), otherwise, which would have been accepted lack of economic value (Wills and Napier-Munn, 2006).

In general, sulfide minerals are found in nature associating each other as copper sulfide ores with moderate to high pyrite content, copper-zinc and lead-zinc ores containing low to high pyrite content, and complex copper-lead-zinc ores (Bulatovic, 2007). Based on their major constituents, complex sulfide ores containing copper, lead, zinc, and iron are grouped into three main categories as siliceous ores, lead rich ores, and pyritic ores. Selective concentration (flotation) of such ores, particularly pyritic types, rather difficult due to impact of a variety of factors related to surface chemistry of the minerals, interaction of reagents used in the process with minerals, oxidation problems, chemistry of the aqueous environment, and grinding conditions, etc. (Majima, 1969; Gibson and Kelebek, 2014). Considering the fact that flotation has been developed nearly a hundred years ago and consequently have reached the highest level in today’s beneficiation technology not only due to theoretical knowledge but also owing to empirical studies that conducting such studies further to enhance the concentration of sulfide, or any other type, minerals by flotation would be very useful for the development of mineral industries.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Definition and History of Flotation

Flotation is defined as a concentration process relying on establishing a difference between the surface properties of minerals to separate valuables from the gangue ones (Gupta and Yan, 2006; Wills and Napier-Munn, 2006).

Essentially, the invention of flotation as an industrial process dates back to 19th century that the advancements occurred since mid-1850's are considered as to have played a great role in bringing the technology to the present level. During the period from 1850 to 1900, mineral industries experienced a series of inevitable improvements due to the demand for minerals and metals. Introduction of the new mining and processing technologies such as dynamites, steam-driven shovels, ball mills, and other processing equipment helped mineral processing industry overcome the stagnancy experienced in the past two centuries. However, even with these improvements, it was impossible to obtain high-grade concentrates with the existing gravity separation equipment. Despite the fact that small-scale flotation studies were conducted in this period, the developments forming the basis of flotation as an industrial application occurred in the following twenty-five-year time period. Starting from 1900, industrial-scale flotation plants were installed and succeeded to obtain concentrates rich in sulfide metals such as lead and zinc in Australia and copper in the western side of the Unites States. After 1960, with the development of on-stream analysis systems and new technology, and higher capacity equipment, flotation have become the most significant and versatile mineral beneficiation technique (Lynch *et al.*, 2007).

Concentration of metals such as copper, lead, zinc, cobalt, nickel, molybdenum, etc. in the form of sulfides, oxides, and carbonates is the most important application area of flotation, which permits treatment of these metallic ores, generally found in low grades and possess complex natures. On the other hand, applicability of flotation is not limited to the concentration of metallic ores that the concentration of non-metallic industrial minerals (e.g. fluorite, barite, clay and silicate minerals) and the cleaning of solid fuels (e.g. coal and oil shale) are accomplished through flotation (Leja, 2004).

2.2 Fundamentals of Flotation

The theory behind flotation is based on a three-phase system, consisting of solid (mineral particles), liquid (water), and gaseous (air bubbles) phases. The separation, or recovery, of mineral particles through flotation includes three mechanisms as; the selective attachment of mineral particles to air bubbles, the mechanical entrainment of mineral particles in water to enter the froth, and the entrapment of mineral particles in the froth. The first mechanism, also called as true flotation, is the most important phenomenon, through which most of the valuable particles are recovered as concentrate. However, the latter two are also responsible for the recovery of particles in the concentrate product and affect grade unfavorably since, unlike true flotation, these two mechanisms contribute the movement of unwanted (gangue) particles into the froth phase (Gupta and Yan, 2006; Wills and Napier-Munn, 2006).

In true flotation, separation of mineral particles occur in accordance with their surface characters, i.e. wettability, such that for the mineral particles to float, their surfaces should be hydrophobic, while for the mineral particles intended to be depressed (remain in the pulp) their surfaces should display hydrophilic character. Thus, hydrophobic (water-repellent) particles attach to air bubbles created in the pulp and ascend upwards to the froth phase, whereas hydrophilic (air-repellent) mineral particles remain in the system during flotation (Warren, 1985; Zheng *et al.*, 2006; Wang and Peng, 2013). Illustration of flotation mechanism is given in Figure 2.1.

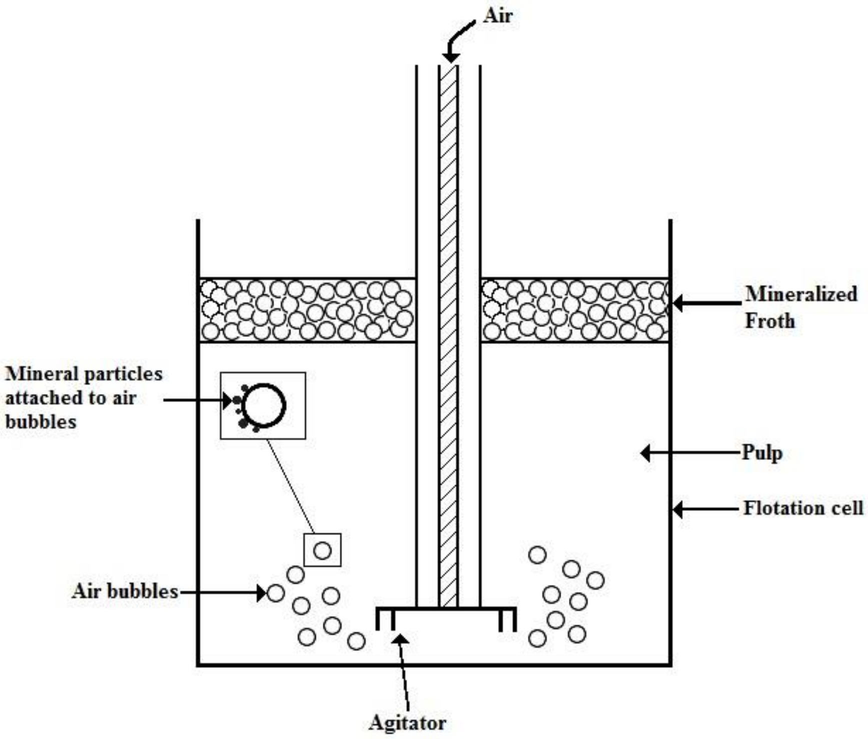

Figure 2.1 Illustration of flotation mechanism

In general, valuable mineral particles are transferred to the froth phase; therefore, unwanted particles remain in the system as gangue, the process is called direct flotation. On the contrary, flotation might conducted in such a manner that gangue particles gain hydrophobic character and move upwards into the froth phase, while valuable ones being hydrophilic stay in the pulp phase, then the flotation is called as reverse flotation (Wills and Napier-Munn, 2006).

The possibility of achieving a selective flotation is heavily dependent on the wetting properties of surfaces of mineral particles. The degree of wetting, a terms used to describe the extent of surface wetting by a liquid, or vice-versa the extent of displacement of water from the surface of mineral particle, is defined by the term contact angle. As it has been mentioned, flotation is a process in which solid, liquid and gaseous phases are present and contacting each other; therefore, between these phases a line of contact occurs. Similarly, contact angle is used to describe the properties of the contact formed between mineral particle, water, and air bubble (Matis, 1995; Gupta and Yan, 2006; Wills and Napier-Munn, 2006). Illustration of the contact between the three phases of flotation and the contact angle are given Figure 2.2.

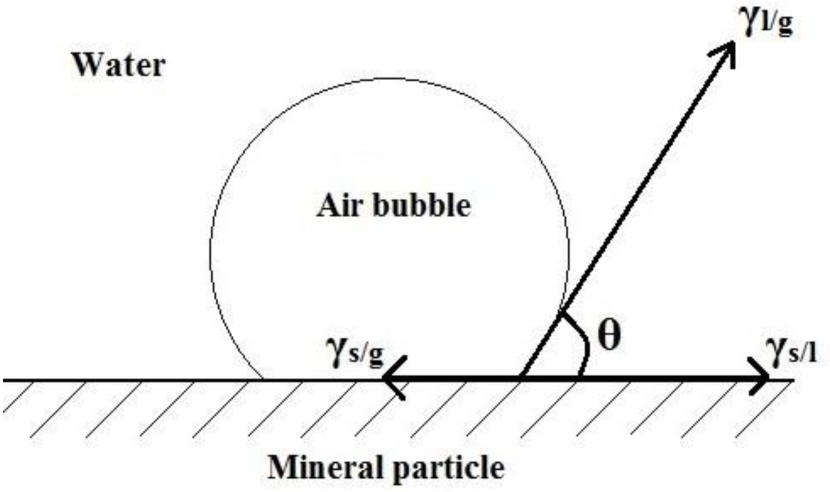

Figure 2.2 Three phase flotation systems and contact angle, θ

In Figure 2.2, $\gamma_{s/g}$, $\gamma_{l/g}$, and $\gamma_{s/l}$ denotes the interfacial tensions, or alternatively the surface energies, between the solid-gas (mineral particle-air bubble), liquid-gas (water-air bubble), and solid-liquid (mineral particle-water) interfaces. In addition, θ is the contact angle between the interfaces. The equilibrium condition is established by the balance between the interfacial tensions and is defined by Young's equation given in Equation 1 (Young, 1805).

$$\gamma_{s/g} = \gamma_{s/l} + \gamma_{l/g} \cdot \cos\theta \tag{1}$$

Due to the fact that measurement of $\gamma_{s/g}$ is rather difficult, Equation 1 is useless to determine the surface property of a solid particle (Adam, 1957). Therefore, another expression is used, Dupre's equation, and is given in Equation 2 (Dupre, 1869).

$$\Delta G = \left(\gamma_{l/g} + \gamma_{s/l}\right) - \gamma_{s/g} \tag{2}$$

In Equation 2, ΔG denotes the free energy change per unit area, which corresponds to the displacement of water by air bubble. In general, ΔG is replaced by the term "work of adhesion" between solid (mineral particle) and gas (air bubble), meaning the work required for removing the air bubble from the particles surface to create separate interfaces between water-air bubble and mineral particle-water. The expression of work of adhesion between solid and gas phases in terms of contact angle is given Equation 3.

$$W_{s/g} = \gamma_{l/g}(1 - \cos\theta) \tag{3}$$

In three-phase flotation system, a mineral particle having a contact angle greater than 90° is defined as a hydrophobic surface, whereas a particle surface which forms a contact angle less than 90° represents a hydrophilic surface. Theoretically, contact angle might be 0° and 180°, meaning that the surface of the particle is entirely wetted by water and air bubble completely displace water, respectively (Matis, 1995; Gupta and Yan, 2006; Wills and Napier-Munn, 2006). However, in nature, the maximum contact angle is observed with Teflon as 108°. Naturally hydrophobic minerals are not common that a few of the examples are coal, molybdenite, sulfur, and talc, which have contact angle values less than that of Teflon (Fuerstenau and Raghavan, 2007). On the other hand, most of the minerals, as in the form they found in nature, are hydrophilic, and this is the reason behind the fact that their surface properties should be changed, in other words, contact angles of such mineral should be increased prior to flotation if the intention is to concentrate these minerals in the froth phase.

2.3 Flotation Reagents

In order to achieve a selective separation between the minerals through flotation, a variety of flotation reagents (surfactants), having distinct functions in the process, are used. Flotation reagents are classified into three main groups as collectors, frothers, regulators (modifiers).

2.3.1 Collectors

Collectors, also called as promoters, are utilized to selectively render a particle surface hydrophobic, i.e. providing suitable conditions for the attachment of a mineral particle to an air bubble and for the recovery of that particle in the froth product. In accordance with their dissociation ability in water, collectors might be ionizing (heteropolar) or non-ionizing (non-polar) (Glembocki and Plaskin, 1961).

Ionizing (heteropolar) collectors are organic substances consisting of non-polar and polar groups in their structures. The non-polar part of a collector is either a short-chain or a long-chain hydrocarbon radical possessing hydrophobic (water-repellent) character, while the polar portion displays hydrophilic character, thus dissociates into its ions in aqueous media and reacts with water. In order to render a particle surface water-repellent, the polar part of a collector is oriented towards the particle surface, whereas the non-polar part towards water. Adsorbed collector molecules, therefore, provide water-repellency to the particle surface (Wills and Napier-Munn, 2006; Bulatovic, 2007). Ionizing collectors are further grouped into two as cationic and anionic collectors according to the type of ions responsible from the hydrophobic character induced to the particle surface.

Cationic collectors have a cation (positive charge) in their hydrophilic ends when introduced into aqueous media. Amines are included in cationic collectors, the primary amines being the most important ones. Contrary to cationic collectors, anionic collectors, which possess an anion (negative charge) in their hydrophilic ends, are most common types of ionizing collectors. Depending of the structure of their solidophilic group, which connects the hydrophobic hydrocarbon radical and hydrophilic end of a collector, anionic collectors are classified as oxyhydryl collectors and sulfydryl (thiol) collectors. Principally, oxyhydryl collectors are used for the flotation of non-sulfide minerals such as silicates, carbonates, oxides. On the other hand, sulfydryl collectors are applied for the recovery of sulfide minerals through flotation. (Crozier, 1992).

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In the flotation applications of sulfide base and precious metals, approximately 70,000 tonnes of sulfydryl collectors are consumed annually. Xanthates are the major type of sulfydryl collectors and each year 60,000 tonnes of various types of xanthates are used in flotation. Sodium ethyl xanthate, sodium isopropyl xanthate, sodium isobutyl xanthate, potassium ethyl xanthate, and potassium amyl xanthate are the most important examples of xanthate group collectors. Other forms of sulfydryl collectors, such as dithiophosphates (the second major type of thiol collectors), thionocarbamates, dithiocarbamates, dithiophosphinates, xanthogen formates, etc., are less common as compared to xanthates. Xanthates are powerful and less expensive collectors, however, dithiophosphates are more selective than xanthates. In general, xanthates and dithiophosphates are utilized in combination for the flotation of sulfide ores at low dosages since recovery, grade, and selectivity of the sulfide metals can be increased using the mixture of these collectors in flotation process (Adkins and Pearse, 1992; Lotter and Bradshaw, 2010).

Non-ionizing collectors, essentially hydrocarbon substances insoluble in water due to their non-polar character, are obtained from crude oil or coal. The function of non-ionizing collectors is explained by a mechanism that they cover a particle surface by adhesion to render its surface hydrophobic. Non-ionizing collectors are utilized for the flotation of naturally water-repellent mineral such as coal, elemental sulfur and molybdenite. Some typical examples of the non-ionizing collectors are fuel oil and kerosene (Bulatovic, 2007). General classification of collectors used in flotation is given in Figure 2.3.

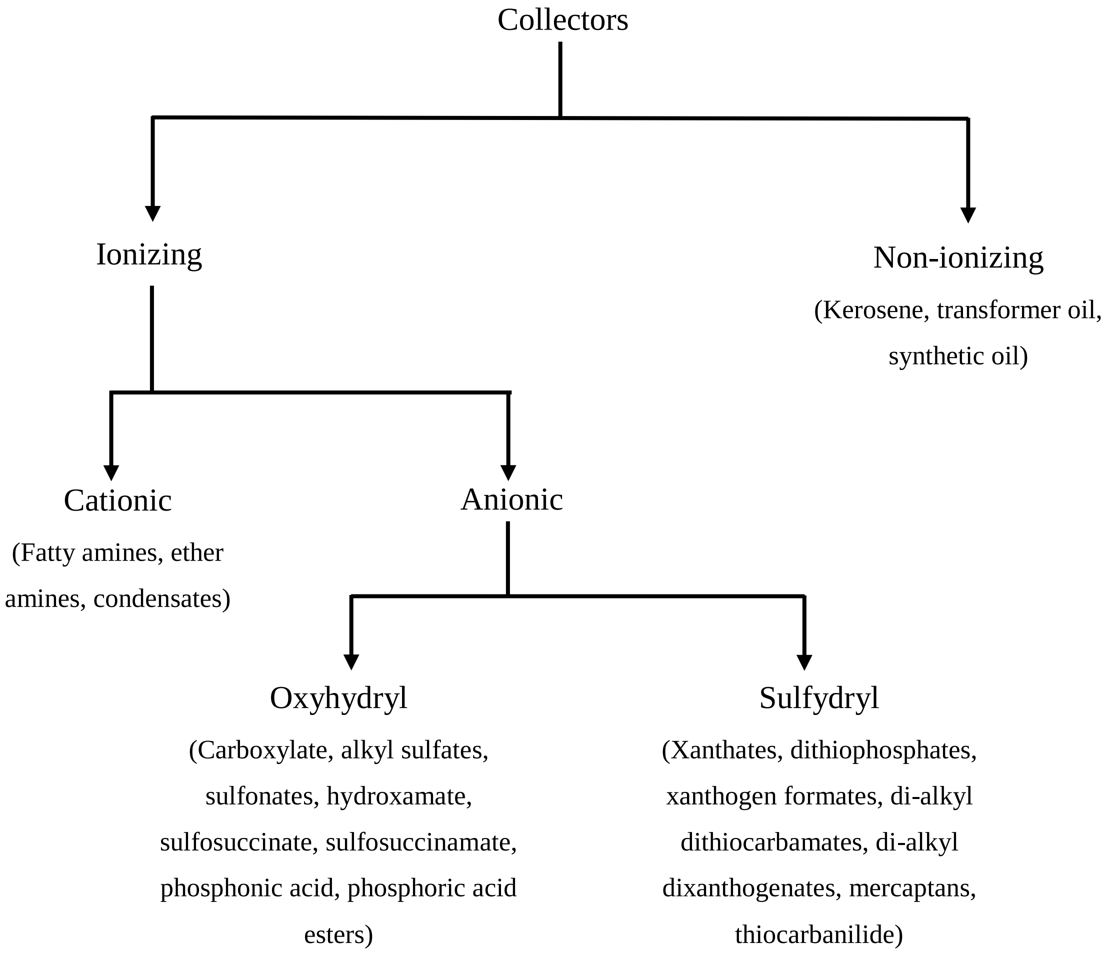

Figure 2.3 General classification of collectors

2.3.2 Frothers

Frothers, similar to ionizing collectors in terms of their structure, are heteropolar surface-active agents (surfactants) that adsorb at the water-air interface to reduce the surface tension of water. Heteropolar structure of frothers leads to an organization in flotation process that their polar (hydrophilic) parts are oriented towards the water phase, while non-polar (hydrophobic) portions towards air bubbles. Therefore, frothers provide a stability to air bubbles by enhancing their film strength so that air bubbles could carry mineral particles upwards to the froth product without experiencing any breakage. In addition, frothers contribute to the preservation of fine air bubbles by opposing to the coalescence of individual ones (Bulatovic, 2007).

Based on their activities at different pH values, frothers are classified into three groups as acidic, neutral, and basic frothers, among which the neutral ones are the most widely used and the most important (Dudenkov and Bakinov, 1966). Acidic frothers, having two main groups as phenols and alkyl sulfates, function at low pH values, while basic frothers, such as pyridine base, are useful in alkaline environment. Neutral frothers, applicable in both acidic and alkaline pH, are extensively used in the flotation of metallic ores, oxidic and industrial minerals. The typical examples of neutral frothers are cyclic alcohols, aliphatic alcohols, alkoxy paraffins and glycols (Bulatovic, 2007). The type and the concentration of a frother, the size and the extent of hydrophobicity of a mineral particle, and the amount of slimes are all affecting the characteristics of froth created during flotation (Subrahmanyam and Forssberg, 1988; Johansson and Pugh, 1992).

2.3.3 Regulators

The main purpose of using flotation regulators is ensuring the selectivity of mineral recovery in flotation by controlling (either increasing or decreasing) the adsorption activities of the collectors on the surfaces of mineral particles. Therefore, utilization of flotation regulators (modifiers) have a vital importance particularly in the flotation of complex ores, in which selective concentration is the major concern. Flotation regulators are either organic or inorganic substances divided into three main classes as activators, depressants, and pH modifiers (Gupta and Yan, 2006; Wills and Napier-Munn, 2006; Bulatovic, 2007).

Activators are the compounds providing suitable conditions for the adsorption of a collector on the surface of a mineral particle. Independent of their type and concentration, some collectors might be useless to change the surface property of a mineral, i.e. they do not render the mineral surface hydrophobic. Therefore, floatability of such minerals is only improved by the addition of activators, which alter the chemistry of the surfaces of minerals and help the selective attachment of collectors on those surfaces (Wills and Napier-Munn, 2006; Bulatovic, 2007).

In order to give a typical example, sphalerite, one of the most important sources of zinc, should be activated prior to flotation due to the fact that the surface of sphalerite displays low floatability character with sulfydryl collectors. Copper sulfate ($CuSO_4$) is used to change the surface property of sphalerite so that its copper-activated surface reacts with xanthate to form insoluble copper-xanthate compound, more insoluble (water-repellent) as compared to sphalerite-xanthate compound (Gaudin, 1957; Finkelstein and Allison, 1976; Finkelstein, 1997; Laskowski *et al.*, 1997). However, activation of sphalerite is only achieved at certain concentrations of copper sulfate that using excessive amounts of copper sulfate may result in reduction in sphalerite recovery (Boulton *et al.*, 2005).

Sodium sulfide (Na_2S) is another activator used as a sulfidizing agent in the flotation of oxidized metallic minerals that the flotation of such minerals are accomplished satisfactorily using a sulfydryl type collector following the activation (Bulatovic, 2007). In addition, sodium sulfide is used to enhance flotation characteristics of chalcopyrite and copper-activated sphalerite in the collectorless flotation applications (Yoon, 1981; Luttrell and Yoon, 1984). The salts such as barium chloride ($BaCl_2$) and lead nitrate ($Pb(NO_3)_2$) are also used as activators for the flotation of barite and stibnite, respectively (Lager and Forssberg, 1989; Bulatovic, 2014).

Depressants are another group of flotation regulators that their function in the process is rendering the surface of minerals hydrophilic to prevent their recovery in the froth product. The most extensively used depressants in the flotation of sulfide minerals are sodium cyanide ($NaCN$), zinc sulfate ($ZnSO_4$), ferrous sulfate ($FeSO_4$), sodium sulfite (Na_2SO_3), sulfur dioxide (SO_2), sodium metabisulfite ($Na_2S_2O_5$), and potassium dichromate ($K_2Cr_2O_7$).

Sodium cyanide is regarded as an effective depressant for iron and zinc sulfides, and it is particularly used as a depressant for pyrite (FeS_2), an easily floatable mineral deteriorating the grade of metal concentrates (Ball and Rickard, 1976; Prestidge *et al.*, 1993). Zinc sulfate prevents the activation of sphalerite surfaces by other metal ions, such as copper, lead, and silver, present in the pulp and causes coagulation of sphalerite particles, which reduces the mechanical entrainment (Cao and Liu, 2006). When it is used in combination with sodium cyanide, ferrous sulfate is also effective for depressing pyrite (Kostovic and Vucinic, 2016). Sulfoxy species such as sodium sulfite, sodium metabisulfite and sulfur dioxide are used extensively for the depression of galena, pyrite, and sphalerite at neutral pH values during copper flotation (Yamamoto, 1980; Pattison, 1983; Misra *et al.*, 1985; Grano *et al.*, 1997; Houot and Duhamet, 1992). Chromate and dichromate salts such as potassium dichromate are used in the flotation of complex sulfide ores to depress galena (Okada and Majima, 1971).

Slimes, particles generally smaller than 20 μm in size, cause natural depression effect to the particles by coating their surfaces. In order to overcome the slime coating problem, sodium silicate (Na_2SiO_3) is used since it leads to the dispersion of slime particles in the pulp, i.e. removing them from the surfaces of valuable minerals by increasing their electrical double layer charge. In general, sodium silicate is utilized to depress siliceous gangue minerals and non-sulfide minerals, such as calcite, fluorite, and scheelite (Wills and Napier-Munn, 2006; Bulatovic, 2007).

The last group of flotation reagents are pH regulators, used to adjust the hydrogen and the hydroxyl ion concentration in the flotation pulp. The surface charge of the mineral particles, the possibility of collectors to adsorb on the surfaces of minerals, and the ionization behaviour of collectors are the important parameters for the selective separation of minerals through flotation that they are heavily affected the by the pH of the pulp. Isoelectric point of a mineral is defined as the pH value at which it carries no charge. Below or above their isoelectric points, particles gain surface charge, either positive or negative, thus, it leads to a change in the adsorption possibility of collectors, carrying a charged (polar) part, on the surfaces of mineral particles. In addition, the stability of the collectors depends majorly on the pH of the flotation pulp, meaning that they change the surface characteristics of a particle at only certain pH values. For instance, xanthates, collectors used extensively in the flotation of sulfide minerals, function at alkaline medium that the surface of pyrite might be activated by copper ions; therefore, it reacts with xanthates and gains hydrophobicity at low pH values. In general, pH should be greater than 11 to depress pyrite effectively (Bushell and Krauss, 1962; Voigt *et al.*, 1994; Buckley *et al.*, 1989; Shen *et al.*, 1998). In order to increase the pH of a flotation pulp to the desired alkaline level, lime (CaO), calcium hydroxide ($Ca(OH)_2$), soda ash (Na_2CO_3), and caustic soda (NaOH) are used. On the other hand, sulfuric acid (H_2SO_4) is the most widely used acid to lower the pH of the flotation medium (Wills and Napier-Munn, 2006; Bulatovic, 2007).

2.4 Origin and Geology of Complex Copper-Lead-Zinc Sulfide Ores

Sulfide ores, hosting the naturally occurring metal-sulfur minerals, are the main sources of base and precious metals in the world. Mainly, sulfide ores may contain one or more of the major sulfide minerals that the list of the eight of major sulfide minerals, which form nearly 95 % of sulfide ore deposits, together with their chemical formula and the principal elements derived from them are given in Table 2.1 (Craig and Vaughan, 1990).

Table 2.1 The major metal sulfide minerals

Mineral	Formula	Principal Elements Extracted
Arsenopyrite	$FeAsS$	Gold (Au), Arsenic (As)
Chalcopyrite	$CuFeS_2$	Copper (Cu)
Galena	PbS	Lead (Pb)
Pentlandite	$(Fe,Ni)_9S_8$	Nickel (Ni), Cobalt (Co)
Pyrite	FeS_2	Cobalt (Co), Gold (Au), Sulfur (S)
Pyrrhotite	$Fe_{1-x}S$	Nickel (Ni)
Sphalerite	ZnS	Zinc (Zn)
Fahlerz (Tetrahedrite)	$Cu_{12}Sb_4S_{13}$	Copper (Cu), Antimony (Sb), Silver (Ag), Arsenic (As)

Chalcopyrite, galena, and sphalerite are some of the most important sulfide minerals, present in the complex form as lead-zinc ores, copper-zinc ores, and copper-lead-zinc ores (Cox and Singer, 1992). Therefore, these type of complex sulfide ores display great similarities in terms of origin and additionally may contain some precious metals such as gold and silver in significant amounts. For copper-lead-zinc minerals bearing complex sulfide ores, hydrothermal vein deposits, massive sulfide deposits, and sedimentary deposits are regarded as the most significant types despite the fact that complex sulfide ores are found in several other different types of geological formations (Bulatovic, 2007).

The complex copper-lead-zinc ores in hydrothermal vein deposits are found in vein fillings and replacements and formed due to the circulation of chloride-rich brines, a type of hydrothermal fluids, extracting, transporting, and finally precipitating the metal sulfide minerals originated from the magmatic sources and the host rocks. These types of ores contain coarse-grained (1 mm to 2 cm) aggregates of chalcopyrite, galena, sphalerite, and pyrite, having banded to massive texture. In terms of mineralogy, tetrahedrite is also common in small amounts as a valuable mineral, and gangue minerals such as calcite, quartz, dolomite, barite, fluorite, sericite, and chlorite are mainly present in these deposits. In general, sphalerite, pyrite, and gangue minerals such as quartz, calcite, and fluorite are found in these deposits in euhedral form, while galena is usually present in anhedral form. Chalcopyrite is often observed contained by sphalerite in the form of rows of small blebs that the condition is called as chalcopyrite disease (Craig and Vaughan, 1994).

Massive sulfide ores have different variations such as coarse-grained ores, finely disseminated ores, refractory ores, altered and oxidized ores, and additionally pyrrhotite copper-lead-zinc ores (found exclusively in certain locations) that the processing of these ores is highly problematic due to their distinct characteristics in terms of mineralogy and texture. Coarse-grained massive sulfide ores mainly consist of sphalerite, and to a lesser extent galena and chalcopyrite. In addition, pyrite occurs in these types of ores in fine to coarser sizes. Altered and oxidized massive ores display similar characteristics as coarse-grained massive ores; however, they contain additional oxidized and altered minerals. Disseminated massive sulfide ore deposits contain significant amounts of pyrite, hosting chalcopyrite, galena, and sphalerite in its cavities and fractures. Refractory massive sulfide ores very complex to treat that the coarse sphalerite particles involve other sulfide minerals, chalcopyrite and pyrite occurring in very fine sizes, while galena is relatively free of chalcopyrite and pyrite inclusions (Bulatovic, 2007).

Sedimentary deposits are the second major group of complex copper-lead-zinc ore deposits chalcopyrite, galena, and sphalerite being the main valuable minerals, displaying open space and replacement textural patterns. In terms of grain size, chalcopyrite, galena, and sphalerite are coarse and the liberation of these minerals is sufficiently achieved at sizes about 60% passing 75 µm in spite of the fact that a part of these ores might be in fine sizes, leading to the significant problems regarding the selective concentration. Pyrite, marcasite, quartz, calcite, and dolomite are the most common gangue minerals observed in the sedimentary sulfide ore deposits, which might also contain a variety of other minerals such as bornite, chalcocite, covellite, pyrrhotite, magnetite, etc. (Hagni, 1990).

2.5 Complex Copper-Lead-Zinc Sulfide Reserves in Turkey

The complex copper-lead-zinc sulfide deposits of Turkey were discovered mainly in northeastern Anatolia, around Artvin, Rize, Trabzon, Giresun, and Ordu provinces. In addition, Turkey has copper-lead-zinc sulfide deposits in Kastamonu, Balıkesir, Çanakkale, Malatya, Siirt, and Elazığ. General Directorate of Mineral Research and Exploration (MTA) reported that total proven and probable copper, lead, and zinc reserves of Turkey were approximately 1.8 M tonnes, 0.86 M tonnes, and 2.3 M tonnes, respectively (MTA, 2013).

Particularly Artvin province, located in the Black Sea Region, is one of the most important sources of poly-metallic deposits, containing copper, lead, zinc, gold, and silver metals. Poly-metallic deposits in the region are classified into four main types as volcanogenic massive sulfide type (VMS), vein type, epithermal type, and skarn type deposits. Locations, reserve amounts, and metal assays of some of the important complex sulfide deposits in the Artvin region are given in Table 2.2 (MTA, 2010).

Table 2.2 Important complex sulfide deposits in Artvin region

Deposit	Proven+Probable Reserve Amount (M tonne)	Metal Assay
Borçka-Akarşen	0.66	3.2% Cu, 1.5 g/t Au, 28 g/t Ag
Hopa-Peronit-Abana	0.24	0.89% Cu%, 2-12% Zn
Kafkasör-Cerattepe	3.90	5.2% Cu, 1.2 g/t Au, 25 g/t Ag
Merkez-Sinkot	5.00	0.39% Cu
Merkez-Seyitler	2.81	1.68% Cu, 2.51 Zn%, 0.35 g/t Au, 36.84 g/t Ag
Murgul-Anayatak	18.0	1.59% Cu
Murgul-Çakmakkaya	16.6	0.99% Cu
Şavşat-Meydancık	0.34	1.36% Cu, 0.38% Pb, 3.21% Zn

In the Şavşat region, Dereiçi (Meydancık) complex sulfide ore is an example of vein type deposit that the mineralization observed in the Dereiçi deposit is grouped into three main groups as, sphalerite-galena-chalcopyrite-pyrite veins, milky quartz-chalcopyrite-sphalerite-galena-pyrite veins, and chalcopyrite-pyrite veins. In addition chalcopyrite, galena, and sphalerite, other major valuable minerals present in the ore deposit are chalcocite, covellite, and tetrahedrite. The gangue minerals of the deposit are pyrite, quartz, sericite and calcite (Soylu and Erler, 1999).

2.6 Flotation of Complex Copper-Lead-Zinc Sulfide Ores

Selective beneficiation of complex copper-lead-zinc sulfide ores through flotation is a very complicated, multiphase, and chemically reactive hydrodynamic process having a variety of both controllable and uncontrollable parameters determining the overall performance (Rogers, 1962; Chander, 1999). The loss of metals to the tailings during sulfide ore flotation is regarded as the biggest problem of the sulfide metal flotation plants (Cramer, 2001).

For the concentration of complex sulfide ores, variables such as mineralogy and complexity of the ore, size and chemistry of mineral crystals, and concerns related to concentration and recovery of precious metals (e.g. gold and silver), frequently found in sulfide minerals determine the type of flotation process applied. Mainly, three basic approaches, sequential flotation of copper-lead-zinc, bulk copper-lead flotation followed by zinc flotation of bulk tailings, and sequential copper-lead-zinc flotation after conducting bulk copper-lead-zinc flotation, are utilized widely for the selective flotation of complex sulfide ores.

2.6.1 Sequential Copper-Lead-Zinc Flotation

Among the processing plants concentrating the complex copper-lead-zinc sulfide ores, only around 10% are operated utilizing the sequential copper-lead-zinc flotation. Despite the fact that this method is costly as compared to the bulk copper-lead flotation method, better results are obtained in terms of the recovery of precious metals like gold and silver in the sequential process. As the name of the method implies, the selective concentration of complex sulfide ore is started with the depression of galena and sphalerite, meaning the recovery of copper is accomplished first. Sequential flotation method is further categorized into three main methods based on the combination of flotation reagents used in the process, as bisulfite method, soda ash-SO_2, or alternatively lime-SO_2 method, and starch-lime method (Bulatovic, 2007).

During the copper concentration, sodium metabisulfite ($Na_2S_2O_5$) and zinc sulfate ($ZnSO_4$) are used to depress galena and sphalerite, respectively (Bulatovic, 2007). Following the depression of galena and sphalerite, various collectors such as ethyl xanthate or dithiophosphate are used separately or in combination for the flotation of copper minerals (Thom, 1961). For the separation of lead from zinc, galena is floated in the second circuit using soda ash (Na_2CO_3) as pH regulator, sodium cyanide (NaCN) for the depression of both pyrite and sphalerite, and a dithiophosphate type collector for the flotation of galena. In the last circuit of sequential flotation systems, in which sphalerite is recovered, pH is adjusted using lime (CaO), the activation of sphalerite is obtained using copper sulfate ($CuSO_4$), and sphalerite is floated with xanthate or dithiophosphate type collector (Thom, 1961; Bulatovic, 2007).

Soda ash-sulfurous acid method starts with the grinding of ore with soda ash to depress pyrite and the pH of the medium readjusted by SO_2 to below neutral pH to depress galena and to increase the recovery of chalcopyrite. Subsequently, for the flotation of copper mineral, thionocarbamate or dithiophosphate type collectors is used depending on the pH of the pulp and the nature of the ore. Alternatively, lime might be used in the grinding stage that higher lime additions are resulted in higher SO_2 consumption for adjusting pH and lead to higher selectivity between chalcopyrite and galena in some plants. In order to separate galena and sphalerite, sodium metabisulfite is used as the galena depressant in this method (Bulatovic, 2007).

Starch-lime method is conducted for the selective separation of complex sulfide ore, which includes precious metals and pre-activated sphalerite. These types of ores are ground with lime and starch, subsequently the pH is modified between 4.5 and 5.5 using SO_2. Oxidized starch is added to depress galena (Allen and Bourke, 1978; Schnarr, 1978; Misra *et al.*, 1985). Ethyldithiocarbamate and dithiophosphates are the examples of collectors utilized for the copper flotation in the starch-lime method. Lead flotation is conducted using soda ash as a pH regulator, zinc oxide (ZnO) and sodium cyanide as zinc depressants, and xanthate-dithiophosphate combination as collectors.

Recovery of zinc is done at the last stage that lime and copper sulfate are used as a pH regulator and as a zinc activator, respectively (Bulatovic, 2007).

2.6.2 Bulk Copper-Lead Flotation

The most widely utilized method for the selective separation of complex copper-lead-zinc sulfide ores is the bulk copper-lead flotation, i.e. depression of zinc in the first place, and subsequent copper-lead separation through flotation. For the separation of the bulk copper-lead concentrate obtained in the first stage of the method might be done by depressing either copper or lead. The decision regarding the types and the dosages of reagents being used is made relying on many variables of the ore (e.g. geology, mineralogy, grade, mining practice, etc.) that a variety of flotation chemicals are used in the bulk copper-lead flotation systems (Bulatovic, 2007).

Lime is used as the pH modifier in the flotation circuits when the overall process is carried out at alkaline pH. However, soda ash – SO_2 and lime – SO_2 combinations are also applicable in many plants; particularly the latter option is used when the sulfide ore is partially oxidized. The types of main depressants change in accordance with the type of pH regulator that sodium sulfite – sodium sulfide depressant combination is used when the pH regulator is lime; while sodium cyanide and zinc sulfate are used as the principal depressants in the flotation systems in which pH is controlled using soda ash. However, depending on the type of ore, the abovementioned pH regulator-depressant combinations might be changed and different selections might be applied. In the first stage of bulk copper-lead flotation, xanthates, dithiophosphates, dithiocarbamates, and mercaptans are used generally in combination (Bulatovic, 2007; Fuerstenau, 2007).

In order to separate copper and lead, two main methods are followed. In the first method, lead is recovered in the froth product, whereas copper is depressed using sodium cyanide or its combinations with other possible depressants depending on the grade and recovery concerns of the ore. Sodium cyanide is regarded as an effective chalcopyrite depressant when it is used in high concentrates at alkaline pH. This process is alternatively called as cyanide method. In the second method utilized to concentrate lead and copper separately, lead is depressed using several reagents such as potassium dichromate ($K_2Cr_2O_7$), sodium dichromate ($Na_2Cr_2O_7$), sodium sulfite, and sodium metabisulfite, etc (Bulatovic, 2007; Fuerstenau, 2007).

For the recovery of zinc from the bulk copper-lead flotation tailings, lime (pH regulator), copper sulfate (activator), and various collector types (xanthates, dithiophosphates, etc.) are used (Bulatovic, 2007; Fuerstenau, 2007).

2.6.3 Bulk Copper-Lead-Zinc Flotation and Subsequent Selective Flotation

In the presence of copper sulfide minerals, sphalerite might be activated by copper ions; therefore, depressing of sphalerite might not be obtained sufficiently (Finkelstein, 1997). In addition, some of the complex sulfide ores are composed of clay minerals in considerable amounts that slime may interrupt the possible reaction between the mineral and depressant, i.e. depression of such slime-coated minerals might not be managed (Leja, 2004). On such conditions, bulk copper-lead flotation or sequential copper-lead-zinc flotation without desliming the ore are not applicable; therefore, bulk copper-lead-zinc flotation is conducted (Bulatovic, 2007).

2.7 Important Aspects in Complex Sulfide Ore Flotation

Beneficiation of a complex sulfide ore deposits through flotation is affected by several parameters that not paying attention on those parameters prior to flotation may have great impacts on the process in terms of selectivity, grade, and recovery. In the simplest sense, particle size of the ground sulfide ore, the grinding environment, and the oxidation problems of the sulfide minerals can be regarded as the examples of the most important pre-concentration parameters influencing the whole process.

2.7.1 Particle Size of Ground Sulfide Ore

Grinding of an ore, liberating the valuable mineral particles, is an important aspect for all beneficiation processes. For sulfide metallic ores, liberation is usually accomplished at very fine sizes. Besides particle liberation, fine sizes are required in flotation process since the size of the mineral particles affects the bubble loading phenomena, collision of particle with air bubbles and subsequent attachment, such that the number of particles loaded per bubble decreases as the size of an individual particle increases (Bradshaw and Connor, 1996). For an effective bubble loading, medium sized particles are preferable since they form smaller and stable bubbles (Feng and Aldrich, 1999).

Grinding of a sulfide ore more than required may result in undesired results during flotation. Natural floatability of a sulfide mineral is heavily affected by its size that they display their floatable character only in limited size ranges. In addition, reduction of particles size may increase the possibility of mechanical entrainment, i.e. unvaluable fine particle might be recovered in the froth product (Trahar, 1981). Generation of slimes is more possible in fine grinding that slime coating of valuable particles is an unfavorable condition, which decreases the flotation selectivity (Muster and Prestidge, 1995).

2.7.2 Grinding Environment in Sulfide Ore Flotation

Controllable or uncontrollable parameters encountered during the grinding of a sulfide ore have several impacts on the flotation system that the interaction between the grinding media and the mineral particles, the grinding method, pre-conditioning the ore in the mills affect the nature of the process both chemically and physically.

During the grinding, galvanic interactions (coupling) occur between the sulfide minerals, and between the minerals and the steel grinding media (Rao and Finch, 1988; Cheng and Iwasaki, 1992; Li and Iwasaki, 1992; Cheng *et al.*, 1993). Galvanic interaction takes place due to the difference in the rest potentials of the metallic mineral particles that the minerals having higher rest potentials acts as a cathode, drawing electrons from the minerals that possess lower rest potentials. Therefore, galvanic interactions alter the activity of minerals and prevents the possible reactions with collectors, influencing the efficiency of flotation. Similarly, steel media might cause galvanic coupling with the minerals due to the fact that mild steel has lower rest potential as compared to those of common sulfide minerals. For instance, chalcopyrite is heavily affected by the galvanic interaction between steel grinding media, causing the formation of iron hydroxides on chalcopyrite surfaces by increasing the iron level and lowering the dissolved oxygen concentration in the pulp. Another impact of galvanic coupling is on pH of the pulp that the consumption of hydroxyl ions in the pulp to form precipitates with iron lowers the pH of the pulp. (Bruckard *et al.*, 2011).

Common practice in sulfide ore flotation is grinding the ore in steel rod mills or ball mills in wet conditions. However, using fully autogenous mills might give better results in copper flotation in terms of recovery (Thornton, 1973; Bruce, 1976; Petruk and Hughson, 1977; Forssberg *et al.*, 1988). In addition, dry grinding prior to flotation of copper minerals enhances the grade and recovery of copper as compared to wet grinding (Lepetic, 1974; Hoberg, *et al.*, 1985; Martin *et al.*, 1991; Feng and Aldrich, 2000).

Pre-conditioning the ore in the mills is done by the addition of collectors, lime, and cyanide. Addition of collectors during milling has several advantages as minimizing the galvanic interaction and increasing the adsorption of collector onto mineral surfaces before they are oxidized (Yelloji Rao and Natarajan, 1988; Bruckard *et al.*, 2011). The recovery of chalcopyrite and the depression of pyrite can be enhanced by the addition of lime during grinding (Grano, 2010). Sodium cyanide is commonly added during milling in copper mineral flotation process to depress pyrite, however, addition of the excessive amounts of cyanide might results in reduction of copper recovery (Grano *et al.*, 1994).

2.7.3 Oxidation Problems in Sulfide Ore Flotation

Oxidation of the surfaces of sulfide minerals is considered as one of the most important parameters that the surfaces of sulfide metals are prone to oxidation in both wet and dry conditions. Oxidation of surfaces adversely affects the natural floatable characters of the minerals, e.g. chalcopyrite (Luttrell and Yoon, 1984).

Among chalcopyrite, galena, sphalerite, pyrite, the surface of pyrite is oxidized more rapidly than that of other three sulfide minerals during dry grinding. Following pyrite, the surface of chalcopyrite is oxidized more quickly when it is exposed to air. Oxidation of galena and sphalerite takes longer time that the latter has the slowest oxidation rate during grinding in dry conditions. On the other hand, when they are exposed to distilled water after being ground in dry conditions, the surfaces of pyrite, galena, and sphalerite do not display any surface degradation, while the surface of chalcopyrite is oxidized that iron hydroxide or iron oxyhydroxide are formed within the first layers its surface (Brion, 1980). In addition, oxidation of complex sulfide ore is enhanced by the presence of pyrite (Majima, 1969).

Unintended flotation of gangue particles or conversely undesired depression of valuable minerals due to oxidation may result in obtaining low-grade concentrates and high smelting costs.

CHAPTER 3

STATEMENT OF THE PROBLEM

The objective of this study is to investigate the amenability of Artvin-Dereiçi complex sulfide ore to concentration by flotation method. Sulfide metallic ores contain one or more of the metal sulfides, chalcopyrite, galena, sphalerite, and pyrite being the most important examples. Flotation is one of the most comprehensive and the most widely used mineral processing technique which allows treating complex ores having fine grain size, low grade, distinct chemistry and mineralogy. Therefore, the primary goal in this study is to obtain metallic minerals present in Artvin-Dereiçi ore as selective separate concentrate products with marketable metallurgical features. In this manner, this study consists of three main phases. These are:

1. Determining the characteristics of Artvin-Dereiçi ore in terms of mineralogy and metal assay
2. Preparation of the ore samples to be used in flotation
3. Concentration of the ore through flotation to determine its amenability and the optimum flotation conditions

CHAPTER 4

MATERIALS AND METHODS

4.1 Complex Sulfide Ore Samples

Complex sulfide ore samples obtained from Artvin-Dereiçi reserve were used in the flotation based concentration studies. Approximately 180 kg's of ore was delivered in the form of drill cores in sealed boxes. This study for determining the concentration possibility of Artvin-Dereiçi ore through flotation consisted of three main stages as mineralogical and geometallurgical investigations and assessment of findings for concentration tests, preparation of ore samples for concentration tests, and concentration of the ore using flotation.

4.1.1 Mineralogical-Petrographical Investigations and Assessment of Findings for Concentration Tests

4.1.1.1 Optical Microscope Analysis

Firstly, drill cores obtained from the ore were carefully examined and the image of the delivered drill core samples is given in Figure 4.1. Rock pieces that represent specific mineralogical formations and sections in the reserve were retrieved from drill cores and sorted into distinctive groups of mineralogy and appearance (texture, color, luster, etc.). Each group was subjected to a secondary and a more precise examination to select samples for preparing polished sections. The goal was to evaluate the mineralogy of the reserve extensively, hence any rock piece that possessed specific and distinctive physical features were selected for preparing polished sections.

The polished sections were examined under optical microscope to define mineralogical formations and characteristics that would provide critical information regarding flotation concentration of Artvin-Dereiçi ore. Mineralogical-petrographical investigations were conducted to identify:

1. Mineralization in the reserve, valuable minerals, gangue minerals, and associated rocks, i.e. minerals that include targeted metals with potential value, unvaluable associations as well as other minerals that would impact flotation concentration.
2. Modes of occurrence of significant minerals in the ore, distribution, characteristic grain size, and grain shape of these minerals.
3. Association modes of significant minerals (associated, locked/encapsulated, free, etc.)
4. Possible liberation size of valuable minerals in the ore based on their modes of occurrence and associations.

Figure 4.1 Classification of drill cores

The images taken under the optical microscope to examine the mineralogy and the petrography of seven different polished sections are presented in Figures 4.2 – 4.43.

The images taken for the first polished section showed that the sample was a vein-type hydrothermal ore specimen involving sphalerite, chalcopyrite, pyrite, galena, and fahlerz as ore minerals as well as pyrite, calcite, and quartz as the major gangue minerals.

Sphalerite was the most common and major metallic ore mineral in this specimen. Sphalerite occurred in the form of coarser particles locked with decomposed chalcopyrite entities and showed cataclastic structure (Figures 4.2 and 4.3). The fractures and veins in sphalerite particles were filled mainly by carbonate minerals (calcite, dolomite) as well as younger minerals such as quartz, chalcopyrite, galena, and fahlerz (Figures 4.2 and 4.4). Calcite and calcite-quartz veins that cut across sphalerite occurred with a broad range of widths (Figures 4.2, 4.5, and 4.6). In sphalerite particles, euhedral pyrite entities and inclusion crystals of quartz were also observed with limited extents and these were relatively older minerals. The size of such entities were commonly less than 0.1 mm.

Chalcopyrite was less common compared to sphalerite that some part of chalcopyrite occurred as decomposed ultrafine entities (a few μm in size) encapsulated in coarser sphalerite grains (Figures 4.2, 4.3, and 4.5). Due to extremely fine sizes, liberation of such chalcopyrite particles from sphalerite through conventional grinding techniques seemed unlikely. It was anticipated that these ultrafine chalcopyrite entities would be recovered with coarser sphalerite particles and might cause presence of copper in the zinc concentrate. The rest of chalcopyrite was generally coarse, but also occurred in varying particle sizes (Figures 4.2 – 4.4, 4.6, and 4.7). These particles occurred as replacements in sphalerite and sutured with sphalerite, pyrite, and other gangue minerals. A majority of this group of chalcopyrite particles were coarser than 0.1 mm while some chalcopyrite particles finer than 0.1 mm were also observed.

Galena was observed at a lesser extent as compared to sphalerite and chalcopyrite. Galena, being a younger ore mineral, occurred mainly as fills in the fractures and veins of other major minerals in the specimen (Figures 4.3, 4.4, 4.6, and 4.8). Galena particles were mostly finer than 0.1 mm and the width of galena veinlets were mostly less than 30-40 μm.

Fahlerz (tennantite-tetrahedrite) was very rarely observed. Fahlerz was seen mainly in the fractures of other minerals and particularly sutured with chalcopyrite.

Pyrite was in limited quantity in this specimen. Pyrite particles occurred in varying sizes, and as euhedral and subhedral particles. Pyrite was the oldest metallic mineral in Artvin-Dereiçi ore, and therefore occurred as inclusions in sphalerite, chalcopyrite, and gangue minerals (Figures 4.2 – 4.4, 4.6, and 4.7). Coarsest pyrite crystals were approximately 0.4-0.5 mm. Occasionally, pyrite particles occurred in gathered form as sutured grains (Figures 4.6 and 4.7). When encapsulated in sphalerite and chalcopyrite, the size of pyrite crystals was generally less than 0.1 mm.

Calcite was abundant in this specimen. Calcite filled the fractures and voids in or between ore minerals (particularly sphalerite), as well as quartz. Calcite veins and crystals occurred in a broad range of widths and sizes. Fine grinding would be required to achieve sufficient liberation between some thin calcite veins and sphalerite particles.

Quartz was identified at a lesser extent than calcite. Quartz occurred in varying particle sizes, as older crystals in euhedral form. The coarsest quartz particles were 0.4-0.5 mm. Quartz particles were observed as inter-sutured entities as well as sutured with calcite and ore minerals. In addition, quartz might occur as inclusion crystals in the ore minerals and occasionally in the form of veins cutting across the ore minerals.

It was concluded that the mineralization was probably of hydrothermal vein type. The significant ore minerals in this specimen were sphalerite and chalcopyrite, which occurred at a lower extent. Liberation of sphalerite and chalcopyrite from gangue minerals and quartz would require fine grinding down to 0.1 mm, while liberation of galena and fahlerz, which were rarely observed in this specimen, would require grinding to sizes much finer than 0.1 mm.

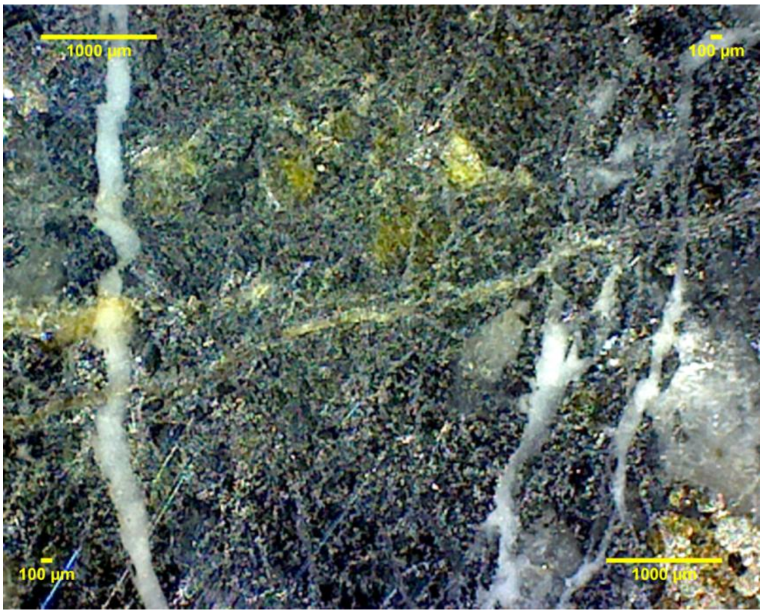

Figure 4.2 Presence of sphalerite, chalcopyrite and pyrite, ultrafine and disseminated chalcopyrite entities, various metallic minerals and gangue fillings in fractures, gangue veinlets

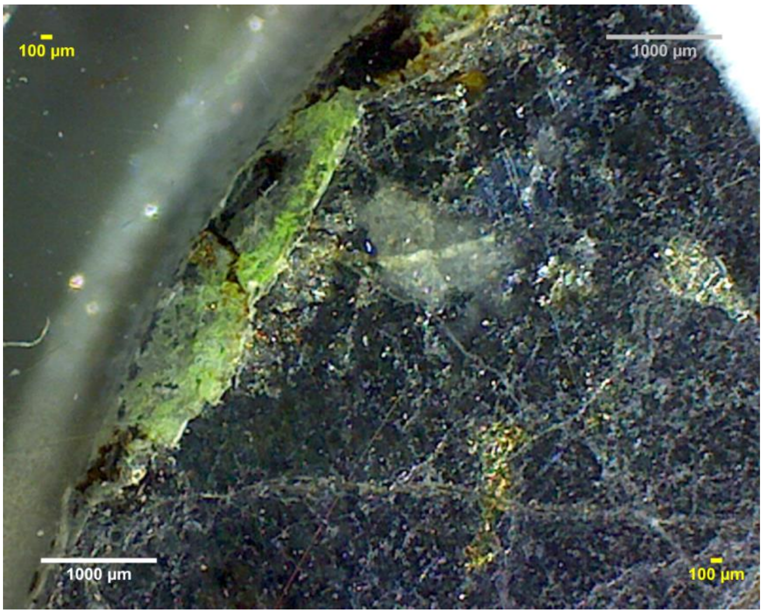

Figure 4.3 Presence of sphalerite, chalcopyrite, pyrite, randomly distributed very fine chalcopyrite and galena entities

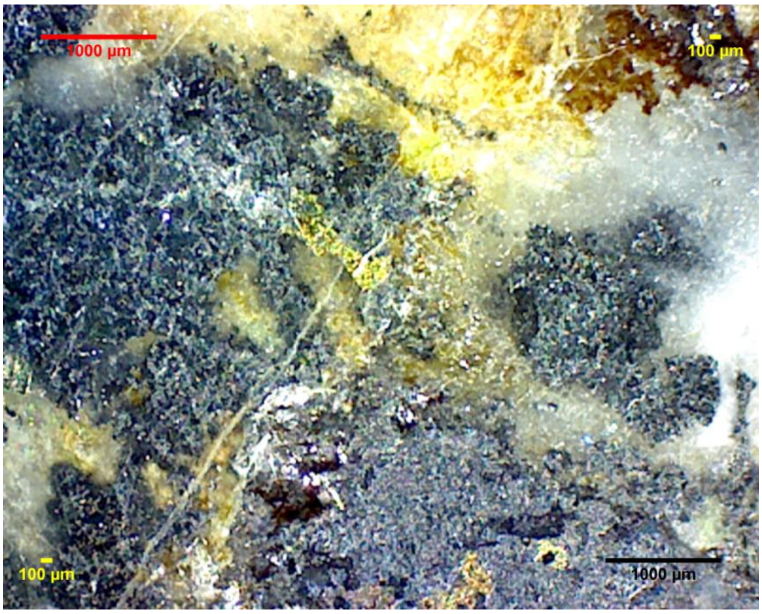

Figure 4.4 Chalcopyrite and occasional pyrite, galena and gangue mineral fillings in fractures

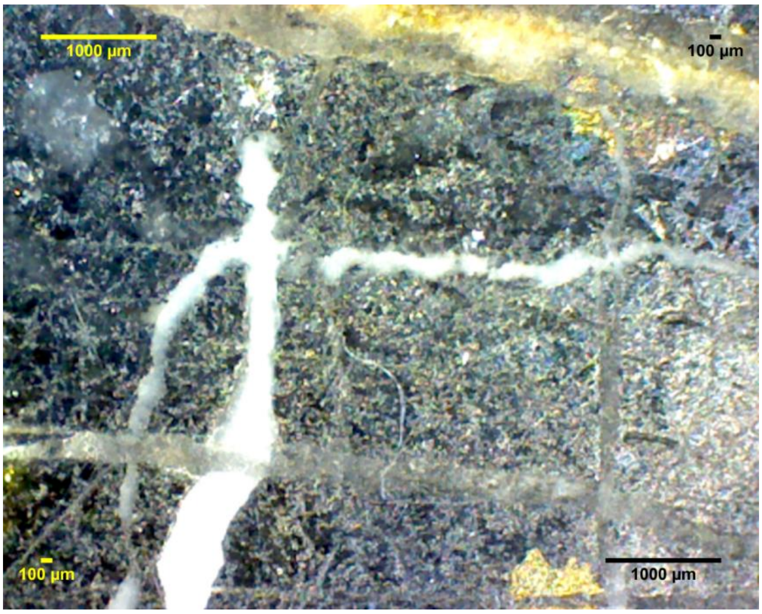

Figure 4.5 Gangue veins with various widths, disseminated fine and ultrafine chalcopyrite particles

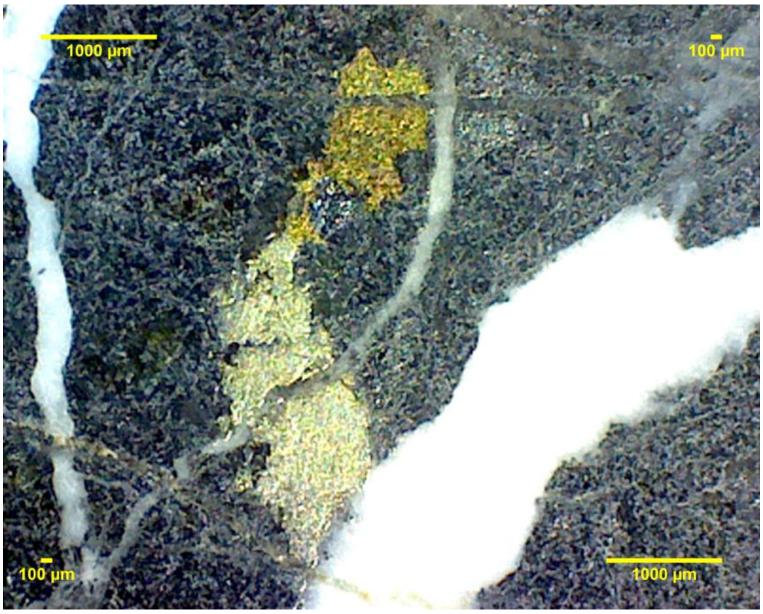

Figure 4.6 Gangue veins with various widths, chalcopyrite, pyrite and some galena in sutured form

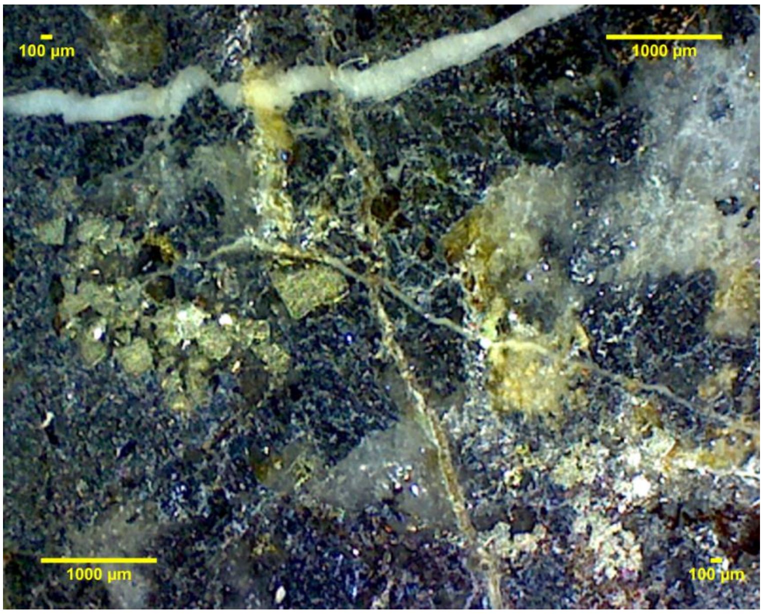

Figure 4.7 Chalcopyrite particles in different sizes, fine chalcopyrite particle groups; fine pyrite particles in groups and sutured form

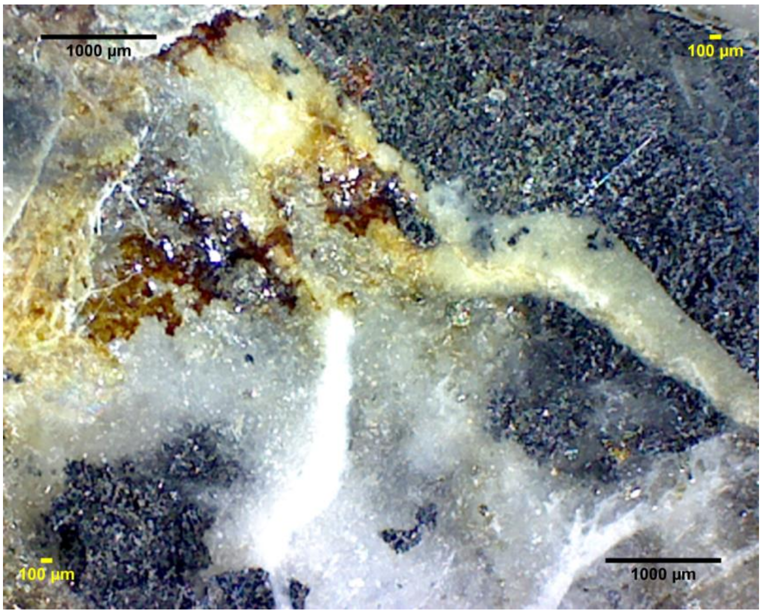

Figure 4.8 Presence of galena between minerals and in voids

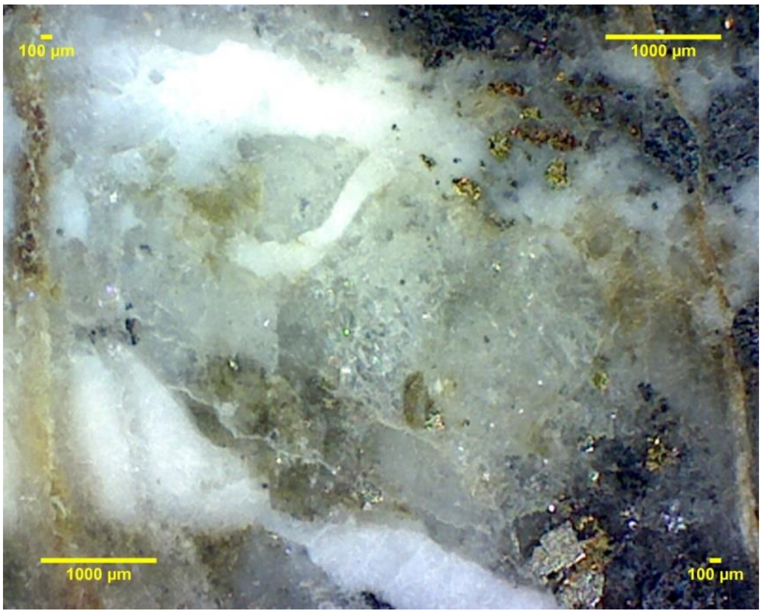

Figure 4.9 Presence of calcite and quartz, chalcopyrite and pyrite particles in different sizes

The images taken for the second polished section revealed that the host rock has been hydrothermally altered, i.e. has been totally silicified, sericitized, chloritized, carbonatized, sphenized, and pyritized. The specimen totally lost its structural-textural features and its original mineral composition due to intensive hydrothermal alteration.

Main metallic minerals in the specimen were pyrite and rutile (Figures 4.10 – 4.13). Pyrite was seen in as euhedral and subhedral crystals. Pyrite occurred in the form of disseminated crystals in the altered host rock. Occasionally pyrite was observed in gathered form as sutured grains. Coarsest pyrite crystals were approximately 0.6-0.7 mm (Figures 4.10 – 4.12). In some pyrite crystals, rutile and gangue inclusions were observed. Rutile was rare in this specimen in the form of single fine grains or as groups of fine grains. At some sections, rutile has transformed into sphene (titanite) and remained as relicts in sphene grains (Figures 4.10 – 4.13). Limonite was also very rarely observed in this specimen. Limonite occurred as a secondary mineral due to the superficial alteration of the original rock. Limonite was observed as fills in the fractures and as veins in the voids of the host rock (Figures 4.10 – 4.12).

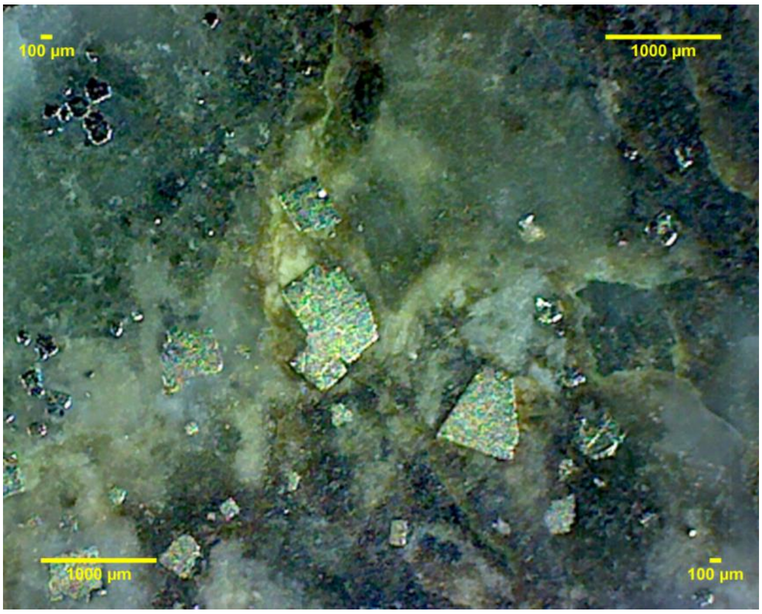

Figure 4.10 Pyrite particles in different sizes, fine rutile particles, occasionally in groups, occasional limonite veins

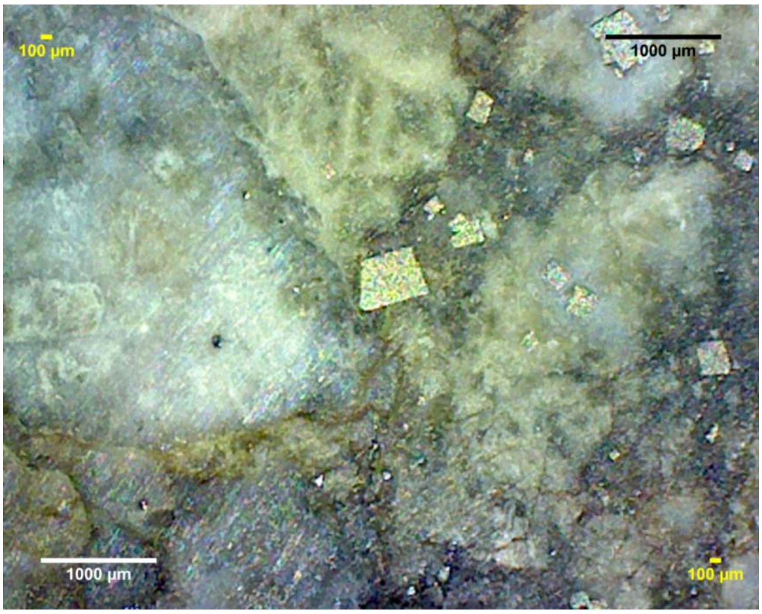

Figure 4.11 Pyrite in different sizes, fine rutile particles, occasional limonite veins

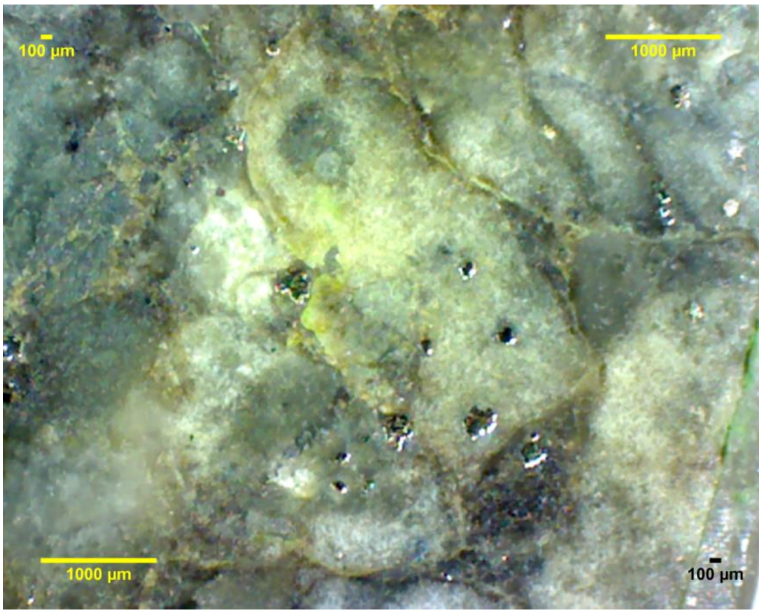

Figure 4.12 Fine pyrite and rutile particles, occasional limonite veins

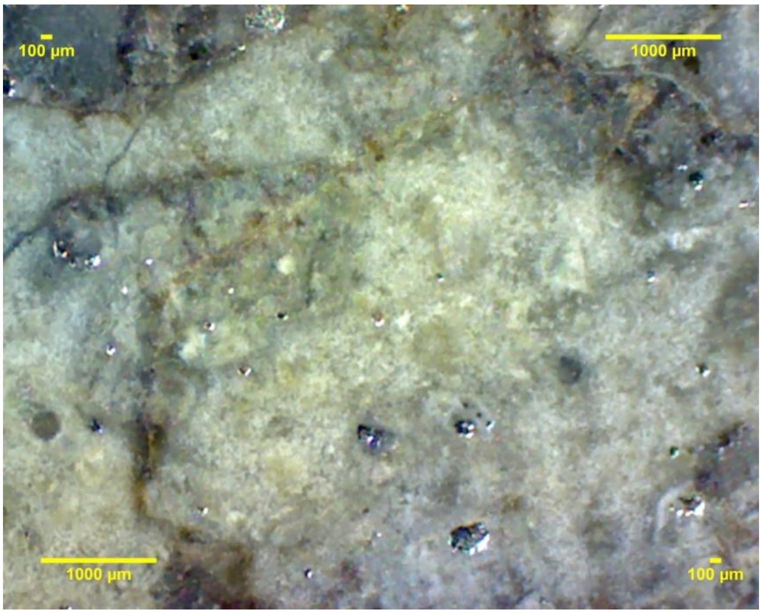

Figure 4.13 Fine and ultrafine pyrite and rutile particles

The optical microscope images of the third polished section showed the abundance of sphalerite and relatively lesser extents of chalcopyrite, pyrite, and galena as the significant metallic minerals in the specimen. Major gangue minerals were quartz and calcite.

Abundance of sphalerite was seen in this specimen (Figures 4.14 – 4.19). Sphalerite particles were coarse and included the decomposed chalcopyrite particles. The fractures in the cataclastic sphalerite particles were filled with gangue minerals (excluding pyrite) and other ore minerals. Sphalerite particles also involved inclusions of quartz and pyrite crystals.

Chalcopyrite was occasionally seen in this specimen. The majority of chalcopyrite particles occurred between and in the fractures of sphalerite, quartz and pyrite particles, in varying sizes (Figures 4.14 – 4.17). The coarsest chalcopyrite particles were 1.5-2 mm (Figures 4.14 and 4.15). Inside chalcopyrite particles, quartz, pyrite, sphalerite crystals and grains were observed as inclusions. In addition, chalcopyrite was partially observed as decomposed particles inside sphalerite.

Galena was another ore mineral in this specimen. Galena was mainly observed in the fractures of sphalerite while presence of galena in the fractures of chalcopyrite, pyrite, and quartz was also seen (Figures 4.14 – 4.18). Galena generally occurred in the form of fine particles and thin veins and the coarsest galena grains were approximately 0.3-0.35 mm.

Pyrite was rarely observed in this specimen as euhedral and subhedral crystals. Pyrite crystals mainly occurred in chalcopyrite particles with partial occurrence in sphalerite and other gangue minerals (Figures 4.14, 4.16, 4.17, and 4.19). Coarsest pyrite crystals were 0.2-0.25 mm. Occasionally pyrite was observed as inter-sutured crystals (Figure 4.17).

Calcite was the most abundant gangue mineral in this specimen. Calcite filled the voids between ore minerals and quartz crystals as well as cataclastic fractures. Calcite crystals broadly varied in size.

Quartz was less as compared to calcite. Some quartz crystals were euhedral. Quartz crystals occurred in varying sizes and were inter-sutured or sutured with ore minerals. Sphalerite and chalcopyrite particles involved inclusions of quartz crystals.

It was concluded that the specimen included sphalerite, some chalcopyrite, and rare amounts of galena. Sphalerite particles were generally very coarse, whereas chalcopyrite particles were relatively finer as compared to sphalerite. Liberation of sphalerite and chalcopyrite from pyrite and other gangue minerals would require grinding down to 0.10-0.15 mm.

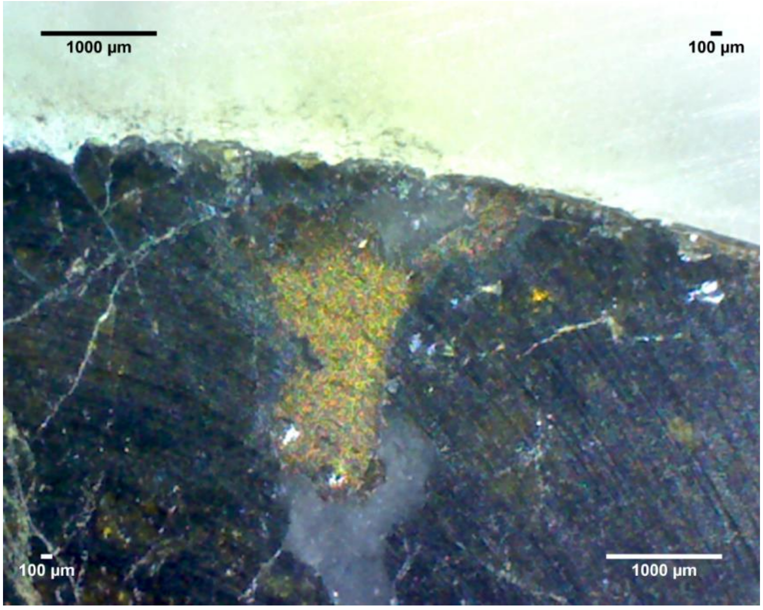

Figure 4.14 Sphalerite; coarse and fine chalcopyrite, fine galena, also, presence of fine pyrite entities inside chalcopyrite particles

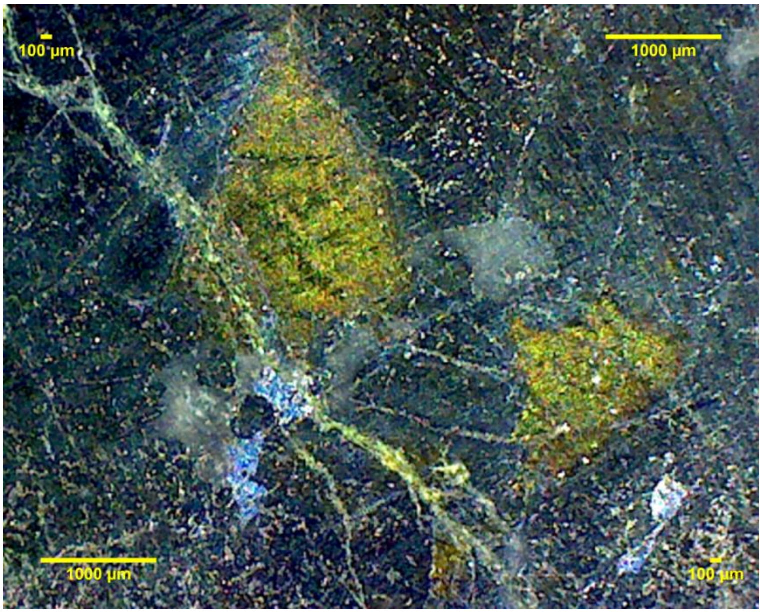

Figure 4.15 Different sized (coarse, fine, ultrafine) chalcopyrite particles in sphalerite, fine galena particles and veins with chalcopyrite fills

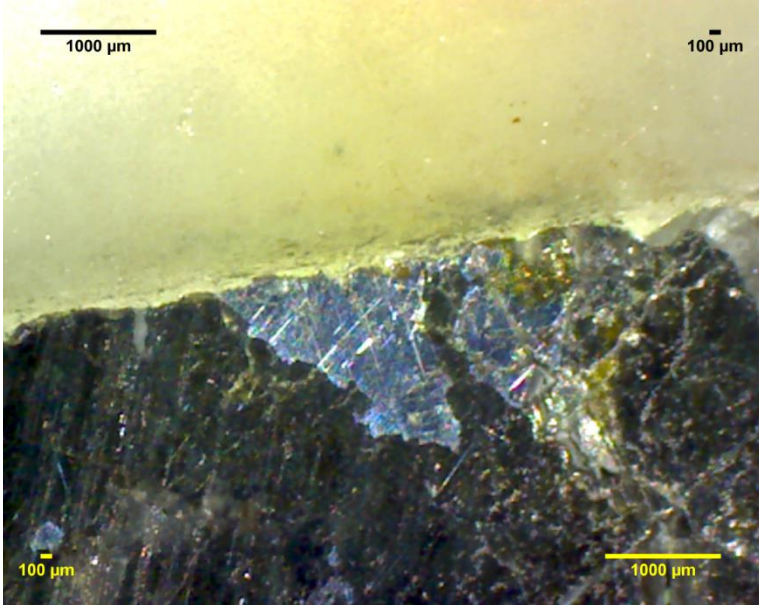

Figure 4.16 Sphalerite, chalcopyrite, galena and pyrite in sutured form

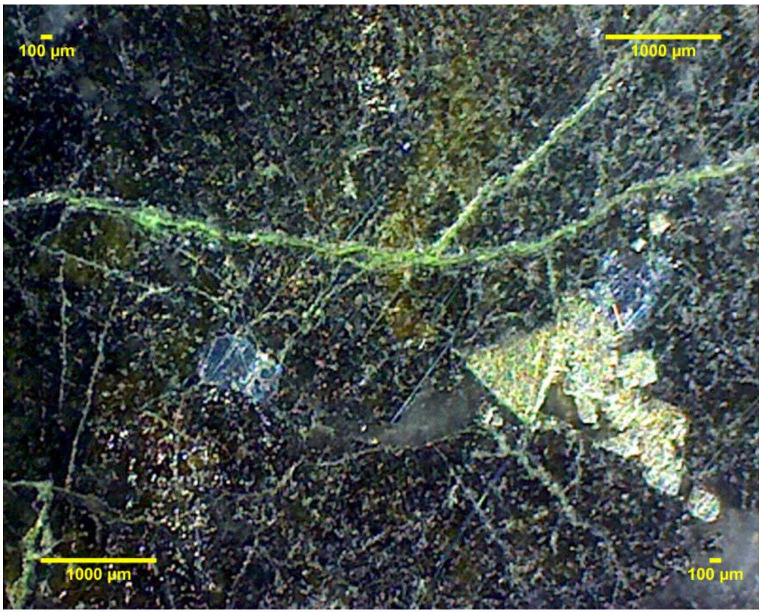

Figure 4.17 Sphalerite, different sized pyrite particles in groups and sutured form, chalcopyrite and galena particles, ultrafine, disseminated chalcopyrite particles

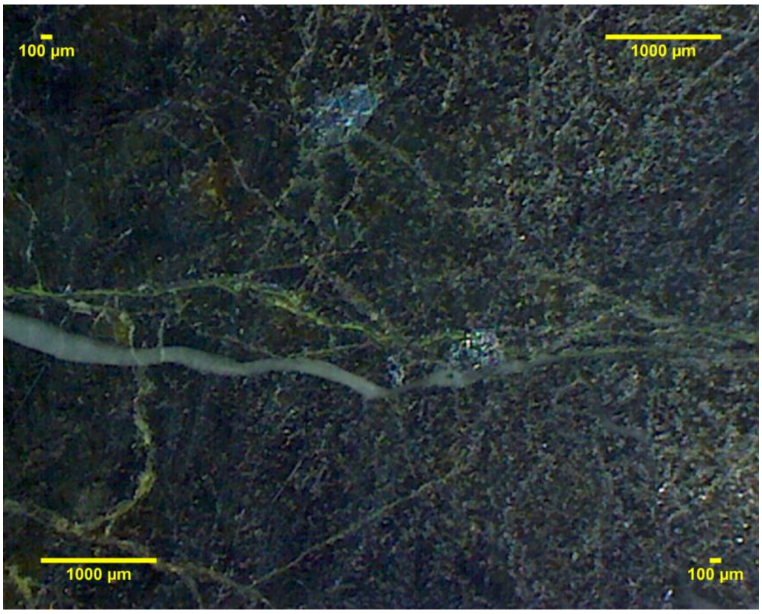

Figure 4.18 Gangue mineral veins, thin chalcopyrite veins and occasional presence of galena particles

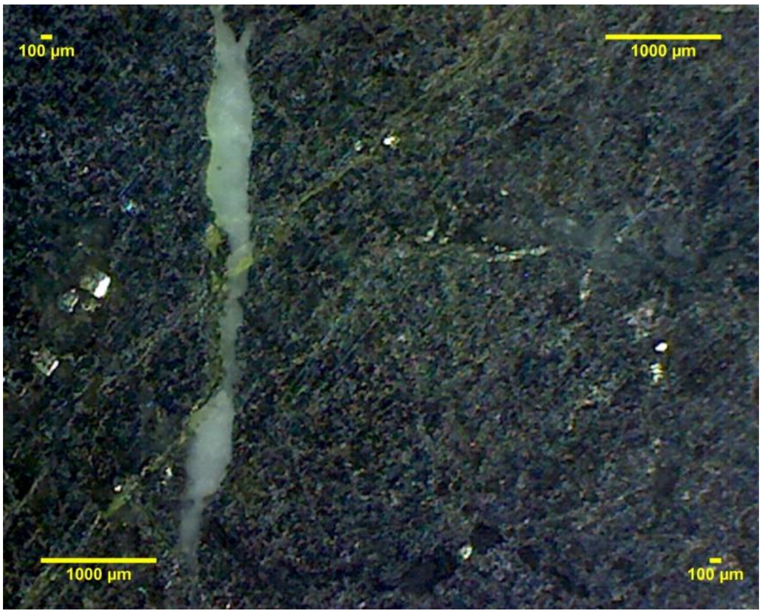

Figure 4.19 Gangue mineral veins, fine and ultrafine pyrite particles

The images of the fourth polished section showed that the specimen consisted of pyrite, chalcopyrite, fahlerz, sphalerite, rutile as metallic minerals and quartz, chlorite, sericite, and calcite as gangue minerals.

Chalcopyrite were observed abundantly in this specimen (Figures 4.20 – 4.26). Chalcopyrite particles were generally coarse, anhedral (Figures 4.22 – 4.24) with some particles finer than 0.1 mm (Figures 4.21, 4.25, and 4.26). Between quartz and pyrite crystals, chalcopyrite particles finer than 40-50 µm were also seen (Figures 4.20, 4.25, and 4.26).

Fahlerz was very rare and occurred mainly in the fractures of cataclastic pyrite particles and occasionally as fine entities sutured with chalcopyrite. A majority of fahlerz particles were finer than 35-40 µm.

Sphalerite was very rare in this specimen and occurred as sutured with pyrite, chalcopyrite and quartz. The coarsest sphalerite particles were 0.3-0.35 mm while a majority of sphalerite particles were finer than 100-150 μm.

Rutile, occurring in chlorite, in the form of single, fine entities or as groups of particles, was very rare in this specimen (Figure 4.21).

Pyrite occurrence was very common in this specimen that pyrite crystals were euhedral and subhedral and occurred in varying sizes. Pyrite crystals were mainly disseminated and occasionally occurred as inter-sutured crystals in groups (Figures 4.20 – 4.26). Pyrite was the oldest sulfide mineral in this ore and occasionally showed cataclastic structure. The coarsest pyrite crystals were approximately 2 mm (Figures 4.20 and 4.22). The voids between pyrite crystals were filled with gangue minerals, while the fractures in pyrite crystals were filled with quartz.

Quartz was the most abundant gangue mineral in this specimen. Quartz occurred as inter-sutured crystals and sutured with ore minerals. Quartz crystals varied in size and shape. Some quartz particles were euhedral. Quartz was occasionally observed as inclusion crystals in pyrite and chalcopyrite.

Chlorite and sericite were formed due to the alteration of gangue rock. These minerals were occasionally observed between quartz and ore minerals. Some part of chlorite was formed due to the hydrothermal alteration of mafic-minerals (such as amphibole, biotite) in the gangue rock. Sericite was formed due to the alteration of feldspars.

It was concluded that the most significant mineral in the specimen was chalcopyrite. Sphalerite and fahlerz were rarely observed. Liberation between the ore minerals and the gangue portions would require grinding down to 0.1 mm. At this grinding size, limited extent of chalcopyrite might remain sutured with pyrite and other gangue minerals.

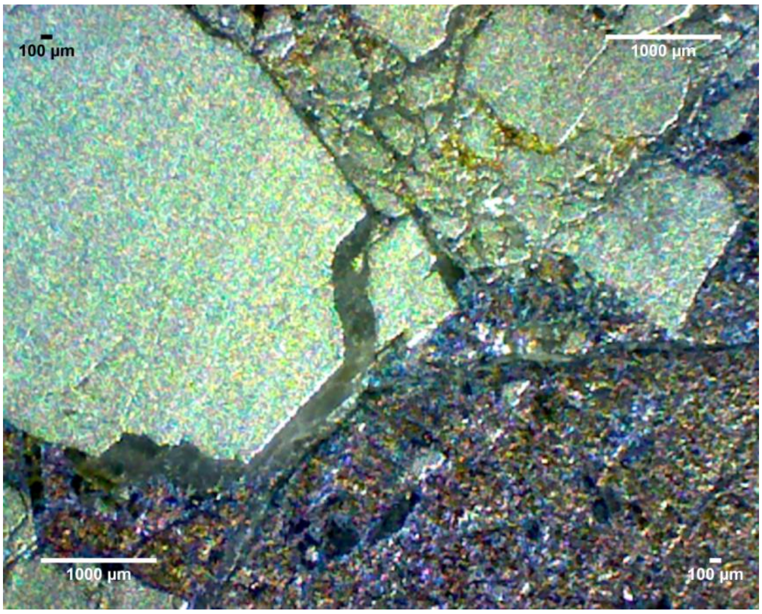

Figure 4.20 Pyrite particles in different sizes, chalcopyrite and other metallic minerals between pyrite particles

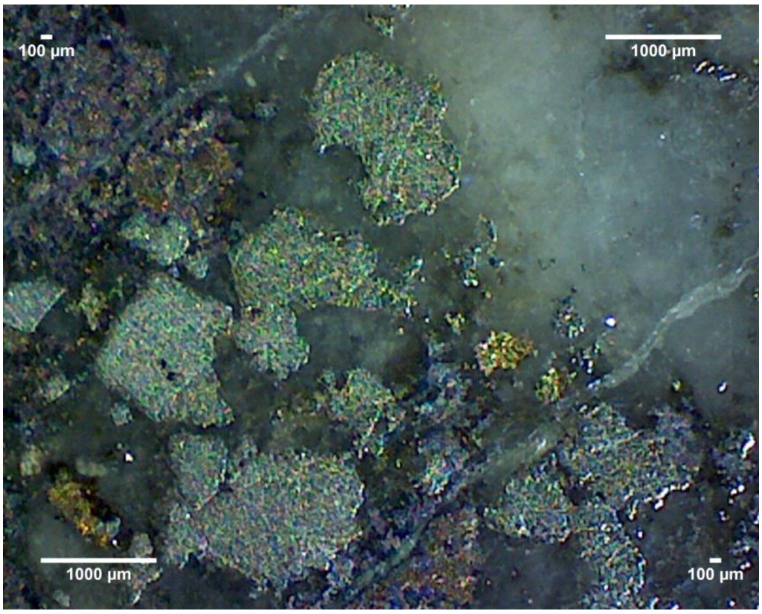

Figure 4.21 Pyrite particles in different sizes, finer chalcopyrite particles and presence of ultrafine rutile in gangue

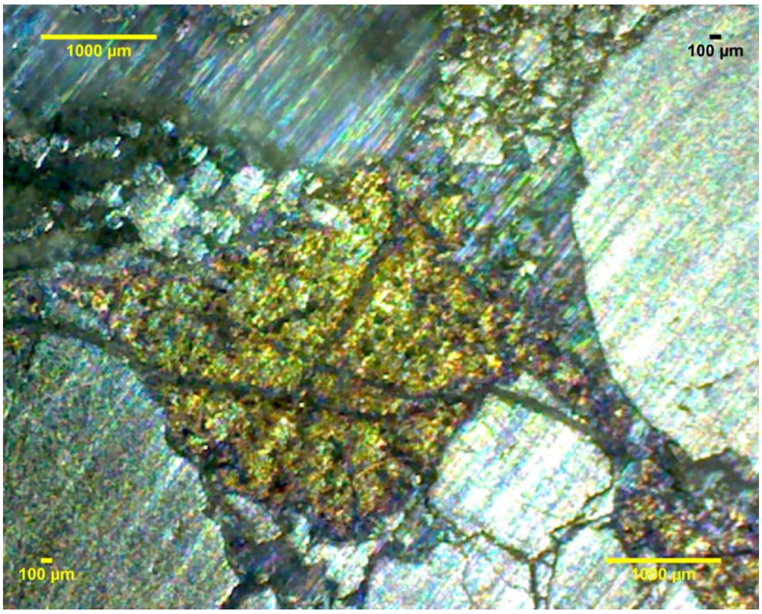

Figure 4.22 Pyrite particles and presence of chalcopyrite between pyrite particles

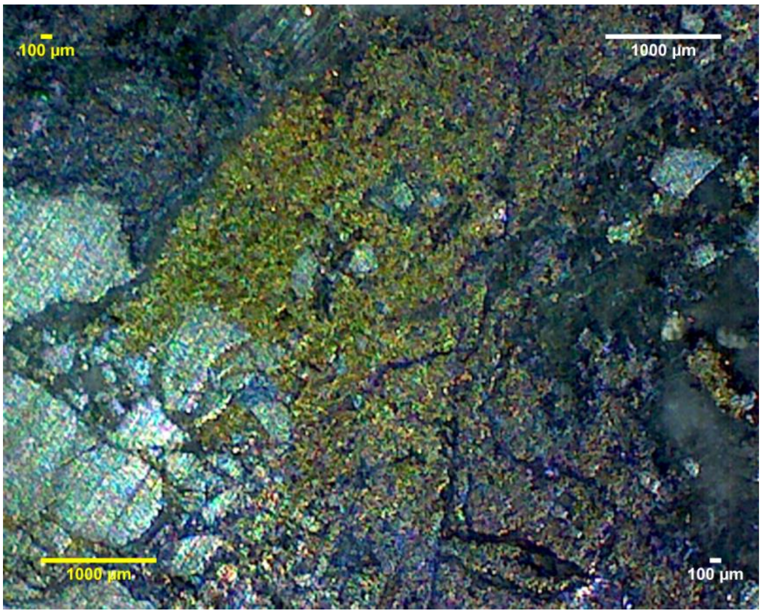

Figure 4.23 Presence of pyrite and chalcopyrite

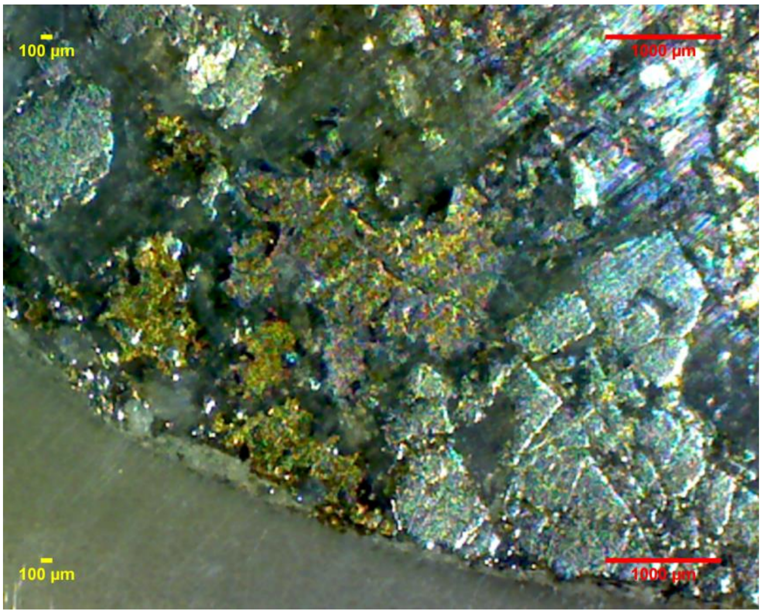

Figure 4.24 Presence of chalcopyrite and pyrite in different sizes and occasionally in sutured form

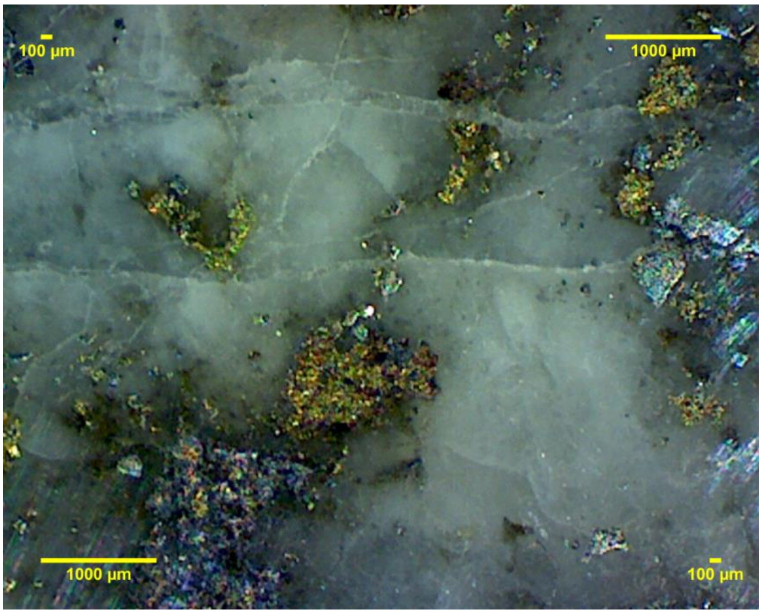

Figure 4.25 Chalcopyrite and pyrite particles with different sizes and occasional presence of ultrafine rutile entities in gangue

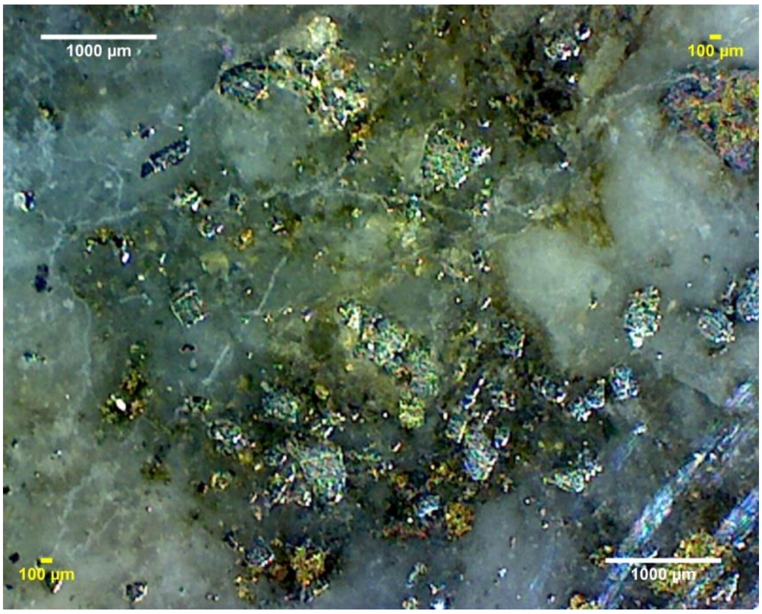

Figure 4.26 Chalcopyrite and pyrite particles with different sizes in gangue

The optical microscope images belong to the fifth polished section showed the presence of pyrite as a metallic mineral. Quartz and calcite were observed as the gangue minerals. Pyrite occurred as euhedral, subhedral crystals in disseminated and partially in inter-sutured form (Figures 4.27 – 4.29). Size of pyrite crystals varied from 10-15 µm to 0.7-0.8 mm, displaying partially cataclastic (fractured-fragmented) texture.

Major gangue minerals in the specimen were quartz and calcite (Figures 4.27 – 4.29). Quartz was particularly abundant and quartz crystals varied in size with the coarsest crystals approximating 1 mm. Some quartz crystals occurred in euhedral form inside calcite. Extent of calcite was relatively lower in this specimen. Similar to quartz, calcite filled the fractures and the voids in and between pyrite crystals.

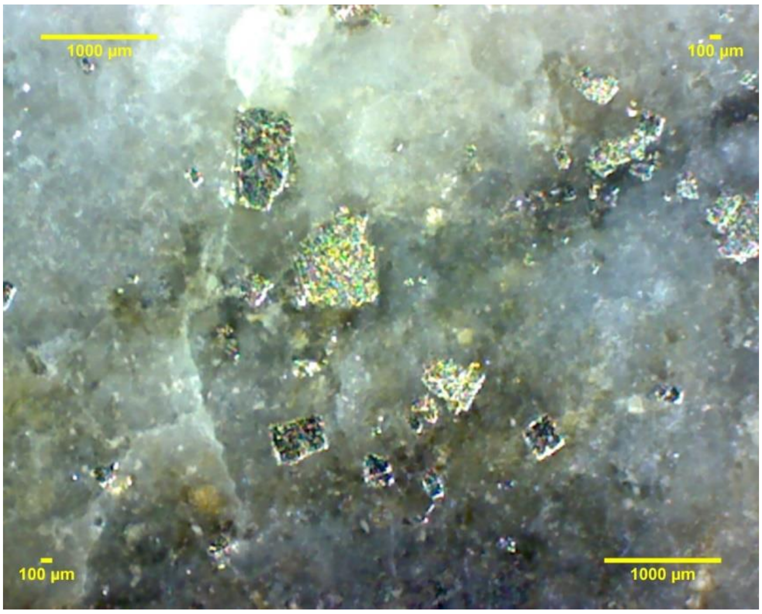

Figure 4.27 Disseminated pyrite particles in gangue minerals (calcite and quartz), Pyrite particles occur in different sizes and occasionally in sutured form

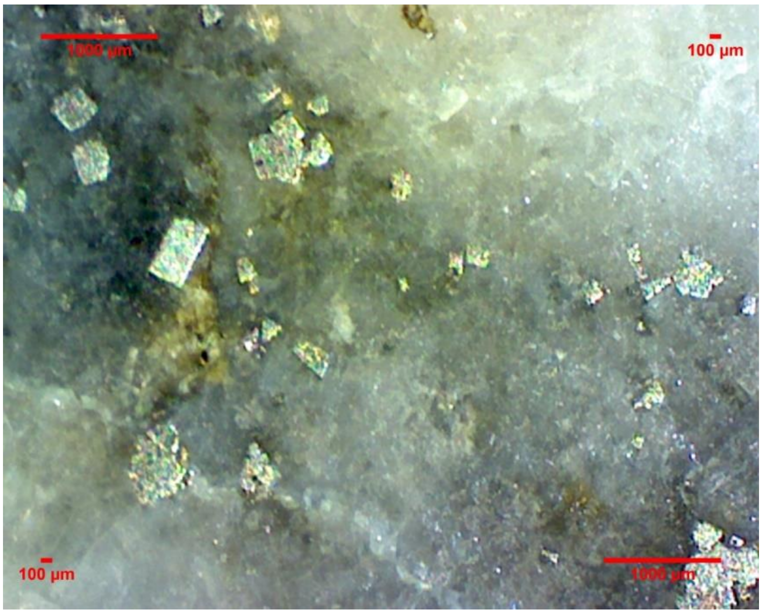

Figure 4.28 Disseminated pyrite particles in gangue minerals (calcite and quartz), Pyrite particles occur in different sizes and in sutured form

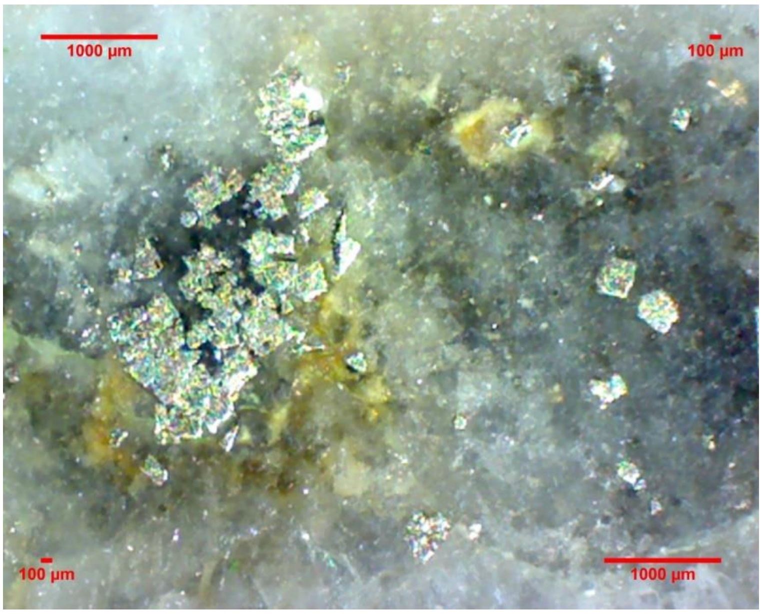

Figure 4.29 Intensive pyrite presence in quartz and calcite, pyrite particles occur as single entities, in groups and in sutured form

The optical microscope images of the sixth polished section revealed sphalerite, pyrite, chalcopyrite, and galena as the metallic minerals and quartz and calcite as gangue minerals.

Sphalerite was abundantly seen in this specimen (Figures 4.30 – 4.32). Sphalerite, including decomposed chalcopyrite grains, occurred in varying sizes and between pyrite and other gangue minerals (Figure 4.33). Sphalerite occurred generally as relatively coarse grains and rarely finer than 0.1 mm. Some sphalerite particles were as coarse as 1.5-2 mm (Figures 4.30 and 4.31). Inside sphalerite particles, pyrite and quartz were observed as inclusion crystals (Figures 4.32 and 4.33).

Chalcopyrite was seen at a lesser extent. Chalcopyrite occurred in different particle sizes (Figures 4.30 – 4.34, 4.36, 4.37) and between pyrite and other gangue minerals (Figures 4.31, 4.32, 4.36, and 4.37). Chalcopyrite occurred generally as relatively coarse grains and rarely finer than 0.1 mm. Some chalcopyrite presence was also identified in the fractures inside sphalerite particles (Figure 4.38).

Galena was very rare in this specimen. Galena was observed as sutured with sphalerite and chalcopyrite. Size of galena particles varied from 20-25 μm to 0.2-0.25 mm (Figures 4.33, 4.34, 4.36, 4.38, and 4.39). Galena was the youngest ore mineral in this specimen and replaced other ore minerals.

Pyrite was very common in this specimen (Figures 4.30, 4.32, and 4.34). Pyrite crystals were euhedral and subhedral and occurred in varying sizes and mostly in disseminated form. Some pyrite crystals occurred in gathered form as inter-sutured grains (Figures 4.30 and 4.32). Pyrite was identified as the oldest mineral in the paragenesis. The coarsest pyrite crystals were 0.5-0.6 mm (Figure 4.34) and the finest ones were 15-20 μm (Figure 4.35).

Calcite was another common gangue mineral in this specimen. Calcite crystals occurred with varying sizes, in the form of fills in the fractures and the voids of metallic minerals and quartz crystals. Inside calcite, euhedral quartz crystals were observed.

Quartz, as a gangue mineral, was less common compared to calcite. Quartz was occasionally observed as euhedral inclusion crystals in metallic minerals (such as sphalerite and chalcopyrite) as well as in calcite. The euhedral quartz crystals in sphalerite and chalcopyrite were generally finer than 150 μm, while those in calcite were coarser, approximating 0.4-0.5 mm.

It was concluded that in this specimen, sphalerite and chalcopyrite were observed as the main ore minerals. Galena was rarely observed. Approximately 90-95% of the sphalerite and chalcopyrite particles were coarser than 0.1 mm. In order to achieve liberation of sphalerite and chalcopyrite, grinding Artvin-Dereiçi ore down below to 0.1 mm would be sufficient.

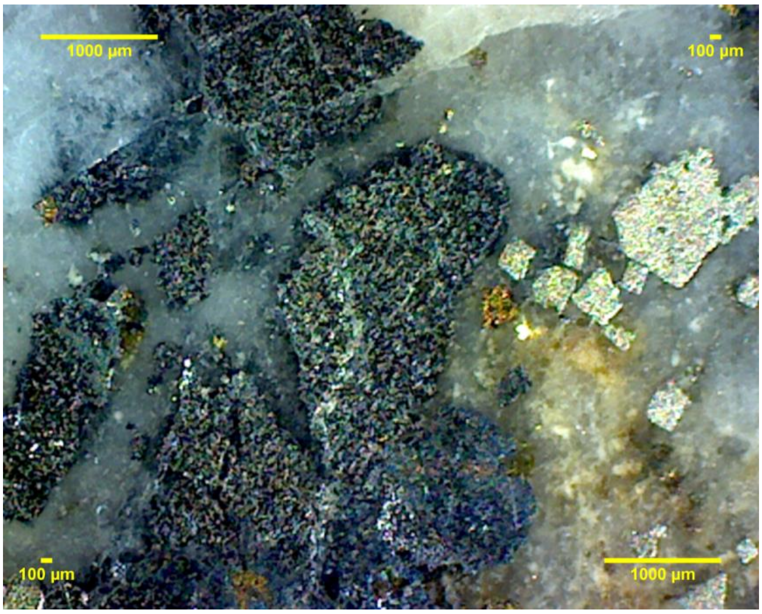

Figure 4.30 Sphalerite, pyrite, chalcopyrite and fine galena particles

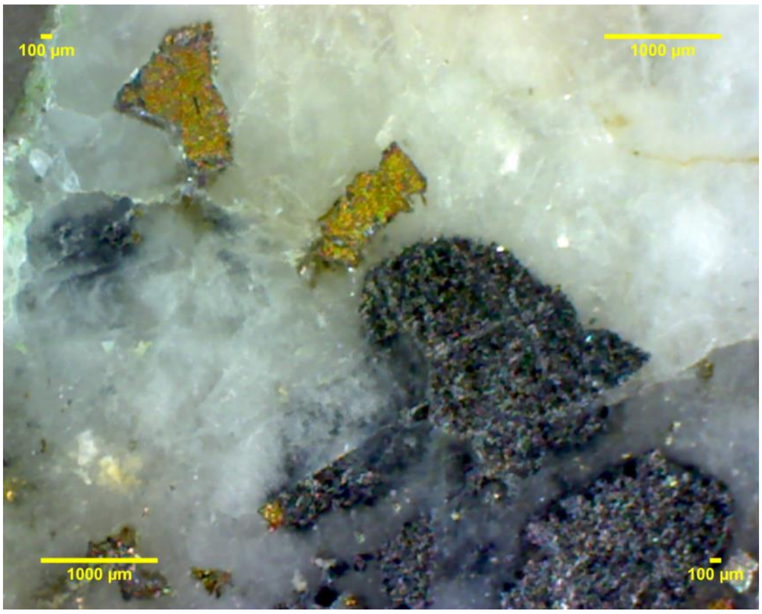

Figure 4.31 Coarse sphalerite, medium sized chalcopyrite and traces of ultrafine pyrite

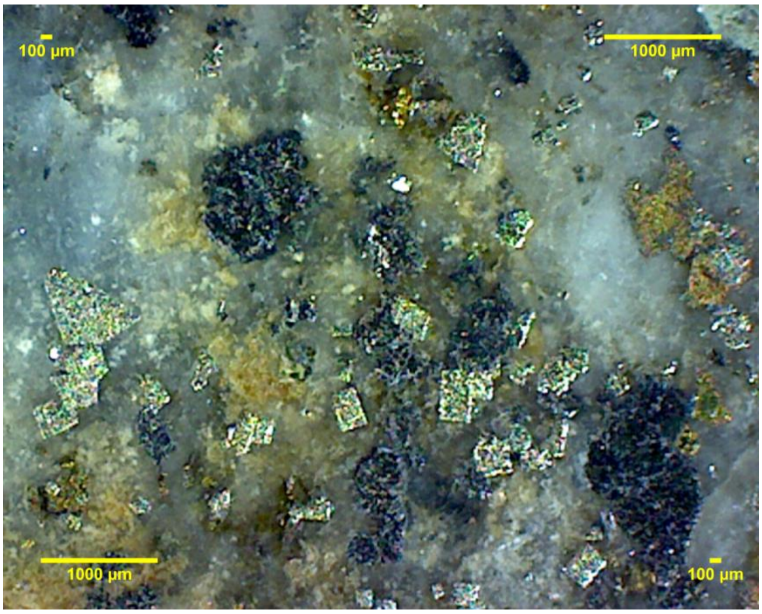

Figure 4.32 Presence of sphalerite, chalcopyrite and intensive pyrite in different sizes

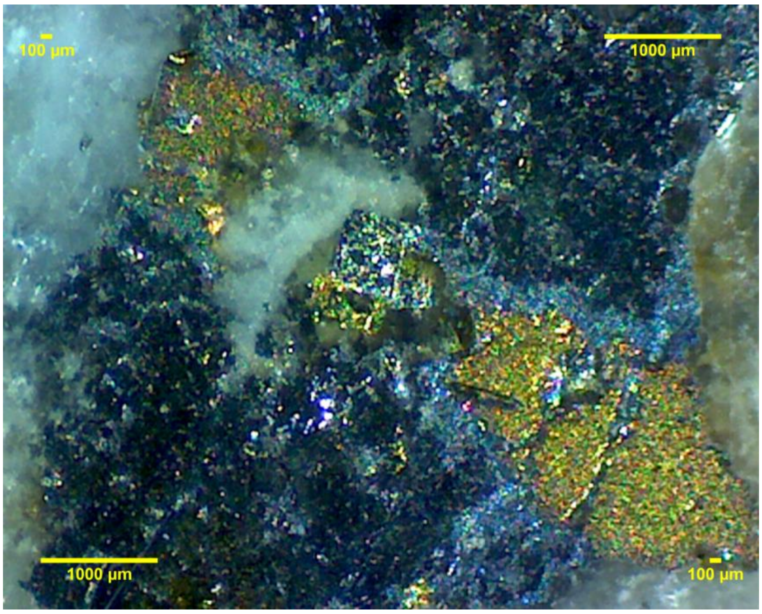

Figure 4.33 Sutured chalcopyrite, galena and pyrite

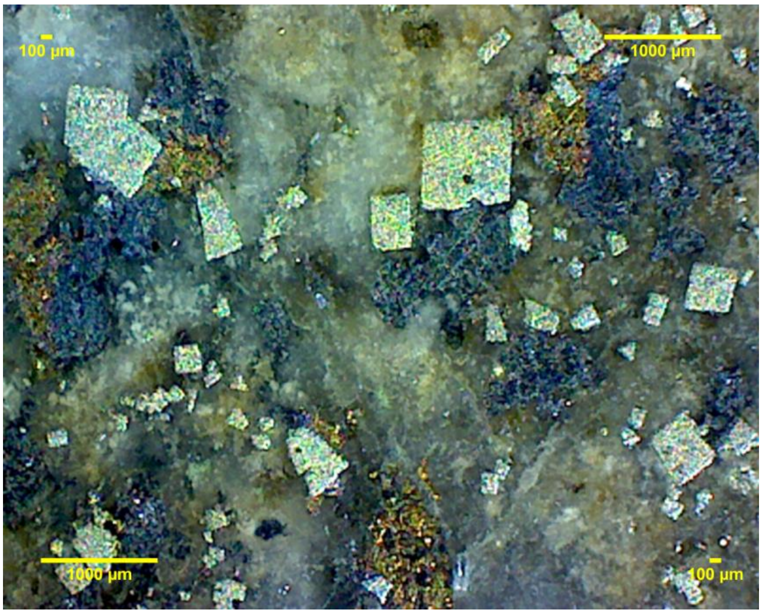

Figure 4.34 Coarse, medium and fine sized pyrite particles, chalcopyrite and sphalerite particles and fine sutured galena particles with chalcopyrite

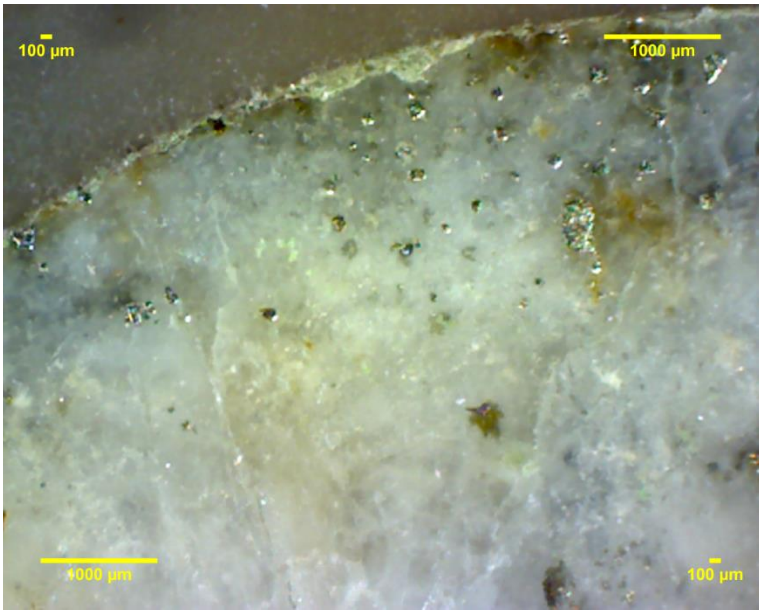

Figure 4.35 Calcite, quartz and disseminated ultrafine pyrite particles, traces of ultrafine galena

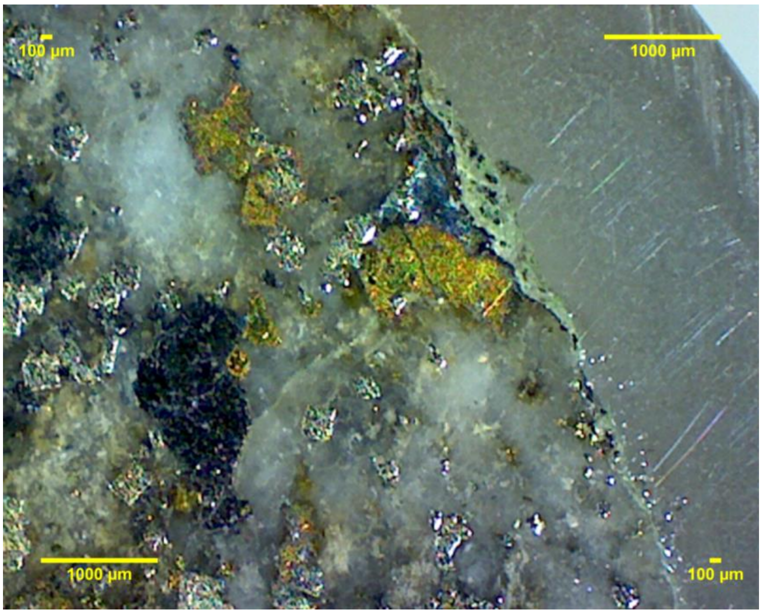

Figure 4.36 Chalcopyrite and pyrite particles in different sizes, coarse sphalerite and ultrafine galena entities

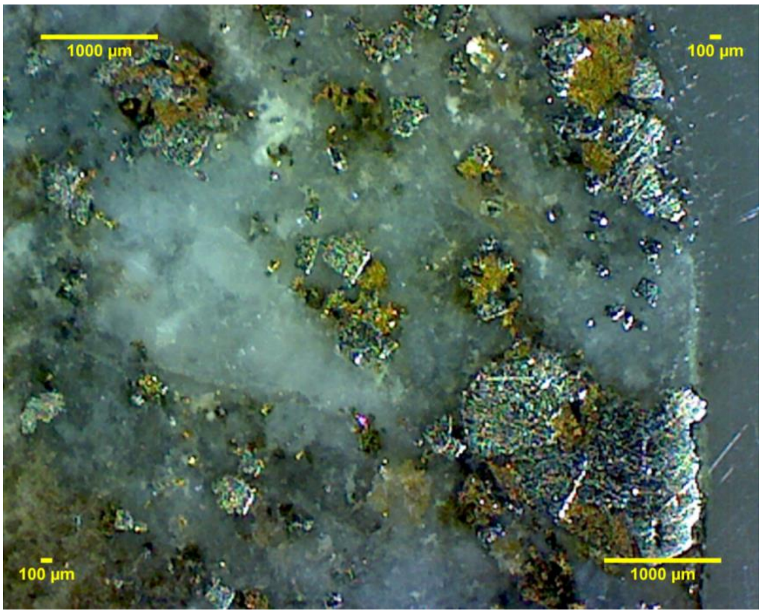

Figure 4.37 Chalcopyrite and pyrite particles and sutured chalcopyrite and pyrite forms in gangue minerals

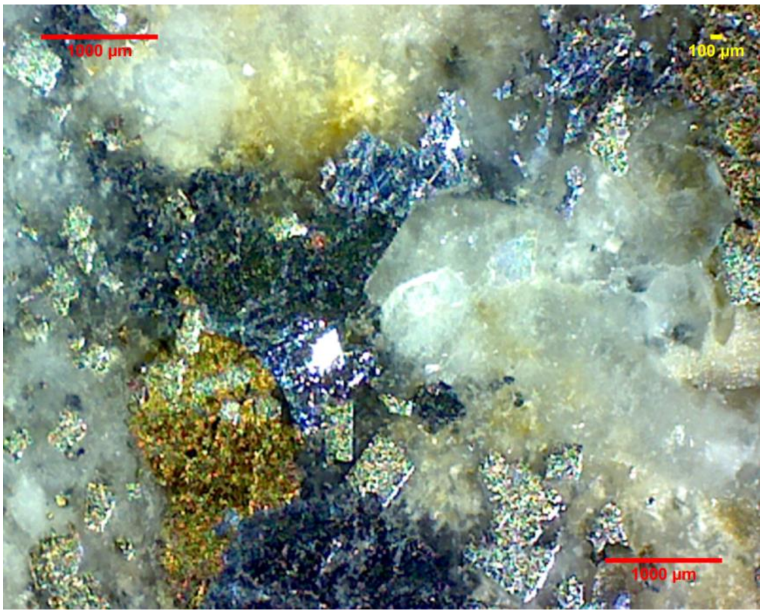

Figure 4.38 Chalcopyrite particles and sutured galena and pyrite forms in sphalerite with calcite and quartz

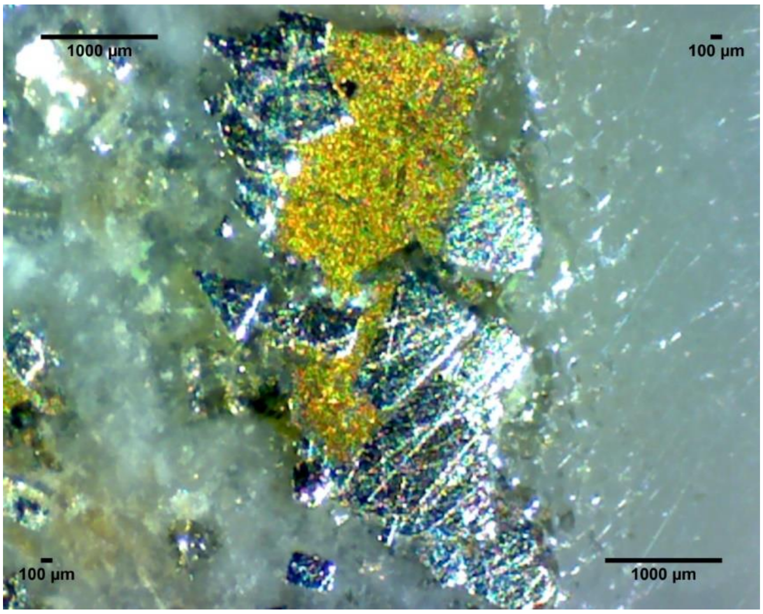

Figure 4.39 Chalcopyrite and galena in sutured form

The images taken for the seventh polished section showed that the original composition as well as the original structural-textural features of the rock has entirely changed due to intensive hydrothermal alteration. Gangue rock has incurred intensive silicification, chloritization, sericitization, sphenization, and pyritization.

Pyrite and rutile were the major metallic minerals (Figures 4.40 – 4.43). Pyrite was particularly abundant and occurred as euhedral, subhedral, and skeleton-form crystals with varying sizes (Figures 4.40 and 4.41). Some pyrite crystals occurred in gathered, inter-sutured form (Figure 4.42). Existence of pyrite veins that cut across the altered rock was also noticed. Pyrite crystals were commonly fine in size where the coarsest crystals approximate 0.2-0.25 mm. Rutile was rarely observed (Figure 4.41) in the form of single or groups of fine particles (Figures 4.41 and 4.43). Rutile has formed due to the alteration of mafic minerals (amphibole, biotite, etc.) that consisted of titanium in their crystal structures as well as alteration of ilmenite. Some rutile grains have transformed into sphene (titanite) and remained as relicts in sphene.

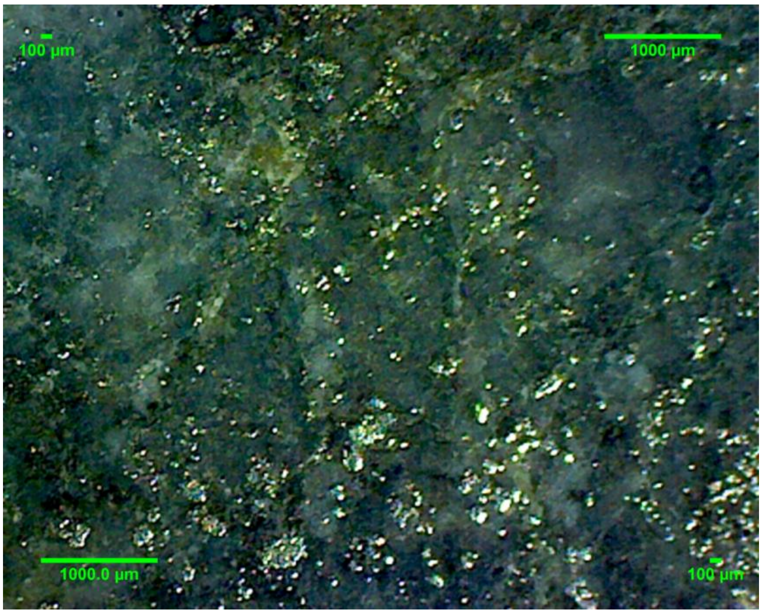

Figure 4.40 Intensive pyrite particles in fine and ultrafine sizes

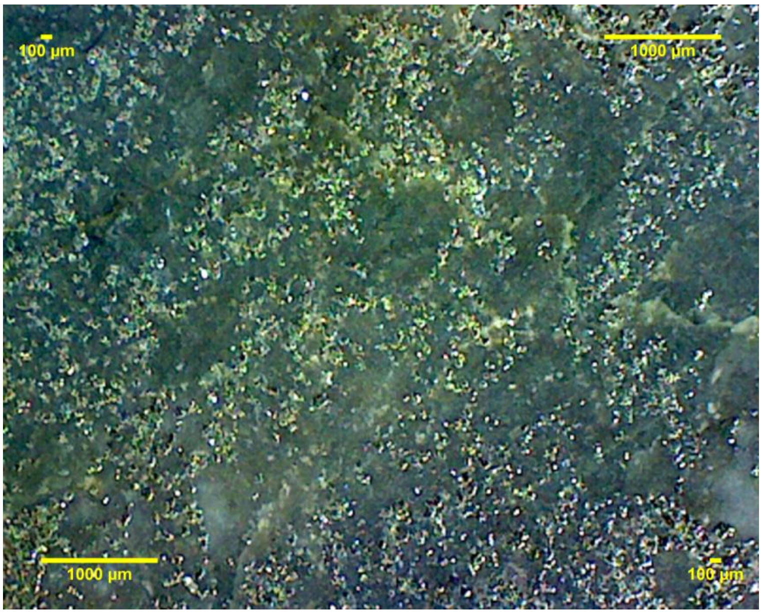

Figure 4.41 Fine and ultrafine pyrite and rutile particles and groups

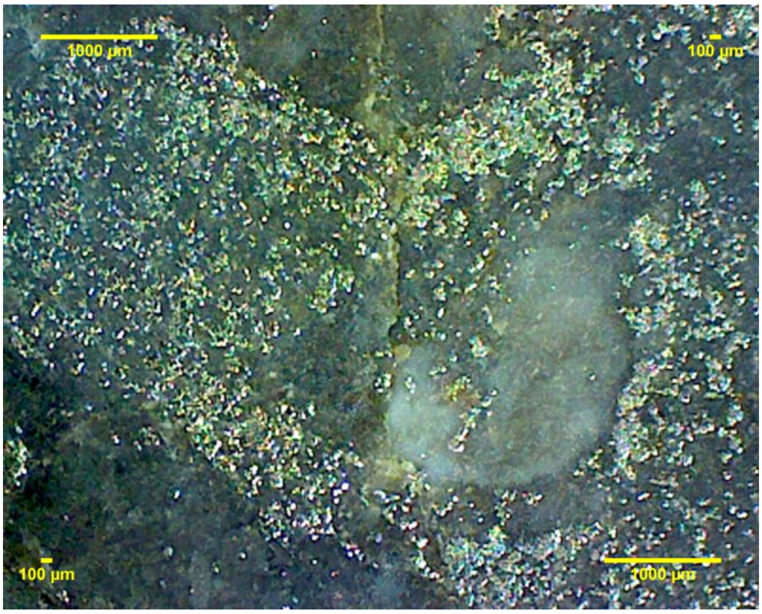

Figure 4.42 Fine and ultrafine pyrite particles and groups, sutured pyrite particles occasionally with fine and ultrafine rutile particles and groups, presence of quartz and chlorite

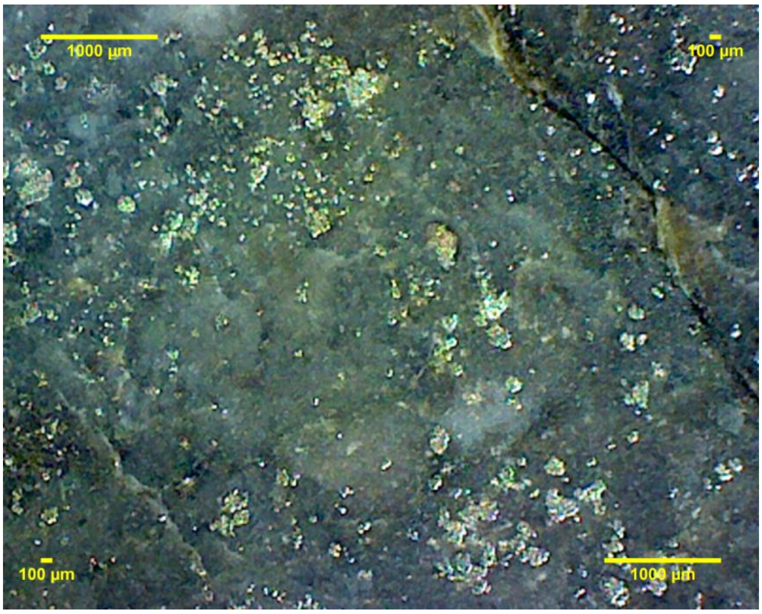

Figure 4.43 Disseminated fine and ultrafine pyrite particles occasionally with fine and ultrafine rutile particles

An overall assessment of the mineralogical-petrographic examinations and investigations on the images retrieved from the polished sections provided the following conclusions:

1. The metallic minerals with potential economic values in Artvin-Dereiçi ore are as follows: Copper mineral is chalcopyrite; lead mineral is galena; zinc mineral is sphalerite. The mineralogical-petrographic investigation did not show any other metallic values with economic potential (such as gold, silver, etc.). The fahlerz and rutile, seen in some specimens, are in trace quantities and of no economic significance in this ore.

2. The major gangue minerals in this ore are pyrite and siliceous and carbonaceous minerals (quartz and calcite).

3. In terms of metallic minerals with potential economic value, the ore is mainly comprised of sphalerite. In sphalerite mineralization, relatively finer chalcopyrite and galena entities were identified.

4. The metallic minerals with potential economic values were identified in a range of particle sizes. Considering flotation, sphalerite is generally the coarsest (>100 µm), chalcopyrite is generally finer than sphalerite. Chalcopyrite was also observed as coarser grains occasionally and as ultrafine (<10 µm) entities disseminated inside sphalerite grains. The size of galena grains are generally around 100 µm or finer. It should be noted that grinding and liberation of ultrafine chalcopyrite entities is not viable. In addition to the presence of these metallic sulfides in the form of single, distinctive particles, they also occur in sutured with or as inclusions in other mineral grains. These observations dictate that achieving sufficient liberation through fine grinding is a pre-requisite for effective concentration of Artvin-Dereiçi ore using flotation.

5. In the view of the observations related to mineralization of valuable minerals and their particle sizes, subjecting the ore to controlled grinding to a P_{100} size of 100 µm would be beneficial. The ground product constitutes the flotation feed. For concentration of this ore using flotation, two methodologies were applied:

   i. Following grinding for liberation of valuable metallic minerals from gangue components, obtaining a bulk flotation concentrate enriched in terms of all targeted metals (galena, chalcopyrite, and sphalerite) while rejecting pyrite (FeS_2) as much as possible. This bulk flotation concentrate would therefore correspond to a ‘‘Pb-Cu-Zn pre-concentrate’’. After this primary flotation stage, obtaining selective Pb, Cu, Zn concentrates (with the highest metal grades and recoveries possible), through a series of flotation stages.

   ii. Following grinding, obtaining a bulk Pb-Cu concentrate, enriched in terms of galena and chalcopyrite, while depressing sphalerite and pyrite to the highest possible extent. After this primary flotation stage, obtaining selective Pb, Cu, Zn concentrates (with the highest metal grades and recoveries possible), through a series of flotation stages.

As noted above, considering all three metallic sulfides, it could be expected that a liberation size of ≈100 µm would yield effective results in selectively achieving Pb, Cu and Zn concentrates through flotation concentration of Artvin-Dereiçi ore.

4.1.1.2 XRD Analysis

In order to examine the mineralization of Artvin-Dereiçi complex sulfide ore, XRD study was conducted. The aim of such study is to support the presence of minerals determined by optical microscope images. Mineralogical analysis of head Artvin-Dereiçi ore sample showed that the minerals present in the samples were chalcopyrite, galena, sphalerite, pyrite, quartz, calcite, and dolomite and its X-ray diffractogram is given in Figure 4.44.

Quartz was the dominating mineral phase in the sample and was responsible for the most intense peaks at 26.7° and 20.9°. In addition, relatively less intense characteristic peaks of quartz were observed at 36.6°, 39.5°, 40.3°, 42.5°, 45.8°, 50.2°, 54.9°, 60.0°, 67.8°, and 68.4°. Other gangue minerals in the ore sample were investigated as two carbonate minerals, calcite and dolomite. The characteristic peak of dolomite was of moderate intensity and observed at 31.0°, while the characteristic peak of calcite was of lower intensity and seen at 36.0°. The main characteristic peaks of sphalerite and pyrite were in overlapping position that the peaks belong to sphalerite and pyrite was seen at 28.6°, 33.1°, and 47.5°. In addition, pyrite was observed at its characteristics peaks at 37.1° and 40.8°, having very low intensities. Considering the copper and lead amount in the head sample, the characteristic peaks of chalcopyrite and galena were only observable in very low intensities. Presence of chalcopyrite was seen at the peak positioned at 29.4, whereas the characteristic peaks of galena were observed at 26.1° and 30.1°.

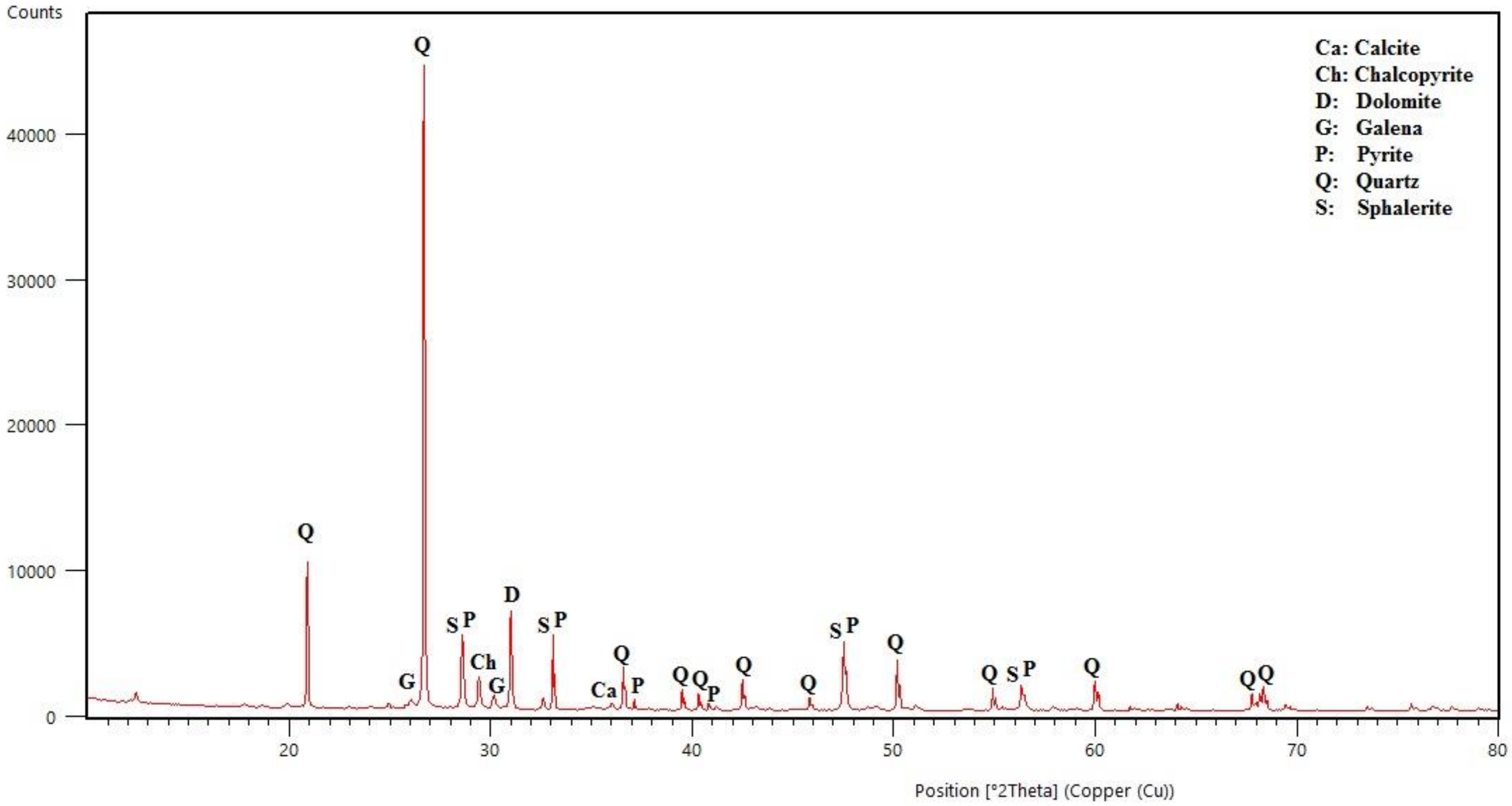

Figure 4.44 X-ray diffractogram of Artvin-Dereiçi ore head sample

4.1.2 Geo-metallurgical Investigations

Representative drill core samples were taken from each drill depth interval and assayed for lead (Pb), copper (Cu) and zinc (Zn) to characterize the drill logs with respect to their metal contents. The numbers of the drill logs, the depth intervals within each drill log and Pb, Cu and Zn assays of the core samples are given in Appendix A (Table A.1).

Assay results revealed that the cumulative Pb, Cu and Zn assay of the core samples fluctuate in a range between 0.135% and 37.24%. The mean of total Pb, Cu, and Zn assay is 8.85%. This implies that the reserve is consisted of various zones with an abundance of metallic sulfides as well as sections with marginally low Pb, Cu and Zn grades. The weighted average of Pb, Cu, and Zn assay of the ore is 8.71%. The weighted average assay is calculated based on the thickness of drill depth intervals given in Table A.1.

4.1.3 Preparation of Ore Samples (Feed) for Concentration Tests

After obtaining samples for preparing polished sections, Artvin-Dereiçi ore drill cores were entirely subjected to particle size reduction by crushing using both jaw and roller crushers. The crushed ore was put into a cone-shaped ore pile for representative sampling (Figure 4.45). From this pile, four representative samples were taken for determining the lead (Pb), copper (Cu) and zinc (Zn) grades of the run-of-mine ore (head assays), i.e. the valuable metal content of Artvin-Dereiçi ore. The head assays are presented in Table 4.1. The remaining ore pile was further divided into representative portions with approximately equal weights for grinding (Figure 4.45). Each representative portion was separately packed and sealed with nitrogen to avoid surface oxidation of ore particles.

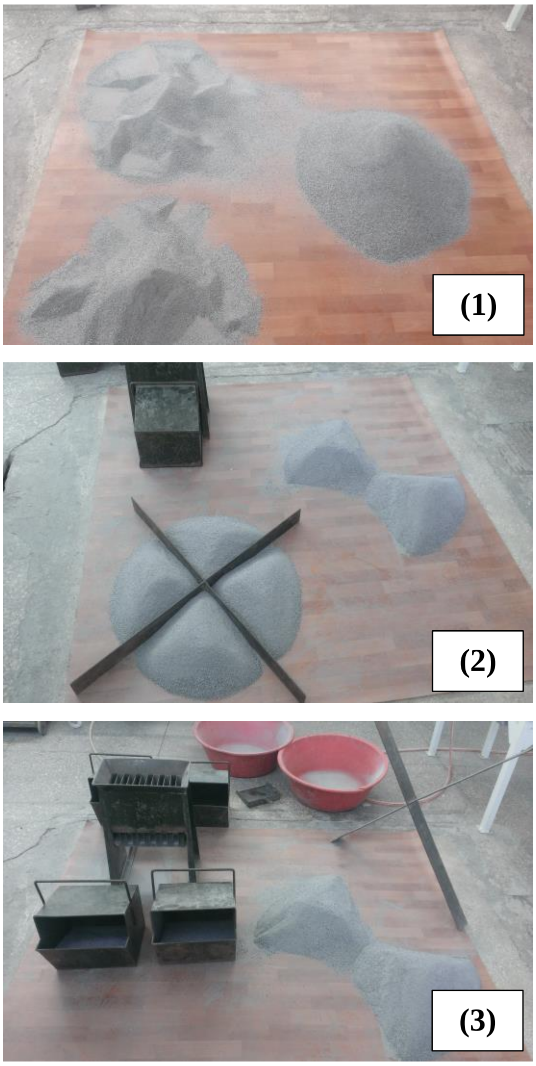

Figure 4.45 Preparation of Artvin-Dereiçi ore for grinding and subsequent flotation testing: (1) Blending the ore pile after crushing, (2) Dividing the pile into representative fractions by Cone & Quartening, (3) Using Riffle type sampler for further dividing the ore into smaller representative fractions

Table 4.1 Lead (Pb), copper (Cu) and zinc (Zn) assays of run-of-mine Artvin-Dereiçi ore

Assay	Sample 1	Sample 2	Sample 3	Sample 4	Mean
Cu (%)	1.48	1.45	1.36	1.45	1.43
Pb (%)	0.98	1.12	1.07	1.05	1.05
Zn (%)	6.42	6.40	6.12	6.35	6.32

Detailed steps of ore preparation for concentration tests explained below in further details:

1. The ore was divided into representative 5-5.5 kg portions, after crushing it to -2 mm. Each portion was packed and sealed separately under inert conditions (by supplying N_2) to avoid undesired surface oxidation of particles. Each representative portion constitute the feed for one flotation test (after grinding to liberation size).

2. Mineralogical investigations showed sufficient liberation of targeted minerals when the ore was ground to -100 µm. The grinding time required to reduce the ore from -2 mm to -100 µm was identified. In this respect the ore was subjected to wet grinding tests for 5, 10 and 15 minutes in a laboratory rod mill under controlled conditions. For the grinding tests, a pulp that consisted of approximately 350 g of -2 mm ore at 60% solids (by weight) was prepared as the grinding feed. As grinding media, stainless steel rods with different diameters were used (9 x 18 mm Ø, 5 x 25 mm Ø, 2 x 38 mm Ø). Particle size distribution of the ore after each grinding period was determined.

3. For concentration, the ore was ground just prior to each and every flotation test for the specified grinding period (i.e. the grinding period that yielded -100 µm sized feed). As previously noted, grinding the ore just prior to flotation was extremely critical to avoid oxidation of particle surfaces. Once the grinding was completed, the pulp was immediately transferred to the flotation cell to initiate the concentration test.

Grinding the ore to achieve sufficient liberation of targeted minerals is of major importance in achieving an effective flotation concentration. The laboratory rod mill used for grinding the ore for flotation tests is shown in Figure 4.46. The particle size distributions of the ore after 5, 10 and 15 minutes of grinding are presented in Tables 4.2 – 4.4 and shown graphically in Figure 4.47.

Figure 4.46 Laboratory rod mill used for grinding the ore

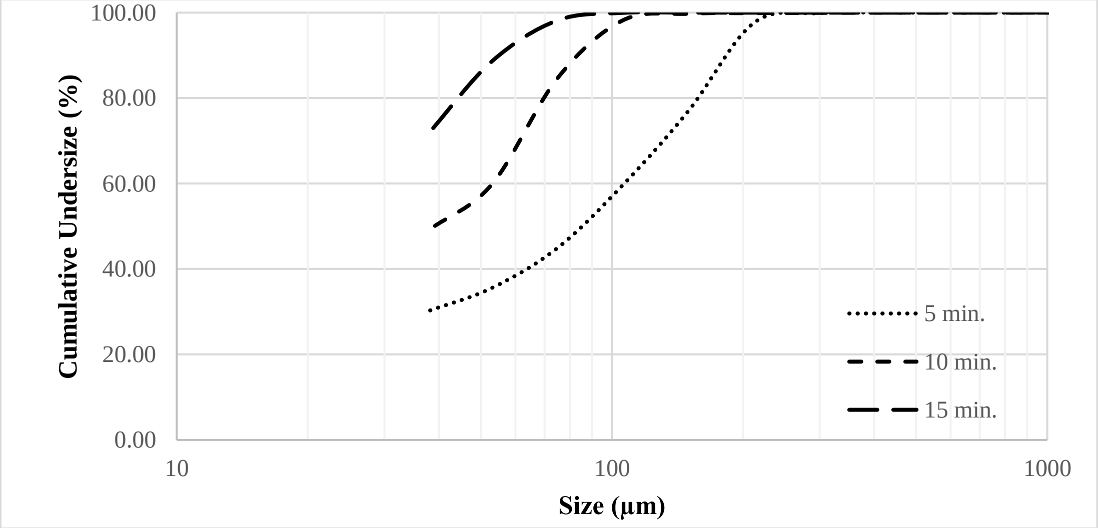

Figure 4.47 Particle size distribution of Artvin-Dereiçi ore with respect to different grinding periods

Table 4.2 Particle size distribution of -2 mm Artvin-Dereiçi ore after 5 minutes grinding

Particle Size Fraction	Weight (%)	Sieve Size (μm)	Cumulative Undersize (%)
-600 +425 μm	0.00	425	100.00
-425 +300 μm	0.11	300	99.89
-300 +212 μm	2.27	212	97.63
-212 +150 μm	20.57	150	77.05
-150 +106 μm	17.36	106	59.69
-106 +75 μm	14.74	75	44.95
-75 +53 μm	9.37	53	35.58
-53 +38 μm	5.35	38	30.23
-38 μm	30.23		
Total	100.00		

Table 4.3 Particle size distribution of -2 mm Artvin-Dereiçi ore after 10 minutes grinding

Particle Size Fraction	Weight (%)	Sieve Size (μm)	Cumulative Undersize (%)
-600 +425 μm	0.00	425	100.00
-425 +300 μm	0.05	300	99.95
-300 +212 μm	0.07	212	99.88
-212 +150 μm	0.14	150	99.74
-150 +106 μm	1.53	106	98.22
-106 +75 μm	13.54	75	84.68
-75 +53 μm	24.84	53	59.85
-53 +38 μm	10.68	38	49.17
-38 μm	49.17		
Total	100.00		

Table 4.4 Particle size distribution of -2 mm Artvin-Dereiçi ore after 15 minutes grinding

Particle Size Fraction	**Weight (%)**	**Sieve Size (µm)**	**Cumulative Undersize (%)**
-212 + 150 µm	0.00	150	100.00
-150 + 106 µm	0.04	106	99.96
-106 + 75 µm	1.76	75	98.19
-75 + 53 µm	9.58	53	88.62
-53 + 38 µm	16.74	38	71.87
-38 µm	71.87		
Total	100.00		

The results in Tables 4.2 – 4.4 showed that the ore remains to be relatively coarser than the liberation size after five minutes grinding (the amount of +106 µm sized material is >55 %), while grinding for 15 minutes resulted in overgrinding and a product finer than required. In view of particle size distributions, grinding for 10 minutes provided the most favorable results considering the liberation size, amongst the three different grinding periods tested. It was decided that the ore should be ground for 10 minutes to prepare feed for flotation tests. As previously mentioned, fresh grinding just before flotation testing is extremely important for metallic sulfides with chalcopyrite that its surface is very liable to being oxidized and surface oxidation may cause additional challenges in the concentration of complex sulfide ores.

4.1.4 Concentration of the Ore by Flotation

Concentration of targeted metals (Cu, Pb, and Zn) in Artvin-Dereiçi ore was accomplished through flotation method. Batch, laboratory scale flotation tests were conducted using a Denver type flotation machine and a one-liter flotation cell. The lab-scale flotation machine used in the tests is shown in Figure 4.48. All tests were conducted using approximately 350 grams of ore at 35% solids by weight in the pulp. Before each test, the ore was ground wet and tests were done immediately after grinding to avoid surface oxidation of the ground particles. Other test conditions, such as the reagents and their dosages, pulp pH were subjected to change at different phases of the study and given in Appendix B-I. Following the flotation, the concentrate (float) and tailing (depressed) products were dried in a laboratory type furnace at 75°C. After drying, the weights of the products were recorded and assayed for Cu, Pb, Zn and Fe. Using the product weights, Cu, Pb, Zn and Fe assays, material balance tables for the tests were constructed and the metallurgical performance of each test was identified in terms of grade-recovery values. In the tests, technical grade reagents and chemicals were used and these are listed in Table 4.5.

Figure 4.48 Denver type laboratory flotation machine used in the tests

Table 4.5 Chemicals and reagents used at various phases of the study

Reagent				
pH Modifiers	**Depressants**	**Collector (promoter)**	**Activator**	**Frother**
Sodium carbonate (Na_2CO_3) (Merck)	Zinc sulfate ($ZnSO_4$) (Merck)	Potassium Amyl Xanthate (PAX)	Copper sulfate ($CuSO_4$) (Panreac)	F-533 (Cytec)
Calcium oxide (CaO) (Merck)	Sodium cyanide (NaCN) (Merck)	Sodium Isopropyl Xanthate (SIPX)		
	Sodium sulfite (Na_2SO_3) (Merck)	Aerophine 3418A (Cytec)		
	Sodium metabisulfite ($Na_2S_2O_5$) (Merck)			

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Obtaining a Rougher Concentrate prior to Selective Flotation

5.1.1 Use of Zinc Sulfate ($ZnSO_4$) as Sphalerite Depressant

Firstly, use of zinc sulfate ($ZnSO_4$) and sodium cyanide (NaCN) as depressants was attempted to depress sphalerite (ZnS) and pyrite (FeS_2), respectively. The goal was to obtain a rougher flotation concentrate, enriched in Cu and Pb and a tailings product enriched in Zn and Fe. A series of flotation tests were conducted in which $ZnSO_4$ dosage was varied at a pulp pH of 9.5 and using potassium amyl xanthate (PAX) and Aerophine 3418A as collectors. Pulp pH was adjusted using sodium carbonate (Na_2CO_3). In the tests, NaCN dosage was one fifth (1:5) of $ZnSO_4$ dosage, changed between 200-600 g/t (Table 5.1). Total collector dosage was 100 g/t and this dosage consisted 25 g/t 3418A and 75 g/t PAX in all tests. Test conditions and metallurgical results are presented in Tables 5.1 and 5.2, respectively.

Table 5.1 Variation of $ZnSO_4$ dosage and other test conditions

Test	**$ZnSO_4$ (g/t)**	**NaCN (g/t)**	**pH**	**3418A+PAX (g/t)**
1	200	40	9.5	100
2	400	80	9.5	100
3	600	120	9.5	100

Assay results showed that, as $ZnSO_4$ dosage increased, Zn grade of the concentrate decreased, i.e. sphalerite was increasingly depressed. Further, with the increase in $ZnSO_4$ dosage, the amount of the concentrate product decreased. It was mentioned that NaCN addition dosage was increased with increasing $ZnSO_4$ usage to maintain a constant NaCN:$ZnSO_4$ ratio of 1:5. Use of higher NaCN dosages seemed to increase depression of pyrite, but at a limited extent. Besides, use of higher NaCN dosage obviously resulted in depression of chalcopyrite, i.e. loss of Cu with the tailings. Therefore, the decrease in Fe grade of the concentrate might be due to the loss of chalcopyrite to the tailings product (at least, to some extent), rather than an increase in pyrite depression. In view of the results, it is obvious that the dosages of $ZnSO_4$ and NaCN as depressants are critically important in the flotation of this ore. Variation of $ZnSO_4$ dosage did not influence flotation behavior of galena such that concentrates with outstanding Pb recoveries were obtained at all test conditions and it was favorable that the loss of Pb in the tailings product was quite limited (Table 5.2).

Table 5.2 Metallurgical results with respect to $ZnSO_4$ dosage

Test	**Product**	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
		g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Test 1 **$ZnSO_4$ 200 g/t** **NaCN 40 g/t**	**Concentrate**	92.99	26.94	3.85	99.30	3.90	79.54	5.29	22.24	19.28	64.35
	Tailings	252.13	73.06	0.01	0.70	0.37	20.46	6.82	77.76	3.94	35.65
	Total	345.12	100.00	1.04	100.00	1.32	100.00	6.41	100.00	8.07	100.00
Test 2 **$ZnSO_4$ 400 g/t** **NaCN 80 g/t**	**Concentrate**	87.15	25.18	3.85	94.19	2.18	40.01	4.92	19.35	17.56	54.67
	Tailings	258.93	74.82	0.08	5.81	1.10	59.99	6.90	80.65	4.90	45.33
	Total	346.08	100.00	1.03	100.00	1.37	100.00	6.40	100.00	8.09	100.00
Test 3 **$ZnSO_4$ 600 g/t** **NaCN 120 g/t**	**Concentrate**	79.30	22.02	3.82	85.70	1.85	29.82	4.52	15.48	17.12	46.25
	Tailings	280.75	77.98	0.18	14.30	1.23	70.18	6.97	84.52	5.62	53.75
	Total	360.05	100.00	0.98	100.00	1.37	100.00	6.43	100.00	8.15	100.00

5.1.2 Use of Zinc Sulfate ($ZnSO_4$) as Sphalerite Depressant and Sodium Isopropyl Xanthate (SIPX) as Collector

This stage of study included tests in which sodium isopropyl xanthate (SIPX) was used as a collector instead of potassium amyl xanthate (PAX) in the Xanthate-3418A combination. Other conditions were equivalent to those in the previous phase that in order to depress sphalerite and pyrite, zinc sulfate and sodium cyanide were used, respectively. In the tests, NaCN dosage was one fifth of $ZnSO_4$ dosage and $ZnSO_4$ dosage was changed between 200-600 g/t (Table 5.3). Pulp pH was adjusted as 9.5 using sodium carbonate (Na_2CO_3). Total collector dosage was 100 g/t in all tests with 25 g/t 3418A and 75 g/t SIPX. Test conditions and metallurgical results are presented in Tables 5.3 and 5.4, respectively.

Table 5.3 Use of SIPX instead of PAX and variation of $ZnSO_4$ dosage

Test	**$ZnSO_4$ (g/t)**	**NaCN (g/t)**	**pH**	**3418A+SIPX (g/t)**
1	200	40	9.5	100
2	400	80	9.5	100
3	600	120	9.5	100

The metallurgical results obtained when SIPX was used, were similar to those obtained with PAX that both the amount of the concentrate and the metal grades tended to decrease by increasing the depressant dosages (Table 5.3). The reductions observed in the grades and recoveries of Zn and Fe were favorable, but the reductions in the recoveries of Pb and Cu were undesired.

Table 5.4 Metallurgical results when SIPX is used and with respect to $ZnSO_4$ dosage

Test	**Product**	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
		g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Test 1 **$ZnSO_4$ 200 g/t** **NaCN 40 g/t**	**Concentrate**	72.00	20.54	4.99	97.73	3.26	47.81	5.74	18.36	9.99	25.24
	Tailings	278.52	79.46	0.03	2.27	0.92	52.19	6.60	81.64	7.65	74.76
	Total	350.52	100.00	1.05	100.00	1.40	100.00	6.42	100.00	8.13	100.00
Test 2 **$ZnSO_4$ 400 g/t** **NaCN 80 g/t**	**Concentrate**	64.99	18.57	4.85	90.21	2.25	29.27	5.51	15.94	9.52	21.63
	Tailings	284.92	81.43	0.12	9.79	1.24	70.73	6.63	84.06	7.87	78.37
	Total	349.91	100.00	1.00	100.00	1.43	100.00	6.42	100.00	8.18	100.00
Test 3 **$ZnSO_4$ 600 g/t** **NaCN 120 g/t**	**Concentrate**	56.82	16.26	4.78	77.46	2.03	23.26	5.25	13.24	9.22	18.28
	Tailings	292.73	83.74	0.27	22.54	1.30	76.74	6.68	86.76	8.00	81.72
	Total	349.55	100.00	1.00	100.00	1.42	100.00	6.45	100.00	8.20	100.00

It was seen that PAX had higher collecting ability as compared to SIPX (Tables 5.2 and 5.4). A comparison at the same depressant dosages showed that higher amount of concentrate could be obtained when PAX and 3418A combination was used as collectors. It should also be noted that with PAX and 3418A combination, apparently higher Cu recoveries were obtained as compared to the use of SIPX and 3418A combination (Tables 5.2 and 5.4). In addition, higher decrease in Pb grade with increasing depressant dosage was another negative result of SIPX and 3418A usage. These observations implied that no significant advantage could be achieved associated with the use of SIPX instead of PAX. It might be argued that, with SIPX, Fe grades in the concentrate product were lower compared to the case where PAX was used and this might seem as the only advantage of SIPX over PAX. However, due to lower amount of concentrates, and reduced Pb and Cu recoveries, this advantage is obsolete. To conclude, despite better performance of SIPX in reducing the Fe grade in the concentrate, due to the lower concentrate amount and reduced selectivity between Pb, Cu and Zn with SIPX, it was decided that PAX would be used as the xanthate type collector in the further stages of the study.

5.1.3 Change of Pulp pH

In this phase, the effect of increasing the pulp pH on the metallurgical performance was investigated. It was observed that sodium carbonate (Na_2CO_3) failed to increase the pulp pH beyond 9.8-9.9 and calcium oxide (CaO) was used as the pH modifier to achieve higher alkalinities of pH 10.5 and 11.2. To depress sphalerite and pyrite, zinc sulfate (600 g/t) and sodium cyanide (120 g/t) were used, respectively Total collector dosage was 100 g/t in all tests with 25 g/t 3418A and 75 g/t PAX. Test conditions and metallurgical results are presented in Tables 5.5 and 5.6, respectively.

Table 5.5 Change of pulp pH and other test conditions

Test	**$ZnSO_4$ (g/t)**	**NaCN (g/t)**	**pH**	**3418A+PAX (g/t)**
1	600	120	10.5	100
2	600	120	11.2	100

Table 5.6 Metallurgical results with respect to pulp pH

Test	**Product**	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
		g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Test 1 **$ZnSO_4$ 600 g/t** **NaCN 120 g/t** **pH 10.5**	**Concentrate**	78.12	22.40	3.78	85.17	2.02	32.71	4.18	14.65	15.10	41.76
	Tailings	270.56	77.60	0.19	14.83	1.20	67.29	7.03	85.35	6.08	58.24
	Total	348.68	100.00	0.99	100.00	1.38	100.00	6.39	100.00	8.10	100.00
Test 2 **$ZnSO_4$ 600 g/t** **NaCN 120 g/t** **pH 11.2**	**Concentrate**	77.20	22.01	3.82	83.05	2.10	33.43	4.12	14.14	13.18	35.63
	Tailings	273.56	77.99	0.22	16.95	1.18	66.57	7.06	85.86	6.72	64.37
	Total	350.76	100.00	1.01	100.00	1.38	100.00	6.41	100.00	8.14	100.00

Increasing the pulp pH to more alkaline levels higher than 9.5 improved depression of sphalerite, but this improvement was limited (Tables 5.2 and 5.6). Metallurgical results obtained at pH 10.5 and 11.2 were similar except for the Fe grade and recovery (Table 5.6). A slight decrease in Pb recovery at pH 11.2 was obtained, this, in fact, was an expected result due to the use of CaO for adjusting pulp pH. It should be noted that at 120 g/t NaCN dosage, pyrite was more effectively depressed at pH 11.2 compared to pyrite depression at pH 10.5 and 9.5 (Tables 5.2 and 5.6). This was favorable and showed the necessity for a highly alkaline pulp pH for effective depression of pyrite of Artvin-Dereiçi ore.

Use of NaCN for pyrite depression might also cause depression of chalcopyrite, an undesired side effect of NaCN usage resulting in the loss of Cu values to the tailings. To test this possibility, tests in which only $ZnSO_4$ was used as a depressant (at high dosages) for depressing sphalerite, i.e. NaCN was not added in these tests. Hence, in these tests possibility of pyrite depression solely by highly alkaline pH was attempted. Pulp pH was adjusted to 11.2 using CaO in these tests. Test conditions and metallurgical results are presented in Tables 5.7 and 5.8, respectively.

Table 5.7 Variation of $ZnSO_4$ as the only depressant at pH 11.2 and other test conditions

Test	**$ZnSO_4$ (g/t)**	**pH**	**3418A+PAX (g/t)**
1	1000	11.2	100
2	2000	11.2	100

Table 5.8 Metallurgical results with respect to $ZnSO_4$ as the only depressant at pH 11.2

Test	**Product**	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
		g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Test 1 **$ZnSO_4$ 1000 g/t** **pH 11.2**	**Concentrate**	75.04	21.07	4.50	94.49	6.32	93.88	4.69	15.43	25.34	66.41
	Tailings	281.17	78.93	0.07	5.51	0.11	6.12	6.86	84.57	3.42	33.59
	Total	356.21	100.00	1.00	100.00	1.42	100.00	6.40	100.00	8.04	100.00
Test 2 **$ZnSO_4$ 2000 g/t** **pH 11.2**	**Concentrate**	70.08	20.28	4.40	91.80	6.22	90.82	4.50	14.19	24.00	60.30
	Tailings	275.50	79.72	0.10	8.20	0.16	9.18	6.92	85.81	4.02	39.70
	Total	345.58	100.00	0.97	100.00	1.39	100.00	6.43	100.00	8.07	100.00

Comparison of the metallurgical results in Tables 5.6 and 5.8 clearly showed the influence of the use of NaCN on chalcopyrite and pyrite. As NaCN helped depressing pyrite, it incidentally caused depression of chalcopyrite to some extent. This caused some loss of Cu to the tailings, i.e. reduction of Cu content of the concentrate product. In the case in which NaCN was not used, the undesired loss of Cu to the tailings was quite lower compared to the tests with NaCN addition (Table 5.8). However, as mentioned previously, without NaCN, the Fe content of the concentrate increased, affecting the metallurgical quality of the concentrate negatively. In addition, when NaCN was not used, the Zn grade of the concentrate was also higher compared to the tests conducted using NaCN, another disadvantage incurred in the tests without NaCN.

Another observation in these tests was that increasing the $ZnSO_4$ dosage from 1000 to 2000 g/t did not provide a remarkable improvement in depressing sphalerite (Table 5.8). $ZnSO_4$ alone could not provide the level of sphalerite depression achieved with $ZnSO_4$ and NaCN together, even when added at high dosages. Accordingly, it was clarified that NaCN was necessary as a depressant for this ore, but it should be used at limited dosages and in a controlled manner.

In view of these findings, another series of tests were conducted at alkaline pulp pH of 11.2 (adjusted by CaO) using high dosages of $ZnSO_4$ (1000 & 2000 g/t) and limited NaCN (40 g/t) as depressants. Test conditions and metallurgical results are presented in Tables 5.9 and 5.10, respectively.

The amount of sphalerite in the concentrate was slightly lower when higher $ZnSO_4$ dosages were used, while the Fe grade of the concentrate significantly decreased as compared to the tests without NaCN (Tables 5.8 and 5.10). Besides, with 40 g/t NaCN, the incidental depression of chalcopyrite was quite limited. This also avoided undesired recovery decrease of Cu in the concentrate product. No apparent benefit could be achieved in terms of sphalerite depression when $ZnSO_4$ dosage was increased from 1000 to 2000 g/t (Table 5.10).

Table 5.9 Use of high $ZnSO_4$ dosages with limited NaCN and other test conditions

Test	**$ZnSO_4$ (g/t)**	**NaCN (g/t)**	**pH**	**3418A+PAX (g/t)**
1	1000	40	11.2	100
2	2000	40	11.2	100

Table 5.10 Metallurgical results with respect to $ZnSO_4$ dosage with limited NaCN

Test	**Product**	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
		g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Test 1 **$ZnSO_4$ 1000 g/t** **NaCN 40 g/t** **pH 11.2**	**Concentrate**	71.74	20.60	4.52	92.14	5.86	86.37	4.18	13.55	15.84	40.18
	Tailings	276.44	79.40	0.10	7.86	0.24	13.63	6.92	86.45	6.12	59.82
	Total	348.18	100.00	1.01	100.00	1.40	100.00	6.36	100.00	8.12	100.00
Test 2 **$ZnSO_4$ 2000 g/t** **NaCN 40 g/t** **pH 11.2**	**Concentrate**	70.12	20.05	4.40	91.69	5.92	83.19	4.16	12.97	16.12	40.02
	Tailings	279.56	79.95	0.10	8.31	0.30	16.81	7.00	87.03	6.06	59.98
	Total	349.68	100.00	0.96	100.00	1.43	100.00	6.43	100.00	8.08	100.00

This again verified that even when high $ZnSO_4$ dosages were used, the Zn grade of the concentrate could not be pulled below 4%. It was also confirmed that NaCN was required for effective depression of pyrite present in this ore, however, addition could be as low as 40 g/t. Using higher NaCN dosages would reduce Fe recovery in the concentrate to as low as 35-36%, but this also caused undesired depression of chalcopyrite and loss of Cu to the tailings. In addition, using an alkaline pH (pH>11.0) clearly enhanced depression of pyrite (Table 5.10).

5.1.4 Use of Sodium Sulfite (Na_2SO_3) as Sphalerite Depressant

Upon the observation that the Zn grade of the concentrate could not be reduced sufficiently, the alternative use of sodium sulfite (Na_2SO_3) (instead of zinc sulfate) for depressing sphalerite was investigated. In these tests, NaCN was also utilized to depress pyrite. Test conditions are summarized in Table 5.11. In this phase, firstly, tests with 100 and 200 g/t Na_2SO_3 and 20 and 40 g/t NaCN (NaCN dosage was adjusted as one fifth of Na_2SO_3 dosage) were conducted. The goal was effectively depressing sphalerite and pyrite while keeping the undesired depression of galena and chalcopyrite at minimum level. In addition to these tests, a third experiment was also conducted where Na_2SO_3 and NaCN were used at equal dosages (50 g/t of each depressant), as shown in Table 5.11. To enable direct comparison with the $ZnSO_4$-NaCN case, tests were done at a pulp pH of 9.5 (with Na_2CO_3 as the pH modifier) and using the PAX and 3418A collector combination (75 g/t + 25 g/t). Metallurgical results of these tests are presented in Table 5.12.

Table 5.11 Variation of Na_2SO_3 dosage and other test conditions

Test	**Na_2SO_3 (g/t)**	**NaCN (g/t)**	**pH**	**3418A+PAX (g/t)**
1	100	20	9.5	100
2	200	40	9.5	100
3	50	50	9.5	100

Table 5.12 Metallurgical results with respect to Na_2SO_3 dosage

Test	Product	Weight		Pb		Cu		Zn		Fe	
		g	%	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
Test 1 **Na_2SO_3 100 g/t** **NaCN 20 g/t** **pH 9.5**	**Concentrate**	93.12	26.59	3.72	98.54	4.48	85.28	4.48	18.93	16.02	52.17
	Tailings	257.12	73.41	0.02	1.46	0.28	14.72	6.95	81.07	5.32	47.83
	Total	350.24	100.00	1.00	100.00	1.40	100.00	6.29	100.00	8.16	100.00
Test 2 **Na_2SO_3 200 g/t** **NaCN 40 g/t** **pH 9.5**	**Concentrate**	90.56	26.12	3.82	96.43	4.40	83.83	4.40	18.14	15.12	48.14
	Tailings	256.12	73.88	0.05	3.57	0.30	16.17	7.02	81.86	5.76	51.86
	Total	346.68	100.00	1.03	100.00	1.37	100.00	6.34	100.00	8.21	100.00
Test 3 **Na_2SO_3 50 g/t** **NaCN 50 g/t** **pH 9.5**	**Concentrate**	91.02	26.07	3.59	98.44	4.33	82.23	4.56	19.08	14.27	45.12
	Tailings	258.12	73.93	0.02	1.56	0.33	17.77	6.82	80.92	6.12	54.88
	Total	349.14	100.00	0.95	100.00	1.37	100.00	6.23	100.00	8.24	100.00

Use of Na_2SO_3 instead of $ZnSO_4$ provided better results in depressing sphalerite, i.e. in reducing the Zn grade of the concentrate. Almost equivalent amounts of concentrates were obtained using 100 and 200 g/t Na_2SO_3 and 200 g/t $ZnSO_4$, but both the Zn grade and recovery in the concentrate were lower when Na_2SO_3 was added (Tables 5.2 and 5.12). In addition, use of Na_2SO_3 resulted in lower Fe grade and recovery in the concentrate accompanied with improvements in the Cu grade and recovery of the concentrate. It should also be noted that increasing the Na_2SO_3 dosage from 100 to 200 g/t did not yield significant differences in the metallurgical performance regarding Cu, Pb and Zn (Table 5.12). However, at 100 g/t Na_2SO_3 dosage, the Fe grade of the concentrate was higher compared to the test with 200 g/t Na_2SO_3. This was linked with the addition of lower NaCN dosage (20 g/t) when 100 g/t Na_2SO_3 was used. When equivalent dosages of NaCN and Na_2SO_3 were added (i.e. 50 g/t of each depressant), the Fe grade of the concentrate was slightly lower (due to increased NaCN dosage from 40 to 50 g/t). An overall evaluation of these three tests with Na_2SO_3 implied that use of 50 g/t Na_2SO_3 and 50 g/t NaCN as depressants were optimum.

5.1.5 Modifying Pulp pH During Grinding when Sodium Sulfite (Na_2SO_3) was used as Sphalerite Depressant

In this phase of the research, the pH was modified during wet grinding the ore for flotation tests. For pH modification, 0.7 g of CaO (≈2 kg/t) was added to the mill (rather than the flotation cell) at the start of the grinding period. After grinding, the feed slurry was transferred to the flotation cell and pulp pH was measured. Pulp pH was measured in the range of 10.20 and 10.28 in all the tests in this stage. Test conditions are summarized in Table 5.13. In this phase, Na_2SO_3 and NaCN were used as depressants. In the tests the previously applied ratio of 1:5 was preserved for NaCN and Na_2SO_3 dosages. Also, an additional test in which equivalent dosages of NaCN (50 g/t) and Na_2SO_3 (50 g/t) was performed. In all the tests, PAX and 3418A collector combination was used as 75 g/t and 25 g/t, respectively (Table 5.13). Metallurgical results of the tests in this phase are presented in Table 5.14.

Table 5.13 Variation of Na_2SO_3 dosage when pH was modified during grinding and other test conditions

Test	**Na_2SO_3 (g/t)**	**NaCN (g/t)**	**pH**	**3418A+PAX (g/t)**
1	100	20	Modified during grinding using 0.7 g CaO (≈2 kg/t)	100
2	200	40		100
3	50	50		100

pH modification during grinding yielded a concentrate (float) enriched in Cu, Pb and Zn, i.e. all targeted metals in this work. This corresponded to a bulk pre-concentrate product in which Cu, Pb and Zn grades were upgraded at exceptional recovery levels. This bulk pre-concentrate constituted the feed for further stages of flotation to recover Pb, Cu and Zn separately and selectively. Another opportunity associated with obtaining this bulk Cu-Pb-Zn pre-concentrate was the early rejection of gangue minerals just at the beginning of the flotation process, i.e. through the rougher flotation stage. This would enable installation and use of smaller capacity flotation machines, better process control, savings in energy consumption and use of lower amount of reagents in the prospective full-scale flotation concentration of Artvin-Dereiçi ore.

After assessing the results with respect to reagent dosages, it was seen that increasing the Na_2SO_3 dosage from 100 to 200 g/t reduced the weight of the concentrate to some extent and increased sphalerite depression slightly. Hence, the Zn recovery in the concentrate was a little lower when 200 g/t Na_2SO_3 was used. A limited decrease in the Cu recovery of the concentrate was also observed with 200 g/t Na_2SO_3. This was possibly due to the incidental depression of extremely fine chalcopyrite particles locked in sphalerite entities. One particular result obtained in these tests was the reduction of Fe grade of the concentrate with increase in NaCN dosage. A Fe grade as low as low as 8.12% could be achieved in the concentrate product when 50 g/t of NaCN was used along with 50 g/t Na_2SO_3, as depressants (Table 5.14).

Table 5.14 Metallurgical results with respect to Na_2SO_3 dosage when pH was modified during grinding

Test	**Product**	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
		g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Test 1 **Na_2SO_3 100 g/t** **NaCN 20 g/t** **pH 10.20**	**Concentrate**	101.64	29.11	3.40	96.54	4.42	91.90	19.24	87.39	13.32	47.44
	Tailings	247.56	70.89	0.05	3.46	0.16	8.10	1.14	12.61	6.06	52.56
	Total	349.2	100.00	1.03	100.00	1.40	100.00	6.41	100.00	8.17	100.00
Test 2 **Na_2SO_3 200 g/t** **NaCN 40 g/t** **pH 10.22**	**Concentrate**	98.85	28.27	3.35	92.96	4.24	86.99	18.72	83.39	10.97	37.78
	Tailings	250.80	71.73	0.10	7.04	0.25	13.01	1.47	16.61	7.12	62.22
	Total	349.65	100.00	1.02	100.00	1.38	100.00	6.35	100.00	8.21	100.00
Test 3 **Na_2SO_3 50 g/t** **NaCN 50 g/t** **pH 10.28**	**Concentrate**	93.08	26.60	3.56	94.85	5.12	96.37	22.32	93.31	8.12	26.32
	Tailings	256.78	73.40	0.07	5.15	0.07	3.63	0.58	6.69	8.24	73.68
	Total	349.86	100.00	1.00	100.00	1.41	100.00	6.36	100.00	8.21	100.00

The requirement for a highly alkaline pH for effectively depressing the pyrite in Artvin-Dereiçi ore was previously identified. In this respect, the test in which equivalent dosages of Na_2SO_3 and NaCN (50 g/t of each) was repeated with increased CaO addition from 0.7 to 1.4 grams (4 kg/t). The objective was to repeat the test at a higher alkalinity. With increased CaO addition at the start of grinding, pulp pH was recorded as 11.55. The test conditions and metallurgical results of this test are presented in Tables 5.15 and 5.16, respectively.

Increasing the pulp pH to 11.5 yielded a much lower Fe grade in the concentrate as compared to the tests at pulp pH of 10.20-10.28 (i.e. 0.7 g CaO addition) (Tables 5.14 and 5.16). This again confirmed that a highly alkaline pulp pH was essential for depression of pyrite in Artvin-Dereiçi ore. In other words, with the given test conditions, the rougher pre-concentrate product (the bulk Pb, Cu, and Zn concentrate to be used as feed for further selective flotation stages) was significantly cleaned from pyrite. This was critically important and favorable for the success of the subsequent flotation stages on Artvin-Dereiçi ore in achieving selective Pb, Cu and Zn concentrates.

5.1.6 Use of Sodium Metabisulfite ($Na_2S_2O_5$) as Sphalerite Depressant

In this phase, sodium metabisulfite ($Na_2S_2O_5$) was used as an alternative to zinc sulfate ($ZnSO_4$) to depress sphalerite. Use of NaCN was maintained for depressing pyrite. The test conditions in this phase are summarized in Table 5.17. The goal was to obtain a concentrate enriched in Pb and Cu (i.e. a bulk Pb-Cu concentrate), while depressing sphalerite and pyrite to reduce the Zn and Fe grades of the concentrate to a minimum. A series of tests were conducted, gradually varying the $Na_2S_2O_5$ dosage between 50-400 g/t. In view of the previous findings and observations, in all the tests; 50 g/t of NaCN was used, pulp pH was modified using CaO to $pH \geq 11.2$, and PAX and 3418A combination (75 g/t + 25 g/t) was added as collectors (Table 5.17). Metallurgical results are presented in Table 5.18.

Table 5.15 pH modification during grinding using higher CaO dosage and other test conditions

Test	Na_2SO_3 (g/t)	NaCN (g/t)	pH	3418A+PAX (g/t)
4	50	50	Modified during grinding using 1.4 g CaO (≈4 kg/t)	100

Table 5.16 Metallurgical results when pH modification was done during grinding using higher CaO dosage

Test	Product	Weight		Pb		Cu		Zn		Fe	
		g	%	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
Test 1 **Na_2SO_3 50 g/t** **NaCN 50 g/t** **pH 11.55**	**Concentrate**	87.68	24.73	3.68	93.79	5.55	97.85	24.12	92.74	6.80	20.58
	Tailings	266.93	75.27	0.08	6.21	0.04	2.15	0.62	7.26	8.62	79.42
	Total	354.61	100.00	0.97	100.00	1.40	100.00	6.43	100.00	8.17	100.00

Table 5.17 Variation of $Na_2S_2O_5$ dosage and other test conditions

Test	**$Na_2S_2O_5$ (g/t)**	**NaCN (g/t)**	**pH**	**3418A+PAX (g/t)**
1	50	50	≥11.2	100
2	100	50	≥11.2	100
3	200	50	≥11.2	100
4	400	50	≥11.2	100

Increasing the $Na_2S_2O_5$ dosage caused a decrease in the weight of the concentrate product. Particularly, the decrease in the concentrate weight, when the $Na_2S_2O_5$ dosage was increased from 200 to 400 g/t, was remarkable. With increasing $Na_2S_2O_5$ dosage, lower Zn and Fe grades were achieved in the concentrate. Although this was positive, the reductions in Pb and Cu recoveries in the concentrate should be noted as an adverse influence. This implied that with higher $Na_2S_2O_5$ dosages depression of sphalerite and pyrite was more effective, however, undesired depression of galena and chalcopyrite became an issue. In addition, when 50 g/t $Na_2S_2O_5$ was used, the Zn grade of the concentrate was comparatively higher as compared to other $Na_2S_2O_5$ dosages. This showed that sufficient depression of sphalerite could not be achieved when $Na_2S_2O_5$ dosage was 50 g/t (Table 5.18).

An evaluation of the tests in this phase suggested 100 g/t $Na_2S_2O_5$ as the optimum dosage. The concentrate obtained at this dosage had less than 4% Zn, while Pb and Cu recoveries in the concentrate were outstanding (>98%). When it was considered that the concentrate obtained in this phase (i.e. the rougher Pb-Cu concentrate) would constitute the feed for subsequent stages of selective flotation, high Pb and Cu recoveries and a Zn grade <4% in the pre-concentrate were significant achievements. Overall, it could be deduced that $Na_2S_2O_5$ was a better sphalerite depressant than $ZnSO_4$ for Artvin-Dereiçi ore.

Table 5.18 Metallurgical results with respect to $Na_2S_2O_5$ dosage

Test	**Product**	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
		g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Test 1 **$Na_2S_2O_5$ 50 g/t** **NaCN 50 g/t** **pH ≥ 11.20**	**Concentrate**	115.12	32.86	3.26	98.76	4.38	99.54	4.76	24.91	11.22	44.10
	Tailings	235.25	67.14	0.02	1.24	0.01	0.46	7.02	75.09	6.96	55.90
	Total	350.37	100.00	1.08	100.00	1.45	100.00	6.28	100.00	8.36	100.00
Test 2 **$Na_2S_2O_5$ 100 g/t** **NaCN 50 g/t** **pH ≥ 11.20**	**Concentrate**	110.74	31.28	3.41	98.73	4.79	98.20	3.40	16.74	12.01	45.31
	Tailings	243.26	68.72	0.02	1.27	0.04	1.80	7.70	83.26	6.60	54.69
	Total	354.00	100.00	1.08	100.00	1.53	100.00	6.35	100.00	8.29	100.00
Test 3 **$Na_2S_2O_5$ 200 g/t** **NaCN 50 g/t** **pH ≥ 11.20**	**Concentrate**	98.12	28.01	3.45	93.07	4.84	94.01	3.19	14.10	12.10	40.70
	Tailings	252.14	71.99	0.10	6.93	0.12	5.99	7.56	85.90	6.86	59.30
	Total	350.26	100.00	1.04	100.00	1.44	100.00	6.34	100.00	8.33	100.00
Test 4 **$Na_2S_2O_5$ 400 g/t** **NaCN 50 g/t** **pH ≥ 11.20**	**Concentrate**	68.12	19.45	3.60	71.88	5.66	75.23	3.11	9.56	12.28	28.89
	Tailings	282.12	80.55	0.34	28.12	0.45	24.77	7.10	90.44	7.30	71.11
	Total	350.24	100.00	0.97	100.00	1.46	100.00	6.32	100.00	8.27	100.00

5.2 Assessment of the Flotation Tests for Recovering a Rougher Concentrate

In this first phase, which aimed at recovering a rougher concentrate (a bulk pre-concentrate enriched either in Pb and Cu or in Pb, Cu, and Zn) to be used as a feed for subsequent stages of selective flotation, type of reagents (particularly the sphalerite depressants) and pulp pH significantly affected the results.

As mentioned previously, this first phase mainly investigated the applicability of the following two methods:

1. In the first method, the objective was recovering the galena and chalcopyrite in the froth product while depressing sphalerite and pyrite. Therefore, the froth product of this phase, relatively enriched in Pb and Cu (bulk Pb-Cu concentrate), constituted the feed for subsequent flotation stages to obtain separate Pb and Cu concentrates selectively. The depressed product of this phase, relatively enriched in Zn and Fe, constituted the feed for subsequent flotation stages to obtain a selective Zn concentrate, while rejecting pyrite with the maximum possible extent.

2. The second method aimed at obtaining a bulk pre-concentrate that was enriched in all targeted minerals in this study, i.e. a froth product that consisted of chalcopyrite, galena and sphalerite with the highest possible extent. This bulk Cu-Pb-Zn pre-concentrate constituted the feed for subsequent flotation stages to obtain separate Pb, Cu and Zn concentrates, selectively. Similar to the first method, maximum rejection of pyrite was also essential.

It was seen that, use of NaCN was necessary for effective depression of pyrite in both methods. Use of high NaCN dosages would increase pyrite depression; however, this also increased incidental depression of chalcopyrite, causing the loss of Cu. Hence, controlled use of NaCN was critical for Artvin-Dereiçi ore.

Depression of sphalerite was identified as the major challenge in this first phase of the study. Even when high dosages of the well-known sphalerite depressants were used, depression of sphalerite remained relatively limited. This was attributed to two possibilities:

- It was well established that surfaces of sphalerite particles were highly liable to being activated by Cu ions from the chalcopyrite particles. Due to this undesired activation, the surfaces of sphalerite particles mimicked the behavior of chalcopyrite in the flotation pulp, interacted with the collectors and were recovered with the froth product instead of being depressed.

- Mineralogical investigations revealed the presence of broadly distributed very fine (<10 μm) chalcopyrite particles locked within relatively coarser sphalerite entities. These ultrafine chalcopyrite particles might act as active sites, causing undesired adsorption of collectors on sphalerite and eventual recovery of sphalerite particles through the froth phase.

Among the reagents used zinc sulfate ($ZnSO_4$), sodium sulfite (Na_2SO_3), sodium metabisulfite ($Na_2S_2O_5$), $ZnSO_4$ was found to be the least effective for sphalerite depression. $Na_2S_2O_5$ provided the highest sphalerite depression. When $Na_2S_2O_5$ was used, the Zn grade could be reduced down to 3% at a very low Zn recovery (12%) in the concentrate product. Accordingly, use of $Na_2S_2O_5$ was decided to depress sphalerite in the selective flotation tests. Using $Na_2S_2O_5$, optimum metallurgical results were obtained with the conditions that 100 g/t $Na_2S_2O_5$ and 50 g/t NaCN as depressants, 75 g/t PAX and 25 g/t 3418A as collectors, pulp pH ≥ 11.2 (Table 5.18).

In the second method, where a bulk Cu-Pb-Zn pre-concentrate was obtained, metal grades and recoveries were highly promising. In this method optimum results were obtained with the following conditions that 50 g/t Na_2SO_3 and 50 g/t NaCN as depressants, 75 g/t PAX and 25 g/t 3418A as collectors, pulp pH of about 11.5. It should be emphasized again that adjusting the pulp pH during grinding is of critical importance in this second method. The mechanism that caused effective recovery of sphalerite due to pH adjustment during grinding was an aspect that requires further research. In the aforementioned optimum flotation conditions for this method, Pb, Cu and Zn recoveries in the pre-concentrate were higher than 92% and pyrite could be effectively depressed (Table 5.16).

5.3 Selective Flotation Tests

5.3.1 Selective flotation after obtaining a bulk Cu-Pb-Zn pre-concentrate

In the first method to obtain selective metal concentrates, the goal was to recover a bulk Cu-Pb-Zn pre-concentrate through rougher flotation and then obtaining separate Pb, Cu and Zn concentrates through subsequent selective flotation stages. The flowsheet of this method and the sequence of flotation stages applied is shown in Figure 5.1. The flotation conditions for each stage are provided in Tables 5.19 – 5.23. Metallurgical results for each flotation stage and mass balance for the products are given in Table 5.24. In addition, Figure 5.2 sketches the flowsheet of this method, the flow of the product streams along with Pb, Cu, Zn, and Fe grades and recoveries achieved after each stage.

In this method, pulp pH was modified during grinding, by adding lime (CaO). The effectiveness of this method relies on the early rejection of gangue minerals at a significant extent at the rougher flotation stage. This enables conducting further selective flotation stages on reduced amount of feed, i.e. on the bulk Cu-Pb-Zn pre-concentrate (Figure 5.1, Table 5.19). This pre-concentrate constituted only approximately 24.5% (by wt.) of the starting feed. In the pre-concentrate, all targeted metals were obtained with high recoveries (>92%) and upgraded grades (4.22% Pb, 5.79% Cu, 24.54% Zn). In addition, in this first stage pyrite was effectively depressed and separated from the pre-concentrate (Table 5.24 and Figure 5.2).

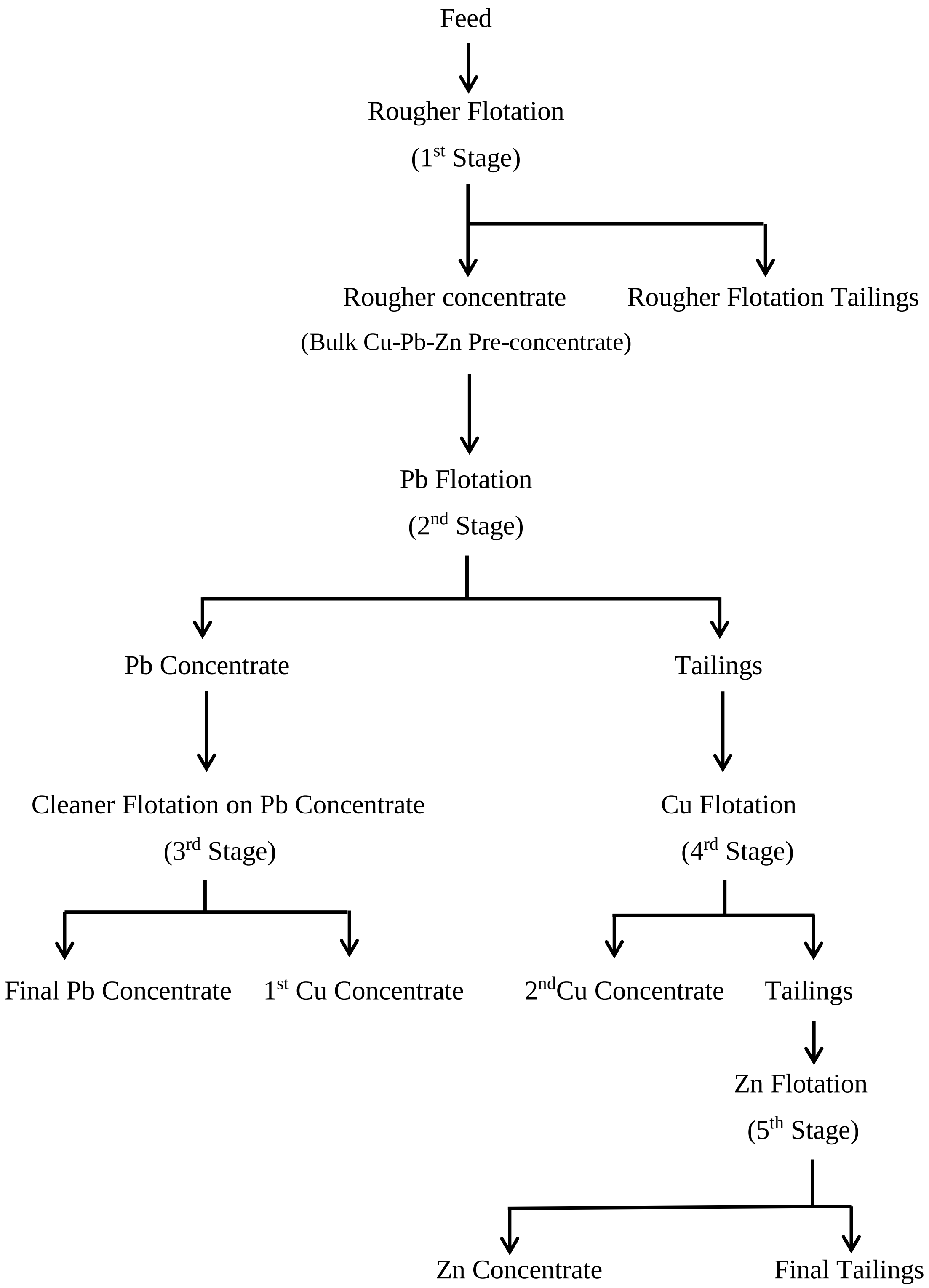

Figure 5.1 Flowsheet of selective flotation after obtaining a bulk Cu-Pb-Zn pre-concentrate

Table 5.19 Rougher flotation (1st stage) for obtaining Cu-Pb-Zn pre-concentrate

1st STAGE Rougher Flotation – Bulk Cu-Pb-Zn Pre-concentrate				
pH		**pH Modifier**		
11.40		CaO – Added at the start of grinding		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	Na_2SO_3	50	Sequential	10
	NaCN	50		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Bulk Cu-Pb-Zn Flotation		
	Time	5 min		
Products	Bulk Cu-Pb-Zn pre-concentrate and tailings			

Table 5.20 Pb flotation (2nd stage) for obtaining Pb concentrate

2nd STAGE Pb Flotation: Pb Concentrate from 1st stage (rougher flotation) concentrate				
pH		**pH Modifier**		
11.22		CaO		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	600	Sequential	15
	$Na_2S_2O_5$	100		
	NaCN	50		
Collector	3418A	25		5
Frother	F-533	50		
Flotation	**Type**	Pb Flotation		
	Time	3 min		
Products	Pb concentrate and tailings			

Table 5.21 Pb cleaner flotation (3rd stage) for obtaining final Pb concentrate

3rd STAGE Pb Cleaner Flotation: Final Pb Concentrate from 2nd stage (Pb flotation) concentrate			
pH		**pH Modifier**	
11.20		CaO	
Reactive		**Dosage (g/t)**	**Conditioning Time (min)**
Depressant	NaCN	250	10
Flotation	**Type**	Pb Cleaner Flotation	
	Time	1.5 min	
Products	Final Pb concentrate and tailings (1st Cu concentrate – tailings enriched in Cu)		

Table 5.22 Cu flotation (4th stage) for obtaining Cu concentrate

4th STAGE Cu Flotation: Cu Concentrate from 2nd stage (Pb flotation) tailings				
pH			**pH Modifier**	
11.25			CaO	
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	600	Sequential	10
	$Na_2S_2O_5$	100		
Collector	3418A	10		5
Flotation	**Type**	Cu Flotation		
	Time	1.5 min		
Products	2nd Cu concentrate and tailings			

Table 5.23 Zn flotation (5^{th} stage) for obtaining Zn concentrate

<table>
<tr><th colspan="4">5th STAGE
Zn Flotation: Zn Concentrate from 4th stage (Cu Flotation) tailings</th></tr>
<tr><th colspan="3">pH</th><th>pH Modifier</th></tr>
<tr><td colspan="3">11.28</td><td>CaO</td></tr>
<tr><th colspan="2">Reactive</th><th>Dosage (g/t)</th><th>Conditioning Time (min)</th></tr>
<tr><td>Depressant</td><td>NaCN</td><td>25</td><td>10</td></tr>
<tr><td>Activator</td><td>$CuSO_4$</td><td>500</td><td>15</td></tr>
<tr><td>Collector</td><td>3418A</td><td>25</td><td>5</td></tr>
<tr><td>Frother</td><td>F-533</td><td>25</td><td></td></tr>
<tr><td rowspan="2">Flotation</td><td>Type</td><td>Zn Flotation</td><td></td></tr>
<tr><td>Time</td><td>3 min</td><td></td></tr>
<tr><td>Products</td><td colspan="3">Zn concentrate and tailings</td></tr>
</table>

Table 5.24 Metallurgical results of selective flotation after obtaining a bulk Cu-Pb-Zn pre-concentrate

Product	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Rougher Flotation Circuit										
Rougher Flotation Concentrate	258.92	24.45	4.22	96.47	5.79	97.40	24.54	92.43	9.63	28.39
Rougher Flotation Tailings	799.97	75.55	0.05	3.53	0.05	2.60	0.65	7.57	7.86	71.61
Rougher Flotation Circuit Total	1058.89	100.00	1.07	100.00	1.45	100.00	6.49	100.00	8.29	100.00
Pb Circuit										
Final Pb Concentrate	60.46	5.71	16.75	89.32	0.25	0.98	0.95	0.84	6.18	4.26
1st Cu Concentrate (Pb Cleaner Tailings)	58.53	5.53	0.97	5.01	23.25	88.43	1.05	0.89	20.76	13.83
Pb Flotation Tailings	139.93	13.21	0.17	2.14	0.89	8.09	44.55	90.69	6.47	10.30
Pb Circuit Total	258.92	24.45	4.22	96.47	5.79	97.40	24.54	92.43	9.63	28.39
Zn Circuit										
2nd Cu Concentrate	10.54	1.00	1.02	0.95	9.05	6.20	2.12	0.32	11.48	1.38
Final Zn Concentrate	124.37	11.75	0.10	1.10	0.23	1.89	49.93	90.35	5.93	8.40
Zn Flotation Tailings	5.02	0.47	0.22	0.10	0.02	0.005	0.39	0.03	9.06	0.52
Zn Circuit Total	139.93	13.21	0.17	2.14	0.89	8.09	44.55	90.69	6.47	10.30
Entire Circuit Total	1058.89	100.00	1.07	100.00	1.45	100.00	6.49	100.00	8.29	100.00

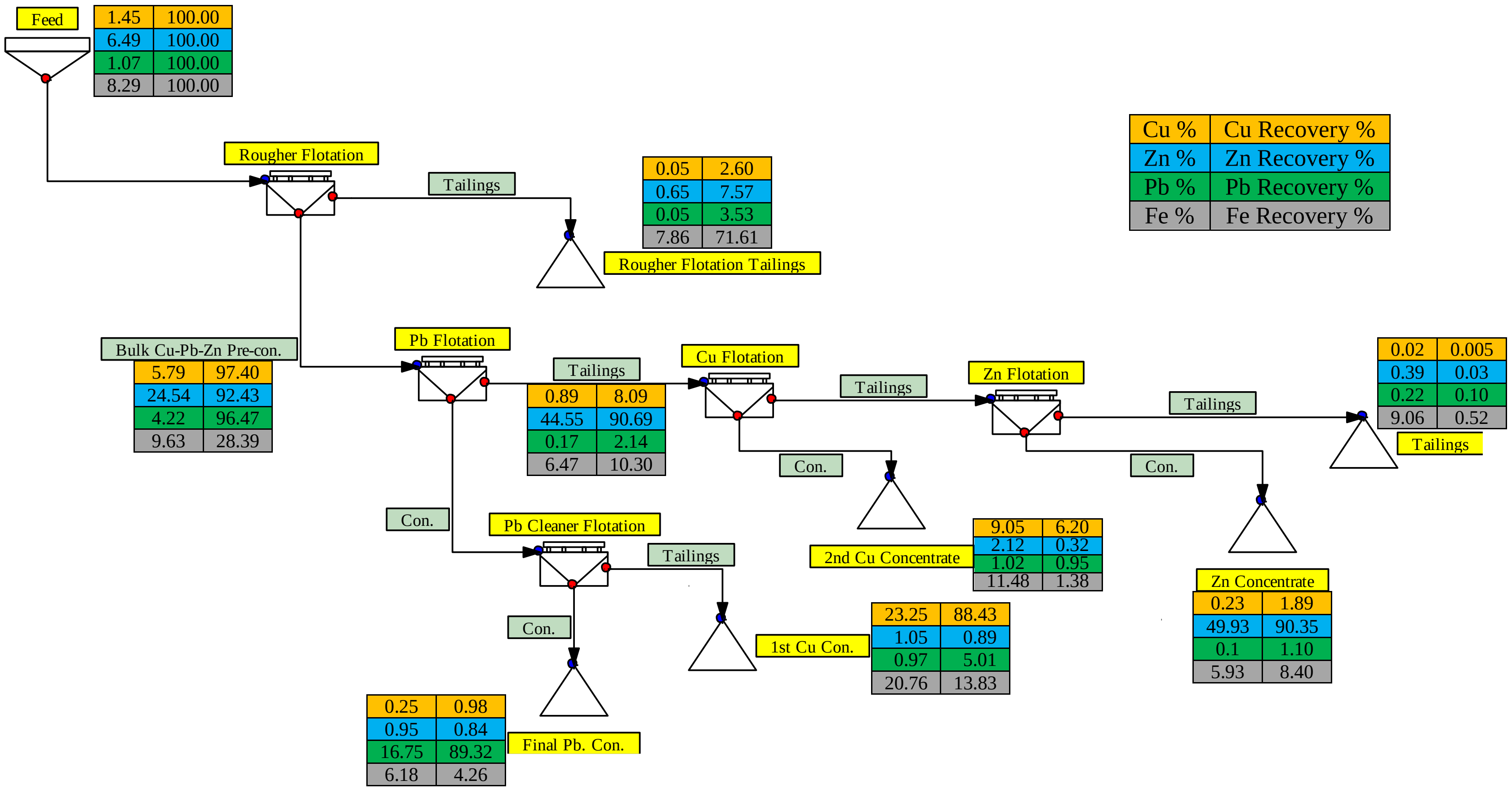

Figure 5.2 Flowsheet of selective flotation after obtaining a bulk Cu-Pb-Zn pre-concentrate and metallurgical results at various concentration stages

After achieving the bulk pre-concentrate through rougher flotation, the 2nd stage in the flowsheet was initiated. The primary objective in the 2nd stage was obtaining a selective Pb concentrate, i.e. a froth product that was enriched in galena. (Figures 5.1 and 5.2). The flotation conditions of the 2nd stage are presented in Table 5.20 and metallurgical results are given in Table 5.24. The tailings of the 2nd stage constituted the feed for the subsequent flotation stages to obtain selective Cu and Zn concentrates (Figures 5.1 and 5.2). In the overall flowsheet, Cu concentrates were obtained as two different products at two different stages. These were depicted as '1st Cu Concentrate' and '2nd Cu Concentrate' in the flowsheets (Figure 5.1 and 5.2). After obtaining a Pb concentrate (the froth product of 2nd stage, Figure 5.1), this concentrate was subjected to cleaner flotation (3rd stage, Figure 5.1) to further increase the Pb grade. The tailings of the 3rd stage was a product enriched in chalcopyrite, i.e. the 1st Cu concentrate in the applied flowsheet (Figures 5.1 and 5.2). The tailings of 2nd stage (Pb flotation), involved significant extent of Zn and Cu. These tailings were subjected to Cu flotation prior to selective Zn flotation stage. The Cu flotation is represented as the 4th stage in the flowsheet. The concentrate of the 4th stage, thus, corresponded to the 2nd Cu concentrate and the tailings constituted the feed for the 5th flotation stage, i.e. selective Zn flotation (Figures 5.1 & 5.2). The target in the 4th flotation stage was to enhance Cu recovery and to send a feed with minimum content of metals other than Zn to the 5th flotation stage.

As a result of 2nd stage (Pb flotation) and subsequent 3rd stage (cleaner flotation on Pb concentrate) a Pb concentrate with 16.75% Pb at 89.32% recovery was obtained (Table 5.24, Figure 5.2). The tailings of the 2nd stage corresponds to the 1st Cu concentrate, as noted above, that assayed 23.25% Cu at 88.43% recovery.

The conditions for the 4th and 5th stages of flotation are presented in Tables 5.22 and 5.23, respectively. The froth product of the 4th stage was the 2nd Cu concentrate assaying 9.05% Cu at 6.20% recovery (Table 5.24, Figure 5.2). The 5th stage involved activation of sphalerite particles using $CuSO_4$. This application successfully yielded a high-recovery (90.35%) Zn concentrate assaying approximately 50% Zn. The pyrite content in this product was fairly low (Table 5.24, Figure 5.2).

In order to evaluate the Cu content in the ore more effectively, it is possible to combine the 1st Cu concentrate (23.25% Cu, 88.43% recovery) and 2nd Cu concentrate (9.05% Cu, 6.20% recovery) to obtain a combined Cu concentrate. This product assayed 21.08% Cu at 94.77% recovery.

5.3.2 Selective flotation after obtaining a bulk Cu-Pb concentrate

In the second method conducted to obtain selective Pb, Cu and Zn concentrates, firstly a bulk Cu-Pb was obtained (1st flotation stage), in which sphalerite was intentionally depressed to obtain a tailings product enriched in Zn. Subsequent flotation stages in this flowsheet included the treatment of the bulk Cu-Pb concentrate to obtain selective Pb and Cu concentrates and treatment of the tailings to obtain selective Zn concentrate. The tailings of the 1st flotation stage (for obtaining a bulk Cu-Pb concentrate), therefore, constituted the feed for Zn flotation stage. The flowsheet for this method is presented in Figure 5.3, in addition to Figure 5.4, sketching the flowsheet of this method, the flow of the product streams along with Pb, Cu, Zn, and Fe grades and recoveries achieved after each stage. Each flotation stage along with applied conditions are presented in Tables 5.25 – 5.28. Metallurgical results for each flotation stage and mass balance for the products are given in Table 5.29.

In the 1st flotation stage, through which obtaining a bulk Cu-Pb concentrate while depressing sphalerite and pyrite was targeted, a froth product assaying 3.31% Pb and 4.87% Cu was obtained (Figures 5.3 and 5.4). The recoveries for both Pb and Cu were quite promising, 98.73% for Pb and 99.30% for Cu. The tailings of the 1st flotation stage became enriched in Zn, assaying 7.64 % Zn at 83.41% recovery (Table 5.29, Figure 5.4). The Fe grade in the concentrate was higher than that of tailings, most probably owing to the iron content of chalcopyrite. Yet, the Fe recovery in the tailings was higher, indicating depression of pyrite at the 1st flotation stage (Table 5.29, Figure 5.4).

In the 2nd flotation stage, the goal was achieving a froth product enriched in Pb, with maximum depression of chalcopyrite, as required for the separation between galena and chalcopyrite (Figure 5.3). Depression of chalcopyrite was for enriching the tailings in Cu since the tailings of this stage constituted the feed for the 3rd flotation stage. The 3rd stage targeted to produce a selective Cu concentrate (Figure 5.3).

As the froth product of the 2nd stage, a Pb concentrate, assaying 45.57% Pb at 96.81% recovery was achieved. It should also be noted that the Cu and Zn contents of the Pb concentrate were quite low (Table 5.29 and Figure 5.4). This implied an effective selectivity that favored the recovery of Pb could be achieved.

In the 3rd flotation stage, a froth product, i.e. a Cu concentrate that assayed 19.10% Cu at 98.79% recovery was obtained. The Pb and Zn contents of the Cu concentrate were very low and pyrite could be effectively rejected (Table 5.29 and Figure 5.4). In view of these results, a good level of selectivity in producing a Cu concentrate could also be achieved through this flowsheet.

The 4th flotation stage aims at recovering a selective Zn concentrate (Figure 5.3). As noted previously, sphalerite activation by adding copper sulfate ($CuSO_4$) to the pulp was applied prior to the flotation to render sphalerite floatable. This activation was critical and necessary to obtain selectivity towards sphalerite, while rejecting other gangue components. As a result, a froth product with outstanding Zn grade of 54.32% at 80% recovery was obtained. In addition, the Cu, Pb and Fe contents of this concentrate were quite low, pointing to a highly selective Zn flotation process (Table 5.29, Figure 5.4).

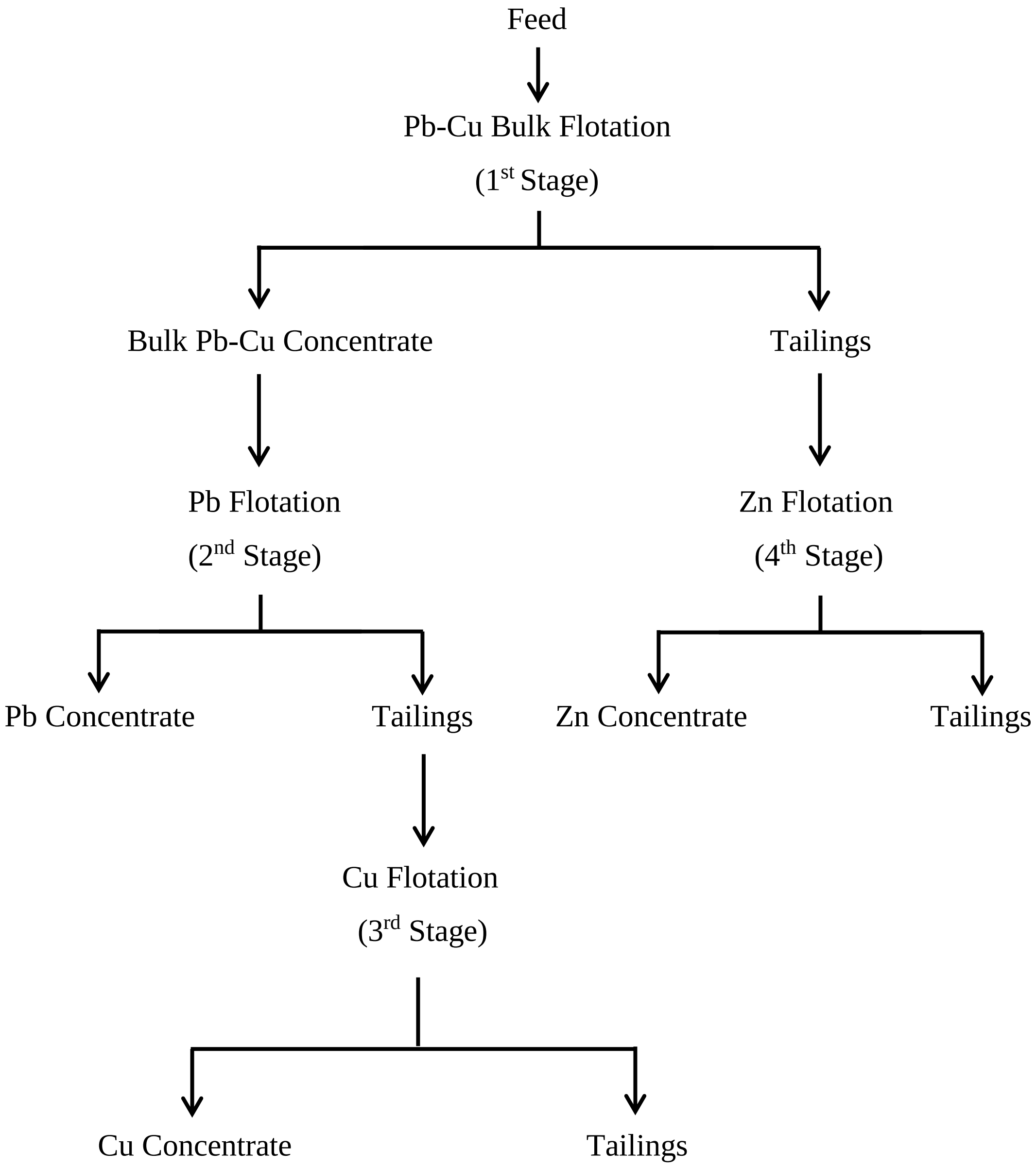

Figure 5.3 Flowsheet of selective flotation after obtaining a bulk Pb-Cu concentrate

Table 5.25 Rougher flotation (1st stage) for obtaining Pb-Cu concentrate

1st STAGE Pb-Cu Bulk Flotation				
pH		**pH Modifier**		
11.32		CaO		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$Na_2S_2O_5$	100	Sequential	10
	NaCN	50		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher Flotation		
	Time	5 min		
Products	Bulk Pb-Cu Concentrate and tailings (enriched in Zn)			

Table 5.26 Pb flotation (2nd stage) for obtaining Pb concentrate from Pb-Cu bulk flotation

2nd STAGE Pb Flotation: Pb Concentrate from 1st stage (Pb-Cu bulk flotation) concentrate			
pH		**pH Modifier**	
11.25		CaO	
Reactive		**Dosage (g/t)**	**Conditioning Time (min)**
Depressant	NaCN	250	10
Flotation	**Type**	Pb Flotation	
	Time	3 min	
Products	Pb concentrate and tailings (enriched in Cu)		

Table 5.27 Cu flotation (3rd stage) for obtaining final Cu concentrate

<table>
<tr><th colspan="4">3rd STAGE
Cu Flotation: Cu Concentrate from 2nd stage (Pb Flotation) tailings</th></tr>
<tr><th colspan="3">pH</th><th>pH Modifier</th></tr>
<tr><td colspan="3">11.22</td><td>CaO</td></tr>
<tr><th colspan="2">Reactive</th><th>Dosage (g/t)</th><th>Conditioning Time (min)</th></tr>
<tr><td>Depressant</td><td>NaCN</td><td>50</td><td>10</td></tr>
<tr><td>Collector</td><td>3418A</td><td>10</td><td>5</td></tr>
<tr><td>Frother</td><td>F-533</td><td>50</td><td></td></tr>
<tr><td rowspan="2">Flotation</td><td>Type</td><td>Cu Flotation</td><td></td></tr>
<tr><td>Time</td><td>1.5 min</td><td></td></tr>
<tr><td>Products</td><td colspan="2">Cu concentrate and tailings</td><td></td></tr>
</table>

Table 5.28 Zn flotation (4th stage) for obtaining Zn concentrate

<table>
<tr><th colspan="4">4th STAGE
Zn Flotation: Zn Concentrate from 1th stage (Pb-Cu bulk Flotation) tailings</th></tr>
<tr><th colspan="3">pH</th><th>pH Modifier</th></tr>
<tr><td colspan="3">11.25</td><td>CaO</td></tr>
<tr><th colspan="2">Reactive</th><th>Dosage (g/t)</th><th>Conditioning Time (min)</th></tr>
<tr><td>Depressant</td><td>NaCN</td><td>25</td><td>10</td></tr>
<tr><td>Activator</td><td>$CuSO_4$</td><td>500</td><td>15</td></tr>
<tr><td>Collector</td><td>3418A</td><td>25</td><td>5</td></tr>
<tr><td>Frother</td><td>F-533</td><td>25</td><td></td></tr>
<tr><td rowspan="2">Flotation</td><td>Type</td><td>Zn Flotation</td><td></td></tr>
<tr><td>Time</td><td>3 min</td><td></td></tr>
<tr><td>Products</td><td colspan="2">Zn concentrate and tailings</td><td></td></tr>
</table>

Table 5.29 Metallurgical results of selective flotation after obtaining a bulk Pb-Cu concentrate

Product	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Pb-Cu Circuit										
Pb+Cu Concentrate	336.38	31.69	3.31	98.73	4.87	99.30	3.28	16.59	11.88	45.72
Tailings	725.08	68.31	0.02	1.27	0.02	0.70	7.64	83.41	6.54	54.28
Pb-Cu Circuit Total	1061.46	100.00	1.06	100.00	1.55	100.00	6.26	100.00	8.24	100.00
Pb Circuit										
Pb Concentrate	23.94	2.26	45.57	96.81	0.07	0.10	0.32	0.12	9.88	2.71
Tailings	312.44	29.43	0.07	1.92	5.24	99.20	3.50	16.48	12.04	43.02
Pb Circuit Total	336.38	31.69	3.31	98.73	4.87	99.30	3.28	16.59	11.88	45.72
Cu Circuit										
Cu Concentrate	85.36	8.04	0.12	0.91	19.10	98.79	2.05	2.63	17.85	17.43
Tailings	227.08	21.39	0.05	1.01	0.03	0.41	4.05	13.85	9.85	25.59
Cu Circuit Total	312.44	29.43	0.07	1.92	5.24	99.20	3.50	16.48	12.04	43.02
Zn Circuit										
Zn Concentrate	97.47	9.18	0.05	0.43	0.05	0.32	54.52	80.00	2.70	3.01
Tailings	627.61	59.13	0.02	0.84	0.01	0.38	0.36	3.41	7.14	51.27
Zn Circuit Total	725.08	68.31	0.02	1.27	0.02	0.70	7.64	83.41	6.54	54.28
Entire Circuit Total	1061.46	100.00	1.06	100.00	1.55	100.00	6.26	100.00	8.24	100.00

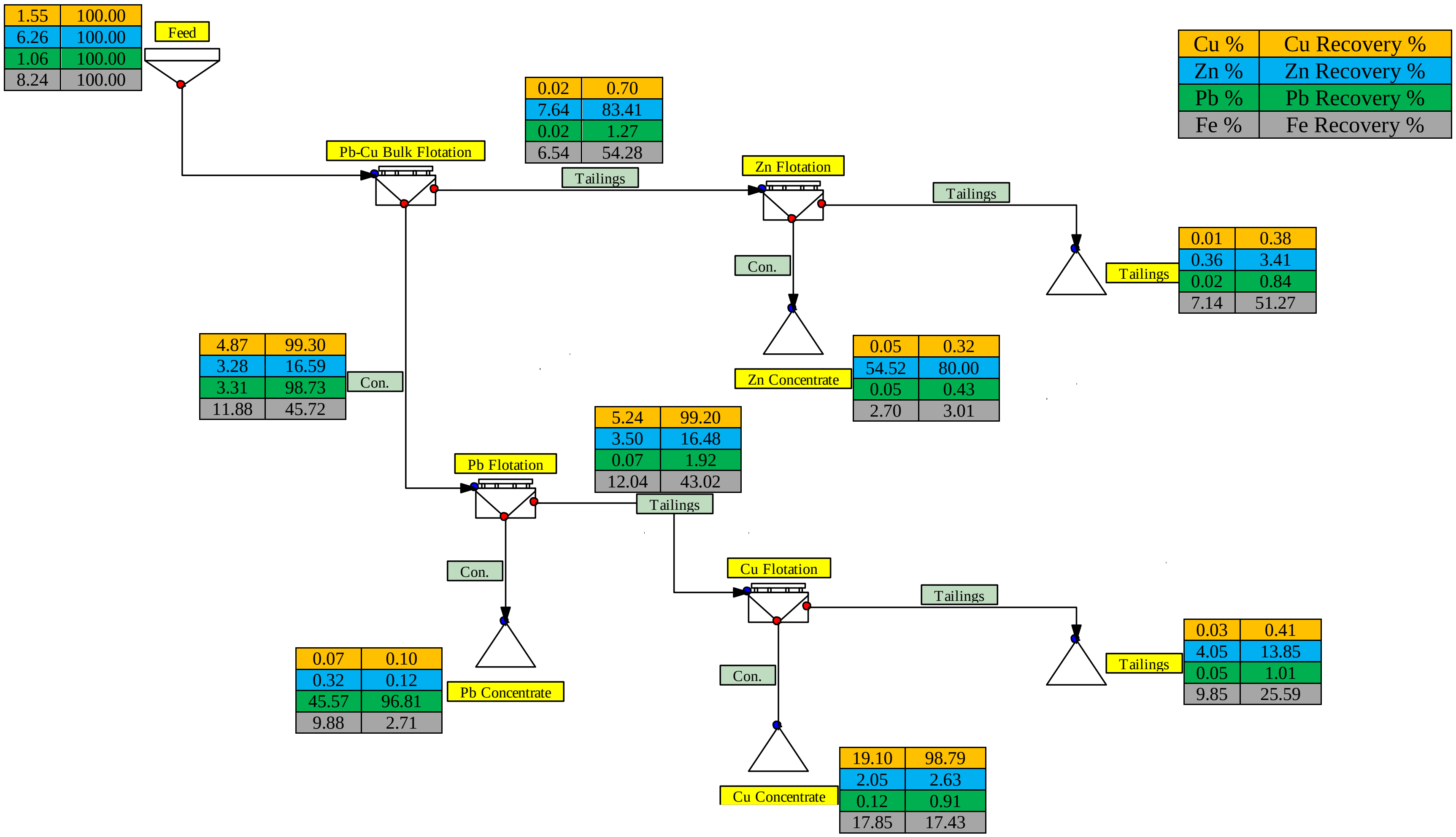

Figure 5.4 Flowsheet of selective flotation after obtaining a bulk Pb-Cu concentrate and metallurgical results at various concentration stages

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

In this research, the amenability of Artvin-Dereiçi complex sulfide ore to flotation was investigated through batch laboratory flotation tests. The objective was to evaluate the opportunity of achieving selective lead (Pb), copper (Cu) and zinc (Zn) concentrates with the highest possible metallurgical performance.

Mineralogical and geo-metallurgical investigations revealed that the major metallic minerals with potential economic value are galena (PbS), chalcopyrite ($CuFeS_2$), and sphalerite (ZnS), while significance of gold or silver were not observed. The major metallic gangue mineral in the ore was pyrite (FeS_2).

The ore was relatively rich in terms of copper (Cu) and zinc (Zn) contents with significant presence of chalcopyrite and sphalerite, as the major copper and zinc minerals, respectively. The copper and zinc assays of the run-of-mine ore were 1.40-1.45%, and 6.35-6.45%, respectively. The lead (Pb) grade in the ore was approximately 1%, which was relatively low and implied that, obtaining an upgraded lead concentrate with marketable grade and recovery values from this ore was appeared to be a challenge.

In upgrading Artvin-Dereiçi ore using flotation, two major challenges were encountered. The first one was depressing pyrite and reducing the pyrite content, thus, the Fe grade of the concentrates and the second one was related to depressing sphalerite in achieving selective copper (Cu), lead (Pb), and zinc (Zn) concentrates.

In depressing pyrite, use of sodium cyanide proved effective. However, adjusting the NaCN dosage was critical since excess use of this reagent caused incidental depression of chalcopyrite, eventually causing loss of copper with the gangue minerals.

The difficulty in depressing sphalerite was attributed to both undesired and uncontrolled activation of the surfaces of sphalerite particles by copper (Cu) ions in the flotation pulp and to the finely distributed chalcopyrite entities locked and homogenously distributed within coarser sphalerite particles. In both cases, sphalerite mimicked the flotation behavior of chalcopyrite and interacted with collectors used for the recovery of chalcopyrite. Consequently, sphalerite was recovered along with chalcopyrite and galena in the froth phase and represented a challenge against achieving the targeted selectivity. In this study, $Na_2S_2O_5$ provided the most favorable results in depressing sphalerite. Both methods and flowsheets applied for selective flotation, yielded zinc concentrates with marketable grade and recovery values.

As stated in details previously, two methods were applied distinctively to selectively achieve metal concentrates with marketable metallurgical features:

- Obtaining a bulk Cu-Pb-Zn pre-concentrate at the first stage of flotation, subsequently obtaining selective (separate) Pb, Cu and Zn concentrates through series of flotation stages.

- The conventional approach, i.e. obtaining a bulk Pb-Cu concentrate at the first stage of flotation by depressing sphalerite (ZnS). Obtaining selective Pb concentrate and Cu concentrates in the second flotation stage. Finally, activating sphalerite and obtaining a selective Zn concentrate in the third flotation stage. Both methods proved effective in this research.

With the first method, a copper concentrate assaying 21.08% Cu at 94.77% recovery, a zinc concentrate assaying approximately 50% Zn at 90.35% recovery were obtained.

The Fe grades in these concentrates showed that pyrite was successfully cleaned. In other words, Cu and Zn concentrates were achieved with marketable Cu and Zn assays at quite high recoveries. The selective lead concentrate obtained through this method also had low pyrite content, yet the Pb grade was relatively low. This was attributed to the low Pb grade of the run-of-mine ore, i.e. the extremely low lead content (approximately 1%) of the flotation feed. Flotation could increase Pb grade from 1% to approximately 17%, which in fact, corresponded to remarkable upgrading. Yet, a higher Pb grade was required for a marketable Pb concentrate. A viable option would be recovering lead within the copper concentrate, rather than attempting the recovery of a selective Pb concentrate as a separate product. This is a very common strategy in the concentration of complex sulfide ores with low Pb grades, because in many smelting schedules, additional payments apply to lead values in copper concentrates.

The second methodology was a conventional route for beneficiation of complex metallic sulfides with lead, copper and zinc values. In this method, a copper concentrate assaying 19.10% Cu at 98% recovery, a zinc concentrate assaying 54.50% Zn at 80% recovery were obtained. Besides outstanding metallurgical results for copper and zinc, this method could also yield a selective lead concentrate with quite higher Pb grade at excellent recovery. The lead grade could be upgraded from 1% to 45.6% at 96% recovery. The Fe grade in the Pb concentrate was low, implying effective rejection of pyrite. In other words, in addition to obtaining high grade Cu and Zn concentrates with high recoveries, the upgrading of lead was favorable with the second method. It was presumed that application of a few additional cleaner flotation stages on this Pb concentrate (45.6% Pb) would further increase Pb grade above 50% with limited decrease in recovery.

An overall assessment of the findings suggests that a significant opportunity exists for the concentration of Artvin-Dereiçi complex-sulfide ore through flotation. Results reveal that it is possible to obtain copper and zinc concentrates with marketable grades and exceptional recoveries. The lead concentrate also approximated a marketable grade at a high recovery. It should be noted that the tests in this study established the flotation behavior of the given ore. Therefore, the following are suggested for future work to improve metallurgical achievements by flotation further:

1. Flotation concentration of Artvin-Dereiçi ore is promising. However, some aspects of the research could be further improved in the next possible phase. For instance, a possibility exists for further increasing the grade of the final Pb concentrate above 50%. This could be attempted by extending this study with an intensive cleaning-re-cleaning flotation scheme on the Pb concentrate obtained in this research.

2. The flotation tests conducted are laboratory scale ‘‘batch’’ trials. The results of these are useful in defining the basic flotation behavior of this ore; however, provide limited information regarding the concentration in a plant-scale flotation circuit. The batch laboratory tests in this research do not assess process alternatives that include various configurations of rougher, scavenger, cleaner and/or recleaner cells/stages applicable in plant-scale operation. The flotation behavior identified in this preliminary research, hence, should be further developed with tests that are specifically designated for designing plant-scale flotation circuit for Artvin-Dereiçi ore.

3. In addition, ‘‘locked-cycle’’ flotation testing, using the favorable flotation conditions determined in this research, is required to simulate possible plant-scale flotation of Artvin-Dereiçi ore. The results obtained with locked-cycle testing are also essential to verify metallurgical performance obtained by batch-tests.

4. As an alternative to the single grind size (P_{100} is 100 μm) applied for flotation in this research, alternative flotation circuits starting with a coarser preliminary grind size (e.g. feed with P_{100} is 150 μm to the rougher stage) and include re-grinding of the middling particles to a finer grind, should be assessed. Such applications may enhance the liberation between metallic and gangue components and positively influence metallurgical achievements.

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APPENDICES

APPENDIX A

DRILL WELLS AND CORES OF ARTVİN-DEREİÇİ ORE AND CORRESPONDING CUMULATIVE PB, CU, ZN ASSAYS

Table A.1 Pb, Cu and Zn assays of the core samples

Drill Well No	Start (m)	End (m)	Interval (m)	Cu (%)	Zn (%)	Pb (%)	Cu+Pb+Zn Assay (%)
1	148.00	148.30	0.30	1.42	5.86	2.24	9.52
	148.30	148.50	0.20	1.08	6.89	0.30	8.27
	148.50	148.70	0.20	1.22	0.67	0.57	2.45
	148.70	149.00	0.30	0.07	0.11	0.04	0.21
2	144.40	144.70	0.30	2.11	6.32	1.53	9.96
	177.30	177.50	0.20	2.64	14.10	0.11	16.85
	178.10	178.45	0.35	2.05	9.86	1.13	13.04
3	144.30	144.60	0.30	1.74	16.50	0.50	18.74
	146.90	147.20	0.30	1.23	7.71	0.97	9.91
	147.20	147.40	0.20	0.49	3.66	0.44	4.59
	147.40	147.70	0.30	1.24	8.38	0.73	10.35
	147.70	148.00	0.30	0.29	1.74	0.13	2.16
	148.00	148.50	0.50	0.57	4.06	0.27	4.90
	148.50	149.00	0.50	0.09	0.38	0.05	0.53
	176.70	177.00	0.30	3.78	25.10	8.36	37.24
	177.00	177.40	0.40	5.21	9.02	14.60	28.83

Table A.1 Cont'd

Drill Well No	Start (m)	End (m)	Interval (m)	Cu (%)	Zn (%)	Pb (%)	Cu+Pb+Zn Assay (%)
4	147.50	148.00	0.50	0.73	7.23	0.88	8.84
	151.20	151.40	0.20	1.56	7.28	0.66	9.50
	151.80	151.95	0.15	1.23	23.10	1.08	25.41
5	170.90	171.25	0.35	2.79	17.80	0.97	21.56
	171.40	172.10	0.70	1.20	13.70	0.42	15.32
6	15.60	16.20	0.60	1.31	5.28	0.77	7.36
	16.20	16.85	0.65	1.08	6.49	0.40	7.97
	18.40	19.00	0.60	1.61	0.19	0.05	1.85
7	15.45	15.80	0.35	1.97	5.71	0.39	8.07
	15.80	16.30	0.50	0.75	1.28	0.56	2.59
	17.40	17.80	0.40	0.50	0.21	0.04	0.75
	18.75	19.20	0.45	0.69	0.42	0.08	1.20
	20.75	20.90	0.15	1.05	0.03	0.01	1.09
8	51.30	51.60	0.30	0.85	2.88	0.38	4.11
9	50.50	50.90	0.40	1.21	19.50	0.61	21.32
	50.90	51.15	0.25	0.96	2.15	0.20	3.31
10	172.20	172.70	0.50	0.33	0.75	0.38	1.45
11	107.50	107.85	0.35	4.88	5.67	0.92	11.47
	268.30	268.50	0.20	1.21	0.79	0.64	2.63
	272.00	272.15	0.15	1.83	0.27	0.15	2.24
12	34.15	34.30	0.15	0.03	0.46	0.38	0.87
	114.80	115.05	0.25	0.42	7.00	1.08	8.50
13	56.05	56.45	0.40	0.10	1.02	0.58	1.70
	115.50	115.80	0.30	0.56	6.86	0.98	8.41
14	120.50	121.00	0.50	0.03	0.08	0.03	0.14

APPENDIX B

USE OF ZINC SULFATE ($ZnSO_4$) AS SPHALERITE DEPRESSANT, FLOTATION PROCEDURE AND CONDITIONS AND METALLURGICAL RESULTS

Table B.1 Use of $ZnSO_4$ as sphalerite depressant, Test 1-flotation procedure and conditions

Test Conditions				
Feed Amount		345.12 g		
Flotation Cell		1 liter		
Agitation Rate		≈1150 rpm		
Initial pH		≈8-8.20		
pH		9.5		
pH Modifier		Na_2CO_3		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	200	Sequential	10
	NaCN	40		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	92.99 g (26.94 %)		
	Tailings	252.13 g (73.06%)		

Table B.2 Use of $ZnSO_4$ as sphalerite depressant, Test 1-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	92.99	26.94	3.85	99.30	3.90	79.54	5.29	22.24	19.28	64.35
Tailings	252.13	73.06	0.01	0.70	0.37	20.46	6.82	77.76	3.94	35.65
Total	345.12	100.00	1.04	100.00	1.32	100.00	6.41	100.00	8.07	100.00

Table B.3 Use of $ZnSO_4$ as sphalerite depressant, Test 2-flotation procedure and conditions

Test Conditions	
Feed Amount	346.08 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.15
pH	9.5
pH Modifier	Na_2CO_3

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	400	Sequential	10
	NaCN	80		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	87.15 g (25.18%)		
	Tailings	258.93 g (74.82%)		

Table B.4 Use of $ZnSO_4$ as sphalerite depressant, Test 2-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	87.15	25.18	3.85	94.19	2.18	40.01	4.92	19.35	17.56	54.67
Tailings	258.93	74.82	0.08	5.81	1.10	59.99	6.90	80.65	4.90	45.33
Total	346.08	100.00	1.03	100.00	1.37	100.00	6.40	100.00	8.09	100.00

Table B.5 Use of $ZnSO_4$ as sphalerite depressant, Test 3-flotation procedure and conditions

Test Conditions	
Feed Amount	360.05 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.20
pH	9.5
pH Modifier	Na_2CO_3

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	600	Sequential	10
	NaCN	120		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	79.30 g (22.02%)		
	Tailings	280.75 g (77.98%)		

Table B.6 Use of $ZnSO_4$ as sphalerite depressant, Test 3-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	79.30	22.02	3.82	85.70	1.85	29.82	4.52	15.48	17.12	46.25
Tailings	280.75	77.98	0.18	14.30	1.23	70.18	6.97	84.52	5.62	53.75
Total	360.05	100.00	0.98	100.00	1.37	100.00	6.43	100.00	8.15	100.00

APPENDIX C

USE OF ZINC SULFATE ($ZnSO_4$) AS SPHALERITE DEPRESSANT AND SODIUM ISOPROPYL XANTHATE (SIPX) AS COLLECTOR, FLOTATION PROCEDURE AND CONDITIONS AND METALLURGICAL RESULTS

Table C.1 Use of $ZnSO_4$ as sphalerite depressant and SIPX as collector, Test 1-flotation procedure and conditions

Test Conditions	
Feed Amount	350.52 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	≈8.00
pH	9.5
pH Modifier	Na_2CO_3

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	200	Sequential	10
	NaCN	40		
Collector	3418A	25	1	5
	SIPX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	72.00 g (20.54%)		
	Tailings	278.52 g (79.46%)		

Table C.2 Use of $ZnSO_4$ as sphalerite depressant and SIPX as collector, Test 1-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	72.00	20.54	4.99	97.73	3.26	47.81	5.74	18.36	9.99	25.24
Tailings	278.52	79.46	0.03	2.27	0.92	52.19	6.60	81.64	7.65	74.76
Total	350.52	100.00	1.05	100.00	1.40	100.00	6.42	100.00	8.13	100.00

Table C.3 Use of $ZnSO_4$ as sphalerite depressant and SIPX as collector, Test 2-flotation procedure and conditions

Test Conditions	
Feed Amount	349.91 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.10
pH	9.5
pH Modifier	Na_2CO_3

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	400	Sequential	10
	NaCN	80		
Collector	3418A	25	1	5
	SIPX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	64.99 g (18.57%)		
	Tailings	284.92 g (81.43%)		

Table C.4 Use of $ZnSO_4$ as sphalerite depressant and SIPX as collector, Test 2-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	64.99	18.57	4.85	90.21	2.25	29.27	5.51	15.94	9.52	21.63
Tailings	284.92	81.43	0.12	9.79	1.24	70.73	6.63	84.06	7.87	78.37
Total	349.91	100.00	1.00	100.00	1.43	100.00	6.42	100.00	8.18	100.00

Table C.5 Use of $ZnSO_4$ as sphalerite depressant and SIPX as collector, Test 3-flotation procedure and conditions

Test Conditions				
Feed Amount		349.55 g		
Flotation Cell		1 liter		
Agitation Rate		≈1150 rpm		
Initial pH		8.08		
pH		9.5		
pH Modifier		Na_2CO_3		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	600	Sequential	10
	NaCN	120		
Collector	3418A	25	1	5
	SIPX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	56.82 g (16.26%)		
	Tailings	292.73 g (83.74%)		

Table C.6 Use of $ZnSO_4$ as sphalerite depressant and SIPX as collector, Test 3-metallurgical results

Metallurgical Results	Weight		Pb		Cu		Zn		Fe	
	g	%	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
Concentrate	56.82	16.26	4.78	77.46	2.03	23.26	5.25	13.24	9.22	18.28
Tailings	292.73	83.74	0.27	22.54	1.30	76.74	6.68	86.76	8.00	81.72
Total	349.55	100.00	1.00	100.00	1.42	100.00	6.45	100.00	8.20	100.00

APPENDIX D

CHANGE OF PULP pH, FLOTATION PROCEDURE AND CONDITIONS AND METALLURGICAL RESULTS

Table D.1 Change of pulp pH, Test 1-flotation procedure and conditions

Test Conditions				
Feed Amount		348.68 g		
Flotation Cell		1 liter		
Agitation Rate		≈1150 rpm		
Initial pH		8.15		
pH		10.5		
pH Modifier		CaO		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	600	Sequential	10
	NaCN	150		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	78.12 g (22.40%)		
	Tailings	270.56 g (77.60%)		

Table D.2 Change of pulp pH, Test 1-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	78.12	22.40	3.78	85.17	2.02	32.71	4.18	14.65	15.10	41.76
Tailings	270.56	77.60	0.19	14.83	1.20	67.29	7.03	85.35	6.08	58.24
Total	348.68	100.00	0.99	100.00	1.38	100.00	6.39	100.00	8.10	100.00

Table D.3 Change of pulp pH, Test 2-flotation procedure and conditions

Test Conditions	
Feed Amount	350.76 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.12
pH	11.2
pH Modifier	CaO

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	600	Sequential	10
	NaCN	150		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	77.20 g (22.01%)		
	Tailings	273.56 g (77.99%)		

Table D.4 Change of pulp pH, Test 2-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	77.20	22.01	3.82	83.05	2.10	33.43	4.12	14.14	13.18	35.63
Tailings	273.56	77.99	0.22	16.95	1.18	66.57	7.06	85.86	6.72	64.37
Total	350.76	100.00	1.01	100.00	1.38	100.00	6.41	100.00	8.14	100.00

APPENDIX E

VARIATION OF $ZnSO_4$ AS THE ONLY DEPRESSANT AT pH 11.2, FLOTATION PROCEDURE AND CONDITIONS AND METALLURGICAL RESULTS

Table E.1 Variation of $ZnSO_4$ as the only depressant at pH 11.2, Test 1-flotation procedure and conditions

Test Conditions				
Feed Amount		356.21 g		
Flotation Cell		1 liter		
Agitation Rate		≈1150 rpm		
Initial pH		8.12		
pH		11.2		
pH Modifier		CaO		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	1000		10
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	75.04 g (21.07%)		
	Tailings	281.17 g (78.93%)		

Table E.2 Variation of $ZnSO_4$ as the only depressant at pH 11.2, Test 1-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	75.04	21.07	4.50	94.49	6.32	93.88	4.69	15.43	25.34	66.41
Tailings	281.17	78.93	0.07	5.51	0.11	6.12	6.86	84.57	3.42	33.59
Total	356.21	100.00	1.00	100.00	1.42	100.00	6.40	100.00	8.04	100.00

Table E.3 Variation of $ZnSO_4$ as the only depressant at pH 11.2, Test 2-flotation procedure and conditions

Test Conditions	
Feed Amount	345.58 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.20
pH	11.2
pH Modifier	CaO

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	2000		10
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	70.08 g (20.28%)		
	Tailings	275.50 g (79.72%)		

Table E.4 Variation of $ZnSO_4$ as the only depressant at pH 11.2, Test 2-metallurgical results

Metallurgical Results	Weight		Pb		Cu		Zn		Fe	
	g	%	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
Concentrate	70.08	20.28	4.40	91.80	6.22	90.82	4.50	14.19	24.00	60.30
Tailings	275.50	79.72	0.10	8.20	0.16	9.18	6.92	85.81	4.02	39.70
Total	345.58	100.00	0.97	100.00	1.39	100.00	6.43	100.00	8.07	100.00

APPENDIX F

USE OF HIGH $ZnSO_4$ DOSAGES WITH LIMITED NACN AT pH 11.2, FLOTATION PROCEDURE AND CONDITIONS AND METALLURGICAL RESULTS

Table F.1 Use of high $ZnSO_4$ dosages with limited NaCN at pH 11.2, Test 1-flotation procedure and conditions

Test Conditions				
Feed Amount		348.18 g		
Flotation Cell		1 liter		
Agitation Rate		≈1150 rpm		
Initial pH		8.15		
pH		11.2		
pH Modifier		CaO		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	1000	Sequential	10
	NaCN	40		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	71.74 g (20.60%)		
	Tailings	276.44 g (79.40%)		

Table F.2 Use of high $ZnSO_4$ dosages with limited NaCN at pH 11.2, Test 1-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	71.74	20.60	4.52	92.14	5.86	86.37	4.18	13.55	15.84	40.18
Tailings	276.44	79.40	0.10	7.86	0.24	13.63	6.92	86.45	6.12	59.82
Total	348.18	100.00	1.01	100.00	1.40	100.00	6.36	100.00	8.12	100.00

Table F.3 Use of high $ZnSO_4$ dosages with limited NaCN at pH 11.2, Test 2-flotation procedure and conditions

Test Conditions	
Feed Amount	349.68g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.10
pH	11.2
pH Modifier	CaO

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$ZnSO_4$	2000	Sequential	10
	NaCN	40		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	70.12 g (20.05%)		
	Tailings	279.56 g (79.95%)		

Table F.4 Use of high $ZnSO_4$ dosages with limited NaCN at pH 11.2, Test 2-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	70.12	20.05	4.40	91.69	5.92	83.19	4.16	12.97	16.12	40.02
Tailings	279.56	79.95	0.10	8.31	0.30	16.81	7.00	87.03	6.06	59.98
Total	349.68	100.00	0.96	100.00	1.43	100.00	6.43	100.00	8.08	100.00

APPENDIX G

USE OF SODIUM SULFITE (Na_2SO_3) AS SPHALERITE DEPRESSANT, FLOTATION PROCEDURE AND CONDITIONS AND METALLURGICAL RESULTS

Table G.1 Use of Na_2SO_3 as sphalerite depressant, Test 1-flotation procedure and conditions

Test Conditions	
Feed Amount	350.24 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.09
pH	9.5
pH Modifier	Na_2CO_3

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	Na_2SO_3	100	Sequential	10
	NaCN	20		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	93.12 g (26.59%)		
	Tailings	257.12 g (73.41%)		

Table G.2 Use of Na_2SO_3 as sphalerite depressant, Test 1-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	93.12	26.59	3.72	98.54	4.48	85.28	4.48	18.93	16.02	52.17
Tailings	257.12	73.41	0.02	1.46	0.28	14.72	6.95	81.07	5.32	47.83
Total	350.24	100.00	1.00	100.00	1.40	100.00	6.29	100.00	8.16	100.00

Table G.3 Use of Na_2SO_3 as sphalerite depressant, Test 2-flotation procedure and conditions

Test Conditions	
Feed Amount	346.68 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.12
pH	9.5
pH Modifier	Na_2CO_3

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	Na_2SO_3	200	Sequential	10
	NaCN	40		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	90.56 g (26.12%)		
	Tailings	256.12 g (73.88%)		

Table G.4 Use of Na_2SO_3 as sphalerite depressant, Test 2-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	90.56	26.12	3.82	96.43	4.40	83.83	4.40	18.14	15.12	48.14
Tailings	256.12	73.88	0.05	3.57	0.30	16.17	7.02	81.86	5.76	51.86
Total	346.68	100.00	1.03	100.00	1.37	100.00	6.34	100.00	8.21	100.00

Table G.5 Use of Na_2SO_3 as sphalerite depressant, Test 3-flotation procedure and conditions

Test Conditions	
Feed Amount	349.14 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.12
pH	9.5
pH Modifier	Na_2CO_3

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	Na_2SO_3	50	Sequential	10
	NaCN	50		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	91.02 g (26.07%)		
	Tailings	258.12 g (73.93%)		

Table G.6 Use of Na_2SO_3 as sphalerite depressant, Test 3-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	91.02	26.07	3.59	98.44	4.33	82.23	4.56	19.08	14.27	45.12
Tailings	258.12	73.93	0.02	1.56	0.33	17.77	6.82	80.92	6.12	54.88
Total	349.14	100.00	0.95	100.00	1.37	100.00	6.23	100.00	8.24	100.00

APPENDIX H

MODIFYING PULP pH DURING GRINDING WHEN SODIUM SULFITE (Na_2SO_3) WAS USED AS SPHALERITE DEPRESSANT, FLOTATION PROCEDURE AND CONDITIONS AND METALLURGICAL RESULTS

Table H.1 Modifying pulp pH during grinding when Na_2SO_3 was used as sphalerite depressant, Test 1-flotation procedure and conditions

Test Conditions				
Feed Amount		349.20 g		
Flotation Cell		1 liter		
Agitation Rate		≈1150 rpm		
Initial pH		8.10		
pH		10.20		
pH Modifier		CaO		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	Na_2SO_3	100	Sequential	10
	NaCN	20		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	101.64 g (29.11%)		
	Tailings	247.56 g (70.89%)		

Table H.2 Modifying pulp pH during grinding when Na_2SO_3 was used as sphalerite depressant, Test 1-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	101.64	29.11	3.40	96.54	4.42	91.90	19.24	87.39	13.32	47.44
Tailings	247.56	70.89	0.05	3.46	0.16	8.10	1.14	12.61	6.06	52.56
Total	349.20	100.00	1.03	100.00	1.40	100.00	6.41	100.00	8.17	100.00

Table H.3 Modifying pulp pH during grinding when Na_2SO_3 was used as sphalerite depressant, Test 2-flotation procedure and conditions

Test Conditions	
Feed Amount	349.65 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.12
pH	10.22
pH Modifier	CaO

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	Na_2SO_3	200	Sequential	10
	NaCN	40		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	98.85 g (28.27%)		
	Tailings	250.80 g (71.73%)		

Table H.4 Modifying pulp pH during grinding when Na_2SO_3 was used as sphalerite depressant, Test 2-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	98.85	28.27	3.35	92.96	4.24	86.99	18.72	83.39	10.97	37.78
Tailings	250.8	71.73	0.10	7.04	0.25	13.01	1.47	16.61	7.12	62.22
Total	349.65	100.00	1.02	100.00	1.38	100.00	6.35	100.00	8.21	100.00

Table H.5 Modifying pulp pH during grinding when Na_2SO_3 was used as sphalerite depressant, Test 3-flotation procedure and conditions

Test Conditions	
Feed Amount	349.86 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.15
pH	10.28
pH Modifier	CaO

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	Na_2SO_3	50	Sequential	10
	NaCN	50		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	93.08 g (26.60%)		
	Tailings	256.78 g (73.40%)		

Table H.6 Modifying pulp pH during grinding when Na_2SO_3 was used as sphalerite depressant, Test 3-metallurgical results

Metallurgical Results	Weight		Pb		Cu		Zn		Fe	
	g	%	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
Concentrate	93.08	26.60	3.56	94.85	5.12	96.37	22.32	93.31	8.12	26.32
Tailings	256.78	73.40	0.07	5.15	0.07	3.63	0.58	6.69	8.24	73.68
Total	349.86	100.00	1.00	100.00	1.41	100.00	6.36	100.00	8.21	100.00

Table H.7 Modifying pulp pH during grinding when Na_2SO_3 was used as sphalerite depressant, Test 4-flotation procedure and conditions

Test Conditions				
Feed Amount		354.61 g		
Flotation Cell		1 liter		
Agitation Rate		≈1150 rpm		
Initial pH		8.10		
pH		11.55		
pH Modifier		CaO		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	Na_2SO_3	50	Sequential	10
	NaCN	50		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	87.68 g (24.73%)		
	Tailings	266.93 g (75.27%)		

Table H.8 Modifying pulp pH during grinding when Na_2SO_3 was used as sphalerite depressant, Test 4-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	87.68	24.73	3.68	93.79	5.55	97.85	24.12	92.74	6.80	20.58
Tailings	266.93	75.27	0.08	6.21	0.04	2.15	0.62	7.26	8.62	79.42
Total	354.61	100.00	0.97	100.00	1.40	100.00	6.43	100.00	8.17	100.00

APPENDIX I

USE OF SODIUM METABISULFITE ($Na_2S_2O_5$) AS SPHALERITE DEPRESSANT, FLOTATION PROCEDURE AND CONDITIONS AND METALLURGICAL RESULTS

Table I.1 Use of Sodium Metabisulfite ($Na_2S_2O_5$) as sphalerite depressant, Test 1-flotation procedure and conditions

Test Conditions	
Feed Amount	350.37 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.12
pH	≥11.2
pH Modifier	CaO

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$Na_2S_2O_5$	50	Sequential	10
	NaCN	50		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	115.12 g (32.86%)		
	Tailings	235.25 g (67.14%)		

Table I.2 Use of Sodium Metabisulfite ($Na_2S_2O_5$) as sphalerite depressant, Test 1-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	115.12	32.86	3.26	98.76	4.38	99.54	4.76	24.91	11.22	44.10
Tailings	235.25	67.14	0.02	1.24	0.01	0.46	7.02	75.09	6.96	55.90
Total	350.37	100.00	1.08	100.00	1.45	100.00	6.28	100.00	8.36	100.00

Table I.3 Use of Sodium Metabisulfite ($Na_2S_2O_5$) as sphalerite depressant, Test 2-flotation procedure and conditions

Test Conditions				
Feed Amount	354.00 g			
Flotation Cell	1 liter			
Agitation Rate	≈1150 rpm			
Initial pH	8.14			
pH	≥11.2			
pH Modifier	CaO			
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$Na_2S_2O_5$	100	Sequential	10
	NaCN	50		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	110.74 g (31.28%)		
	Tailings	243.26 g (68.72%)		

Table I.4 Use of Sodium Metabisulfite ($Na_2S_2O_5$) as sphalerite depressant, Test 2-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	110.74	31.28	3.41	98.73	4.79	98.20	3.40	16.74	12.01	45.31
Tailings	243.26	68.72	0.02	1.27	0.04	1.80	7.70	83.26	6.60	54.69
Total	354.00	100.00	1.08	100.00	1.53	100.00	6.35	100.00	8.29	100.00

Table I.5 Use of Sodium Metabisulfite ($Na_2S_2O_5$) as sphalerite depressant, Test 3-flotation procedure and conditions

Test Conditions				
Feed Amount		350.26 g		
Flotation Cell		1 liter		
Agitation Rate		≈1150 rpm		
Initial pH		8.12		
pH		≥11.2		
pH Modifier		CaO		
Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$Na_2S_2O_5$	200	Sequential	10
	NaCN	50		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	98.12 g (28.01%)		
	Tailings	252.14 g (71.99%)		

Table I.6 Use of Sodium Metabisulfite ($Na_2S_2O_5$) as sphalerite depressant, Test 3-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	98.12	28.01	3.45	93.07	4.84	94.01	3.19	14.10	12.10	40.70
Tailings	252.14	71.99	0.10	6.93	0.12	5.99	7.56	85.90	6.86	59.30
Total	350.26	100.00	1.04	100.00	1.44	100.00	6.34	100.00	8.33	100.00

Table I.7 Use of Sodium Metabisulfite ($Na_2S_2O_5$) as sphalerite depressant, Test 4-flotation procedure and conditions

Test Conditions	
Feed Amount	350.24 g
Flotation Cell	1 liter
Agitation Rate	≈1150 rpm
Initial pH	8.10
pH	≥11.2
pH Modifier	CaO

Reactive		**Dosage (g/t)**	**Conditioning**	**Conditioning Time (min)**
Depressant	$Na_2S_2O_5$	400	Sequential	10
	NaCN	50		
Collector	3418A	25	1	5
	PAX	75	2	5
Frother	F-533	50		
Flotation	**Type**	Rougher		
	Time	5 min		
Products	**Concentrate**	68.12 g (19.45%)		
	Tailings	282.12 g (80.55%)		

Table I.8 Use of Sodium Metabisulfite ($Na_2S_2O_5$) as sphalerite depressant, Test 4-metallurgical results

Metallurgical Results	**Weight**		**Pb**		**Cu**		**Zn**		**Fe**	
	g	**%**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**	**Grade (%)**	**Recovery (%)**
Concentrate	68.12	19.45	3.60	71.88	5.66	75.23	3.11	9.56	12.28	28.89
Tailings	282.12	80.55	0.34	28.12	0.45	24.77	7.10	90.44	7.30	71.11
Total	350.24	100.00	0.97	100.00	1.46	100.00	6.32	100.00	8.27	100.00