UNIVERSIDAD AUTÓNOMA DE SAN LUIS POTOSÍ

Doctorado Institucional en Ingeniería y Ciencia de Materiales

Recovery valuable metals from processing gangue minerals.

TESIS

QUE PARA OBTENER EL GRADO DE

DOCTORADO EN INGENIERÍA Y CIENCIA DE MATERIALES

PRESENTA

Yipeng Zhang

ASESOR

Dr. Alejandro López Valdivieso

PATROCINADO POR CONACyT Beca número 900339

San Luis Potosí , S.L.P. Febrero 2022

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Summary

The wide use of zinc and the exhaustion of traditional sulfide zinc resources provide the motivation to consider oxide zinc mineral resources, however, it is a challenge to be separated from other carbonate minerals by flotation techniques. Therefore, calcium reverse flotation was evaluated as a new flotation method to recover zinc oxide minerals in this literature. The novel collector CaFloatA1 and CaFloatA2, a emulsion mixed by sodium oleate, kerosene and sodium hydroxide, were examined in this study. For comparison, the Ag-CuOx-Ca and Ca flotation were considered as a control tests.

In the control test of Ag-CuO_x-Ca, the collector sodium isopropyl xanthate, frother AF-70 and promoter AP-3418 were carried out for Ag flotation; sodium hydrosulfide, AP-6494 and sodium amyl xanthate for CuO_x flotation; sodium oleate (NaOl) as a collector for Ca flotation. The results showed an insufficient recovery for Ag and CuO_x, only15.7% of Ag, 2.44% of CuO_x in the Ag and Cu concentrate, respectively. But we surprisingly found the Ca flotation recovered 66.46% of calcite, then the calcite recovery was examined in the further Ca flotation.

Three Ca flotation stages were carried out for recovering reversely calcite. 1000 g/t NaOl was added in each Ca flotation stage. The results showed that Ca recovery increased from 61 to 78%, and the ore grade decreased from 8.69 to 1.97% of the tailings, indicating that Ca flotation could recover a large quantity of calcite. Therefore, it is proved that Ca reverse flotation was a promised method to separate calcite from zinc oxide ores.

Recently, studies showed that sodium oleate mixed with the bridging liquid, such as kerosene or benzene, improved the agglomeration of calcite particles, and calcite recovery achieved 98% under the optimal process parameters. Therefore, this kind of collector was carried out to inspect calcite recovery by Ca reverse flotation in this study. The results showed that Ca, Zn recovery and grade increased with NaOl addition

increased by the novel collectors (CaFloatA1) at pH 10, despite the content of zinc oxide ores of sample 1, sample 2 (willemite, Zn_2SiO_4) is different from sample 3, sample 4 (Zincite, ZnO). The maximum Ca recovery was over 90% with 4000 g/t NaOl additions in four samples. The acid leaching tests showed that the acid consumption of Zn pre-concentrate was decreased significantly compared to the original samples. The acid consumption of ores was introduced in this study, which demonstrated that less than 100 Kg/t sulfuric acid was consumed for extracting Zn.

The CaFloatA1 had a perfect performance on the calcite flotation in this literature. The acid consumption of Zn pre-concentrate decreased significantly After Ca reverse flotation compared to the original ores, which indicated that this method can improve economic benefits and decrease the environmental footprint. Therefore, we supposed that CaFloatA1 can be applied in the separation of other metal oxide ores from calcite by froth flotation.

Gold and silver in pyrite are not amenable to recovery by traditional cyanide leaching. In this literature, pyrite concentrates were roasted at different temperatures to improve the recovery of gold and silver by cyanide leaching. Gold and silver recoveries were maximum in the temperature range of 500-600^{o}C due to the higher porosity of calcine, the Au and Ag recovery improved from 25 to 86% and 50 to 77%, respectively. Higher roasting temperatures caused the gold secondary encapsulation and formation of silver ferrite lead to the recoveries decreased. Gold secondary encapsulation was due to the sintering of the calcines. SEM characterization studies of the calcine revealed that the gold included in the pyrite occurs in sizes less than one micron and roasting produced channels in the pyrite exposing the gold particles to the leaching solution. This work also presents a brief review of the pretreatment oxidation processes currently available for the recovery of encapsulated gold in pyrite, namely bio-oxidation, atmospheric and high-pressure leaching with oxygen.

Copper tailing is a solid waste produced from effluent in mining plants. However, a huge amount of copper tailings are collected and stockpiled by mining activity and

process, resulting in the occurrence of failures increase worldwide, in addition, the leached heavy metals in the tailings pose serious pollution to the local resources when exposed to the weathering and natural oxidation environment. On the other hand, such a large number of tailings are regarded as a second resource to recycle valuable metals, such as iron, copper, zinc, etc. As an effective and multifunctional technology, flotation is a widely and commonly used method to treat copper tailings, recover valuable minerals and minimize the environmental footprint. This literature reviews: the potential effects of tailings in the environment, including dust emission, tailing failures, and contamination; factors that influence the performance of copper flotation, including particle size, reagent effects, and clay minerals behavior were also discussed.

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Chapter 1

Recovery zinc oxide ores by calcite reverse flotation using oil/water emulsion as a collector.

1. Introduction

1.1 Current situation of zinc

Zinc was the very first used metal, such as brass, which is an alloy of zinc and copper mixing in different proportions during the early millennium BC(Craddock 1978, Thornton 2007). By now, zinc, one of the most versatile transition metals, has been applied in many fields, such as food, galvanizing, battery, and alloy, etc. It is reported that the total global reserve of zinc is estimated to be 250 million metric tons. Australia owns the largest zinc reserve—an estimated 68 million metric tons. China is the largest zinc producer, approximately 12 million metric tons were produced in 2020, accounting for 33.7% of worldwide zinc production. The United States and China are the largest consumers of zinc. The consumption of zinc grew steadily, reaching over 13.7 million tons. From the data discussed above, the demand for zinc metal has become stronger and stronger owing to the gradual exhaustion of zinc by many industries, especially in the last 30 years (Liu, Wang et al. 2012, Department 2020, Garside 2021).

Zinc naturally occurs in the form of sulfide and oxide. Generally, 95% of zinc is mined and extracted from sulfidic ores, such as sphalerite (ZnS) and marmatite ($Zn_xFe_{1-x}S$). Therefore, after zinc sulfide has been exhausted since the continuous exploitation and utilization, the oxide and silicate resources become alternative options for zinc production and such a process should be developed.

The variety of zinc oxide ores are categorized into three types from an economic point of view: a) ores with hemimorphite as the predominant zinc oxide mineral; b) ores with smithsonite as dominant zinc oxide mineral and c) ores with a mixture of smithsonite and willemite (Bulatovic 2010). Oxide zinc ores contain various forms, such as smithsonite ($ZnCO_3$), hydrozincite ($2ZnCO_3 \cdot 3Zn(OH)_2$), zincite (ZnO), willemite (Zn_2SiO_4) and hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$), etc (Chen, wei Zhao et al. 2009). Froth flotation is the commonly used method for the low grade ores. However, the flotation of oxide minerals, especially the zinc minerals, is more difficult than the flotation of corresponding sulfide minerals, because they are isomorphous with gangues, like calcite-group minerals (Shi, Zhang et al. 2013).

1.2 zinc oxides ores flotation

Both zinc oxide mineral and calcite are similar in many physical and chemical properties, (such as high soluble in the water), which may be replaced partially or fully by each other, resulting in the poor selective separation of zinc oxide from calcite during the flotation (Feng, Wen et al. 2019). Furthermore, the leaching process is the most common method for extracting zinc from oxides ores. However, much more leach solvent is depleted when the ores contain many acid-consuming gangue minerals which are not viable economically. It is feasible and essential to separate these kinds of gangue prior to the leaching process (De Wet and Singleton 2008, Ejtemaei, Gharabaghi et al. 2014). Therefore, in order to improve the flotation performance of zinc oxides, the necessity of newer technology, more novel methods and more effort should be devoted in this field.

The methods for zinc oxides employed in flotation which have been investigated are as follow:

1) Sulfidation by sodium sulfide, flotation by amines as collectors (Kashani and Rashchi 2008, Irannajad, Ejtemaei et al. 2009, Bai, Li et al. 2018);
2) Sulfidation and activation by metal ions, flotation by xanthate as a collector (Rao and Finch 2003, Hosseini and Forssberg 2006);
3) Chelating agents (Bustamante 1979, Marabini, Ciriachi et al. 2007);
4) Other Thiol collectors (Hosseini and Forssberg 2006, Hosseini and Forssberg 2008);

5) Mixed anionic and cationic collectors (Mehdilo, Irannajad et al. 2013);
6) Fatty acid (Irannajad, Ejtemaei et al. 2009, Shi, Feng et al. 2012).

1.2.1 Sulfidation by sodium sulfide, flotation by amines as collectors

The most common and commercial flotation technique for zinc oxides is sulfidation by sodium sulfide, followed by treating with amine collectors. It is reported that in the traditional amine flotation of zinc oxide ores, the consumption of collectors is pretty high because of the hydrophilic surface of minerals (Ejtemaei, Irannajad et al. 2011). In addition, the zinc oxides flotation has lower selectivity since the similar properties of minerals and gangue. To increase the hydrophobicity of the mineral surface, sulfidizing agent, such as sodium sulfide (Na_2S), is utilized in the flotation process. The related dissolution, hydrolysis, and adsorption are participated and occurred on the mineral surface, the equations as follow (Pokrovsky and Schott 2002, Ejtemaei, Gharabaghi et al. 2014):

$$ZnCO_3 = Zn^{2+} + CO_3^{2-} \tag{1}$$

$$Zn^{2+} + OH = ZnOH^{+} \tag{2}$$

$$Zn^{2+} + 2OH = Zn(OH)_{2(aq)} \tag{3}$$

$$Zn^{2+} + 3OH = Zn(OH)_3 \tag{4}$$

$$Zn^{2+} + 4OH = Zn(OH)_4^{2-} \tag{5}$$

$$Na_2S + 2H_2O = 2NaOH + H_2S \tag{6}$$

$$H_2S = H^{+} + HS^{-} \tag{7}$$

$$HS^{-} = H^{+} + S^{2-} \tag{8}$$

$$ZnCO_{3(surf)} + HS^{-} = ZnS_{(surf)} + HCO_3^{-} \tag{9}$$

$$Zn(OH)_{2(surf)} + HS^{-} = ZnS_{(surf)} + H_2O + OH^{-} \tag{10}$$

Therefore, the mildly alkaline condition is required when HS^- is the predominant species in the solution at pH > 7.0 (Bustamante and Shergold 1983), from equation (1-10), HS^- species interact with zinc oxides surface and form a hydrophobic film. Under these conditions, conventional froth flotation can be applied to separate zinc oxide ores by adding effective collectors. In addition, sodium sulfide is a desirable pH regulator at a pH range of 10.5-12. Many studies showed that sodium hydroxide and sodium carbonate are the most common pH regulators for flotation, but zinc hydroxide precipitation and higher costs are the main limitations for utilization (Ejtemaei, Irannajad et al. 2011).

On the other hand, the dosage of sulfidizing agents is another factor that influences the flotation performance. It is reported that larger amounts of sodium sulfide change the zeta potential of minerals more negative, and the value of the isoelectric point decreases, resulting from the HS^- ions adsorbed chemically on the surface of the mineral, then increasing the zinc recovery (Hosseini and Forssberg 2006). Studies showed that there is a controversial point between willemite and smithsonite when overmuch Na_2S is added. Zinc silicate willemite will not be depressed with an excess of sodium sulfide, but the extra sulfide ions have a significant negative effect on the smithsonite recovery (Malghan 1986, Önal, Bulut et al. 2005, Mehdilo, Irannajad et al. 2013).

Amines are the most common cationic collectors for the flotation of zinc oxides. Amine salts and organic ammonium compounds are very sensitive to the pH, for example, high activity in slightly acidic medium and inert in strong alkaline and acidic media. Several amines, such as Flotbel 1, Flotbel CA, Flotble CH-A, Aeroamine, Armac T, Armac S, Armac CD, etc, have been investigated by many studies, the results showed that Armac C was the best collector for the smithsonite recovery, and Armac T enhanced the Zn grade of flotation concentrate, with the mixture ratio of Armac C and Armac T =1:6, the optimal Zn recovery and grade were obtained without any depressant addition (Irannajad, Ejtemaei et al. 2009, Mehdilo, Irannajad et al. 2013). In the case of willemite and hemimorphite flotation, the stearyl anime has the best flotation performance at pH=10.

As shown in Fig.1, amine collectors exist in the form of $RNH_{2(aq)}$ in the pH range of 10.5-12, which is a benefit for sulfidation by sodium sulfide. The predominant species are expected to adsorb on the sulfidized surface of zinc oxides through chelating.

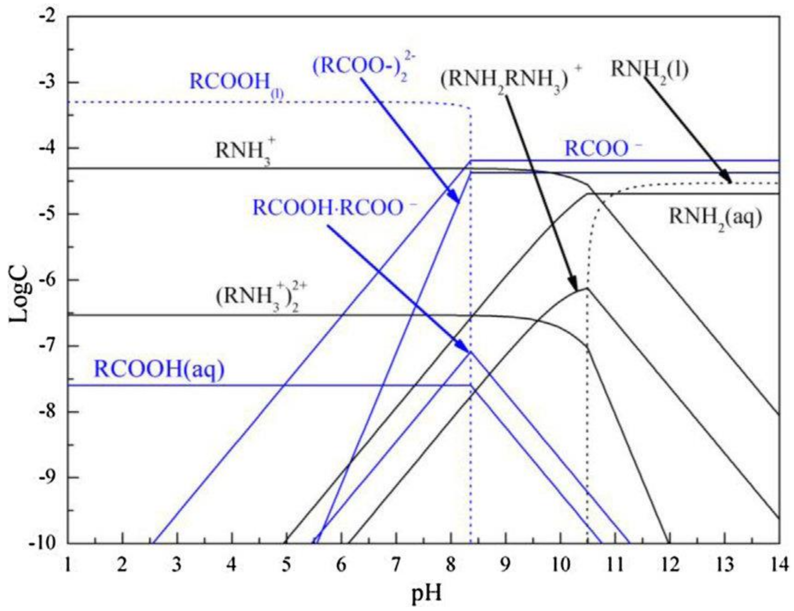


Fig. 1. Speciation of amine collector as a function of pH at a total initial concentration of 0.2mM (Xu, Hu et al. 2015).

Besides the type of amine collectors, conditioning time, depressant types and dosage, dispersants, pH regulator, the concentration of solid, desliming are also important factors for the zinc oxides flotation.

1.2.2 Sulfidation and activation with metal ions, flotation with xanthate as a collector

Xanthates are the most common and effective collectors for sulfide mineral flotation. For the oxide minerals, sulfidation-xanthate to activate metal ions is the most practical method. Generally, copper sulfate is one of the most common activators for zinc oxides flotation. It is suggested that adding $CuSO_4$ in the conditioning stage after pre-treatment with sulfidizer, such as sodium sulfide, then the zinc oxide minerals can be recovered by xanthate collectors. Hosseini et al., (2006a) investigated the influence of potassium amyl xanthate (KAX) on the smithsonite flotation. The results showed that the maximum zinc oxide recovery achieved of 81.3% at pH 10.5, with the KAX concentration of 2.96×10^{-3}M, Na_2S concentration of 2.6×10^{-2}M and $CuSO_4$ concentration of 9.4×10^{-3}M (Hosseini and Forssberg 2006).

The copper ion plays an important role in zinc mineral flotation, an ion exchange between Zn^{2+} and Cu^{2+} occurs on the mineral surface, then a layer of CuS is formed to increase the hydrophobicity of zinc oxides in the pulp (Hosseini and Forssberg 2006).

Unlike the sulfide minerals which have a more hydrophobic surface, short-chain xanthates are not effective collectors for oxide ores flotation, since they are more hydrophilic compared to the long-chain xanthates. The chemical bond between xanthates and metal is the main mechanism for the sulfide mineral flotation, while the ionic bond is more active between metal and oxygen than that between metal and sulfur (Finkelstein 1997), which results in a weak reaction between zinc oxide and short-chain xanthate. Therefore, a longer chain xanthate is required to produce a hydrophobic film for metal oxide flotation (Rao and Finch 2003).

However, when the ore contains many ferric oxide and silica, the poor zinc recovery would be very poor, due to the inadvertent activation of silica by the metal ions. Therefore, the zinc oxide flotation is not selectively separate in practice (Barbery, Cecile et al. 1977, Somasundaran and Wang 2006, Bulatovic 2010, Ejtemaei, Irannajad et al. 2010).

1.2.3 Chelating agents

Chelating reagents are proposed as effective collectors to form stable and selective compounds in the flotation, because of their significant stability, selectivity, and specificity. Chelating reagents contain a large quantity of various organic functional groups which are capable of bonding with metal ions to form one or more rings, namely chelates. Every chelating reagent is characterized by the presence of at least one group that is capable of donating a pair of electrons to the metal to which it is bound. This leads to the formation of rings with ligand bonds other than covalent bonds. In addition, chelating groups are usually inserted into the aromatic ring as well. Thus, these form very stable four- to six-membered rings (Marabini, Ciriachi et al. 2007).

Rinelli and Marabini (Rinelli and Marabini 1973) studied the performance of different concentrations of 8-hydroxyquinoline and zinc sulfate on the smithsonite flotation, which was carried out in a Hallimond tube at pH 7.0. The results showed that smithsonite recovery achieved to 100% by a concentration of oxine was 0.08 g/L.

Although the successful utilization of chelating reagents in the laboratory scale for the pure mineral flotation, there are limitations to the industrial scale, due to (Marabini, Ciriachi et al. 2007):

1) Lack of long-chain hydrocarbon in the molecular
2) Lower selectivity in the heterogeneous phase
3) Deficiency of the thermodynamic and structural criteria to design new chelate type.

1.2.4 Other Thiol collectors such as mercaptans

Mercaptans have been applied in many fields, such as the flotation reagents for lead, copper, and zinc minerals; Rubber vulcanization accelerator; condensation agents in peptide synthesis; free radical polymerization and photoreduction inhibitor of ketones (Ejtemaei, Gharabaghi et al. 2014). Hosseini et al (Hosseini and Forssberg 2011) investigated the effects of mercaptans on the zinc oxide flotation. Methyl mercaptan (CH_3SH; MM), ethyl mercaptan (C_2H_5SH; EM), and hexyl mercaptan ($C_6H_{13}SH$; HM) were assessed as collectors. The results revealed that the maximum smithsonite recovery achieved of 78%, grade of 22.5% by HM at pH 9.0 in a Hallimond tube. However, the MM and EM results showed no significant variation for Zn recovery compared to the HM, because these mercaptans have shorted lengths of hydrocarbon chains. The mercaptans adsorption process involved the rupture of the sulfur-hydrogen bond, reaction with the metal-OH bond, and the formation of a strong sulfur-metal bond. As a weak acid, the ionization of SH and adsorption on the zinc mineral surface is according to the following equation (Hosseini and Forssberg 2006):

$$RSH + H_2O = RS^- + H_3O^+ \tag{11}$$

$$Zn \cdots OH^+ + RS^- = Zn \cdots SR + H_2O \tag{12}$$

1.2.5 Mixed anionic and cationic collectors (xanthates and amines)

The mixture of anionic and cationic collectors was investigated for sulfide minerals (sphalerite, pentlandite, and pyrrhotite (Rao and Forssberg 1997)) and oxide minerals (smithsonite (Hosseini and Forssberg 2007), ilmenite (Tian, Xu et al. 2017), magnesite (Sun, Dai et al. 2021)) flotation, as well as in the separation of alkali feldspars-spodumene(Shu, Xu et al. 2020), water glass (Dong, Jiao et al. 2018), muscovite-quartz (Wang, Sun et al. 2014), etc.

A system that contains two differently charged surfactants is called a cationic system. The processes and phenomena of adsorption and dissolution behavior of anionic and cationic trapping agents must be considered at the interface and the solution phase, e.g. multivalent cation precipitation, micelles formation, a liquid-gas interface film formation, insoluble complexes formed by anions and cations reaction (Ejtemaei, Gharabaghi et al. 2014).

A mixture of octadecylamine acetate (ODA) and sodium amyl xanthate (SAX) was applied for flotation to separate zinc oxide ores from calcite (Luo, Zhang et al. 2020). In smithsonite flotation, the optimum ratio of these two reagents was 3:1 in the presence of 2 mol/L sodium sulfide under pH was 10. The results showed that the mixed collectors co-adsorbed on the surface of sulfidized smithsonite and calcite, while macromolecular sodium alginate (NaAl) as a strong inhibitor which was selectively chemisorbed onto the surface of calcite resulting in its hydrophilicity increased, which improved the separation of smithsonite from calcite. Figure 2. Shows a schematic diagram of the mechanism of adsorption and inhibition of NaAl on calcite and smithsonite by mixed trapping agents.

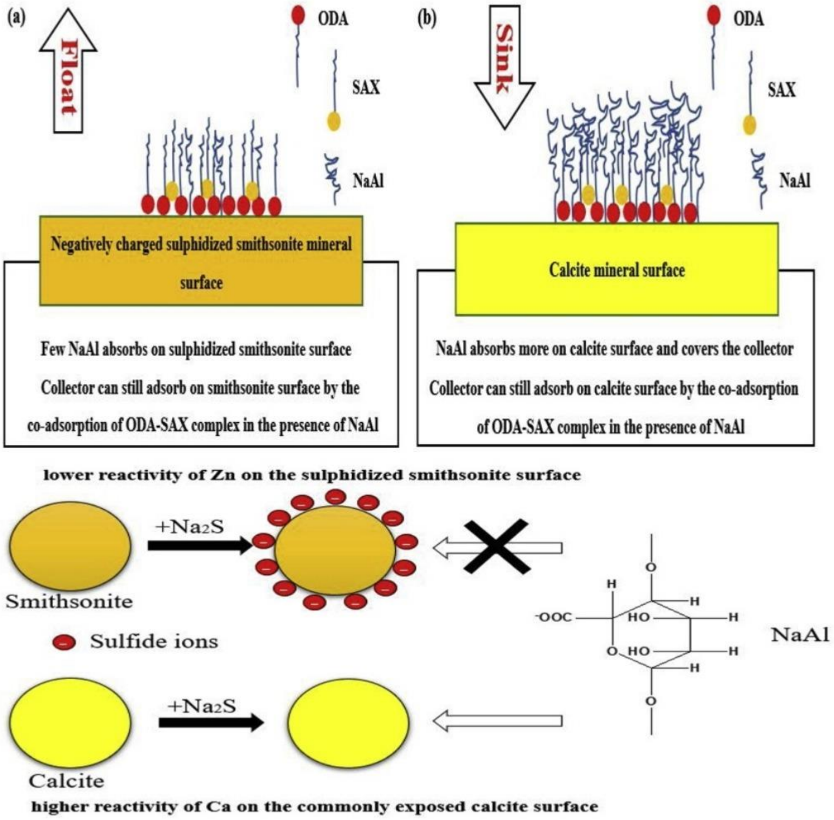


Fig. 2. Schematic diagram of adsorption of mixed collectors and mechanisms of depression by sodium alginate.

1.2.6 Fatty acids

It is reported that for the carboxylic acid, the zinc flotation was not influenced if the gangue is silica or clay minerals, but if the gangue contains calcite and dolomite, the grade of zinc would decrease significantly due to the floatable of calcareous materials (Rey 1979).

Oleic acid or sodium oleate is a long-chain carboxylic acid that is used widely in zinc oxide flotation at a pH of 10. The negative zeta potential increases due to the adsorption of oleic anions on the mineral surface. As revealed by FTIR analyses that the adsorption of oleic acid on the mineral surface is caused by an ion-exchange mechanism (Irannajad, Ejtemaei et al. 2009). Chemical and physical interaction are involved at alkaline environment, while in the acid/base pH range, hydrophobic interaction is the main mechanism of hemimorphite particle aggregation to improve the mineral floatability (Liu, Feng et al. 2015).

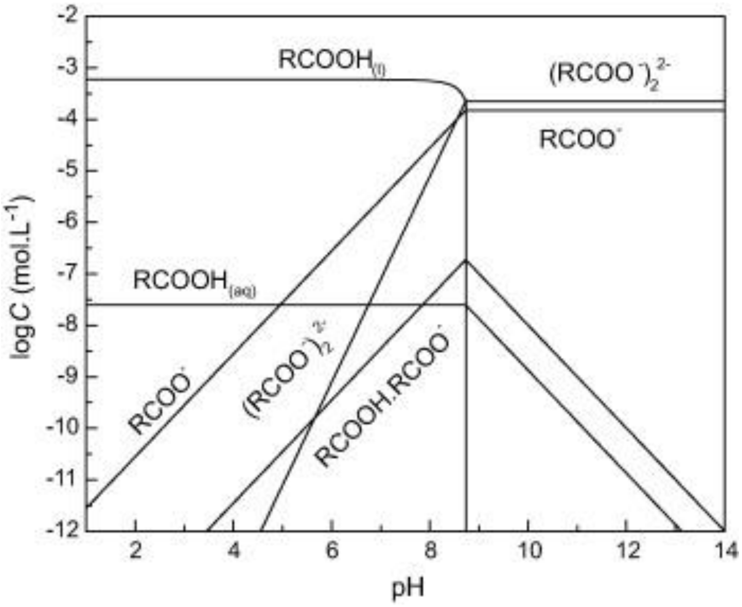


Fig. 3. Species distribution diagram of oleic acid (Yu, Wang et al. 2015).

It is well known that the carboxyl groups (RCOOH) are dependent strongly on the pH value. Figure 3. Shows the species diagrams of oleic acid in the whole pH range, species such as $RCOO^-$ or $(RCOO^-)_2^{2-}$ are predominant species when pH > 9, which may be adsorbed on the surface of Zn oxide ores, The equation can be assumed as follow (Hosseini and Forssberg 2006):

$$Zn(OH)_2 + RCOO^- = Zn^+RCOO^- + OH^- \tag{13}$$

In order to avoid the reduction of zinc grade by gangue minerals in zinc oxide flotation, depressants that have no effect on the valuable zinc oxide are used. It has been characterized that quartz cannot be floated by oleic ions at pH 9 due to the charge repulsion. However, the actual flotation results show that there was no separation between smithsonite and quartz, and both have been floated (Ejtemaei, Irannajad et al. 2010). Ejtemaei et al. (Ejtemaei, Irannajad et al. 2011) used different depressants to depress the flotation of quartz in the presence of oleic acid. They found that quartz can be activated by dissolved ions (especially Pb^{2+} and Zn^{2+}) and floated along with smithsonite. To solve this problem, various depressants have been applied, namely, sodium silicate, sodium sulfide, sodium fluoride, carboxymethyl cellulose (CMC), and starch. It is proved that the CMC was the most successful quartz depressant and not harm the recovery of smithsonite.

Calcite and dolomite were depressed by citric acid in the flotation, but this method has not been applied in any plant practice (Ejtemaei, Gharabaghi et al. 2014). Sodium humate is another depressant for separating smithsonite from calcite in the micro-flotation which obtained a successful result. On the other hand, using SH in flotation of zinc oxide ore, the Ca grade was decreased with the Zn grade fell sharply (Irannajad, Ejtemaei et al. 2009). To understand the mechanisms of these results, we need to thoroughly investigate the effects of dissolved ions on the flotation of calcite and smithsonite surfaces in the presence of oleic acid.

1.3 The mixture of sodium oleate and kerosene

Recently, a mixture of oleic acid and kerosene as a novel emulsion collector has been proposed and investigated on the flotation of coking coal. The results showed that the novel collector had a stronger collectivity than kerosene alone (Zhu, Yin et al. 2020). A similar mixture could be found in other metals flotation, for example, recovery malachite mixture of octyl hydroxamate and kerosene (Li, Rao et al. 2019). However, there is no information about hydrophobic floc-flotation of calcite with the mixture of fatty acid and kerosene.

1.4 Research objective

In industrial practice, sulfidation flotation has been used for zinc mineral separation. However, this strategy has some disadvantages, such as higher reagent consumption, sulfidation control difficulty, and low separation efficiency for lower grade zinc ore. The direct flotation of oxide zinc ore using an anionic collector or mixed anionic/cationic collector shows poor separation between oxide zinc mineral and other calcium carbonate minerals. Therefore, the development of the flotation method zinc oxide ore from calcite is urgently needed. Since the difficulty of separation between zinc oxide ore and gangue contains calcite and dolomite, the reverse flotation of calcium ores is possibly feasible with a fatty acid, because calcite has better floatability due to the chemisorption of fatty acids on surface-active Ca^{2+} sites (Liu, Zhang et al. 2019).

2 Material and Method

2.1 Mineral samples and reagents

Four powder mineral samples were obtained from Minera Rio Tinto, SA. De. CV (Chihuahua, Mexico). These mineral samples were homogenized and split into small samples of 1 kg each. The chemical analysis of these 4 samples was shown in Table 1. which indicated that the zinc content was varied from 1.30% to 5.80% and the calcium content was the highest. X-ray diffraction measurements on these samples showed that the zinc minerals was willemite (Zn_2SiO_4), the calcium minerals were calcite ($CaCO_3$) and composed of other minerals, such as hematite (α-Fe_2O_3), quartz, and gangue minerals (see Figure.1), the willemite could not be detected in sample 2 maybe because of the lowest zinc content.

Table 1. The chemical analysis of four mineral samples

Sample	Cu	Fe	Pb	Zn	Ca	Au	Ag
1	0.64	15.52	0.07	6.86	11.32	0.85	44
2	1.81	14.35	0.19	1.08	17.66	0.39	34.5
3	0.17	10.50	0.013	4.86	21.13	0.42	8.38
4	0.19	2.68	0.017	2.68	20.29	0.34	5.63

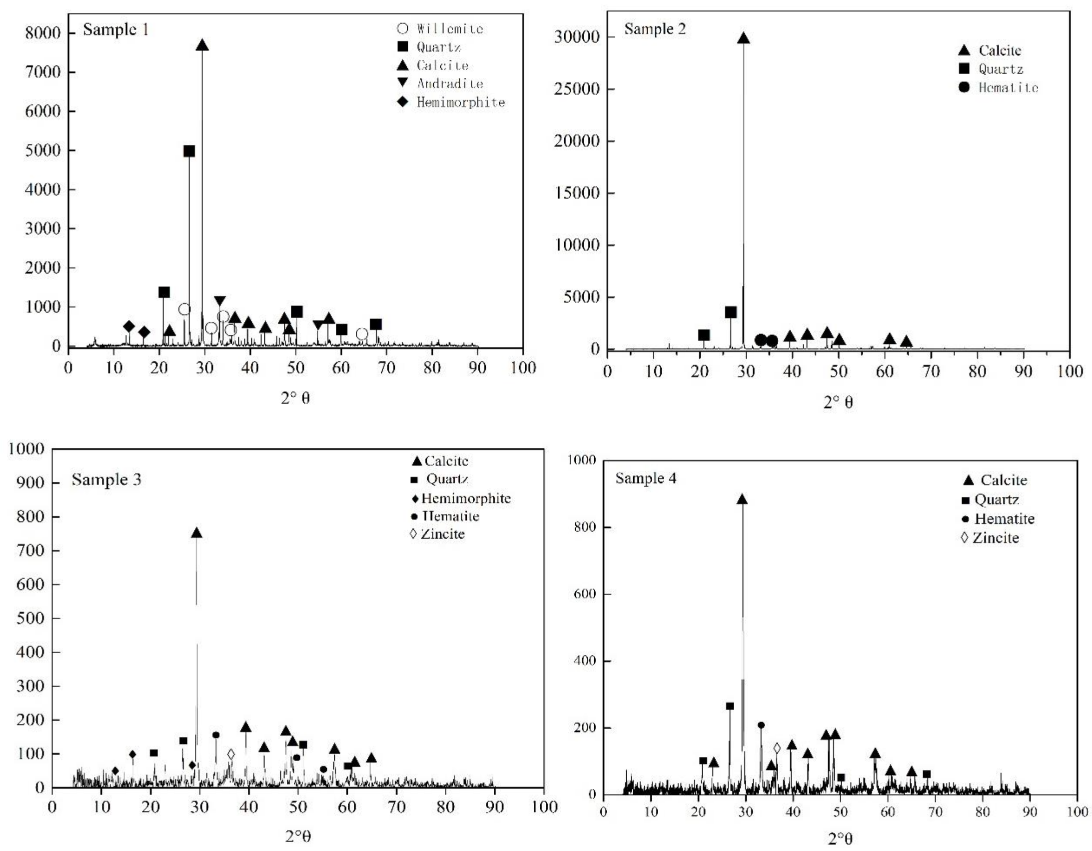


Fig. 4. The XRD spectrum of 4 samples.

Chemically analytical grade reagents were obtained from the following sources: sulfuric acid (H_2SO_4), sodium cyanide (NaCN) sodium hydrosulfide (NaSH), sodium oleate (NaOl, $C_{18}H_{33}NaO_2$), and sodium hydroxide (NaOH) are from J.T.Baker Chemical Company, kerosene is from J.T.Baker; the frother (AF-70 and F-507), collector (potassium amyl xanthate) and promoter (AP-6494 and AP-3418) are from Cytec Industries Inc. Distilled water was used for the preparation of reagents, tap water was used in all the flotation tests and leaching experiments.

2.2 Ag-CuO_x-Ca flotation flowsheet

The experiments were conducted in a self-aerated Denver laboratory flotation cell with a volume of 1235, 2550, and 4980 cm^3. The solid weight was 60%, ores and water were added to the grinding mill and grounded with different concentration promoters then put into the flotation cell. The Ag-CuO_x-Ca beneficiation flowsheet of the test is presented in Figure 5. The concentrate and tailings were filtered, dried, weighed, and assayed for Ag, Cu oxide, Ca, Fe, and Zn.

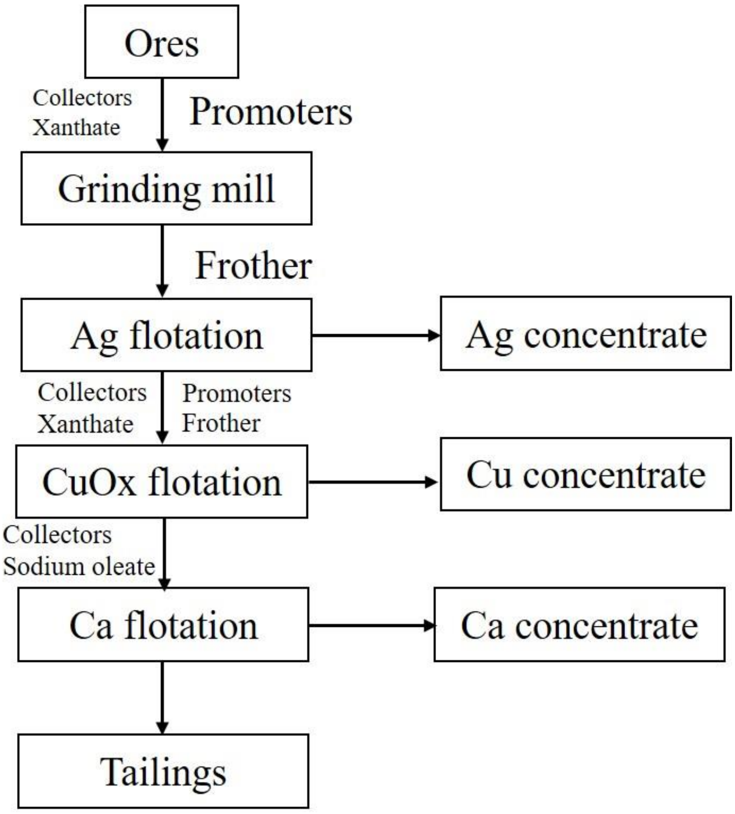


Fig. 5. Ag-CuO_x-Ca flotation flowsheet.

2.3 Calcite reverse flotation flowsheet

The calcite flotation experiments were also conducted in the various Denver flotation cell, the reverse calcium flotation was different from Ag-CuO_x-Ca flotation (see in Figure 6.). The collector (CaFlotA1/A2) for calcium flotation, synthesized by sodium oleate, sodium hydroxide, kerosene, and tap water, was an emulsion solution produced by combining and stirring reagents in the ultrasonic ambient. The difference between collector CaFlotA1 and A2 is the two different concentrations of sodium hydroxide to change the pulp pH. The ratio of sodium oleate and water was 1:10, and the dosage of kerosene was fixed as 350 g/t. The concentrate, middling, and tailings were filtered, dried, weighed, and assayed for Ag, Cu oxide, Ca, Fe, and Zn.

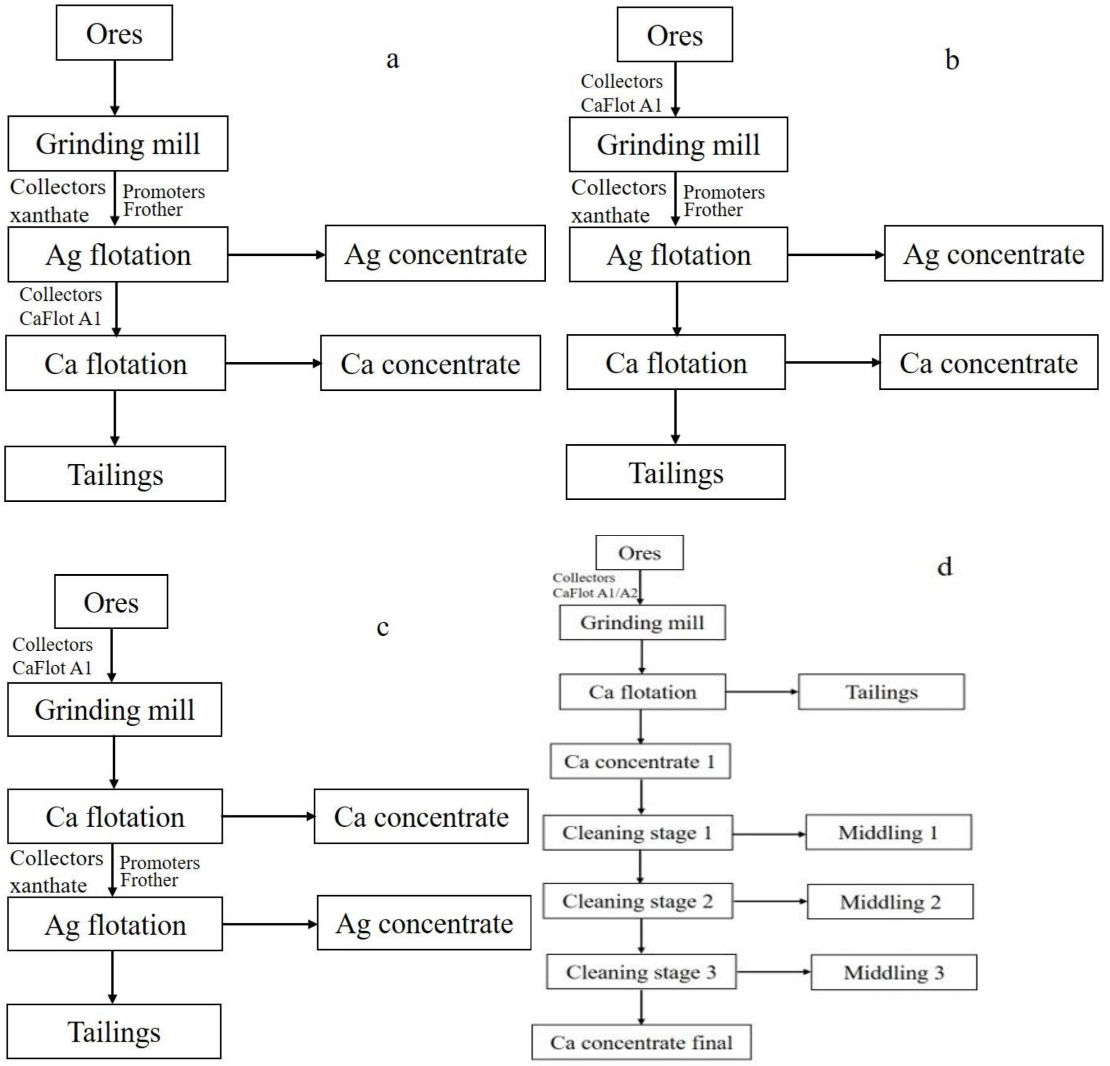


Fig. 6. Calcite reverse flotation flowsheet.

3 Results and discussion

3.1 Size distribution

The grinding time of ores are 2, 3, 5, and 8 min, the particle size distribution was shown in Figure 7.

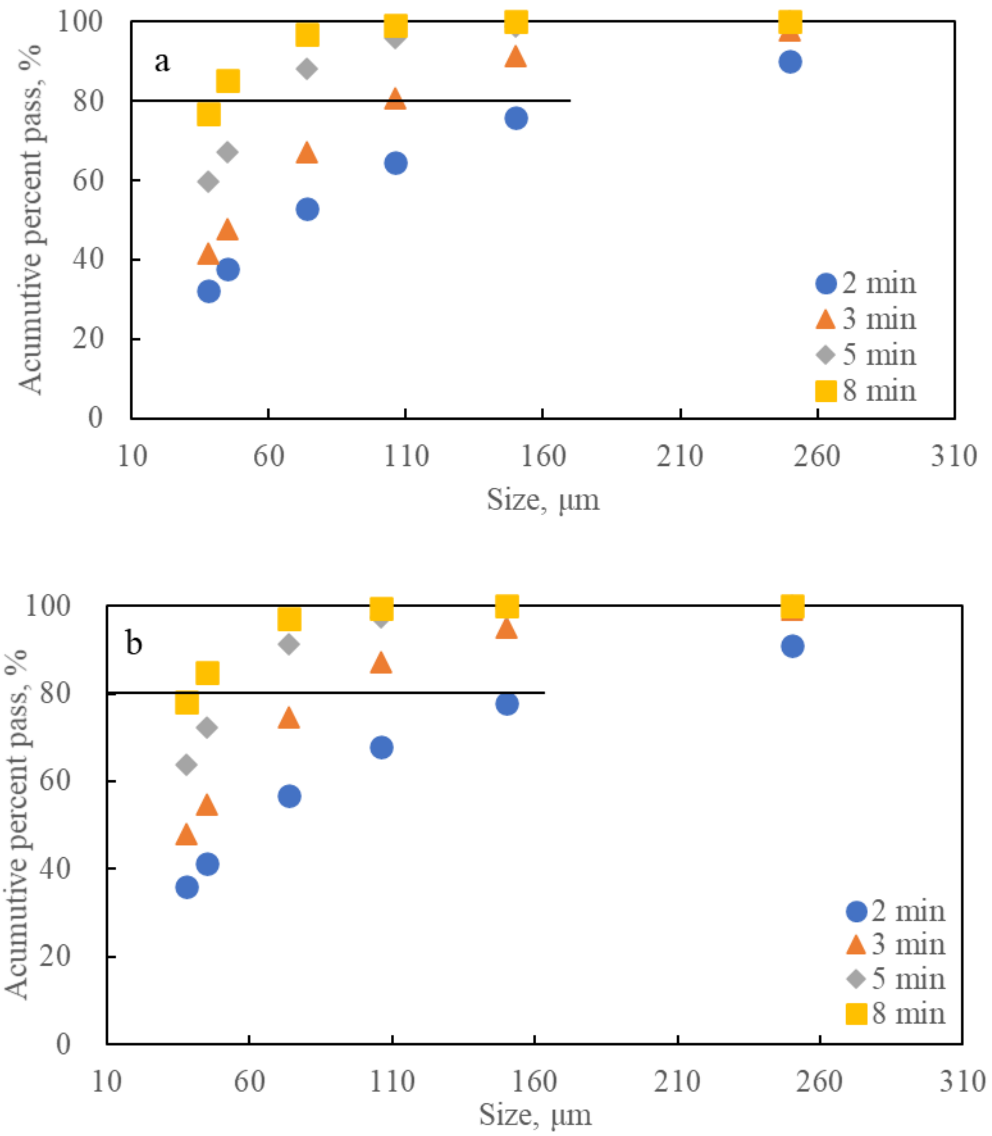


Fig. 7. Particle size distribution of a: Sample 1, b: Sample 2; in the grinding mill with different grinding time: ● : 2 min, ▲ : 3 min, ◆: 5 min, ■ : 8 min.

P80 of each ground sample is shown in Table 2. The results indicated that 3 min is optimal for the calcite reverse flotation because a fine particle grinding is unnecessary for calcite flotation (Deng, Huang et al. 2018), while metal sulfide needs the finer grinding to liberate mineral particles due to finely disseminate or "lock" in slime (Leistner, Peuker et al. 2017).

Table 2. P80 of sample 1 and sample 2 at different grinding times.

P80	Sample 1	Sample 2
	µm	
2 min	189	183
3 min	145	126
5 min	82	61
8 min	40	46

3.2 Ag-CuO_x-Ca flotation

3.2.1 Flotation procedure

In this section, the flowsheet was followed as Figure 5. and the reagents dosage was shown in Table 2. 1 kg ores (sample 1), 50 g/t sodium isopropyl xanthate (X-343), and 30 g/t promoter AP-3418 were added in the grinding mill to increase the contact possibility between the ores and chemicals, the ratio of solid was 60% and the grinding time was 3 min. Before the Ag flotation, 20 g/t frother AF 70 was added during conditioning 1 after the grinding. Ag flotation time was 10 min. NaSH is a widely used sulfidation reagent for copper oxide and zinc oxide (Önal, Bulut et al. 2005, Matsuoka, Mitsuhashi et al. 2020), and also as a depressant for the Cu-Mo system (Chen, Chen et al. 2020). In this study, 530 g/t NaSH was added in the conditioning 2 for 5 min to sulfidize the copper and zinc oxide, then the 100 g/t AP-6494 and 30 g/t sodium amyl xanthate were added to the conditioning 3, the CuO_x flotation time was 6 min. Sodium oleate is a common collector for calcite flotation, to separate calcium minerals, 2000 g/t NaOl was added during conditioning 4, the Ca flotation was 10 min. After the flotation set, the cleaning was applied for Ag and CuO_x concentrate, the cleaning time was 10 min.

Table 3. The flotation stages and reagents dosage in the flotation flowsheet Ag-CuO_x-Ca

Reagents	X-343	AP-6494	AP3418	NaSH	AF70	X350	NaOl
Stages				g/t			
Grinding	50.0		30.0				
Conditioning 1					20.0		
Flotation Ag							
Ag cleaning					20.0		
Conditioning 2				530.0			
Conditioning 3		100.0				30.0	

Flotation CuOx		
CuOx cleaning	20.0	
Conditioning 4		2000
Flotation Ca		

3.2.2 Results and discussion

Table.4 showed that the Ag-CuO_x-Ca flotation had very poor performance, with only 15.7% of Ag in the Ag concentrate, 2.44% of CuO_x in the Cu concentrate, and 66.46% of $CaCO_3$ in the Ca flotation. Meanwhile, almost 52% of the zinc oxide was lost in these Ag, CuO_x and Ca concentrate and middling stages.

Table 4. chemical assays of Ag-CuO_x-Ca flotation of sample 1

Process	**Grade, %**					**Recovery, %**				
	Ag	Cu	Fe	Zn	Ca	Ag	Cu	Fe	Zn	Ca
Ag Conc	1540	1.243	14.4	6.69	11.64	15.70	1.24	0.51	0.55	0.46
Ag Midd	72	0.809	12.8	6.25	12.3	7.06	7.75	4.40	4.90	4.69
CuOx Conc	190	0.53	13.7	4.19	17.89	8.95	2.44	2.26	1.58	3.28
CuOx midd	27	0.542	13.4	4.37	16.08	5.74	11.25	9.97	7.43	13.29
Ca Conc	26	0.263	9.4	3.88	14.29	31.08	30.71	39.37	37.10	66.46
Tailings	36	0.546	14.2	6.93	3.473	31.47	46.62	43.49	48.45	11.81
Total	41.03	0.42	11.71	5.13	10.55	100.00	100.00	100.00	100.00	100.00

3.3 Ag-Ca flotation

3.3.1 Flotation Step

From section 3.2. Ag-CuO_x-Ca flotation, the results showed that calcium flotation recovered more Cu, Zn and Ca in the Ca concentrate. Maybe because the mineral surface was sulfidized by NaSH then floated by the collector. However, only 16.7% of CuO_x was extracted by CuO_x flotation, therefore, the CuO_x flotation was not efficient and this step was removed in the further Ag-Ca flotation.

Ag-Ca flotation step was the same as section 3.2 Ag-CuO_x-Ca flotation, except removing CuO_x flotation, the reagents dosage was shown in Table 5. In this flotation process, the dosage of X-343 and AP-3418 was increased from 50 to 80 g/t, 30 to 60 g/t respectively, in order to increase Ag recovery. The Ca flotation was separated into two parts which each one having a 1000 g/t sodium oleate dosage. The results were shown in Table 6.

Table 5. The flotation stages and reagents dosage in the flotation flowsheet Ag-Ca

Reagents	X-343	AP3418	AF70	NaOl
Stages	g/t			
Grinding	80.0	60.0		
Conditioning 1			10.0	
Flotation Ag				
Ag cleaning				
Conditioning 2				1000
Flotation Ca 1				
Flotation Ca 2				1000

3.3.2 Results and discussion

According to Table 6. the flotation performance has been improved a lot compared to section 3.2, 54.8% of calcite have been recovered in the two calcium flotation, the grades in these two concentrates were 17.88% and 6.74%, and the total Ca grade decreased from 8.62 to 3.23%. Moreover, 77.36% of zinc oxide ores remained in the tailings, and the grade increased to 3.77%. However, the silver still had a poor recovery, only 27% silver in the Ag concentrate and middling, which means that xanthate and AP-3418 had limited effects on the Ag flotation, although increased the double dosage.

Table 6. chemical assays of Ag-Ca flotation of sample 1

Process	Grade, %					Recovery, %				
	Ag	Cu	Fe	Zn	Ca	Ag	Cu	Fe	Zn	Ca
Ag Conc	1230	1.67	15.2	7.75	8.80	15.69	0.66	0.30	0.35	0.38
Ag Midd	53	0.95	12.4	7.03	9.79	12.04	6.45	3.94	4.43	5.47
Ca Conc 1	0.0019	0.4	6.6	2.89	17.88	0.00	7.51	2.18	2.20	31.10
Ca Conc 2	0.0019	0.36	10.3	4.13	6.74	0.00	24.64	17.37	15.67	23.70
Tailings	100	0.49	13.3	7.49	3.23	72.27	60.74	76.21	77.36	39.36
Total	60.19	0.47	10.74	5.55	8.64	100.00	100.00	100.00	100.00	100.00

Indeed, this test improved calcite removal and remained more zinc oxide ores in the tailings, however, the efficiency of removal still did not meet the expected purpose. But it could be concluded that two stages of Ca flotation have floated most of the calcite while expelling the zinc oxide ores in the tailings.

3.4 Ca flotation

3.4.1 Flotation Step

From section 3.3, the two stages of Ca flotation had a perfect performance, therefore, Ag flotation was removed and three Ca flotation stages were applied in this section. 1 Kg of ores was added in a grinding mill with a solid percent of 60%, the grinding time was 3 min. After grinding, the pulp was added into a Denver cell with a 5 min conditioning, the 1000 g/t sodium oleate was added three times before each 10 min Ca flotation. The pulp pH was maintained at 8. The flotation stages and reagents dosage were shown in Table 7.

Table 7. The Ca flotation stages and reagents dosage

Stages	NaOl
Grinding	-
Flotation Ca 1	1000
Flotation Ca 2	1000
Flotation Ca 3	1000

3.4.2 Results and discussion

Table.8 showed that the Ca recovery in these 3 flotations increased from 61 to 78% compared to the results of section 3.3, and the grade decreased from 8.69% of the total to 3.87% in tailings, which removed calcite significantly in this section. However, almost 39% of zinc oxide ores were removed by Ca flotation, although the grade increased to 6.84% in tailings.

Table 8. Chemical assay of Ca flotation of sample 1

Process	Grade, %					Recovery, %				
	Ag	Cu	Fe	Zn	Ca	Ag	Cu	Fe	Zn	Ca
Ca Conc 1	81.00	0.44	6.00	3.63	20.40	23.87	13.77	9.43	10.08	36.94
Ca Conc 2	67.00	0.39	6.30	3.68	16.30	20.56	12.71	10.31	10.64	30.74
Ca Conc 3	53.00	0.54	11.00	6.86	5.72	14.53	15.72	16.09	17.73	9.64
Tailings	43.00	0.57	12.60	6.84	3.87	41.04	57.79	64.17	61.55	22.69
Total	53.43	0.50	10.01	5.67	8.69	100.00	100.00	100.00	100.00	100.00

From this section, the calcium reverse flotation was a promising method to remove calcite and recover zinc in this study. Recently, a mixture of oleic acid and kerosene as a novel emulsion collector has been proposed and investigated on the flotation of coking coal. It is shown that the novel collector had a stronger collectivity than kerosene alone (Zhu, Yin et al. 2020). Once the calcite was treated with sodium oleate, the bridging liquid, such as kerosene and benzene, promotes the agglomeration of the particles. Therefore, the performance of a mixture of sodium oleate, sodium hydroxide, and kerosene was discussed in the next section.

3.5 The effect of pH on the Ca reverse flotation

3.5.1 Flotation step

It is reported that calcite has better floatabillity than zinc oxide ores due to the chemisorption of fatty acid on the activated surface by Ca ions sites (Liu, Zhang et al. 2019, Luo, Zhang et al. 2019). It is widely known that the extent of agglomeration recovery depends on the pH value of the aqueous medium. There is a study that investigated the effects of pH on the calcite recovery by oil agglomeration, the optimal pH to achieve the highest calcite recovery was 10. Therefore, two different pulp pH (8 and 10) were studied in this section.

The volume of kerosene was fixed as 3.36 g/t, the concentration of NaOl was 3000 and 4000 g/t, the ratio of NaOl and water was 1:15, adding 480 or 960 g/t sodium hydroxide as a pH modifier, and classified pH of 10 as CaFloatA1 and pH of 8 as CaFloatA2. The mixed collector was produced in a beaker by combining water, NaOl, kerosene, and NaOH in an ultrasonic environment, keeping stirring until the aqueous medium changed to a milk-like solution.

Both sample 1 and sample 2 were investigated in this section. 1 Kg ores, different concentrations of novel collector, and tap water were added in grinding mill with 60% solid. The grinding time was 3 min. The pulp was subjected to flotation cell after grinding, the pulp pH was maintained as 10, conditioning time was 5 min, and flotation time was 12 min.

3.5.2 Results and discussion

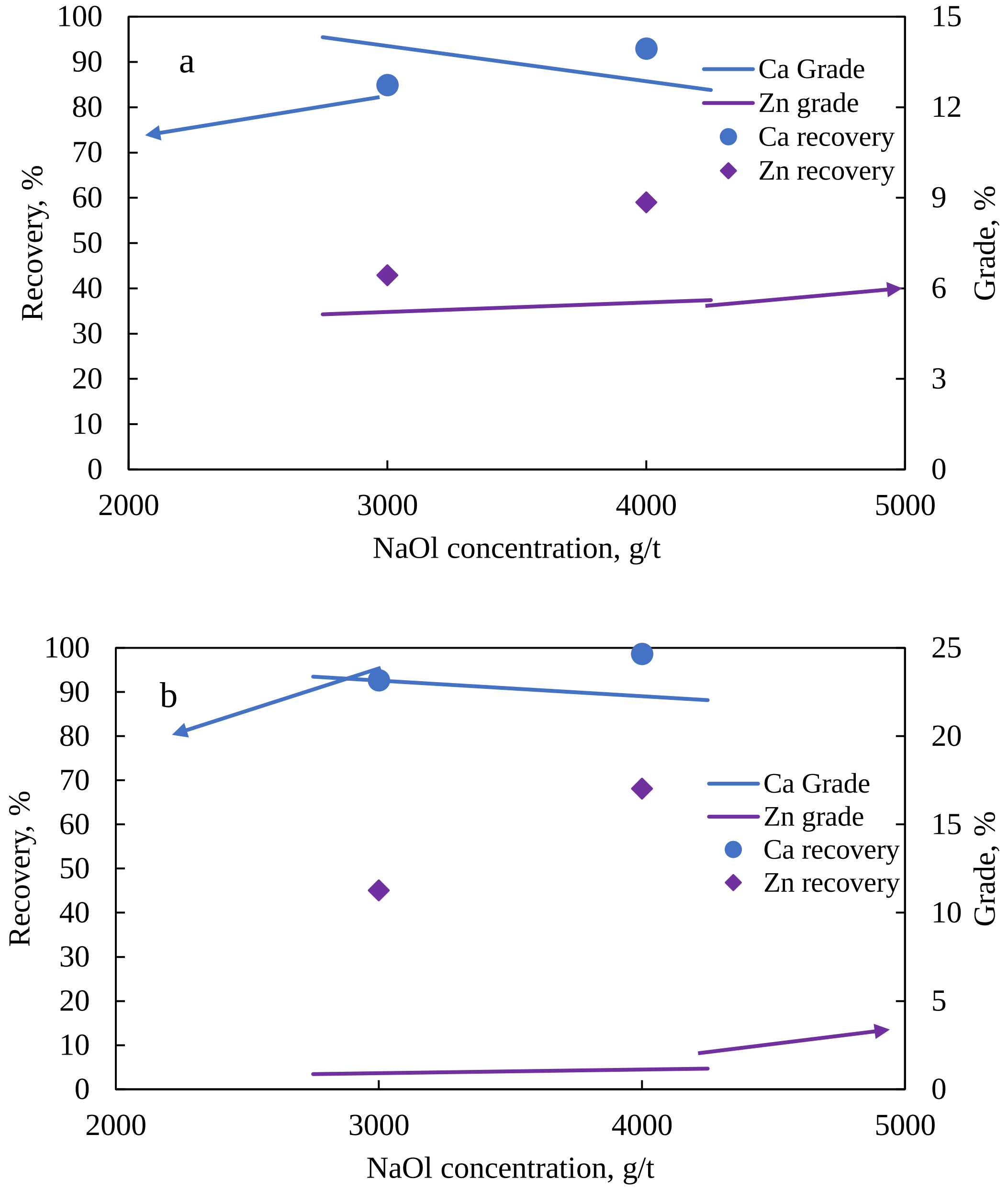
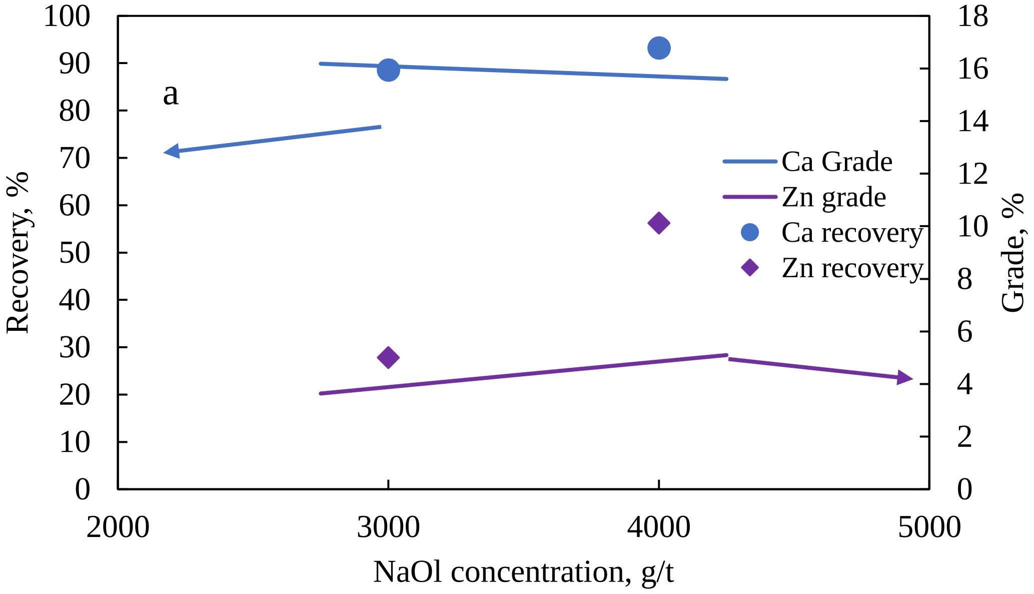


Fig. 8. Effect of CaFloatA2 (in the concentration of 3000 and 4000 g/t, pulp pH= 8.1) on the Ca flotation of zinc pre-concentrate of a): sample 1, b): sample 2, ●Ca recovery, ◆Zn recovery; —Ca grade, —Zn grade.

To investigate the efficiency of CaFloatA2, 3000 and 4000 g/t sodium oleate was studied in this section. The results were shown in Figure 8. The recovery of Ca and Zn increased with NaOl increased. Ca recovery was increased from 77% (in section 3.4) to 84.9% and 92.95%, with 3000 and 4000 g/t NaOl addition in sample 1 (as shown in

Figure 5. a), while the Ca grade decreased with recovery increased, achieved of 14.32% and 12.57%, respectively. Similar results could be found in sample 2 (as shown in Figure 5. b), the calcite recovery achieved over 90% with both NaOl additions, and the grade increased to 23.37% and 22.04%. The results indicated that the CaFloatA2 had a perfect performance for calcite reverse flotation.

However, it is apparent that the zinc recovery and grade were increased with calcite recovery. The zinc recovery was increased to 42.89 and 59% with two different NaOl additions in sample 1, and the grade increased to 5.14% and 5.61%, which means more zinc was expelled into Ca concentrate, the similar tendency of zinc recovery and grade was observed in sample 2, the maximum zinc recovery achieved at 70%. Maybe because the zinc oxide ores were coated by free calcium ions generated by calcite and other calcium ores, then floated by CaFloatA2 with overdosage of sodium oleate (for example, more willemite was recovered by 4000 g/t).



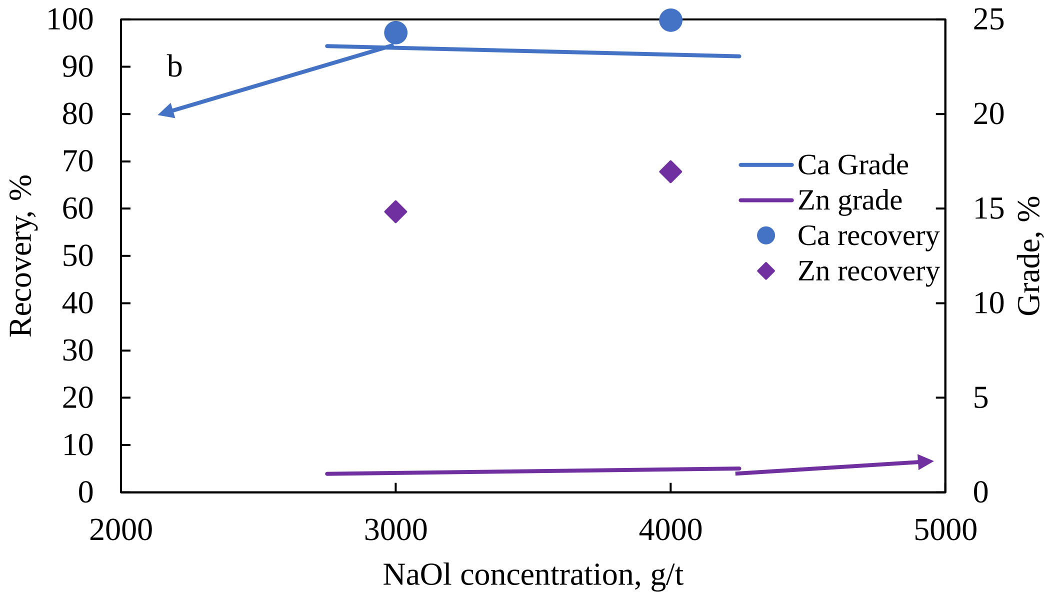


Fig. 9. Effect of CaFloatA1 (in the concentration of 3000 and 4000 g/t, pulp pH=10.2) on the Ca flotation of Ca concentrate of a: sample 1; b: sample 2. ● Ca recovery, ◆ Zn recovery; — Ca grade, — Zn grade.

To verify the effects of pH value on the calcite flotation by agglomeration, one set of experiments was carried out at the pulp pH of 10. The results were shown in Figure 9. Like in Figure 8. Ca and Zn recovery increased with NaOl increased, and both samples had Ca recovery over 90%, and the Ca grade increased in sample 1, from 14.32 to 18.18% in 3000 g/t NaOl addition and 12.57 to 15.6% in 4000 g/t NaOl addition; while increased slightly in sample 2, from 23.37 to 23.59% in 3000 g/t NaOl addition and 22.04 to 23.05% in 4000 g/t NaOl addition. The zinc recovery and grade were decreased compared to the results at pH 8. For sample 1, the zinc recovery decreased from 42.89 to 27.85%, and grade reduced from 5.14 to 3.64% with 3000 g/t NaOl addition, the same downtrend was also observed in 4000 g/t NaOl. However, the recovery and grade were almost the same with the lower NaOl addition, because sample 2 has more calcite and less willemite, calcite particles had more collision possibility with collectors. These results indicated that in this study the best pH value for calcite reverse flotation was 10 and the following experiments were carried out at this pH value.

3.6 improve zinc grade in zinc pre-concentrate

3.6.1 Flotation step

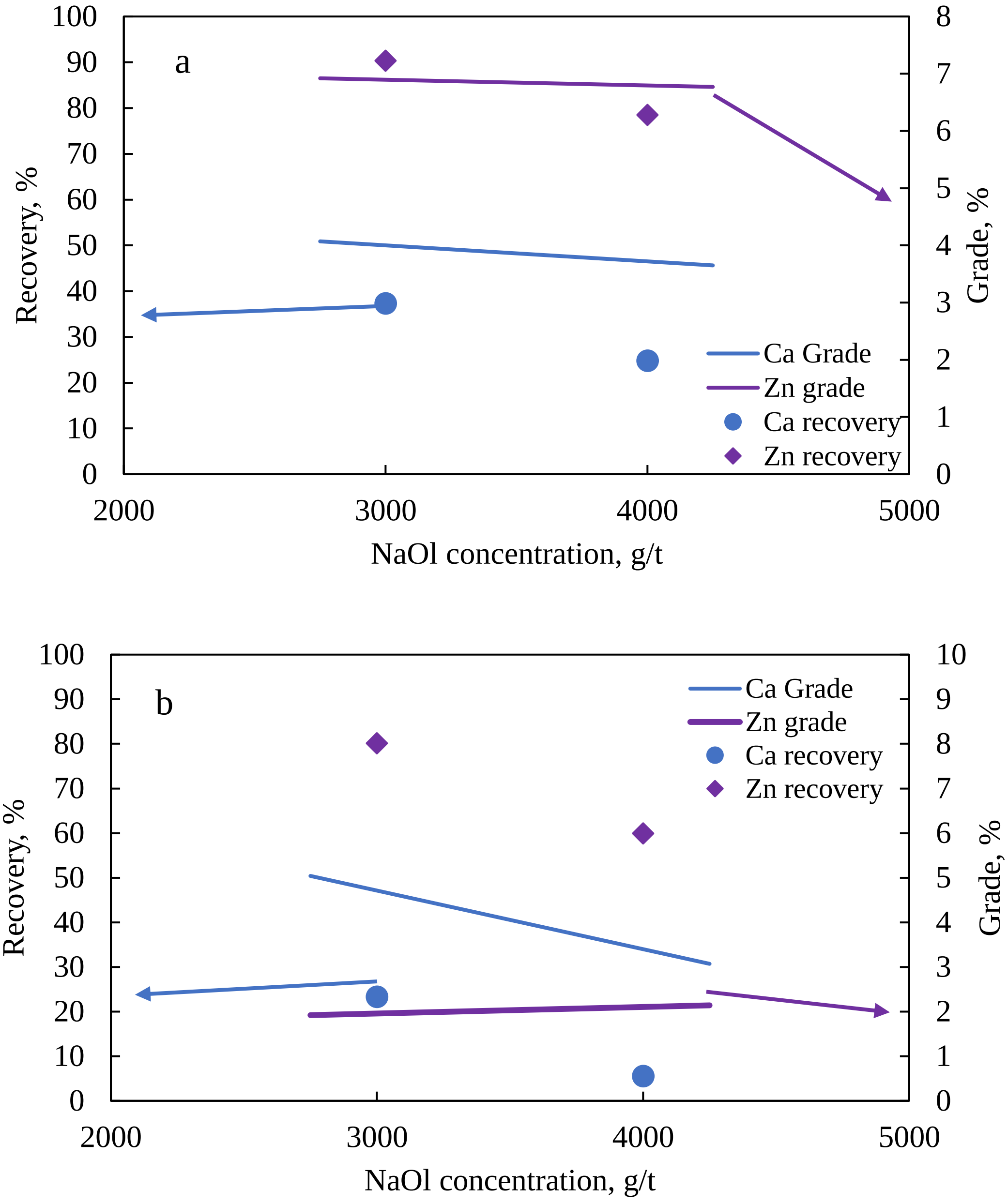
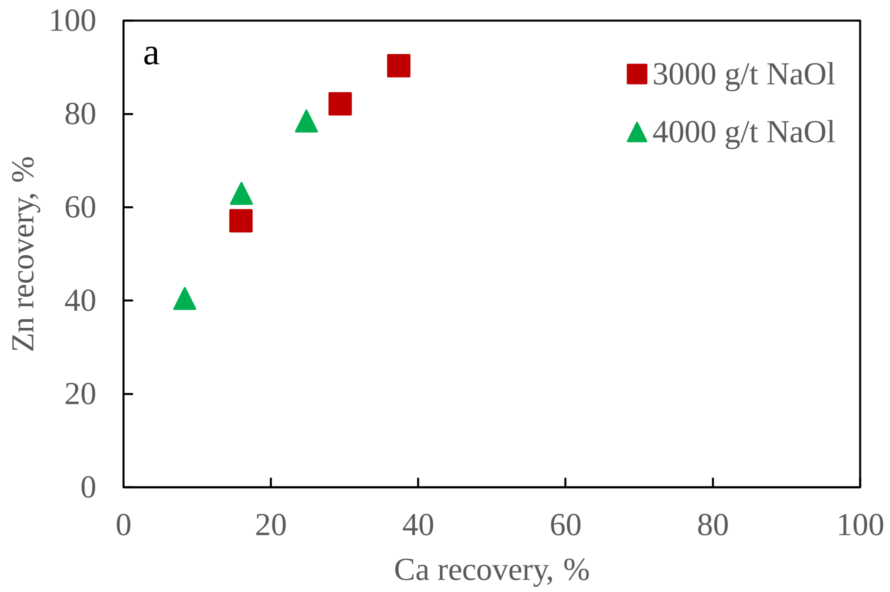


Fig. 10. Zn and Ca recovery and grade of Zn pre-concentrate (tailings+M1+M2) of a: sample 1; b: sample 2. ● Ca recovery, ◆ Zn recovery; — Ca grade, — Zn grade.

The flotation procedure was the same as in section 3.5, two cleaning stages for Ca concentrate was applied for improving Zn grade in zinc pre-concentrate in this section, each cleaning time was 10 min. Tailings, Middling 1 (M1), and Middling 2 (M2) were dried, sampled and chemical assayed for Zn and Ca analysis, the zinc pre-concentrate results were shown in Figure 10.

3.6.2 Results and discussion

Zn and Ca recovery decreased as NaOl increased in CaFloatA2, Zn recovery could be achieved 90.36% in sample 1 with 3000 g/t NaOl addition (shown in Figure 10. a), but it was surprisingly observed that the Zn grade increased to 6.97%, a little grade decreased to 6.77% was found with higher NaOl addition. Ca grade and recovery decreased with NaOl addition increased, from 4.07 to 3.65% and 37.35 to 24.83%, respectively, similar results could be found in Figure 10. b. The linear relationship between Zn and Ca recovery in Zn pre-concentrates (tailings, tailings +M1, tailings+M1+M2) was shown in Figure 11.



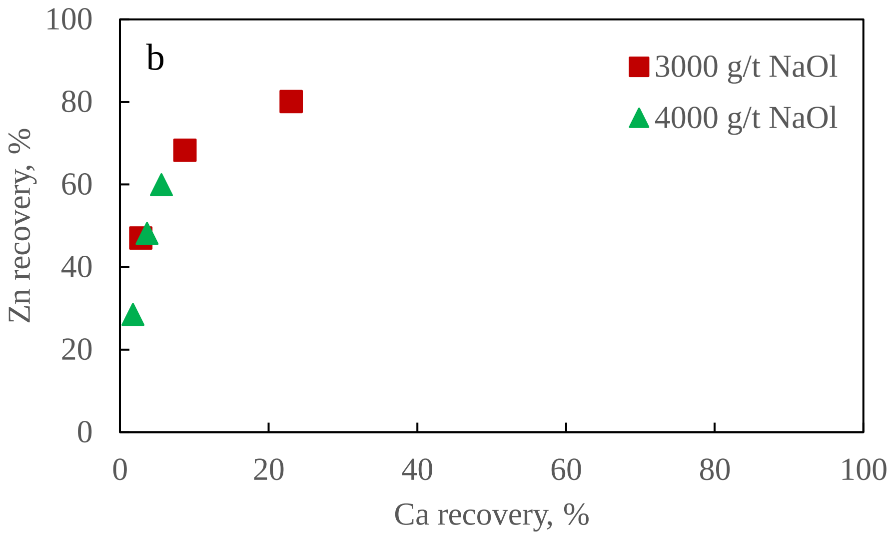


Fig. 11. The linear relationship between Zn and Ca in Zn pre-concentrates of the a: sample 1; b: sample 2, ■ 3000 g/t NaOl, ▲ 4000 g/t NaOl.

Figure 11. showed that Ca recovery and Zn recovery was a positive correlation. Although more calcite was removed by 4000 g/t NaOl in CaFloatA2, less willemite remained in Zn pre-concentrate. In order to extract more willemite, zinc pre-concentrate of samples 1 and 2 with 3000 g/t NaOl was applied to examine zinc recovery by acid leaching experiment.

3.7 Leaching method

3.7.1 Leaching procedure

Sulfuric acid from J.T.Baker was used in this study. It has a concentration of 95% and a density of 1.83 g/ml.

35 g of Zn pre-concentrate (tailings+M1+M2 of 4000 g/t NaOl addition) was added to a beaker with 50 ml of water, then the solution was titrated by a burett with 25 mL H_2SO_4, maintained pH 1.5 one hour. The solid and solution were taken out for analysis after leaching. The results were shown in Table 9.

3.7.2 Results and discussion

Figures 12 and 13 showed that Zn recovery was over 90% in these two original samples and two Zn pre-concentrates, while only over 50% of Cu were extracted, but scarcely iron was recovered. The acid consumption of original sample 1 and sample 2 were 299.11 and 418.05 Kg/t, respectively, which consumed a lot of sulfuric acid due to the high content of calcite. After the calcite reverse flotation, the acid consumption was decreased significantly, with only 158.98 and 105.98 Kg/t sulfuric acid consumed.

The acid consumption of related concentrate (ores) was introduced in this section:

$$V_O = V_c / \frac{100}{w\%\ of\ Zn\ pre-concentrate} \tag{1}$$

Where Vo is the acid consumption of ores, Vc is the acid consumption of concentrate. The acid consumption of ores of two floated samples were 107.42 and 42.22 Kg/t as shown in Figure 12. but 299 and 481 Kg/t were consumed by original sample 1 and 2, which indicated that less sulfuric acid was needed after reverse flotation. It is also indicated that much less sulfuric acid consumed accoding to the ores.

Table 9. Ca grades in original samples and Zn pre-concentrate samples

Samples	Sample 1	Zn pre-conc 1	Sample 2	Zn pre-conc 2
Ca grade	11.32	3.24	21	4.76

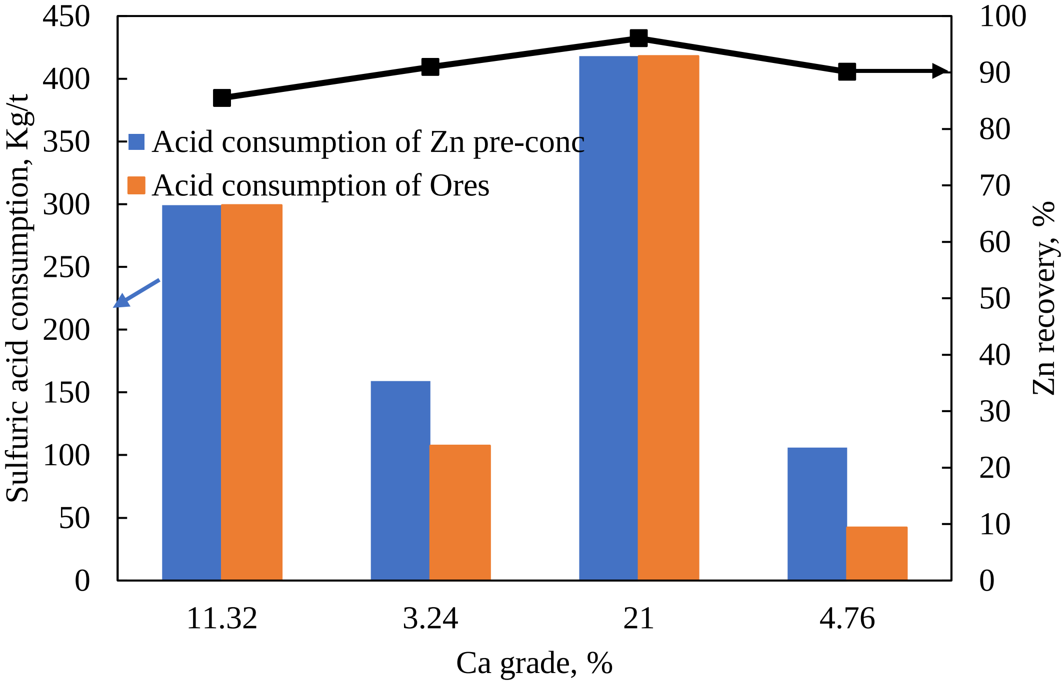


Fig. 12. Zn recovery and acid consumption by original samples and Zn pre-conc. Line: Zn recovery of the original sample and Zn pre-concentrate by sulfuric acid leaching; column: sulfuric acid consumption of each sample.

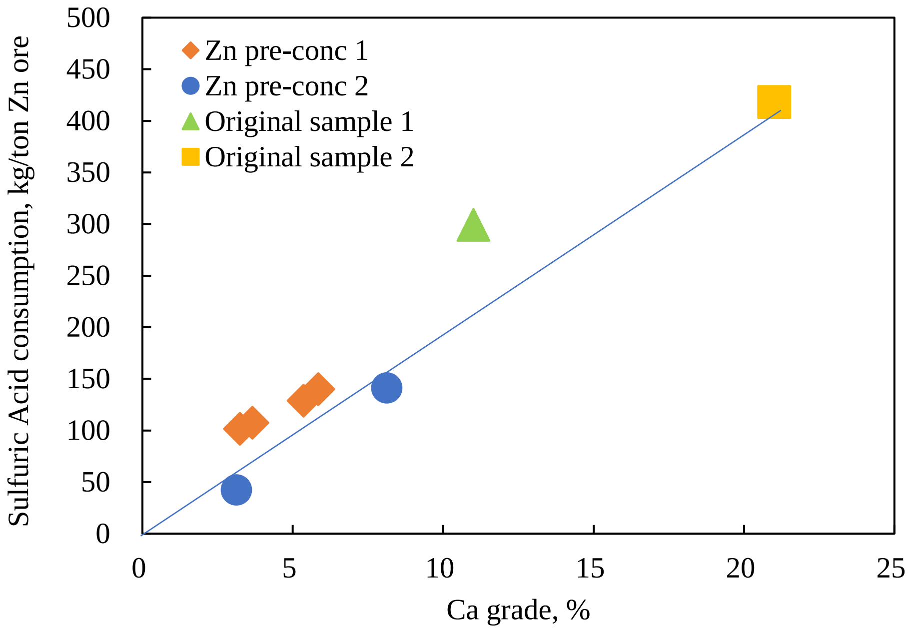


Fig. 13. The relationship between sulfuric acid consumption and Ca grade of Zn pre-concentrate.

Figure 13. showed the relationship between sulfuric acid consumption and Ca grade in the original samples or Zn pre-concentrate. Higher sulfuric acid was consumed when the ores contained higher Ca grade.

It can be concluded that CaFloatA1 was a promising collector for calcite reverse flotation and recovery of zinc oxide ores. To verify this collector on the effects of other zinc oxide minerals, sample 3 and sample 4 were carried out in the further investigation.

3.8 The effects of CaFloatA1 on sample 3 and sample 4

3.8.1 Flotation Procedure

Sample 3 and sample 4 have the same gangue minerals such as calcite and quartz. But the zinc oxide minerals are a little different (see Figure 1.). Willemite and hemimorphite are the main zinc oxide in samples 1 and 2, while samples 3 and sample 4 have zincite (ZnO) besides hemimorphite.

The flotation procedure was the same as in section 3.6, and the flotation kinetics was carried out in this section. Four cleaning stages were carried out for Ca concentrate to recover more zincite and hemimorphite.

3.8.2 Results and discussion

The results of the Ca and Zn flotation kinetics of the two samples were shown in Figure 14. Ca and Zn flotation were very fast before 360s for sample 3 and recoveries were 93.09% and 48.04%, respectively, then the recoveries remained consistent at 94% and 48%.

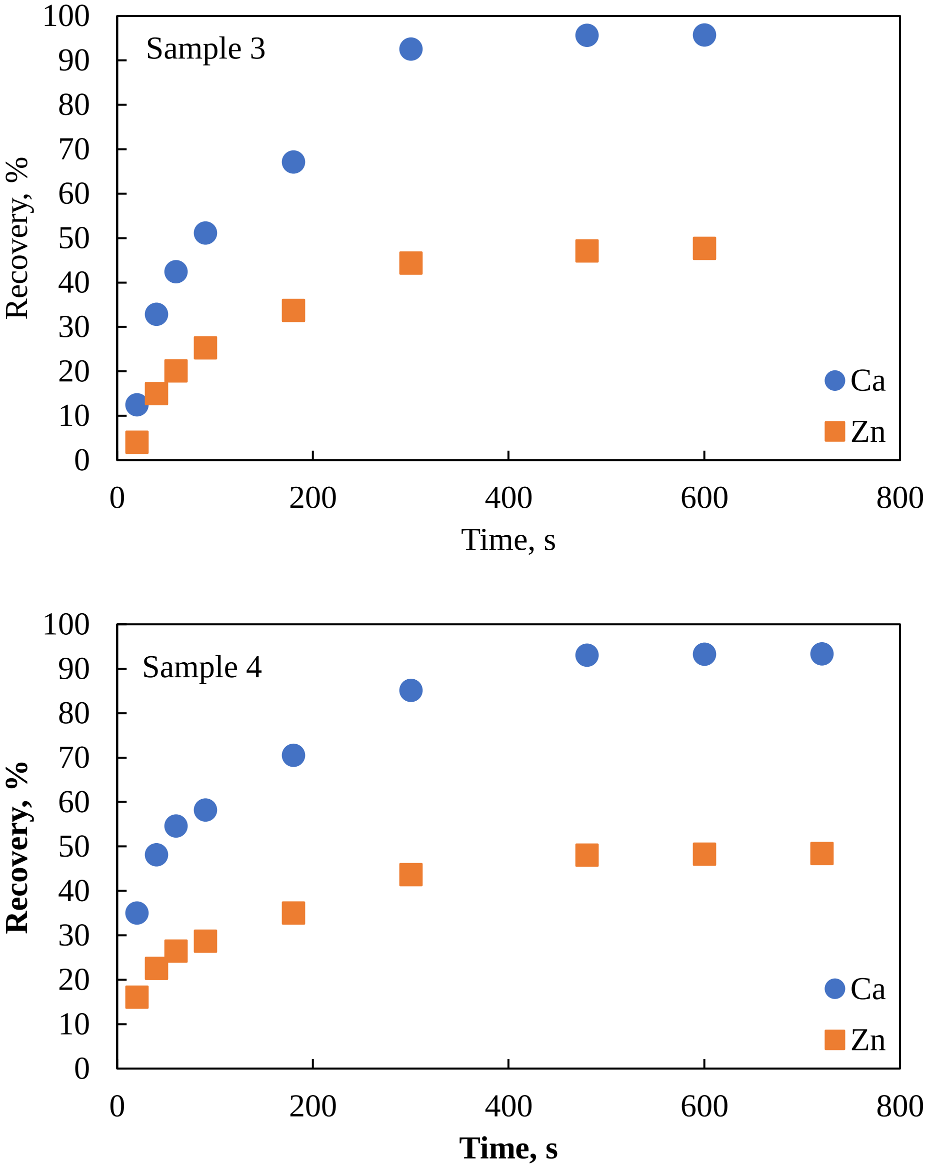


Fig. 14. The Ca and Zn flotation kinetics of sample 3 and sample 4.

While the flotation kinetics of sample 4 was a little different from sample 3, the flotation has not been finished until the time was 480s, the recoveries were maintained constantly at 95.7% of Ca and 47.74% of Zn, respectively.

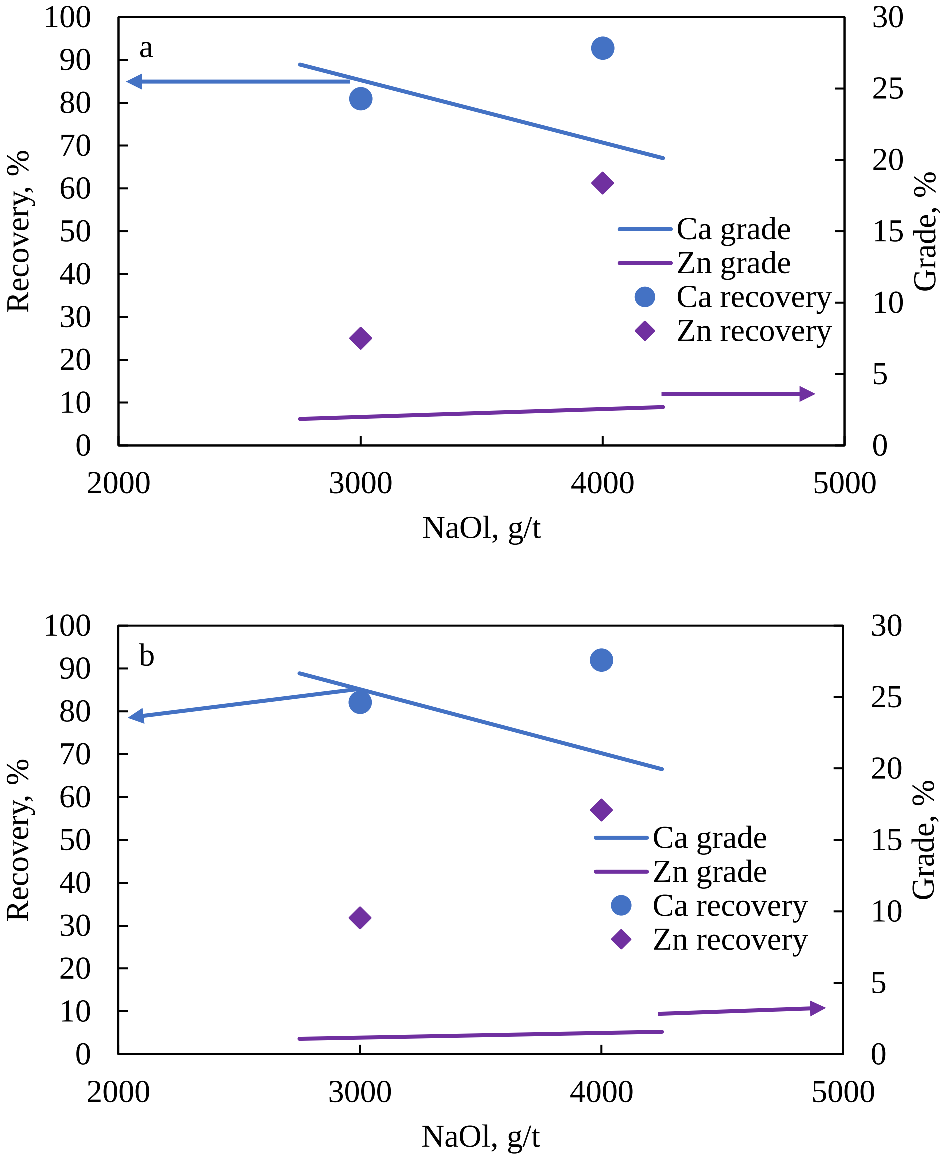
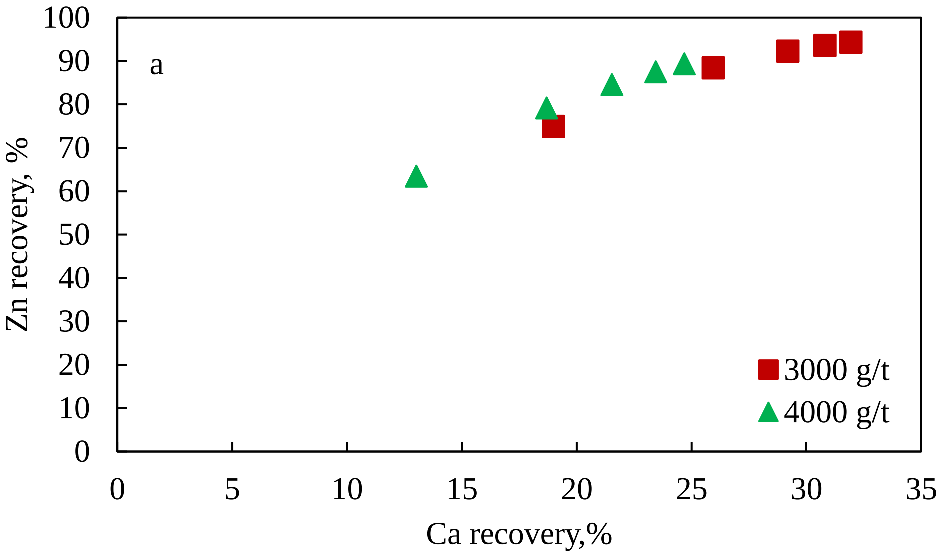


Fig. 15. Effect of CaFloatA1 (in the concentration of 3000 and 4000 g/t, pulp pH=10.2) on the Ca flotation of Ca concentrate of a: sample 3; b: sample 4. ● Ca recovery, ◆ Zn recovery; — Ca grade, — Zn grade.

The Ca and Zn recovery was increased with NaOl concentration increased (as shown in Figure 15.). Over 80% Ca was recovered by 3000 g/t NaOl addition, and increased to 92% in both samples with higher NaOl. The Ca grade decreased from 26.68 to 20.12% of sample 3, 26.66 to 19.95% of sample 4. The Zn recovery was 30% of both samples with 3000 g/t NaOl while more Zn was floated in Ca concentrate with 4000 g/t NaOl addition, 61.31 and 57.01% of sample 3 and sample 4, respectively.

The relationship of Ca recovery and Zn recovery of Zn pre-concentrates (tailings, tailings+M1, tailings+M1+M2, tailings+M1+M2+M3, tailings+M1+M2+M3+M4) were shown in Figure 16. The results showed that Ca recovery and Zn recovery was a positive correlation, the Zn recovery was increased with Ca recovery increasing. Although more calcite was removed by more NaOl in collector CaFloatA1, more zinc oxide ores were expelled which reduced zinc recovery by sulfuric acid leaching.



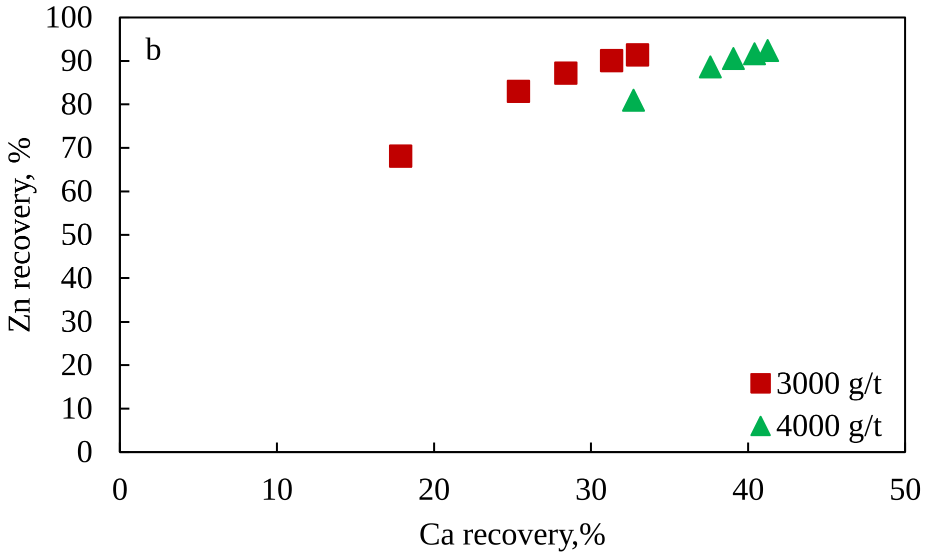


Fig. 16. The linear relationship between Zn and Ca in Zn pre-concentrates of the a: sample 3; b: sample 4, ■ 3000 g/t NaOl, ▲ 4000 g/t NaOl.

3.9 Sulfuric acid leaching tests

3.9.1 Leaching procedure

The leaching procedure was the same as in section 3.8. The leaching kinetics was carried out in this section. 3 different sulfuric acid concentrations (85, 100 and 125 Kg/t) were examined for the extraction and recovery of Zn, the results were shown in Figure 17. The acid consumption of Zn pre-concentrates and ores was shown in Figure 18.

3.9.2 Results and discussion

1) leaching results

As shown in Figure 17, Zn recovery was very high in the initial stage at 3 different concentrations of sulfuric acid, higher Zn recovery was achieved at higher sulfuric acid dosage. It is indicated that after 40 minutes, the Zn recovery was over 90% and the leaching was completed.

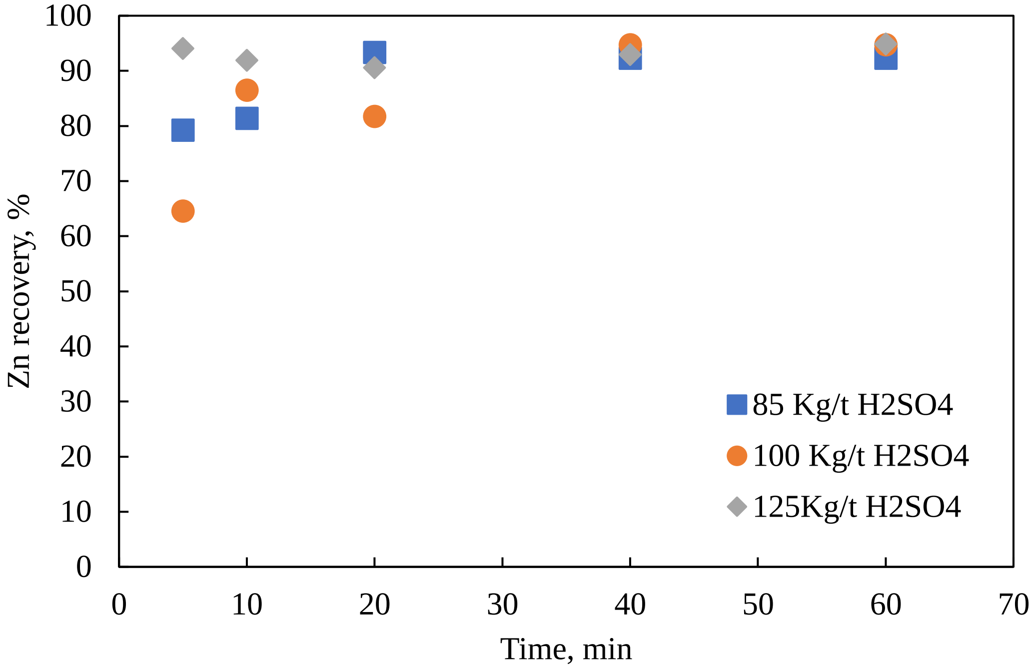


Fig. 17. Leaching kinetics of Zn pre-conc of sample 3 (contains tailings, M1, M2, M3 and M4).

2) acid consumption and Zn recovery in the fixed concentration of sulfuric acid

Table 10 showed the Ca grade in the two original samples and 4 Zn pre-concentrate. After Ca reverse flotation, Ca grade decreased significantly.

Table 10. Ca grades in original samples and Zn pre-concentrate samples

Samples	Sample 3	Zn pre-conc 1	Zn pre-conc 2	Sample 4	Zn pre-conc 2	Zn pre-conc 2
Ca grade, %	21.13	7.52	7.18	20.29	8.33	8.02

From Figure 18. the results showed that the original sample 3 consumed a huge amount of sulfuric acid (377 Kg/t) in the leaching test while only 50% Zn was extracted, After Ca reverse flotation, around 132 and 126 Kg/t H_2SO_4 were consumed by two different Zn pre-concentrates of sample 3, which indicated that acid consumption reduced 65%, the similar results were found in sample 4, 289 Kg/t H_2SO_4 H_2SO_4 was consumed by the original sample. 103 and 97 Kg/t H_2SO_4 was consumed after Ca reverse flotation. Less quantity of acid consumption for the ores compared to the concentrate in the terms of equation 1, 78.68 and 60.57 Kg/t H_2SO_4 were consumed in the Zn pre-concentrate of sample 3, 57.24, and 66.54 Kg/t of H_2SO_4 of sample 4.

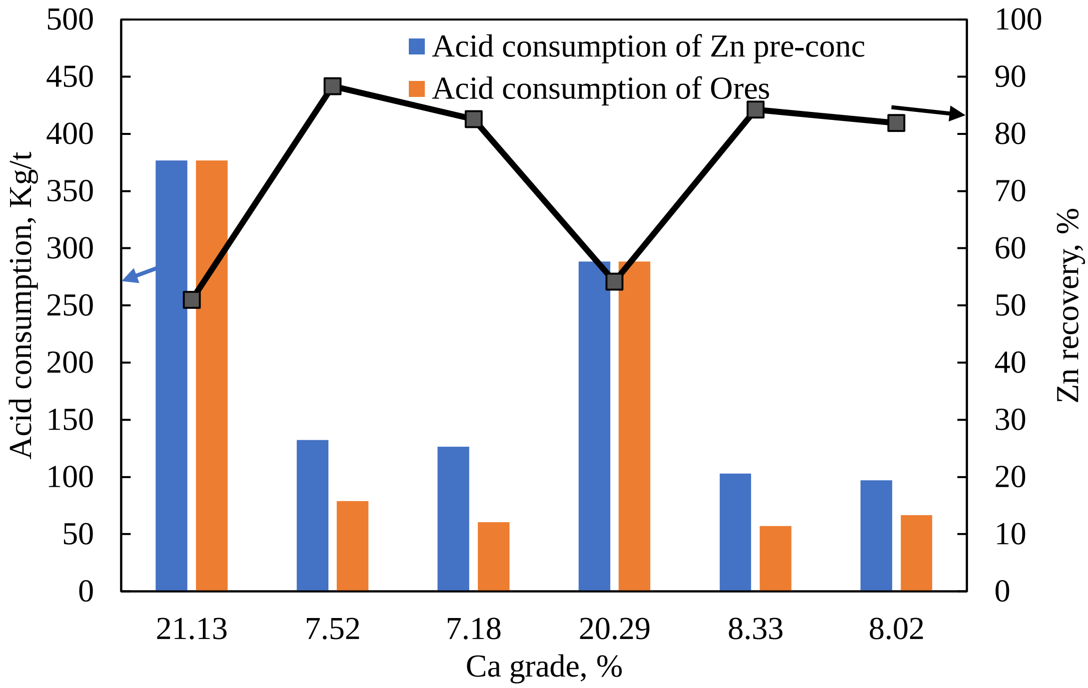


Fig. 18. Zn recovery and sulfuric acid consumption. Line: Zn recovery of the original sample and Zn pre-concentrate by sulfuric acid leaching; column: 🟦 acid consumption of Zn pre-conc; 🟧 acid consumption of ores.

4 Conclusion

The conclusions obtained from this study are as follows:

1. The collector NaOl mixed with kerosene had a good selectively separation calcite in this study, the optimal pulp pH was 10. Over 90% calcite was floated with 4000 g/t NaOl of CaFloatA1 while more zinc oxide ores were removed.
2. The acid consumption decreased significantly after Ca reverse flotation, which could improve economic benefits by reducing chemical reagent dosage.

3. From the different types of zinc oxide minerals in samples 1-4, CaFloatA1 had a perfect selective separation of calcite, which supposed that CaFloatA1 can be applied in the flotation of oxide ores which contain calcite

5 Further investigation

Although we obtained a good result in this study, the NaOl dosage was a little higher, which lead to a higher cost for calcite flotation during the industrial practical production. Therefore, a method or a way to decrease sodium oleate dosage should be proposed and studied in further investigation.

There are more types of bridging liquid such as fuel-oil, spindle oil, etc, which maybe have a better coating effect on calcite than kerosene, therefore, it is necessary to focus on these bridging liquids to explore the performance of the calcite reverse flotation.

Chapter 2

Roasting temperature effect on the recovery of refractory gold and silver in pyrite concentrates

1. Introduction

Gold was used in very ancient times, even before 3400 B.C. It is a relatively special precious metal, with a unique beauty and highly prized for its color. In addition, as a metal with extraordinary malleability and ductility, it is widely used in jewelry, technology and medical applications due to its unique physical and chemical properties (BROOY, LINGE et al. 1994, Syed 2012).

1.1 Gold deposits

Gold is one of the most valuable and rare metals. It is estimated that, to date, only 150,000 tons have been extracted worldwide. In fact, gold is abundant in the 16-kilometer-thick crust of the earth, but only a small amount has been found - about 5 grams per ton. South Africa, North America and Australia are the regions with the highest concentration of gold. Depending on how they were formed, the sediments can be classified as (free version) (Hedenquist, Arribas et al. 2000, Goldfarb, Baker et al. 2005, Phillips and Powell 2009, Goldfarb, Qiu et al. 2019):

1.1.1 Primary gold

The most basic and common classification is that of primary and secondary deposits. Gold from primary deposits is usually embedded in quartz veins. Mining is only economically viable at concentrations above 2.5 grams per ton. Typically, however, the concentration of gold in quartz joints is only 1 gram per tonne.

1.1.2 Secondary gold

When primary gold ore is weathered and eroded by temperature, wind, and water, it is called secondary gold ore. The gold washes out of the rock with the water and collects in the form of fine gold dust or small particles in the shallow water of streams and rivers, known as "nuggets". The formation of the so-called "placer gold" which is also known as "flow gold" or "gold soap".

1.1.3 Epithermal gold

Epithermal gold deposits also belong to the primary gold deposits. This type of gold deposit is mostly found in sedimentary and magmatic rock. At the depth of up to 1500 meters, the gold is found very close to the surface. The gold concentration is between 1 and 10 grams per tonne of rock. The most important epithermal deposits are in Mexico, New Zealand, Peru and Papua New Guinea.

1.1.4 Orogen gold

The orogen gold deposits also belong to the primary gold deposits, and some of the largest gold production mine are of this type. These gold deposits formed because of mountain formation and the depth are between 1200 and 4500 meters. During mountain formation, metamorphic fluids with temperatures between 250 and 400 degrees (mesothermal) typically squeeze silica, gold and metal sulfide into rock fractures. The gold content of such deposits is typically very high, with concentrations of at least 10 grams per ton. Significant deposits of this type are found in areas such as the United States, Africa, and Brazil.

1.2 Refractory

Gold and silver in pyrite are not amenable to recovery by traditional cyanide leaching (Chen et al., 2002), lower recovery could be explained as follow:

1) Gold is locked in reactive gangue minerals, often sulfides, and cannot be fully liberated, even by fine grinding (Xu et al., 2014).
2) Gold occurs with minerals that consume unacceptable quantities of reagents, for example, pyrite and arsenopyrite.
3) Carbonaceous materials that adsorb gold during leaching.
4) Any combination of 1 to 3.

This material is commonly referred as “refractory,” which literally means “difficult to treat.” In addition, sulfide minerals consume oxygen and rob cyanide ions during the cyanidation, leading to insufficient cyanide ions and oxygen concentration for gold and silver recovery. The refractory minerals show a pretty poor gold and silver recovery (typically < 50%) by the conventional cyanidation (Faraz et al., 2014). Therefore, in order to improve the gold and silver recovery, the sulfide matrix structure should be cracked or dissolved to expose the gold and silver to the leaching reagent. Oxidative processes may be used as a pre-treatment for sulfide, carbonaceous, and telluride ores.

The methods that can be used for oxidation are sorted in two main categories: pyrometallurgical and hydrometallurgical. Pyrometallurgical oxidation of sulfide and carbonaceous ores by roasting has been implemented worldwide for decades and is well documented. Hydrometallurgical methods have been developed during the past 25 years, the biological technology and high pressure (acidic and alkaline) are the main process for pyrite oxidation.

1.3 Biological oxidation

Bacterial leaching involves a variety of complex physicochemical processes (e.g. as chemical oxidation, biological oxidation, and galvanic reaction) to oxidise pyrite. There are three types of bio-oxidation, namely 1) direct reaction, where the leaching bacteria oxidize the sulfide minerals directly, 2) indirect reaction, where the sulfides are oxidized by Fe(III) ions produced during bacterial metabolism, and 3) complex reaction, where a mixture of the above two reactions (Tributsch., 2001; Sand et al., 2001).

1.3.1 Mechanisms

The bacteria derive energy from the oxidation of sulfur and iron species. However, they also require nutrients such as oxygen, carbon, and nitrogen to sustain oxidation reactions and cell reproduction. These substances must come from ores or nutrient reagents, etc. Bacteria operate best in a pH range of 1.0 to 1.8..

The oxidation reactions for a generic iron sulfide mineral (FeSx) in acidic media are given as follows (Lorenzo-Tallafigo, Iglesias-González et al. 2019):

$$FeS_x + xO_2 + 2xH_2O \; = \; FeSO_4 + 4xH^+ + (x-1)SO_4^{2-} + (2x+2)e \tag{1}$$

$$4FeSO_4 + \; O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O \tag{2}$$

$$FeS_x + \; Fe_2(SO_4)_3 \; = \; 3FeSO_4 + xS \tag{3}$$

$$2S + \; 3O_2 + \; 2H_2O \; = 2H_2SO_4 \tag{4}$$

Equations (2) and (4) are completely dependent on bacterial catalysis and the bacterial activity is significantly inhibited under environmental conditions. The reaction shown in Equation (3) is essentially chemical reaction, with little or no bacterial involvement. There is evidence that reaction (1) proceeds more rapidly in the presence of suitable bacteria (Lawson and Hulse 1990). The role of bacteria in the oxidation and removal of elemental sulfur produced by Reaction (3) is most important, because without removal of sulphur, sulphur can be present on the mineral surface, preventing further oxidation of the mineral, and may also increase cyanide consumption and reduce gold recovery (Lindström, Gunneriusson et al. 1992).

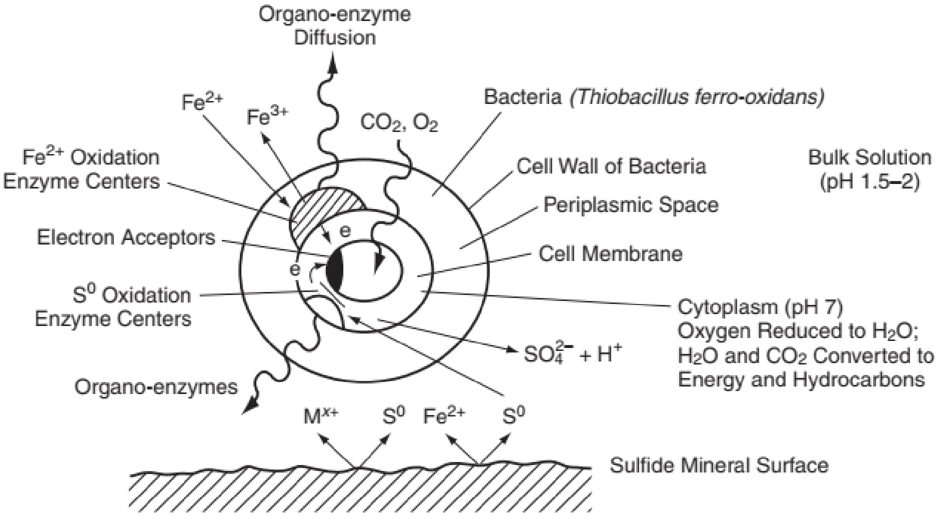


Fig.1 Simplified mechanism for bacteria-catalyzed sulfide oxidation(Marsden and House 2006).

1.3.2 Factors that affect bacterial activity

The oxidation rate is directly related to the activity of the bacteria or “biomass,” which is determined and driven by the solution conditions. These factors are summarized below (Konadu, Mendoza et al. 2020).

1) Temperature (Lindström, Gunneriusson et al. 1992)

Bacterial activity and growth rate are strongly dependent on temperature, and optimum temperature is the decisive condition for bacterial culture and its growth rate. In addition, the high temperature system essentially completely oxidizes elemental and intermediate sulfur species to sulfate, significantly reducing cyanide consumption in subsequent leaching operations compared to low temperature biological operations. However, higher temperature applications will pose additional problems for the reactor materials of construction

2) pH (Asamoah, Skinner et al. 2020)

The optimum pH range for bacterial growth has been proved to be between 2.3 and 2.5. However, a pH of 1.0 to 1.8 is usually maintained to maximize the rate of oxidation and to prevent the formation of obstructive precipitates, such as jarosites. Solution pH is used to control the culture and growth of predominant bacterial species. An optimization process for gold extraction is required, while raw material mineralogy and solution chemistry are also relevant parameters.

3) Pulp density (Fomchenko, Kondrat'eva et al. 2016)

The high pulp density facilitates the tank volume requirements for bio-oxidation, as well as the process economics. However, the maximum pulp density is usually limited by the oxygen transfer rate because the rate increases with increasing mineral content. Bio-oxidation systems for sulfide concentrates operate at a pulp density of 10% to 20% solid. While the ores may be required a higher slurry density, from 25% to 40% solids, because of lower oxygen requirements with the lower sulfide and sulfur content.

4) Solution potential and the ratio of Fe^{2+} and Fe^{3+} (Wu, Huang et al. 2013).

The solution potential and/or Fe^{2+} and Fe^{3+} are important indicators which represent the overall activity, energy, and oxidation efficiency of bacterial metabolism. Generally, a solution potential of 670 mV is obtained in the presence of high Fe^{2+} and Fe^{3+} ratios and early adaptive bacteria. Highly active bacteria in solution owns solution potentials of 950 to 980 mV, with lower Fe^{2+} and Fe^{3+} ratios.

5) The effect of adaption and other species (Aitimbetov, White et al. 2005).

Bacteria can continually adapt to changing environments. When a new feed is introduced into a bacterial culture, such as an unoxidized sulfide ore or concentrate, it takes time for the bacteria to adapt to the material. This process takes from 2 or 3 days to several months, depending on the mineralogy of the material and the slurry property. Fully adapted bacteria will achieve maximum oxidation rates when sufficient sulfide is provided, and environmental conditions are suitable. When the sulfur source is depleted, the bacteria go into dormancy and thus the oxidation rate decreases.

Before introducing a bacterial solution into the process, it is necessary to check for toxic chemicals that encounter the bacterial solution. Construction materials, such as rubber compounds, should also be rigorously tested for any adverse effects for bacteria growth.

6) Effect of shear (Fraser, Walton et al. 1991)

Shear is a very important parameter in bio-oxidation systems due to the need to efficiently disperse the air in the system and to maximize the mass transfer rate in the slurry. However, there is some controversy over the effect of shear on bacteria activity and overall bio-oxidation efficiency. Some studies have shown that the biological oxidation system must be stirred slowly to avoid remove the bacteria from the mineral surface. It is indicated that shear does not significantly affect bacterial activity. Many successful commercial bio-oxidation plants have proved this conclusion and applied higher shear agitation to facilitate oxygen and mass transfer, for example, Wiluna (Australia) and Fairview (South Africa), etc.

7) Nutrient requirements (Murugan, Han et al. 2016)

Nutrients vary depending on the water source and the nature of the solution. Carbon dioxide in the air is a source of carbon which could be used for cell growth and energy conversion, and that carbon dioxide is used to provide oxygen for oxidation. Besides carbon, nitrogen and phosphorous are also require for bacteria. Ammonium sulfate and potassium phosphate are typical nutrients to maintain the bacteria activity.

1.3.3 Species for oxidation

More than 20 species of bacteria have been tested to sulfide bioleaching, such as *Leptospirillum ferrooxidans, Acidianus/Sulfolobus spp. T. thiooxidans, Metallogenium,* and others (Sand et al., 2001). Gold recovery could achieve over 95% when sulfide oxidation of up to 90%, (Shahverdi et al., 2001; Deng and Liao., 2002; Amankwah et al., 2005). There are also studies investigated that organic nutrient in altering community structure, microbial activity and improving oxidation efficiency (Muravyov and Bulaev 2013). Yeast extract increased the bacteria activity enhancing the oxidation of arsenopyrite from 31.1 to 73.5% and that of pyrite from 25.8 to 95.1%. Gold recovery by cyanidation was 67.8 and 93% from the oxidized arsenopyrite and the oxidized pyrite, respectively. The essence of bio-oxidation is the bacteria life activity, which is significantly affected by environmental conditions. Many biological technologies that optimized the environment for bacteria reproduction have been applied for gold sulfide mineral pre-treatment in decades.

1.3.4 Plants that applies the biological oxidation

BacTech's technology has been first used at the Youanmin Deeps, in Western Australia, to treat refractory concentrates grading 5.4 g/t Au (Neale et al., 2000). The throughput is over 120 t/d gold concentrate, achieving gold recoveries between 93 and 95%. After that, it was tested successfully in Bulgaria Ghana and Kazakhstan plan to build a BacTech processing gold plant (Poulin and Lawrence 1996, Neale et al., 2000). On the other hand, Ashanti Gold Mine applied BIOX to process gold concentrate, capacity expanded from 720 t/d (in 1994) to 960 t/d (in 1996) in Ghana. The Kokpatas plant in Uzbekistan is the largest BIOX plant in the world, the designed concentrate treatment capacity was 2138 t/d (Dew et al., 1997; Neale., 2000; Miller et al., 2004; Marsden and House., 2006). There are other Bio-technologies such as the MINBAC, a plant that was constructed in Vaal Reefs in South Africa to process 20 t/d gold concentrate in 1989; the GeoCoat Process designed by Newmont in America to process gold concentrate, achieved sulfide oxidation over 70% and gold recovery over 85%.

The CCGRI process was developed rapidly in China recently in two decades and China National Gold Group Co., Ltd has invested a plant in Liaoning which processed 100 t/d of gold concentrate (Neale et al., 2000, Harvey and Bath., 2007; Wen et al., 2016).

Biotechnology is a promising method for the pre-treatment oxidation of gold refractory sulfides. But it still faces problems that impede its amply application, such as the use of a specific pH, low percent solids in slurries, moderate stirring rate, almost constant temperature, continuous and subtle operation (Kondrat'eva et al., 2012, Sun et al., 2012).

1.3.5 Future application

The low-cost, non-polluting advantages of bio-oxidation can be applied as a process for treating gold-bearing sulfide ores in plants. Research should focus on the specificity bacteria that can maintain high activity at high temperatures to increase processing of more structurally complex ores (especially for processing high sulfur concentrates) improve oxidation efficiency and oxidation rates, and thus reduce capital costs.

1.4 Oxidation with high pressure

Oxidation of pyrite can be undertaken in autoclaves, which generally operate at 170-230°C, and 350-700 KPa of oxygen pressure under acid or alkaline conditions (Fleming., 2009). Processes of pressure oxidation are divided into two types:

(1) acidic oxidation, pyrite is decomposed by sulfuric acid and converted to sulfate and the iron is turned to hematite (Papangelakis and Demopoulos., 1990; Long and Dixon., 2004). The oxidation is as follows (5-8).

$$FeS_2 + O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \tag{5}$$

$$FeS_2 + O_2 + H_2O \rightarrow Fe_2(SO_4)_3 + H_2SO_4 \tag{6}$$

$$Fe_2(SO_4)_3 + FeS_2 + H_2O \rightarrow H_2SO_4 + FeSO_4 \tag{7}$$

$Fe_2(SO_4)_3 + H_2O \rightarrow Fe_2O_3 + H_2SO_4$

(8)

(2) alkaline oxidation, the oxidation products are sulfate and hematite. The oxidation is as follows (9)

$FeS_2 + O_2 + NaOH \rightarrow Fe_2O_3 + Na_2SO_4 + H_2O$

(9)

All these products from either acidic or alkaline oxidation are stable. Their formation is controlled by the operation temperature, pressure, solid/water ratio in the slurry. At 100-160°C, element sulfur would be generated, which is an undesirable product and detrimental for cyanidation. This is because cyanide and S would form thiocyanate ions, resulting in very high cyanide consumption. And thiocyanate has toxic effects on the environment. Therefore, the process requires more energy to increase temperature (over 160°C) to prevent forming element sulfur (Rusanen et al., 2013).

1.4.1 Reaction kinetics

1) Temperature and pressure

Pressure requirements increase with temperature, and it becomes increasingly difficult (and more expensive) to design and operate oxidation systems as temperatures increase. For example, oxidation at a temperature of 250°C requires an operating pressure of approximately 6,200 kPa (Thomas and Pearson 2016). The major issues associated with operation at high temperature and pressure are as follow:

- Limitations of mechanical agitator seal on the pressure vessels.
- Increased corrosion rate.
- Increased capital and operating costs due to higher pressure on equipment.

Operating temperature and pressure are usually maintained at minimally sufficient levels to avoid the elemental sulfur formation, on the other hand, providing the desired oxygen partial pressure to achieve highest sulfide mineral oxidation for cyanide leaching.

2) Extract reagent concentration

The sufficient acid is required to maintain iron concentration in the pulp, avoid excessive precipitation, and keep promising oxidized potential (Fleming 2010). On the other hand, too much acid will require additional and unnecessary neutralization after oxidation, which is expensive. Typically, the acid concentration is maintained around 10 g/L H_2SO_4. Low sulfur minerals (i.e., less than approximately 2.5% S) may require more acid to keep the desired acid concentration. High sulfur materials (i.e., >3% S) generate sufficient acid by decomposition, but the process of acid replenishment is usually limited by the nature of the feed, as dictated by the presence of carbonates. Acid concentration in the discharge slurry can be as high as 60 to 80 g/L after processing (Wu, Ahn et al. 2021).

3) Solution Potential

The solution potential of oxidized slurry provides a good oxidation indicator and a measure of the driving force for the reaction. Several commercial pressure oxidation plants use this data to control process. A slurry or solution potential of 480 mV is equivalent to an Fe^{3+}:Fe^{2+} ratio of 10:1, which indicates that a high degree of oxidation has been achieved (Rusanen, Aromaa et al. 2013).

4) Degree of Agitation

Adequate agitation is required to ensure favourable heat and mass transfer properties. The agitation speed decides the dispersion and retention of oxygen bubbles in the pulp. The degree of agitation strongly depends on reactor and impeller design, slurry properties (i.e., viscosity and density), energy input, and types of impellers. (Mason 1990).

5) Pulp Density

The optimum pulp density for pressure oxidation is a compromise between minimizing the reactor size (i.e., by maximizing pulp density) and maximizing oxygen mass transfer (Long and Dixon 2004). However, element sulfur formation and mineral content also influence the slurry density. For low sulfur ores (<5% S), higher slurry densities of 40% to 53% solids can be used. Minerals with higher sulfide contents must be processed at a lower slurry density, typically 25% to 35% solids, or recycle part of the product to avoid the formation of sulfur. Similarly, ores containing high content of gangue minerals, such as carbonates and clay, also need to be processed at lower densities, resulting in slurry viscosity increased because of the formation of gypsum (Papangelakis and Demopoulos 1990).

6) Particle Size

Oxidation rates increase with higher sulfide surface area, leading to reaction time reduced (Koslides and Ciminelli 1992). Optimal particle size is closely related to the degree of oxidation, reaction time. However, the finer the particle size, the significantly higher the required comminution cost, as well as the cost of the reaction residence time, and the required degree of oxidation. Whole-ore pressure oxidation in industrial operation generally ground to P80 <78 μm, while pressure oxidation of concentrates generally grind P80 <37 μm (Weir, King et al. 1986, Corrans and Angove 1991).

1.4.2 Plants that applies the high-pressure oxidation

McLaughlin plant was the first acidic pressure oxidation plant in the US with a throughput of 2700 t/d ore grading 3.1 g/t Au. Achieved gold recovery of over 90% (Turney et al., 1989; Guinivere., 1984). The Goldstrike mine in northeast Nevada is the largest gold mine in the North. America, with an estimated reserve of 992 tons of gold in an ore averaging 2.8 g/t Au. The operation capacity of the autoclave installation was 12,000 t/d in 2015 and the gold recovery achieved was over 81% (Parga et al., 2012) Pueblo Viejo deposits, in the Sánchez Ramírez, the Dominican Republic is the largest gold mine in America. In 2018 the mine processed 40,105 kt ore, produced 581,000 oz gold, and attained an Au recovery of 89% from ore grading 4.04 g/t Au (Torró et al., 2017). Currently, over 15 pressure oxidation plants have been constructed and operating in the world (Adams., 2016). It has become an important pre-treatment process for gold refractory minerals, but it demands facilities that should be resistant to high temperatures, acid, and corrosion, resulting in higher capital costs. Since the process is under acidic conditions, the oxidized slurry must be neutralized, and the pH adjusted over 10 for gold recovery by cyanidation. (Marsden and House 2006)

The Albion process^{TM} is a newly oxidative leaching process for precious metal recovery at atmospheric pressure. The main processing steps are ultra-fine regrinding and refractory sulfide oxidation by supersonic oxygen at neutral pH. It has been applied in the Ararat plant, Armenia, owned by GeoProMing Ltd, and successfully increased gold recovery from 20% to 95% (Voigt et al., 2015). FLSmidth process is a mechano-chemical leaching process, known as rapid oxidative leach for refractory gold recovery. Unlike the Albion process, ultra-fine grinding is not necessary for this technology. Oxidative leaching is carried out at acidic pH assisted with mechanical energy in a stirred media reactor (SMR) to remove elemental sulfur from the sulfide particle surface. This process has helped Shanta in southwest Tanzania to boost its gold and silver recovery (Mulligan., 2017).

1.5 Oxidation by roasting

Oxidation of refractory sulfide and carbonaceous constituents of ores and concentrates can be achieved pyrometallurgically by roasting in the presence of an oxidizing gas, such as air or oxygen. The objective is to produce a porous iron oxide calcine in which the gold is largely liberated, allowing access to cyanide leach solution and minimizing any reagent-consuming or gold-adsorbing potential of ore constituents.

The different types of ore result in roasting that can use either a single-stage or two-stage process. The single-stage method is direct roasting of the material at presence of air. The two-stage process employs a first stage which produces a porous intermediate product under reducing conditions, then the product is roasted in a second-stage with oxygen atmosphere.

Methods for processing roaster products are essential for maximizing gold recovery, minimizing reagent consumption and reducing environmental pollution.

1.5.1 Sulfide Roasting Chemistry

1) Pyrite

Oxidative roasting releases gold from refractory minerals by converting the iron to iron oxides, the sulfur to sulfur dioxide, which then is used to produce sulfuric acid to prevent SO_2 discharge and reduce environmental concerns (Runkel and Sturm., 2009; Yang et al., 2009; Liu et al., 2014). In pyrite, it has been postulated that gold atoms in the metastable state migrate to a lower energetic site by solid-state diffusion (Filmer., 1982). Oxidation of pyrite is as follow (10-12):

$$FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$$

(10)

$$FeS_2 + O_2 \rightarrow Fe_3O_4 + SO_2$$

(11)

$$Fe_3O_4 + O_2 \rightarrow Fe_2O_3$$

(12)

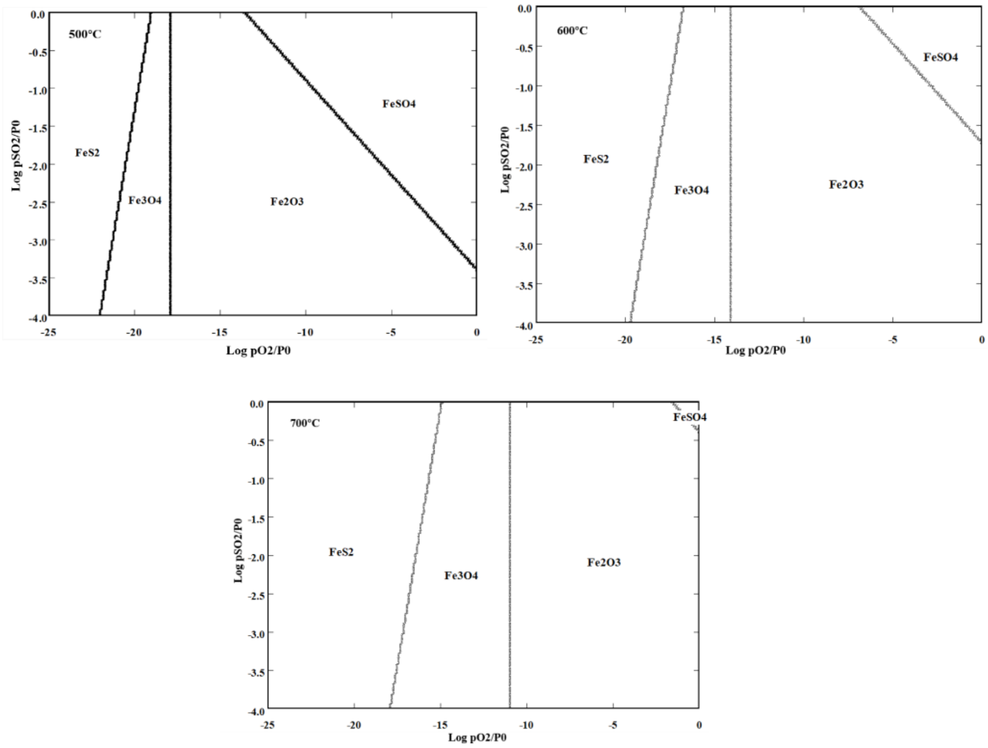


Figure. 2 Stability phase diagram of pyrite roasting at 500, 600 and 700°C built using the (HSC) chemistry 6 software.

The phases that are formed from pyrite oxidation at different temperatures (500, 600 and 700°C) are presented in Figure 2. At the lowest roasting temperature of 500°C, FeSO4 and different iron oxides such as hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) formed as oxidation products. Increasing the temperature to 700°C hematite is the iron oxide terminal phase. Hematite is the ideal product for gold recovery since it is a highly porous matrix with good permeability and accessibility to gold particles. $FeSO_4$ and magnetite are intermediates and undesirable products as they are detrimental by higher cyanide consumption in leaching (Paktunc et al., 2006).

In general, converting pyrite to porous hematite by roasting to generate pores on the concentrate, making possible the contact between gold and leaching solutions. But the gold recovery has never been corrected to the specific surface area of the calcine.

2) Arsenopyrite

The phase–stability diagram for the Fe–As–S–O system at 400°C is shown in Figure 3 (Dunn and Chamberlain 1997). Under oxidizing conditions, low sulfur dioxide content and low temperatures, arsenopyrite converts to magnetite as follows (Dunn, Ibrado et al. 1995):

$$12FeAsS + 29O_2 = 4Fe_3O_4 + 6As_2O_3 + 12SO_2 \tag{13}$$

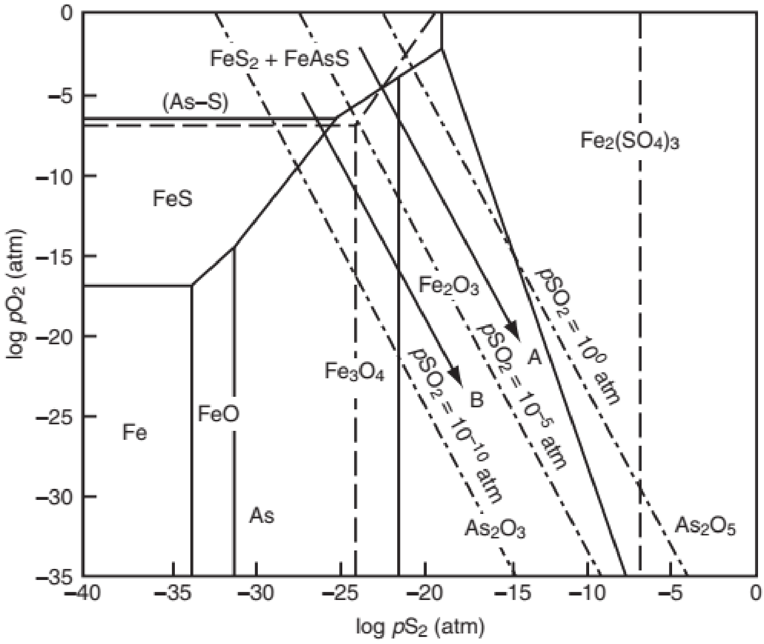


Figure. 3 Phase–stability diagram for As-Fe–S–O system at 400°C

Then the arsenic trioxide may be oxidized to arsenic pentoxide:

$$As_2O_3(s) + O_2(g) = As_2O_5(s) \tag{14}$$

However, it may occur a further undesirable reaction between Fe_2O_3 and As_2O_5 to form ferric arsenate ($FeAsO_4$), which proved to be a non-porous matrix, thus impede cyanide ions access to gold particles and reduce gold extraction (Thomas and Cole 2016):

$$Fe_2O_3(s) + As_2O_5(s) = 2FeAsO_4 \tag{15}$$

The formation of As_2O_5 can be limited by roasting in an anaerobic atmosphere, although it is still necessary to provide sufficient oxygen for primary oxidation of arsenic and sulfur.

1.5.2 Roasting kinetics

The roasting efficiency depends on the response of the cyanide leached gold and silver particles, and to a large extent on the roasting kinetics. where temperature, oxygen and particle size are the main parameters determining the kinetics (Paktunc, Kingston et al. 2006). But maximizing the reaction kinetics does not necessarily lead to maximizing the gold recovery rate.

1) Temperature and Gas

The oxidation rate pyrite and arsenopyrite minerals increases with increasing temperature and oxygen pressure (Li, Zhang et al. 2018). At low temperatures (<450°C), oxidation rates of pyrite and arsenopyrite are very slow. Rates can be only achieved by increasing temperatures >500°C. On the other hand, at very high temperatures >700°C, the porous iron oxide structure that is obtained during oxidation may collapse, leading to encapsulate gold reducing subsequent gold recovery. This process is often referred to as “sintering”. Similar phenomenon can be produced by longer retention time at high, or even marginally high temperatures, commonly referred to as “overroasting.”

In the subsequent cyanidation process, the porosity and specific surface area of the calcined product play an important role in the feasibility of recovering gold particles.

This porosity depends not only on the oxidation rate, but also on the sulfur diffusion rate. The formation of products with higher porosity is favorable at longer reaction residence times. Under high temperature and saturated oxygen conditions, pyrite and arsenopyrite may not have sufficient reaction time for their mineral structures to diffuse to the mineral surface, thus preventing further pore development.

The optimum operating conditions required for the optimal roasting of sulfide ores depend on many factors such as the mineralogy of the material, the roasting vessel, the roasting method and the mineral size distribution. These conditions must be determined by rigorous test work and evaluation.

2) Particle size distribution

During the roasting, coarser particles may be oxidized incompletely, while finer particles may be overroasted and cause sintered. The size distribution of the roaster feed should be maintained as consistent as possible to reduce the amount of finer and coaser particles. The actual mineral size depends on the mineral structure and roasting method. Typically, the ore and concentrate are ground to P80 of 75-150 microns, this particle size that is optimal for gold extraction in the cyanidation process. One of the concentrates could be roasted at coarser sizes (i.e., between 0.25 mm and 1 mm), if necessary the roasted calcine could be grounded again (Wang, Hu et al. 2019).

3) Retention Time

The retention time of pyrite and arsenopyrite in the roaster determines the efficiency of oxidation. Incomplete oxidation may occur if the residence time is too short and excessive feed in the roaster. This may lead to high cyanide consumption during cyanidation, in addition, high gold losses because of calcine remains unexposed to gold particles. However, long retention time could cause overroasting or sintering of calcined minerals, especially for the fine particles (Hammerschmidt, Güntner et al. 2016).

4) Oxidation efficiency

The calcine containing over 85% hematite and less 25% magnetite has been found to be optimal. This indicates that iron or arsenic sulfide oxidation has been achieved completely, but the oxidation of magnetite (Fe_3O_4) to hematite (Fe_2O_3) is not completed (De Michelis, Olivieri et al. 2013). The calcine color is a useful indication of the degree of oxidation: a bright red color refers hematite (maybe very little magnetite) has been generated resulting from overroasting (like discussed above, higher temperature and oxygen content, or longer retention time). However, a very dark brown or black color refers to a magnetite-rich product, which may because of lower temperature and insufficient oxygen, shorter retention time. The effiicient oxidation of magnetite to hematite is important because magnetite is a barely porous product which tends to retain arsenic, sulfur, and occlude gold in the matrix (Qin, Guo et al. 2021).

1.5.3 Application

Roasting can be applied to a wide variety of sulfide, carbonaceous, and telluride ores and concentrates. Roasting has been employed by a number of major gold producers, including Kalgoorlie Consolidated Gidji (Australia) (Fernández, Collins et al. 2010), Fairview and New Consort (South Africa) (Gudyanga, Mahlangu et al. 1999), Campbell Red Lake and Con (Canada), Emperor (Fiji), and, more recently, at Jerritt Canyon, Big Springs, Cortez, Carlin, Goldstrike (all in the United States), and Minahasa (Indonesia) (Dehghani, Ostad-Rahimi et al. 2009).

1.6 Research Objective

Biotechnology is a promising method for the pre-treatment oxidation of gold refractory sulfides. But it still faces problems that impede its amply application, such as the use of a specific pH, low percent solids in slurries, moderate stirring rate, almost constant temperature, continuous and subtle operation

High pressure with oxygen oxidation has become an important pre-treatment process for gold refractory minerals, but it demands facilities that should be resistant to high temperatures, acid and corrosion, resulting in higher capital cost. Since the process is under acidic conditions, the oxidized slurry must be neutralized and the pH adjusted over 10 for gold recovery by cyanidation

Roasting is an alternative option and has been the preferred method to pre-oxidation due to its fast and energetically self-supporting. The aim of this work was to further study the effect of pyrite roasting temperature on the physical and chemical characteristics of the calcine and how these properties influence the gold and silver recovery. The pyrite and calcines were examined by Scanning Electron Microscope (SEM), X-ray diffraction (XRD) and chemical assay. The specific surface area and pore volume of calcines were determined in order to correlate them to the gold and silver recovery by cyanide leaching.

2. Materials and methods

2.1 Materials and reagents

Two Au-pyrite concentrate samples from Chihuahua, México were used in this work. These concentrates were collected from the same gold-pyrite ore, they, therefore, have the same mineralogy. They only differed in the grade of the element components. SEM microscopy reported that they contained pyrite (FeS_2) chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite (ZnS). Calculation based on the elemental chemical assays (Table 1) revealed that sample 1 contains 82.3% FeS_2, 0.2% $CuFeS_2$, 0.4% PbS and 0.7% ZnS, and sample 2 contains 88.9% FeS_2, 0.4% $CuFeS_2$, 1.4% PbS and 2.7% ZnS. And XRD also confirmed that FeS_2 was the main sulfide mineral in the concentrates (Figure 2.). Particle size distribution indicated that the sample size was 80% passing 150 µm. The sodium cyanide used in the gold and silver leaching tests was from J.T.Baker. All leaching tests were using tap water and lime for pH adjustment.

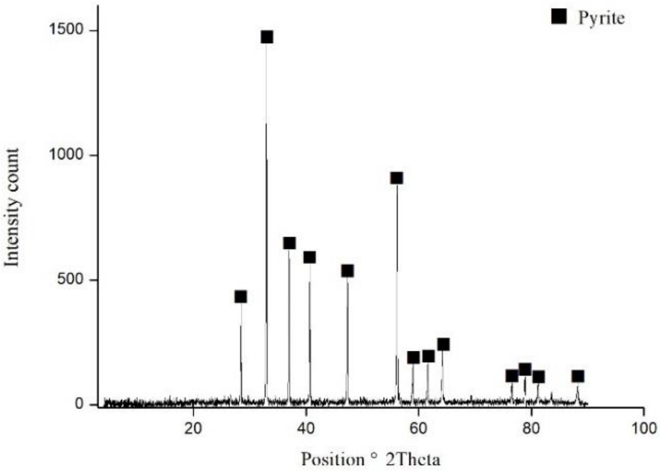


Fig. 2. XRD of pyrite concentrate

Table 1. The chemical composition of Au-pyrite concentrates

Original sample	Amount %						g/t	
	Cu	Pb	Zn	Fe	S	Insoluble	Au	Ag
1	0.07	0.35	0.46	38.5	48.0	5.7	18.2	238
2	0.14	1.20	1.80	41.5	48.0	6.6	14.8	366

2.2 Roasting

Roasting of the pyrite concentrate was carried out in a tube furnace. 35g pyrite was uniformly put on a ceramic container, which was placed into an alumina tube once the temperature achieved the desired value. Roasting tests were performed in the temperature range of 400 to 700°C, and in the time range of 4-6 h. Air was injected into the tube at a flow rate of 10 ml min^{-1}. Outgas from the furnace were directed to a bucket with a sodium hydroxide solution to trap the SO_2. Pre-oxidation was completed until SO_2 stopped emanating which was detected by no pH changes in the sodium hydroxide solution. The calcine was characterized by gold and silver content, surface area, SEM and XRD. Gold and silver recovery from the calcine was determined by cyanide leaching.

2.3 Cyanidation

Cyanidation tests were performed in a 250 mL glass stirring reactor using a 200 mL cyanide solution (concentration was 1,000 mg/L) and 30 g calcine (15%w solid slurry). The slurry pH was adjusted to 10.5-11 and maintained constant throughout the leaching test. Air was continuously injected into the slurry during the leaching test. The O_2 concentration in the slurry was 7.2 ppm throughout the test. The leaching time was 72 h. Afterward, the solid was filtered, dried and prepared for Au and Ag assay.

3 Results and discussion

3.1 Roasting Temperature and Time

Figure 3. shows the XRD diffractogram of the pyrite concentrate and the calcines after roasting at 400, 450, 500, 600 and 700°C, and several time (4 and 6 h). The XRD diffractogram revealed that maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) appeared as the final pyrite oxidation at 450°C and 6 h, while at 400°C no iron oxides were detected meaning very mild pyrite oxidation and longer time was needed for the oxidation process. γ-Fe_2O_3 is a metastable spinel polymorph of hematite (α-Fe_2O_3) and an intermediate product from magnetite to hematite. It has been reported that maghemite renders the mineral refractory and makes a tough gold recovery by cyanidation (Bas et

al., 2015). The formation of the α-Fe_2O_3 present in the roasting temperature up to 500°C, while pyrite oxidation was still not completed during 6 h roasting, neither at 600°C, 4 h. Then pyrite was completely converted to iron oxides when the roasting time increased to 6 h at 600°C and higher temperature. At 700°C, only α-Fe_2O_3 was detected in the calcine.

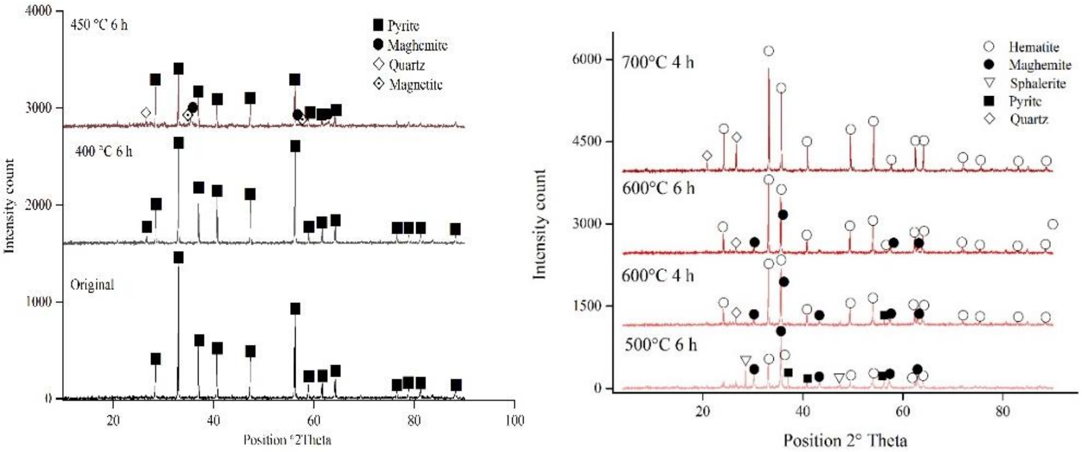


Fig. 3. XRD of original pyrite and calcines from a): original sample, 400 and 450°C; b) 500-700°C

Figure 4. shows SEM photomicrographs of the pyrite sample and calcines at the various roasting temperatures. As noted, a thin layer of iron oxides (γ-Fe_2O_3 and Fe_3O_4) formed on the edge of pyrite particles at 450°C (Fig 4 a-b), which confirmed the species by results in Fig 3 (a). It can be seen that Fe_3O_4 was first formed around the pyrite, then the Fe_3O_4 was oxidized to γ-Fe_2O_3 and α-Fe_2O_3 when the roasting temperature increased. At 500°C (Fig 4 c-d), α-Fe_2O_3 appeared at the particle edge where there were Fe_3O_4, γ-Fe_2O_3 and iron sulfate ($FeSO_4$) as predicted by the diagram shown in Figure 1. The formation of these iron oxides was confirmed by other studies, which reported that γ-Fe_2O_3 was an intermediate product during pyrite oxidation and α-Fe_2O_3 was the final product (Music et al., 1992; Paktunc et al., 2006; Liu et al., 2010). Moreover, α-Fe_2O_3 was the only iron oxide at the roasting temperature of 700°C (Fig 4 e-f). In this

study, we chose 500-700°C to recover gold and silver as the calcine presented distinct iron oxide phases and the aim was to delineate how this affected the metal recoveries.

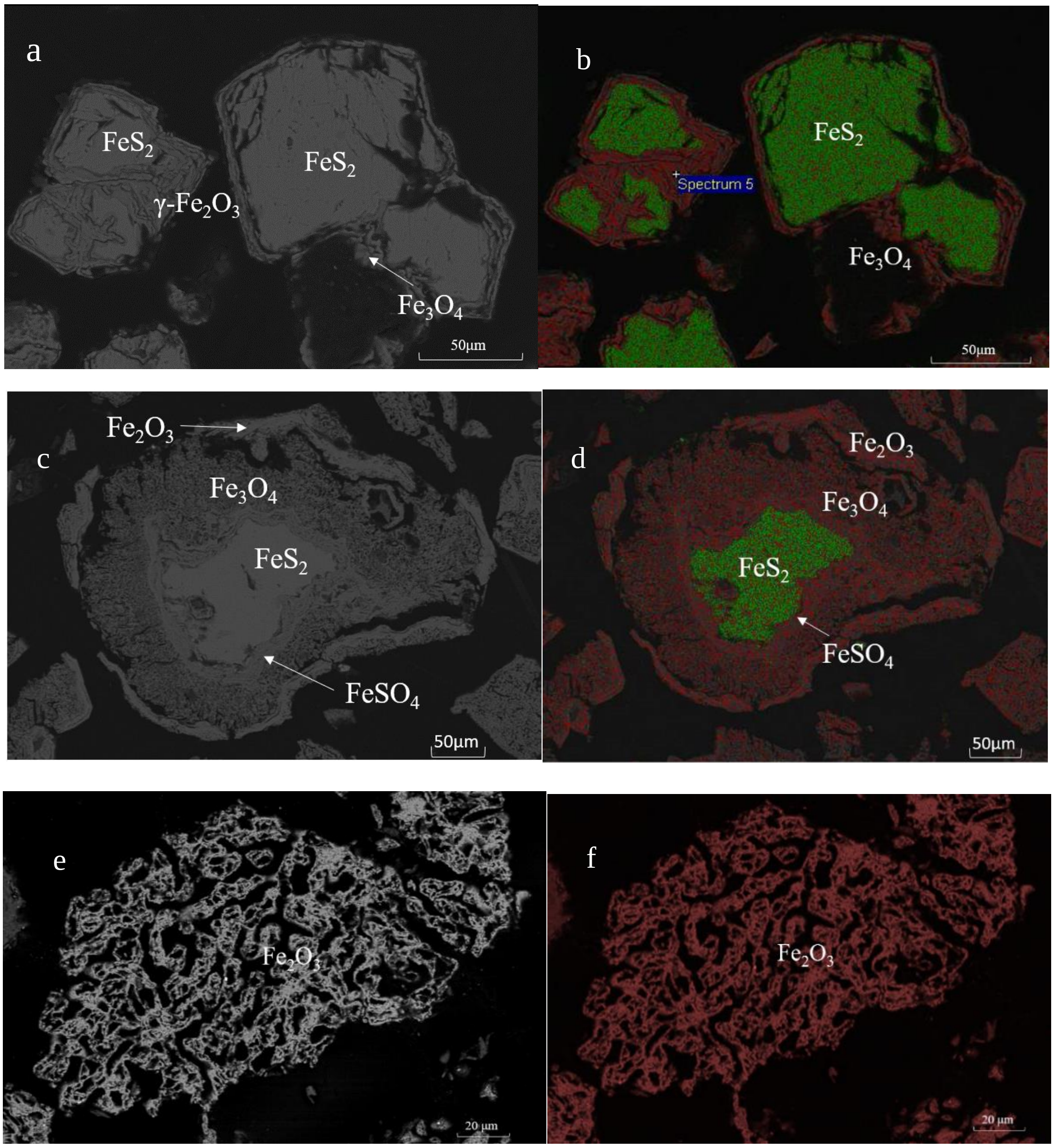


Fig. 4. SEM of process pyrite oxidized in a-b) 450°C, c-d) 500°C and e-f) 700°C; b, d and f were the mapping of calcine, red color dots represent Fe ions and green color dots represent S ions.

Most roasting processes operate above 700°C since this is beneficial for S removal and easy to control in roasting operating processes (Liu et al., 2019). This temperature is reached from the heat evolved during the oxidation of pyrite, which is highly exothermic (Runkel and Sturm., 2009). However, sintering occurs under these conditions of roasting temperatures (Hammerschmidt et al., 2016, Liu et al., 2019). The specific surface area and porosity of the original samples and calcines are presented in Table 2. and Figure 5. The surface area and pore volume of the roasted products, especially the meso and microporosity, increased from 500 to 600°C as compared to that of the original sample. But they significantly decreased as the temperature increased to 700°C, meaning that particles sintering occurred during roasting.

Table. 2. The specific surface area and pore volume of the original and roasting samples in three temperatures.

Sample	Surface area (m^2/g)	Porosity volume (cc/g)	Micro-pore		Meso-pore		Macro-pore	
			Volume (cc/g) $x10^{-3}$	%	Volume (cc/g) $x10^{-3}$	%	Volume (cc/g) $x10^{-3}$	%
Original	0.55	0.001	0	0	2.14	21	2.12	79
500°C	2.76	0.009	0.62	21	1.00	33	0.14	46
600°C	3.31	0.100	1.05	30	0.13	36	0.12	34
700°C	1.68	0.005	0.80	33	0.51	21	0.16	67

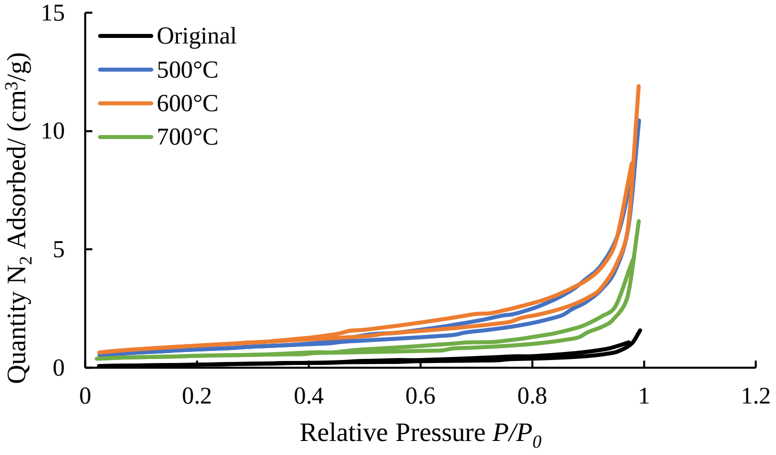


Fig. 5. N_2 Adsorption isotherms of calcines recovered from roasting pyrite at 500, 600 and 700°C.

3.2 Chemical Analysis of Calcines

The mass loss of the original sample and a chemical assay of the calcines are given in Table 3. Increasing the temperature from 500-700°C, the mass loss increased linearly, which confirmed that the S in the pyrite was oxidized to SO_2 gas during the roasting. The S content was reduced significantly from 48% to 11% at 500°C, and only 1.9% S remained in the calcine when the roasting was at 600°C and for 6 h. Due to the different types of original samples, there was still 3.7% sulfur of the product at 700°C, for sample 2. XRD and SEM showed that iron oxides formed during roasting. As a consequence of the mass loss, the grade of Fe, Au and Ag increased in the calcine than original samples. That of Au, increased from 18.2 g/t to 36-30 g/t, supposedly would be exposed easier to leaching solution after roasting (Paktunc et al., 2006; Hammerschmidt et al.,2016; Espiell et al., 1986).

Table 3. Weight loss and chemical analysis of original and calcines samples

Time, h	Temp. °C	Weight Loss, %	Chemical Assay							
			%						g/t	
			Cu	Pb	Zn	Fe	% S	Ins.%	Au	Ag
Sample 1		-	0.07	0.35	0.46	38.5	48.0	5.72	18.2	238
6	500	22	0.07	0.39	0.69	51.5	11.0	9.62	26.8	278
4	600	28	0.08	0.44	0.78	56.0	4.3	10.0	31.0	291
6	600	29	0.08	0.42	0.75	56.0	1.9	10.0	28.5	299
Sample 2		-	0.14	1.20	1.80	41.5	48.0	-	14.8	366
4	700	38.3	0.19	1.51	2.11	50.4	3.7	-	20.8	381

Fig. 6 shows SEM photomicrographs of roasted samples (500-700°C) where a random porous structure can be observed. In addition, it is seen that fine gold and silver particles were exposed, which is beneficial for gold and silver recovery. The size of the gold particles was about one micron and there were particles with an even smaller size. The porous structure of the calcine would definitively allow cyanide solution and oxygen to migrate to the gold and silver particles and dissolve them.

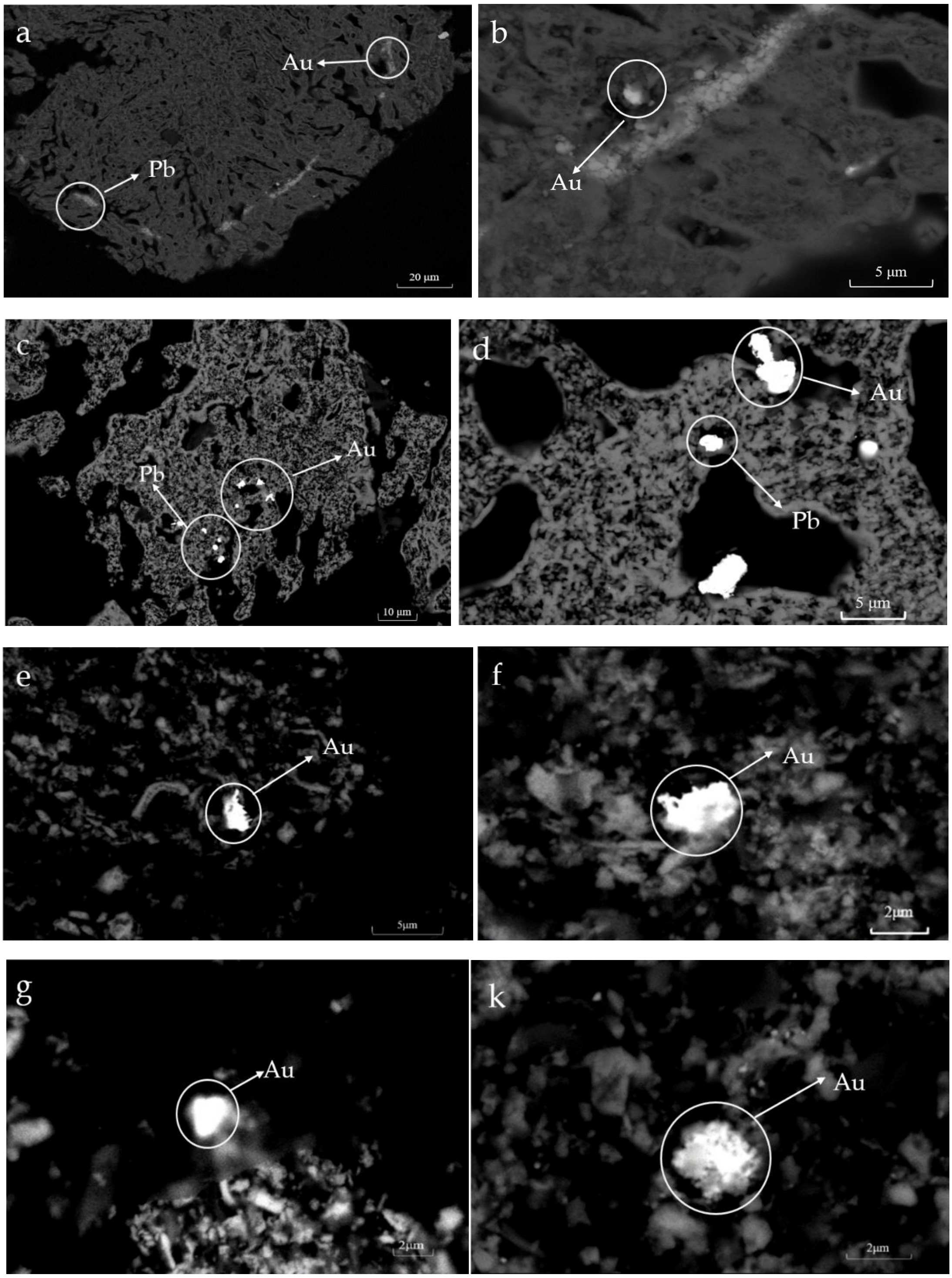


Fig. 6. SEM photomicrographs of roasted samples: (a-b) 500°C, 6 hrs; c-d 600°C 4 hrs; (e-f) 600°C, 6 hrs; g-k 700°C 4 hrs. Porous matrix was iron oxide hematite and the white and shining phases marked by an open circle were gold, without white circles were lead.

3.3 Au and Ag cyanide leaching from calcines

The calcines from the pyrite-sample roasting were treated to cyanide leaching to extract the gold and silver. After roasting, the sample was ground to 0.25 mm and cyanide leached at pH 10.5-11 for 72 h. The gold and silver recovery are presented in Fig 7. The original sample exhibited very poor gold recovery (25%) and Ag recovery (50%). Gold achieved a maximum recovery of 86% at 500°C, while a little decreased at 600°C. Moreover, when the temperature increased to 700°C, gold recovery decreased significantly to 43%. Comparing the gold recovery with the calcine-specific surface area, it was found that gold recovery decreased when the surface area decreased. As the decrease in surface area is due to the sintering of the iron oxides in the calcine, it can be said that gold particles were encapsulated by iron oxides and were no longer accessible to oxygen and cyanide solution. This phenomenon was called secondary gold physical encapsulation (Zhang et al., 2019). Silver recovery achieved maximum at 500 °C to 73% compared with 50% in origin, then decreased when increasing roasting temperature. As noted in Fig 8, SEM characterization revealed the formation of an Ag-Fe-S species ($Fe_{1-x}S$ + Ag_2S + Ag), a ternary eutectic reaction at 600°C, which is characterized by very low mutual solubility both in the liquid and the solid states (Raghavan et al. 2004).

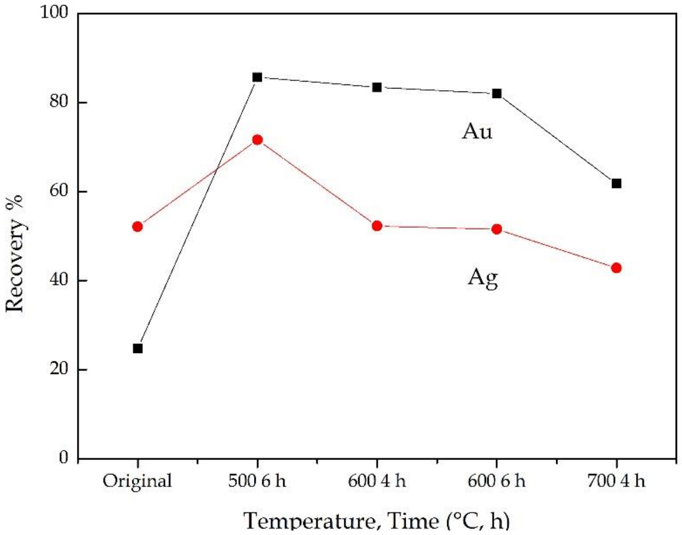
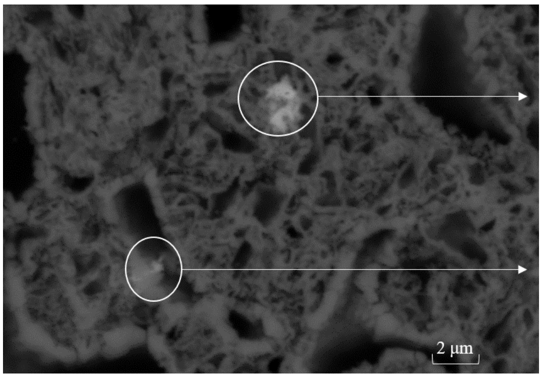


Fig. 7. Recovery of gold and silver from pyrite and roasted pyrite at various roasting temperatures and times.



Element	Weight %	Atomic %
O	27.02	62.24
S	6.56	7.54
Fe	23.65	15.61
Ag	42.76	14.61

Element	Weight %	Atomic %
O	30.67	62.25
S	2.02	2.05
Fe	55.04	32.01
Ag	12.26	3.69

Fig. 8. SEM Photomicrograph of residues after cyanide leaching of calcine obtained by roasting 600°C, 6 h. The white circle indicates the element composition of the phase by EDS.

4 Conclusions

Direct cyanidation on Au-pyrite concentrates only recovery less than 25% Au and 55% Ag, because of their high refractoriness so the pyrite concentrate needed to pre-treat to liberate gold and silver particles. Au and Ag's recovery improved significantly after roasting, an Au recovery of over 85% was attained at 500 to 600°C due to the high porosity of the calcine exposing occluded ultrafine gold to leaching solutions. Above 600°C, the iron oxide in the calcine sintered gave rise to Au recovery decrease. Secondary gold encapsulation occurred under these conditions. Ag recovery increased when the roasting temperature was 500°C, then declined as the temperature above 600°C not because of encapsulation but due to the formation of Ag-Fe-S species, which are not dissolved by cyanide.

Chapter 3

Environmental concerns and flotation performance of copper tailings: a critical review

Abstract

Copper tailing is a solid waste produced from effluent in mining plants. However, copper tailings are collected and stockpiled in a huge amount by mining activity and process, resulting in the occurrence of failures increased significantly in the world, in addition, the leached heavy metal in tailings poses serious pollution to the local resources when exposed to the weathering and natural oxidation environment. On the other hand, such a large number of tailings are regarded as a second resource to recycle willand zinc, etc. As an effective and multifunctional technology, flotation is a widely used method to treat copper tailings, recover valuable minerals and minimize the environmental footprint of tailings. This paper reviews: the potential effects of tailings in the environment, including dust emission, tailing failures, and contamination; factors that influence the performance of copper flotation, including particle size, reagent effects, and clay minerals behavior were also discussed.

Keywords: Copper recovery; Metal recovery; Mineral tailings; Environmental concerns; Acid mine drainage; Froth Flotation;

1 Introduction

Copper, a soft, malleable, and ductile metal with high thermal, electrical conductivity, and low chemical activity, is widely used as a conductor of heat and electricity, building materials and various metal alloys, even decorative art (Northey, Haque et al. 2013, Sverdrup, Ragnarsdottir et al. 2014, Onuaguluchi and Eren 2016). From 1991 to 2019, the total world copper production has been doubled from 9.3 Mt to 18 Mt, at present, the production is over 18 Mt per year but the demand is augmented from 23.6 Mt in 2018 to 29.8 Mt in 2027, leading to the productivity could not meet the demand in the future (Editor 2019). Furthermore, another major challenge is copper head grade deterioration in the mining industry. It is reported that the average copper ore grade is decreased from 1.0% to 0.62% during the last decade and would expect to decrease continuously when higher copper content ores are depleted (Calvo, Mudd et al. 2016). Therefore, it is necessary to develop more efficient processes or discover other potential sources to fill the gap between product and demand.

Tailings, the leftover materials after selectively separating the desirable metals by mining plants, are composed of unwanted clays, wasted water and residual chemical reagent. Generally, many large-scale mines produce more undesirable tailings than valuable minerals. It is reported that 128 to 196 tons of copper tailings would be generated when producing 1 ton of refining copper (Gordon 2002). An estimated 5-7 billion tons of tailings are produced all over the world every year (Edraki, Baumgartl et al. 2014). Literature reported that the cumulative copper tailings have achieved over 2400 billion tons by the end of 2014 in China (Liu, Li et al. 2018). In most cases, the tailings are discharged and cumulated in the form of engineered dams and ponds, in addition, to the higher copper grade in the historic tailing dams due to the lower efficiency of process operation in the past decades. Therefore, tailings have the potential to be one of the sources to recycle and obtain copper. Meanwhile, such valuable metals as iron, molybdenum, aluminum, lead, zinc and mercury are included by the considerable amount of tailings which could be recovered as the second resource (Zhao, Xia et al. 2012).

2 Method

For this study, the Thomson Reuters' Web of Science (WoS), the most recognized website that provides multiple databases for peer-reviewed journal content, was selected to extract publication information. The following search terms are utilized to collect the maximum number of related papers on tailings studies. By searching the keywords “tailings”, “failures”, “contamination” and “flotation”, “recovery”, in the title of articles, the related publication was downloaded. Based on the method above, a total of 12 articles (including reviews) was extracted for tailings failures; 22 articles were extracted for the dust emission and contamination of tailings; and 13 articles were extracted for the copper recovery by flotation of copper tailings from 2013 to January 2020.

3 Environmental concerns

In past decades, copper mine tailings have been generated tremendously in parallel with the ore extract and process. A notable example of tailing reservoir is found in Dexing copper mine, (Jiangxi province, China), where the capacity of tailings slurry impoundment is $8.35*10^9$ tons, currently approximate 10^5 tons of copper tailings are discharged per day, which turn this tailing reservoir into the biggest tailing dam in the Asia (Guo, Huang et al. 2013). Such a significant volume of copper tailings is considered an environmental concern that causes serious outcomes to the surrounding area, for example, 1) dust emission; 2) storage failures; 3) contamination (Ozkan and Ipekoglu 2002, Santander and Valderrama 2019).

3.3 Dust emission

Tailing dams are designed for permanent containment at closure mineral processing, which are also treated as dust sources and persists a long time depending on tailings characteristic (Ozkan and Ipekoglu 2002, Gil-Loaiza, Field et al. 2018). Due to the poor structure of tailings and lack of adequate vegetation cover, when the dam’s surface is exposed to erosion by wind and air, resulting in transportation, dispersion, and transmission of fine tailing particles to nearby soil and water environment (Csavina, Field et al. 2014, Stovern, Guzmán et al. 2016), and most of the tailings contains heavy metal and radionuclide particles, which have adverse effects on adjacent surroundings, including the area for agricultural activities and natural ecological water system (Csavina, Field et al. 2012, Ramirez-Andreotta, Brusseau et al. 2013). Many studies reported that tailings dust dispersion is one of the most vital anthropogenic factors for a local source of windblown particles (Csavina, Landázuri et al. 2011, Csavina, Field et al. 2012, Loh, Sugeng et al. 2016). Dust emission, therefore, could be a significant nuisance problem though its influences seem to be long-standing.

3.4 Storage failures

As mentioned in section 1.1, discharged and deposited mine tailings occupied countless places for storage, including farms and woodlands. The purpose of tailing ponds and dams is to store mining waste safely to protect the surrounding area from pollution and damage. Following points are the reasonable characteristics of susceptible tailing dams: 1) embankments formed with soil, coarse waste, and residual materials from the mining operations; 2) wastewater volume raised as the height of the tailing dams increases; 3) lack of reasonable regulations on design criteria; 4) shortage of monitoring and controlling requirements during mining process; and 5) higher cost of maintenance for tailing dams at entire mining activity (Rico, Benito et al. 2008). It is reported that the total area of mined lands and resources destroyed by tailings is over 2000 ha (Wang, Ji et al. 2017). In addition, the failures of the tailing dams happened very often worldwide. In the past 100 years, the severe failure rate has been increased to a frequency of 5 to 6 (Vogel 2013).

In July 2020, the Hpakan jade mine disaster was the deadliest mining accident in Myanmar, a heap of tailings collapsed into a lake after heavy rain, then a wave of mud and water was generated, resulting in at least 162 people died and 54 people being injured (Htet and Win 2020). In January 2019, there was a catastrophic tailing dam failure in Córrego do Feijão’s, Brumadinho, Brazil. The dam collapsed and released a mudflow leading to 259 people’s death and 19 billion dollars lost, the disaster also destroyed 133.27 ha of native Atlantic forest vegetation and 70.65 ha of permanent protection areas along watercourses (Thompson, de Oliveira et al. 2020). On 12 March 2014, another tailings dam failure has been found in the Tonglvshan mine in Hubei province, China. 200,000 m^3 were released, the flooding approximately 27 ha and at least 2 people dead (Wang, Yang et al. 2018). Historically more than 350 failures have been taken place in the world since 20^{th} and led to human mortality, enormous economic losses, and extensive environmental damage (Azam and Li 2010, Xu, Zhan et al. 2019).

Maintaining the tailing dams and ponds safe and stable are the most critical challenge tasks in the whole mining process. As the public is widely aware of the disaster and issue related to tailings, although the fewer cases showed that the tailings have been discharged directly to the ponds in the developing countries, this practice is no longer acceptable and heavily declined and banned in many countries under more strict monitoring and controlling (Zhang and Stana 2012, Samal, Ray et al. 2013). For example, the disposal guidelines for phosphate tailings were designed and established by the Florida Department of Environment Protection in the USA in 1993 (DEP rule: 62-673.220). The guideline indicated several modifications for using impoundment: 1) limited area for disposal; 2) leachate control;3) cooler ponds, surge ponds and perimeter drainage; 4) vegetation on the topsoil. This guideline did improve the tailings disposal management and limited the polluted content of slurry, however, it imposed only little impact on the larger land requirement and storage failure.

Much joint effort and cooperation, required from government department, design and construction units, and engineering supervision divisions, should be put forward in the future study and investigation for the tailing ponds and dams' stability and safety, to prevent the occurrence of tailing failure, instead of restoring and repairing after the accident. For example, reducing the contaminated solution from seepage when tailings are discharged (including neutralizing slurry, removing toxic chemical reagents and maxima heavy metal recovery); the tailings ponds should be designed with special attention in which any major factors need to be considered, such as site geological condition (hydrological environment), climate change situation (typhoon and heavy rain) and risk prediction (flood and mudslide); on the other hands, the topsoil of tailing dams should be stabilized by enhancing the specific vegetation for the maintenance (Lyu, Chai et al. 2019).

3.5 Contamination

Copper tailings are composed mainly of finer particles and enriched with sulfide minerals, which are easily oxidized and decomposed when exposed to oxygen conditions, water, and microbial species, making the harmful metallic solid more soluble and mobile. Acid mine drainage (AMD) is well known as another environmental concern of tailings due to the oxidation of reactive sulfide minerals, sulfuric acid and iron oxyhydroxides were generated in the oxidizing process, (Murphy and Strongin 2009, Elghali, Benzaazoua et al. 2019, Xu, Zhan et al. 2019). The detrimental outcomes are introduced by AMD such as 1) polluted groundwater; 2) interfered reproduction of plants and animals; 3) corroded public transportation like railway, subway and ships (Mohapatra and Kirpalani 2017, Park, Tabelin et al. 2019).

Mining direct influences groundwater and surface water through the discharged effluent or sewage to water resources and indirectly polluted through the leakage due to AMD. It is reported that the maximum concentration of arsenic in the groundwater was 1466 μg/L in Patna, India, in 2016, exceeding the guide value of 10 μg/L by World Health Organization (WHO) (Chakraborti, Rahman et al. 2016). Uranium is a major element because of its unique nuclear properties. Generally, the U components exist in groundwater through the dissolution of uranium minerals, according to WHO the concentration of U should be less than 30 μg/L in water resources, while the maximum concentration of U in groundwater has been reported of 50 mg/L in the City of Tuba, USA (Abdelouas, Lutze et al. 2000). The groundwater polluted by various heavy metals from tailings is a quite common concern in many countries of the world, such as India, Vietnam, Argentina, Chile, China, Cambodia, Mexico, and the United States (Bhattacharya, Frisbie et al. 2002, Mohapatra and Kirpalani 2017).

The environmental concerns from mine tailings placement and disposal are increasing and attracting international scientific and environmental attention. Currently, several recycling methods in different fields have been advocated. For example, 1) crusts or hardpans (Stumbea, Chicoș et al. 2019); 2) cemented paste backfill (Yao, Liu et al. 2019); 3) building materials (Kim, Lee et al. 2019); 4) agricultural fertilizer; 5) recovery metals (Gandarillas, España et al. 2019). The metals recovery is one of the promised reprocessing technologies since various valuable metals are left in mine tailings. Flotation is a physiochemical process to separate desirable metal from gangue owing to the differences in mineral surface properties in the pulp (Yin, Sun et al. 2017).

4 The Factors effects on the performances of flotation

Flotation has been widely concepted as an efficient and rapid technology to separate the valuable metal from gangue minerals, depending on the particle surface differences, namely hydrophobicity and hydrophilicity. Flotation has been used in mineral plants for processing a large number of metals, such as copper, zinc, lead, iron, nickel and antimony, etc, even non-metal matters, like coal, barite, etc. Due to the utilization of diversity of flotation, especially the multiplex and low grades minerals, this technology could be proposedly used in the reprocessing of tailings minerals (Wills and Finch 2015). However, the challenges presented by mineral and pulp properties, distinct reagents, and gangues are limited to the recovery of minerals.

4.1 Particle size

There is a large number of experimental data showing that flotation and recovery increase with particle size increased. However, most particles in tailing dams are fine or ultrafine, generally less than 50 μm, therefore, it is vital to investigate what is the flotation performance of such materials and how they influence recovery efficiency (Mackay, Videla et al. 2020). Several challenges concluded by current studies of fine or ultrafine particles, such as 1) deplete excessive collectors and frothers and even adsorb others chemically active particles because of the higher surface area (Feng and Aldrich 1999); 2) fine particles have lower collision efficiency with gas bubbles (Miettinen, Ralston et al. 2010); 3) recovery and grade decreased due to the entrainment of floatable and non-floatable particles and water recovery (Subrahmanyam and Forssberg 1988).

Table.1 Summary of the effects of particle size on the copper recovery and grade from the tailings

References	Grade %	Particle size d_{80} (μm)	Grade %	Recovery (%)
(Mackay, Videla et al. 2020)	-	220	1.1	45
(Yin, Sun et al. 2018)	0.45	22.4	19.42	84.58
(Mousavinezhad, Pourghahramani et al. 2018)	0.13	<37	2.7	52
(Mackay, Mendez et al. 2018)	-	225	-	46
(Lv, Wang et al. 2018)	0.57	<74	19.92	84
(Ai, Yan et al. 2018)	-	<74	-	92.28
(Lv, Ding et al. 2015)	0.21	<30	13.01	72.67
(Karimi, Vaghar et al. 2013)	0.716	<74	15.3	90.6

This work summarized the results of the particle size performances on the copper tailings flotation based on the presented papers, the copper recovery and grade were carried out as shown in Table 1. Most of the studies obtained a good copper recovery or grade though the particle size was fine or ultrafine, except for the two types of research (Mackay, Videla, et al. 2020) and (Mousavinezhad, Pourghahramani, et al. 2018) which investigated the relationship of particle size and froth stability. Studies have proved that the negative effects of fine or ultrafine particles could be overcome by other measures, for example

4) Higher impeller speed.

Finer particles would settle down or remain on the surface of valuable minerals in the pulp, on the contrary, rising bubbles would separate fine particles and prevent attaching minerals. At high stirring speed, fine particles and target minerals could be separated from each other due to the higher bubble rising velocity, leading to an increase in the collision possibility of bubbles and minerals (Rodrigues et al., 2001[Cilek, 2009 #82].

2）Fine foam frother

Larger bubbles are prone to trigger turbulence during the flotation when they rise more rapidly, decreasing the probability of bubbles and minerals collision. Small bubbles are expected to raise the possibility of bubble-particle collision, resulting from the larger surface area increasing the bubble’s loading capacity and gas holding-up time within the cell, despite they have a lower relative velocity. Frothers with fine foam were carried out by many studies, aerofroth 65, 70 and MIBC (methyl isobutyl carbonyl) were conducted in the flotation of copper tailings, the results showed that A65 produced finest foams and bubbles size became much smaller when increasing the dosage, and the least turbulence was found in the flotation cell, which thereby obtained the optimum recovery and grade of copper (Mousavinezhad et al., 2018; Tao, 2005).

5) Reducing solid percent

Distinguish from flotation and entrainment, the former is selectively extracted from the cell with rising bubbles, the latter is the process of recovery of both desirable minerals and gangue (Ahmed and Jameson, 1985). Therefore, entrainment is tending to decrease the recovery grade during flotation, especially in the processing of finer particles due to the lower sedimentation velocity. On the other hand, the bubble surface is rapidly filled with fine particles during the pulp containing higher percent solid and then removed from active mode by filling its loading capacity, impeding the copper particles further attach of rising bubbles. Therefore, decreasing the percent solids in the pulp is one of the methods to avoid particle entrainment, because fewer mineral particles are surrounded by fine particles (Mousavinezhad et al., 2018).

4.2 Reagent effects

4.2.1 Pyrite depressants

Copper sulfide and pyrite usually disseminate in the gangue minerals and even immerse as micro-grained particles in the tailings. Therefore, pyrite tends to be floated associated with copper from tailings leading to a decrease in copper recovery grade. Yang et al 2016 investigated that pyrite is depressed significantly with the pH increased from 9 to 12 (Yang, Tong et al. 2016), due to the hydrophilic $Fe(OH)_2$ formation on the surface of pyrite when pH is above 9. In addition, the production of elemental S and dissolution of iron sulfide are responsible for the increased recovery at the pH range of 5 to 9 (Göktepe 2002).

Lime is the most common pH modifier and pyrite depressant in copper flotation (Yin, Sun et al. 2018). However, the large dosage of lime could raise unfavorable concerns, such as 1) excess Ca^{2+} ions are adsorbed by molybdenite ores, observed by Ca concentration larger than the point of reversal of the zeta potential; 2) Ca^{2+} ions could be hydrolyzed to form $Ca(OH)^+$ in the higher pH, which nucleates and co-precipitate on the edges or the faces of minerals (Yin, Sun et al. 2018); 3) high alkaline environment also reduced the desirable Cu recovery. With the consideration of higher lime dosage, limited application (only for non-metallic minerals processing on the industrial scale), and the shortcoming discussed above, the alternative reagent of lime (pyrite depressant) should be put forward.

Humate salt, for example, according to the research by Lv (Lv, Wang et al. 2018), the results showed pyrite was depressed because ammonium humate was prone to be adsorbed chemically with iron to form stable polymeric, and achieved Cu recovery of 84% and a grade of 19.92. Therefore, the ammonium humate was a promising depressor for the processing of tailings containing copper and pyrite. Other organic depressors such as glycerine-xanthate, used for depressing pyrite from chalcopyrite was investigated by Dahongshan Copper Mine (Wang, Qian et al. 2015); Dextrin was also applied for pyrite depressant from sphalerite (Darban 2011); to control reagent cost, the combination of N-(Carboxymethyl) dithiocarbamic acid disodium salt (NDAD) and lime was adopted to depress pyrite (Yin, Sun et al. 2018). The mechanism involved in those organic depressants is hydrophilic functional groups like OH^+, $NH_3^{+,}$ and $COOH^-$ which were pre-adsorbed on the surface of pyrite to form a hydrophilic film, thus leading to separate pyrite from chalcopyrite.

Though the inorganic depressants showed the efficiency of the pyrite depress, the higher dosage and limited environmental and economical utilization are the main concern of applying on the industrial scale. Organic depressors have been considered more promising and favorable. However, the poor selectivity of organic polymers may depress all the sulfides during the flotation. Therefore, organic depressants still have a large gap in optimizing the production and development in the commercial and industrial scope.

4.2.2 Collectors

Xanthates are the most common collectors in the froth flotation of sulfide minerals (Bag, Das et al. 2011). The mechanisms of interaction between sulfide and xanthate have been carried out by many studies: physical and chemical adsorption, surface oxidation, and polarization (Woods 1971, Leppinen 1990, Roos, Celis et al. 1990). Various xanthates have been applied in copper recovery by tailings flotation, such as butyl xanthate; Potassium Amyl Xanthate (Z6), and sodium isopropyl xanthate (Z11). However, xanthates that possess poorer selectivity, and are easier to decompose should be replaced by other collectors. Alkyl thionocarbamate (AERO 3894) has the advantage of solution stability and lower operating pH, which was applied to recover copper against gangue and iron sulfide (Fairthorne, Fornasiero et al. 1996, Lv, Wang et al. 2018), the results showed that Cu recovery achieved 83.1%, as the dosage of Alkyl thiocarbamate was 48 g/t. Sodium salt carbonodithioic acid O-(1,3-dimethylbutyl) ester (COES) is another chalcopyrite collector which has a lower dosage and more selectivity in contrast to xanthate (Yin, Sun et al. 2018), in the optimal collector dosage of 30 g/t, the Cu concentrate grade of 5.21% with 81.2% recovery were obtained.

4.2.3 Activators

Cyanidation developed rapidly since 1887 when John Stewart MacArthur discovered that gold could be dissolved in ores by cyanide solution. The cyanide tailings are the solid residue that remained from plants when extracting gold or other minerals by cyanidation (Lv, Ding et al. 2015). However, the tailings could leave environmental and health risks to the local sources due to the toxicity, on the other hand, valuable metals contained in the residues, such as Cu, Pb, Zn, and Fe, means that the cyanide tailings could be the second resource to recycle. But the recovery of copper can be depressed in the presence of cyanide ions, Duke et al (Duke and Courtney 1952) have carried out the interaction between the copper and cyanide ions, the equations are as followed:

$$Cu^{2+} + 2CN^{-} \rightarrow Cu(CN)_2 \rightarrow CuCN + \frac{1}{2}CN_2 \tag{1}$$

$$CuCN + x\,CN^{-} \rightarrow Cu(CN)_{x+1}^{x-} \tag{2}$$

which further indicated that the hydrophobicity of chalcopyrite could be decreased by cyanide solution, therefore, it is imperative to remove the cyanide-free ions and complexes prior to retrieving valuable minerals. Various kinds of physical and chemical methods were reported for cyanide removal, including natural degradation, chlorination, ozonation, hydrogen peroxide, etc (Khodadad, Teimoury et al. 2008, Kuyucak and Akcil 2013, Han, Zhu et al. 2016). Sodium hypochlorite is an oxidizer to depress the adsorption of Cu(CN), $Cu(CN)_2^-$, and $Fe(CN)_6^{4-}$ on the copper sulfide surface. According to the results by Lv et al, (Lv, Ding et al. 2015) the total cyanide in the solution decreased from 0.37g/t to 0.14g/t with an increment of sodium hypochlorite, the oxidation reactions are as follows:

$$CN^{-} + OCl^{-} + H_2O \rightarrow CNCl^{-} + 2OH^{-} \tag{3}$$

$$2OH^{-} + CNCl^{-} \rightarrow CNO^{-} + Cl^{-} + H_2O \tag{4}$$

$$CN^{-} + OCl^{-} \rightarrow CNO^{-} + Cl^{-} \tag{5}$$

The collector has more possibility to contact with the activated surface of Cu mineral through the above chemical reactions, the results also showed that the copper recovery increased to 95.8% and the grade of 4.14. However, the excess of sodium hypochlorite inhibited the copper recovery, because the OH^- produced in equation 3 made the pulp more alkaline and combine with Zn^{2+} and Fe^{2+} to form a hydrophilic membrane on the surface of chalcopyrite. On the other hand, the element S was generated during oxidizing, then forming a hydrophobic layer to promote the copper flotation, while the S was oxidized to hydrophilic sulfate by the excessive activator.

Copper sulfate ($CuSO_4$) as another activator was adopted for depressing cyanide in the chalcopyrite flotation. The mechanisms involved in activation by copper sulfate were Cu^{2+} reduced to Cu^+ and oxidized S^{2-} to form specie Cu and O_{x}-S^{2-} on the surface of chalcopyrite, collector such as xanthate is adsorbed by these species thereby promoting the copper flotation (Deng, Wen et al. 2014). Yin et al (Yin, Sun et al. 2018) studied the concentration of copper sulfate on the effect of copper flotation. The results showed the copper recovery and grade achieved 85% and 5%, respectively, when the optimal activator dosage was 400 g/t. Another study showed similar results of activation by copper sulfate, which eliminated the depressant effect of cyanide ions, improved the collector (butyl xanthate) adsorption on the surface of chalcopyrite, and promoted the Cu recovery to 93% (Ai, Yan et al. 2018). Copper sulfate has been applied as an activator not only in the metal sulfide fields (like pyrite, sphalerite, and chalcopyrite), but in the non-metallic such as chlorites, lizardite, and quartz.

To Compare with $CuSO_4$, such stronger oxidants as hydrogen peroxide (H_2O_2) destroy the connection of CN^- and sulfide minerals. When moderate H_2O_2 participate in the activation, the equations are as follows (Qiu, Huang et al. 2015):

$$H_2O_2 + \frac{2}{3}Cu(CN) + \frac{2}{3}H^+ \rightarrow \frac{2}{3}Cu^{2+} + \frac{2}{3}OCN^- + \frac{4}{3}H_2O \tag{6}$$

$$H_2O_2 + \frac{2}{5}Cu(CN)_2^- + \frac{2}{5}H^+ \rightarrow \frac{2}{5}Cu^{2+} + \frac{4}{5}OCN^- + \frac{6}{5}H_2O \tag{7}$$

While excessive activator in the pulp, the hydrogen peroxide also oxidizes element S on the chalcopyrite surface to hydrophilic sulfate, the equations are as follows:

$$H_2O_2 + S^{2-} + 2H^+ \rightarrow S + 2H_2O \tag{8}$$

$$H_2O_2 + \frac{1}{3}S + \frac{2}{3}OH^- \rightarrow \frac{1}{3}\ SO_4^{2-} + \frac{4}{3}H_2O \qquad (9)$$

According to the results of Ai et al (Ai, Yan et al. 2018), the optimal dosage was 1,800 cm^3/m^3, the maximum Cu recovery was achieved of 84%, and the recovery decreased significantly when overdosage of activator, the equation 8-9 explained that the element S was oxidized led to decrease the hydrophobicity of chalcopyrite. Therefore, copper sulfate has much better activation effects than hydrogen peroxide on the cyanide copper sulfide.

4.2.4 Clays mineral behavior

Clays are phyllosilicates composed of a varying combination of stacked tetrahedral (T) and octahedral (O) sheets. The different ratios of T and O layers were gathered by strong hydrogen bonds to form various clays. T-O-T structure contains 2 tetrahedral sheets, bonded with one octahedral sheet, and are held together by weak Van der Waals force. Because of the T-O-T structure, talc ($Mg_3(Si_2O_5)_2(OH)_2$) comprises two different surfaces, the basal cleavage surface and the edge. The surface with Si-O-Si bonds exhibits hydrophobicity while the edge with the OH^- groups shows hydrophilicity. Muscovite (KAl_2 $(AlSi_3O_{10})(OH)_2$) also has a T-O-T structure, due to the isomorphic substitution of Si ions by Al ions, then balanced by interlayer K ions resulting in a T-O-T -K- T-O-T layer linked with another T-O-T -K- T-O-T (Farrokhpay, Ndlovu et al. 2018).

The presence of fine and ultra-fine gangue minerals, such as clay and talc, can depress the recovery of valuable metals from flotation (Castillo, Ihle et al. 2019). In addition, the content of clay is various and much higher in tailings, which pose deleterious effects on the froth flotation. The challenge of high content clay, for example, high slurry viscosity, foam barely generated, and few valuable minerals loads on the top of froth (Burdukova, Becker et al. 2008), has raised a topic of interest to the researchers and processing plants (Wang, Peng et al. 2015).

Most researchers attributed the performances of clay minerals to flotation. Due to the basal cleavage face surface occupying 90% of the talc surface and its hydrophobicity, making it is naturally floatable in the processing ores. Furthermore, clays consume more reagents in the pulp because of the high surface area, thereby decreasing the froth stability during the flotation. (Beattie, Huynh et al. 2006, Farrokhpay, Ndlovu et al. 2016, Farrokhpay, Ndlovu et al. 2018). On the other hand, the poor copper recovery from tailings was also because of mineral surface oxidation or contamination by gangue minerals. However, there is only tiny evidence or study about the behavior of gangue minerals on the copper tailings flotation. Desliming or removing the oxidized layer is an improvement in the copper recovery before discarding the tailings. Ultrasonic waves have been proved a promising technology to process the tailings that contained high content clays (Videla, Morales et al. 2016). It is explained that surface cleaning through fluid cavitation produced by ultrasound, results in the collectors effectively adsorbed on the cleaning particles surface.

5 Summary and recommendation

Copper was one of the first metals extracted and used. Copper social demand and supply have increased dramatically in the past decades. However, copper reserve decreased and the head grade deteriorated means that the disparity between demand and supply gets larger.

Copper is one of the few metals that could be recycled repeatedly without any loss of performance, studies showed that 35% of the demand is covered by copper recycling which significantly reduced the need for mining. Recycling has various environmental and economic benefits, such as 1) solid waste diversion, 2) reduced energy consumption and CO_2 emission when processing; 3) mineral conservation; 4) saving costs (Leblanc 2019). However, it is getting more difficult to collect and reprocess the complicated parts which contain copper, such as electronic scrap. Therefore, the idea of copper recycling should be implemented in the new design products of overall fields to facilitate the industry recycling process, on the other hand, regulations and policies should be formulated by the government to encourage the recovery and recycling process (Association 2017).

Resulting from the immature and inefficient technology, the accumulation of copper tailings by mining activity is still a serious matter, The susceptible tailings tams and ponds are designed for storage in the light of current techniques, but a host of environmental issues emerged around the tailing surrounding area. The environmental concerns raised by tailings have become more severe when tailings are discarded irrationally. Tailing impoundments experience failures more frequently due to a lack of appropriate management, regulation, and vegetation. Dust emission is another annoying concern when the dam's surface is weathered and corroded by wind or air. Furthermore, acid mine drainage is resulted from oxidized sulfidic minerals in tailings by natural weathering and chemical percolation, promoting the heavy metal released and permeated into the soil and underground water.

Different methods have been conducted on the tailings re-using and recycling over decades, such as cemented paste backfill, cementitious materials, ceramic substrates, etc. However, to reduce the environmental footprint, the content sulfur of tailings should be evaluated and eliminated before the processes. As an effective and widely used method, many studies have been proved that flotation not only reduces sulfur content but also owns higher efficiency in the process of lower grade minerals, improving the economic benefit of a mining company.

To date, only a few studies have reported copper recovery by hydrometallurgy from tailings, and even fewer for the froth flotation. An encouragement of deep learning and exploring in reprocessing tailings by flotation is proposedly served to reduce the environmental footprint and prevent people health from contamination such as acid mine drainage, especially in those places that possess a large quantity of tailing storages.

It is necessary to determine the type of tailings before the flotation, for example, the sulfide-rich tailings contain much higher sulfur minerals, while the copper slags contain mostly iron oxide, silicon oxide and other oxides. Different recycling and recovery processes should be formulated once the tailing types are determined, such as the apply reagents, grinding procedure, flotation parameters, etc.

Unlike the conventional copper flotation, much more fine or ultrafine particles contained in tailings deteriorate the copper sulfide floatability. Various methods have been studied to improve the copper recovery, such as increasing the stirring speed, changing frothers with finer foam, and reducing solid percent. Grinding also affects sulfide mineral exposure, but more fine particles are generated during the process as well. Therefore, the type of mill, a grinding parameter such as time, atmosphere, dry or wet condition and activity of griding media should be paid more attention to.

It is well known that the chemical reagents, like depressants, activators, and collectors, are also a significant factor that determines copper recovery. However, the common pyrite depressant lime is limited in application. Organic matters which own lower cost and higher efficiency are conducted in many studies, but less selectivity is the principal shortcoming in the mineral process.

Clay and talc are contained in the copper tailings that define as gangue minerals, the poor copper recovery was because of mineral surface oxidation or contamination by gangue. Desliming and removing the oxidized layer are methods to eliminate the gangue effects and improve copper recovery.

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