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The effect of water chemistry on froth stability and surface chemistry of the flotation of a Cu–Zn sulfide ore

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ABSTRACT

Water shortages have a direct impact on the life of many mining and mineral processing operations. Therefore, a good understanding of the effects of water quality on flotation performance is essential. In this study, effects of dissolved ions (both anions and cations) were investigated on the flotation performance of a Cu-Zn complex sulfide ore from Çayeli Bakır İşletmeleri A.Ş. (CBI) (Turkey) by means of batch flotation tests. The results of the flotation tests revealed that accumulation of dissolved metal ions and sulfide ions, mainly in the form of SO_4^{2-} and $S_2O_3^{2-}$, changed both the froth stability and surface chemistry of the sulfide minerals. The froth stability and hence the recovery by entrainment, increased in conjunction with the dissolved ion concentration in water. The presence of dissolved metal ions, such as Cu^{2+} and Pb^{2+}, also increased the flotation rate and recovery of sphalerite. In the case of pyrite, the activation by dissolved metal ions was observed for moderately contaminated recycled water samples. High concentrations of sulfide ions however, counteracted the activation effect and reduced the recovery of pyrite by true flotation.

1. Introduction

Managing water resources has become an increasingly important issue in the world because it is closely related to the quality of human life and environment. Therefore, water reuse is a growing practice in many regions of the world, even in those countries that have not typically been considered to have problems with water scarcity.

A number of research works have focused on the treatment and utilization of recycled process water in mineral processing. In general, the recycled process water can be classified, treated and disposed selectively, and then returned to different sections of flotation operations according to its effect on mineral surface reactions. Such a method could enhance the efficiency, and utilization of wastewater, therefore greatly decreasing costs (Broman, 1980; Forssberg et al., 1985; Rao and Finch, 1989; Basilio et al., 1996; Leavay et al., 2001; Wei et al., 2006).

In mineral processing plants, the process water is recycled from the tailings dams, thickener overflows, dewatering and filtration units. Typical contaminants in the recycle water are the colloid materials (silicates, clays, precipitated metal hydroxides, etc.), ions of base metals, thiosalts, sulfide, sulfite, sulfate, chloride, magnesium, calcium, sodium and potassium, as well as residual reagents such as frothers, collectors and depressants. The recycled water, particularly the water recycled from thickeners, dewatering and filtration units, have increased levels of total dissolved ions and solids (Leavay et al., 2001; Johnson, 2003; Slatter et al., 2009). In these streams, the dissolved ions, suspended solids and flotation reagents have insufficient time to decompose and precipitate. In this case, the concentration of the contaminants can adversely affect flotation performance.

The effect of dissolved ions in recycled water on flotation performance has been investigated by a number of researchers for various ore types. Lui et al. (Lui et al., 1993) reported that the presence of calcium ions and thiosalts improved Cu flotation in a Cu/Zn ore by enhanced depression of pyrite. Kirjavainen et al., (Kirjavainen et al., 2002) showed that the addition of calcium and thiosulfate ions improved copper and nickel floatability after grinding in a steel mill, but resulted in depression of copper and nickel after grinding in a ceramic mill. Activation after steel milling was attributed to the galvanic interactions that occurred. Although, there is limited agreement on the electrochemical mechanisms, a number of researchers have shown the depressing effect of sulfite ions on galena, pyrite and sphalerite (Peres et al., 1981; Yamamoto, 1980; Wang and Forssberg, 1990). Haran et al. (Haran et al., 2008) investigated the effect of triple recycled water on the accumulation of dissolved ions in the recycle water on flotation of copper tailings from the Benambra Mine. An accumulation of organic and inorganic species was observed after using the triple recycled water. This had a detrimental effect on flotation performance.

An accumulation of both organic and inorganic ions in the process water may also affect the froth stability in flotation. A poorly mineralized or over stabilized froth phase could form depending on the type

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Table 1
Characteristics of recycle process water in CBI Flotation Plant.

	Cu (ppm)	Zn (ppm)	Fe (ppm)	Ca (ppm)	Mg (ppm)	Cl^- (ppm)	NO_3– (ppm)	SO_4^{2-} (ppm)	$S_2O_3^{2-}$ (ppm)	Total
Cu recycle Process water	0.54	0.07	0.08	222.5	1.7	5.65	10.64	334.69	341.28	917
Zn recycle Process water	0.02	0.11	0.12	333.7	0.01	4.29	11.35	228.57	16.88	595

and concentration of dissolved species in the recycled water (Rao and Finch, 1989; Castro et al., 2010; Muzenda, 2010). At high electrolyte concentration, bubbles become stable and do not coalescence even in the absence of frother. It has been reported that bubble size measured in saturated brine solutions and seawater without frother and in distilled water at high frother concentrations were similar. Hence, both froth stability and flotation rate increases in solutions containing high concentrations of dissolved ions. However, Kurniawan et al. (Kurniawan et al., 2011) have shown that the enhancement in the flotation performance depends on the type and concentration of the salt. This was attributed to the differences in ion specificity (size and polarizability) of different salts at high concentrations.

In this study, the effects of dissolved ions in process water were investigated on the flotation performance of a Cu-Zn ore from Çayeli Bakır İşletmeleri (CBI) (Turkey) by means of batch flotation tests using synthetic water samples. It is well known that the recycled water becomes progressively more contaminated over time and results in an accumulation of dissolved ions in process water due to the oxidation/dissolution of the sulfide minerals and repeated reagent addition (Laskowski and Castro, 2008; Rey and Raffinot, 1966). Therefore, synthetic water samples were prepared with increasing concentrations of cations (Cu^{2+}, Fe^{2+}, Zn^{2+}, Pb^{2+}) and anions (SO_4^{2-} and $S_2O_3^{2-}$) to simulate the effects of water recycling. The combined effects of the dissolved ions both on froth stability and activation/ depression of the sulfide minerals were discussed.

2. Material and methods

2.1. Flotation tests

A complex Cu-Zn sulfide ore from Çayeli Bakır İşletmeleri A.Ş. (CBI) in Turkey, was used for batch flotation experiments. The main copper mineral is chalcopyrite that is associated with sphalerite, pyrite and minor amounts of galena. The ore contains 3.63% Cu, 4.07% Zn, 0.39% Pb and 25.07% Fe. Approximately 30% of the ore is composed of the non-sulphide minerals, mainly quartz and barite (Ekmekçi et al., 2010).

A representative ore sample was taken from the feed belt of the primary ball mill of the Çayeli Flotation Plant and crushed down to 2 mm using roll crushers. The sample was then split into 1.150 kg batch samples for the flotation experiments and stored in vacuum sealed bags to prevent oxidation of the sulfide minerals. Samples were milled to 80% finer than 38 μm in a ball mill at 60% w/w pulp density just prior to flotation. The flotation tests were then performed at 30% pulp density using a modified 3 L Leeds flotation cell. 30 g/t diisobutyl phosphinate (Cytec 3418A) and 15 g/t MIBC were used as the collector and the frother respectively. The impeller rotation speed and air flow rate were set at 1200 rpm and 3 lt/min respectively. The froth was scrapped manually at 10 second intervals and four concentrates were collected after 0.5, 1.5, 3.5 and 7.5 min of flotation. The mass and water recovery data was also recorded. The froth depth was kept constant at 2 cm by addition of synthetic water during the entire flotation test. The same flotation conditions were applied for all of the tests. Feed, concentrate and tails samples were then analyzed for Cu, Fe and Zn using AAS analysis.

In order to investigate effects of the chemistry of the recycle water on Cu flotation of the Cayeli Cu-Zn ore, four different synthetic recycle process water samples were prepared. Since the circulation of the process water results in a gradual build up of reagents and all dissolved products in the water, the synthetic recycle water samples were prepared accordingly to simulate the real conditions of the Cu and Zn recycle process water streams at the Çayeli Flotation Plant as determined by AAS and Ion Chromatography (equipped with an Ion Pack AS9-HC Model anion column, Table 1). The synthetic water samples were prepared using various salts containing Cu^{2+}, Fe^{2+}, Zn^{2+}, Pb^{2+}, Ca^{2+}, SO_4^{2-} and $S_2O_3^{2-}$ ions. The ionic concentration of the synthetic water samples is given in Table 2. For the four synthetic water samples, the concentration of the dissolved ions increased gradually from Water 1 to Water 4. Water 1 has a similar composition to Çayeli Cu recycle process water.

Although, ferrous iron was also added to the water, e.g. 1 ppm in Water 1 and gradually increased to 8 ppm in Water 4, very little ferrous iron was detected in the recycle water because of the precipitation of ferric hydroxide. Similarly, most of the Pb and Ca ions added to the synthetic water precipitated out and very little remained in ionic form. The precipitates were then separated from the water used in the flotation tests. In spite of some precipitation of Fe, Pb and Ca, the characteristics of the synthetic recycle water samples were considered suitable to simulate the influence of the existing recycled water in the plant and also accumulation of ions in the water (Table 2).

2.2. Data analysis

There are two main recovery mechanisms, namely recovery by true flotation and entrainment that determine the overall recovery and concentrate grade in flotation. The effect of various ions in process water may change both the surface state of the particles and froth phase. While the changes in the surface state, i.e. the degree of hydrophobicity, affect the recovery by true flotation, changes in froth phase will affect the amount of entrainment. Therefore, the contribution of true flotation and entrainment to the overall recovery was decoupled in this study in order to evaluate the effects of water chemistry on mineral activation-depression and froth stability.

The degree of entrainment was calculated using Eq. (1). This was done using the non-sulfide minerals (mainly quartz and barite) as tracer minerals that were evaluated on an unsized basis. For the

Table 2
Ionic concentration of tap water and artificially prepared recycle water samples.

	Cu ppm	Fe ppm	Pb (ppm)	Zn ppm	Ca ppm	SO_4^{2-} ppm	$S_2O_3^{2-}$ ppm	Total Ion (ppm)
Tap water	0.01	0.03	0.02	1.36	82	256	n.a	340
Water 1	0.92	n.a	0.13	1.55	308	281	400	991
Water 2	1.72	0.01	0.26	2.83	576	329	796	1706
Water 3	3.46	0.05	0.71	4.70	1040	432	1787	3269
Water 4	6.90	0.33	2.06	9.55	2037	461	2748	5264

n.a.: below detection limit.