



Flotation of copper sulphide from copper smelter slag using multiple collectors and their mixtures



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ABSTRACT

Present work focuses on the differences in the performances obtained in the froth flotation of copper smelter slag with multiple collector viz. sodium iso-propyl xanthate (SIPX), sodium di-ethyl dithiophosphate (DTP) and alkyl hydroxamate at various dosages. Flotation tests were carried out using single collectors as well as various mixtures of the two collectors at different but constant total molar concentrations. Flotation performances were increased effectively by the combination of collectors. The findings show that a higher copper recovery (84.82%) was obtained when using a 40:160 g/t mixture of sodium iso-propyl xanthate (SIPX) with di-ethyl dithiophosphate compared to 78.11% with the best single collector. Similar recovery improvement (83.07%) was also observed by using a 160:40 g/t mixture of sodium iso-propyl xanthate (SIPX) with alkyl hydroxamate. The results indicate that in both cases DTP and alkyl hydroxamate played important role as co-collector with SIPX for the recovery of coarse interlocked copper bearing particles and has an important effect on the behaviour of the froth phase. However, comparatively higher mass recovery was obtained when hydroxamate was used as a co-collector, accompanied by poorer copper grades. In this context the co-collector DTP is advantageous for the improvement of copper grade and recovery from copper smelter slag.

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1. Introduction

Copper slag is produced during pyrometallurgical production of copper from copper ores. For every tone of metal production about 2.2 t of slag is generated. Dumping or disposal of such huge quantities of slag cause environmental and space problems. During the past two decades attempts have been made by several investigators and copper producing units all over the world to explore the possible utilisation of copper slag. Utilisation and recovery of metal depend on the type of slag. Current options of management of this slag are recycling, recovering of metal, production of value added products and disposal in slag dumps or stockpiles.

In general, the main components in the copper slags are Fe and Si. They amount to 25 to 40% each. Slags usually contain reasonable quantity of valuable metals. Almost all copper slag contains a considerable amount of Cu (0.5 to 3%). They can be treated as secondary resource of metals, rather than an end-waste. Various methods for copper recovery from the copper slags were reported with attention given to beneficiation, pyrometallurgical, hydrometallurgical, and mixed pyro and hydrometallurgical processes. However, among the various processing method, physical separation by froth flotation is widely

applied and some researchers considered flotation as an effective method to recover copper from slag.

Understanding the slag mineralogy and associations of copper in the flotation feed is crucial to optimise operations. Changes in mineralogical composition influence mineral recovery, reagent choice and also help in identifying and explaining possible processing challenges. Lack of accurate mineralogical characterisation of copper slag often leads to low copper recovery. Froth flotation has been utilised over the years in pre-concentrating copper. Even with this technique, there are still some discrepancies in copper recoveries due to the difficulty in selecting the right reagents to impart hydrophobicity to this valuable metal phase. Therefore, for an improved copper recovery by flotation, it is ideal to have a considerable understanding of mineralogy and association of copper in the flotation feed. The mineralogical characterisation should be able to identify the copper-bearing minerals, show how the copper particles are distributed in each fraction and also to show how copper particles are associated with the gangue minerals. Hydrophobicity of copper can be enhanced by the addition of generic collectors for sulphide minerals such as xanthate and dithiophosphates or specific collector for oxide copper minerals such as hydroxamate etc.

Thiol collectors were used in the froth flotation of copper sulphide from the slag. The xanthates, dithiophosphates are classes of thiol collectors that each form different surface products on different copper sulphide minerals. It has been shown that the use of mixtures of thiol

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collectors can have benefits over the use of pure collectors (Bradshaw, 1997; Bradshaw and O'Connor, 1996, 1994; Bradshaw et al., 1998; Heilbig et al., 2000; Rao and Forrsberg, 1997). The use of mixtures is sometimes proposed to produce a synergistic effect. These benefits include lower dosage requirements, improved selectivity, rates and recovery and an increase in the recovery of coarse particles. It has been proposed that these benefits derive from the differences in the behaviour of the thiol collectors on mineral surfaces (Bradshaw and O'Connor, 1996). Bradshaw and O'Connor (2000) and Lotter and Bradshaw (2010) have reviewed many reports, where it has been suggested that such interactions are occurring. It is however often not immediately clear if it is correct to deduce a synergistic effect when mixtures of reagents are shown to result in an unexpected increase in flotation performance. For example, Mingione (1984) investigated the effect of various mixtures of the collector di-iso-butyl dithiophosphate (DTP) and sodium iso-propyl xanthate (SIPX) on an ore that contained platinum group metals (PGMs) and reported that the optimum PGM recovery was obtained with an approximately 70% di-iso-butyl DTP/30% SIPX and attributed the improved results to a collector-collector synergistic interaction.

Valdiviezo and Oliveira (1993) proposed a "more favourable arrangement" of the adsorbing species in a study using a 3:1 ratio of xanthate to oleate. Hanson et al. (1985) used a binary xanthate-glycine system, the glycine encouraged greater adsorption of the xanthate due to the formation of metal glycinate complexes, which react with the xanthate and finally adsorb on the mineral surface. However, it is known that xanthate will adsorb in multiple layers onto a mineral surface and seems to need little encouragement from a co-collector (Goh et al., 2008). Plaskin and Zaitseva (1960) applied radiographic means to quantify the surface distribution of collector molecules. They found that when using single collectors, an increase in dosage did not necessarily result in an increase in the surface coverage of the particles.

McFadzean et al. (2012) showed that mixtures of ethyl xanthate with diethyl dithiophosphate or ethyl dithiocarbamate resulted in large improvements in flotation rate and recovery with pure galena in a microflotation cell. Although the microflotation cell provides valuable insights into the hydrophobicity of the particle-collector pair by indicating how many particles rise to the launder and are collected, it does not include the froth phase effects which are of critical importance in the industrial flotation process. It has been observed that some collectors have frothing properties. Sodium di-isobutyl dithiophosphate was introduced in the South African platinum industry in the 1970s as a co-collector and because of cost savings on frother consumption due to its frothing properties (Lotter and Bradshaw, 2010). The frothing properties of this collector have been ascribed to the presence of residual isobutyl alcohol from the manufacturing process.

Wakamatsu and Numata (1979), used a mixture of butyl xanthate and butyl DTP in the flotation of galena, showed that the DTP adsorbed preferentially from the mixture but this did not affect the mass loaded onto bubbles. Adkins and Pearse (1992), in a study of the flotation of a mixed copper sulphide/oxide ore, showed that a mixture of isopropyl xanthate and dicresyl DTP resulted in enhanced rates and recoveries of copper.

Synergistic effects in flotation were also reported by Finch and Smith (1972). They observed that mixtures of surfactants can cause a greater lowering of surface tension than that predicted for each component in the mixture due to a chemical interaction between the components in the mixture. It should be mentioned that there has been no evidence of any significant chemical interaction taking place between the many different mixtures of thiols studied to date.

The use of alkyl, arylaryl or alkylaryl hydroxamates in the flotation of minerals that chelate with hydroxamate is also known in the industry (Nagaraj, 1988). Hydroxamates are powerful collectors in flotation due to their ability to selectively chelate at the surfaces of minerals that contain titanium, copper, yttrium, lanthanum, cerium, niobium, tantalum, tin, iron and manganese. Mixtures of minerals containing

copper and iron have been successfully beneficiated by flotation using hydroxamates as the collector (Peterson et al., 1965; Fuerstenau et al., 1967). In the United States flotation of chrysocolla and hematite with *n*-octyl hydroxamates and some applications in platinum group metal flotation were studied (Peterson et al., 1965; Fuerstenau et al., 1967; Fuerstenau and Peterson, 1969; Nagaraj, 1992). Evrard and De Cuyper (1975) found the use of alkyl hydroxamates for floating copper-cobalt ores in Africa. Since the latest mining boom over the last few years, many copper oxide deposits have become economically viable for operation and interest has been generated in using alkyl hydroxamates where traditional processing techniques using sulphidisation have failed to produce consistent plant recoveries. Several operations are currently using the alkyl hydroxamates across the world.

In present work, flotation process was applied for the recovery of copper value from copper smelter slag which is generated from Birla Copper Smelter in Dahej, Gujarat situated in western part of India. This paper discusses the differences in the performances obtained in the froth flotation of copper smelter slag with selected collectors such as sodium iso-propyl xanthate (SIPX), Sodium di-ethyl dithiophosphate (DTP) and alkyl hydroxamate at various dosages and the mechanisms responsible. It also evaluates the effectiveness of adding sodium di-ethyl dithiophosphate (DTP) to sodium isopropyl xanthate (SIPX) as a co-collector and the effect of adding of alkyl hydroxamate to sodium isopropyl xanthate (SIPX) as a co-collector in the flotation of a copper slag with a view to investigating whether there was any evidence of a synergistic beneficial effect resulting from the use of the mixture. Flotation tests were carried out using single collectors as well as various mixtures of the two collectors at different but constant total concentration.

2. Material and methods

Copper slag sample containing 1.9% Cu, 51.58% Fe and 12.15% Si was used in this study. The slag was collected from Birla Copper Dahej, Gujarat, India for characterisation and beneficiation studies. The sample was crushed to pass 300 μm size and wet sieved into different size fractions (in micrometre), viz., $-300 + 210$, $-210 + 150$, $-150 + 75$, $-75 + 38$ and $-38 \mu\text{m}$ size. Polished sections of the different size fractions were prepared as per standard section preparation technique. The polished sections were studied by using Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN) (M/s. Intellection Pty. Ltd., Australia). The mode of scanning of the polished sample blocks in QEMSCAN instrument was Trace Mineral Search mode. Mineral chemistry was determined by spot analysis on minerals by Energy Dispersive Spectrometer (EDS) attached to Scanning Electron Microscope. The QEMSCAN is an extremely versatile SEM-based automated mineralogical analysis system. It provides a rapid, digital, quantitative morphological and mineralogical analysis of samples. The system scans population of particle with the electron beam at a pre-determined resolution (from 0.2 μm upwards). The resulting X-ray and backscattered electron signals are then compared with a comprehensive "look-up" table of known minerals and chemical phases to produce a mineralogical identification. Data output is very comprehensive and typically includes quantitative modal mineralogical data to trace mineral levels, calculated chemistry, mineralogical association and liberation data, together with mineralogical maps of the sample. QEMSCAN work was carried out at The Institute of Minerals and Materials Technology, Bhubaneswar, India. Chemical analyses of slag samples were done using X-Ray Fluorescence spectroscopy (XRF).

All batch flotation studies were carried out using lab scale Denver D-12 flotation cell. Slag samples were ground to d_{80} of 75 μm microns particle size and subjected to froth flotation. Impellor speed was kept constant at 1000 rpm. The flotation experiments were performed at 9 pH.

Sodium iso-propyl xanthate (SIPX), Sodium di-ethyl dithiophosphate (DTP) and alkyl hydroxamate are the three collectors used in this study.

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