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Flotation separation of copper sulphides from arsenic minerals at Rosebery copper concentrator

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ABSTRACT

The removal of arsenic bearing minerals from concentrates is becoming more important as environmental laws become ever stricter with regard to smelter emissions. The onus is shifting to concentrate producers to remove these minerals from their product, with penalties applying to materials containing greater than background amounts.

The arsenic content of Rosebery copper flotation feed is mainly present as arsenopyrite (FeAsS), containing approximately 46.0% arsenic with the remainder of the arsenic in copper sulphosalts (tennantite ($Cu_{12}As_4S_{13}$)), in a solid solution series with tetrahedrite ($Cu_{12}Sb_4S_{13}$). Tennantite contains approximately 20.3% arsenic. Characterisation of the rougher and cleaner concentrates obtained during a plant survey showed that the arsenopyrite was appropriately rejected in the copper flotation circuit. However, tennantite showed similar flotation behaviour to the copper sulphide minerals so that the high arsenic content of the final copper concentrate was mainly in the copper sulphosalts. In this study, regrinding the copper rougher concentrate was investigated to reject tennantite in cleaner flotation. It was found that although finer grinding increased the mass fraction in the ultrafine fraction, the tennantite liberation only increased slightly. The copper selectivity against arsenic was improved significantly although the recovery of copper, silver and arsenic was lower. The difference in floatability of copper sulphide minerals and tennantite appears to increase at finer sizes. In this study, pH and Eh were also manipulated to further improve the selectivity of copper flotation against tennantite at fine particle sizes with some promise. In order to find an application in the Rosebery circuit, any changes must have a net economic benefit and the trade-offs and implications are discussed in this paper.

1. Introduction

1.1. Arsenic problems in copper flotation

As metal reserves around the world, and existing mines, get deeper, ore mineralogy is becoming increasingly more complex. In addition, penalty elements such as arsenic, antimony and bismuth are occurring in increasing concentrations. These are highly toxic inorganic pollutants and can cause serious environmental and human health problems. Stringent regulations on smelting emissions are leading to increases in penalty rates for these elements such that many flotation concentrates become difficult to sell to smelters.

Arsenic minerals pose a problem for copper flotation concentrates since they are often associated with copper minerals, display similar flotation behaviour to copper minerals and therefore report to final copper flotation products. Despite extensive research, the rejection of arsenic minerals in copper flotation is still a challenge.

Arsenic sulphide mineralogy in copper deposits has been reviewed by Long et al. (2012). A range of arsenic minerals including arsenopyrite, tetrahedrite, tennantite and enargite occur in various copper deposits in the world. Rejection of arsenic minerals in sulphide flotation has been reviewed by Ma and Bruckard (2009), Plackowski et al. (2012). In general, pre-oxidation of flotation pulp and Eh control during flotation are promising options to separate arsenic from other sulphides.

Pre-oxidation of flotation pulp utilizes the different floatability of arsenic and other valuable minerals after reacting with oxidizing

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agents. Menacho et al. (1993) found that enargite was more resistant to oxidation than chalcopyrite and therefore a pre-oxidation procedure using sodium hypochlorite at pH 11.5 selectively floated enargite while depressing chalcopyrite. Similarly, Huch (1994) used hydrogen peroxide to preferentially oxidise and depress chalcocite while floating enargite. Other researchers such as Fornasiero et al. (2000) and Byrne et al. (1995) also used pre-oxidation to separate copper sulphide minerals from arsenic minerals, but they found that arsenic minerals were more oxidised resulting in depression in the flotation of copper sulphide minerals. For example, by using XPS analysis, Fornasiero et al. (2000) found that enargite and tennantite were oxidised more readily than chalcocite, covellite or chalcopyrite and the copper–arsenic oxides were more stable than non-arsenic containing copper oxides as they measured them in EDTA solutions. In the study by Byrne et al. (1995), the addition of hydrogen peroxide depressed tetrahedrite while chalcopyrite maintained its floatability. These inconsistent reports in literature may be caused by impurities associated with these arsenic and copper minerals that modify the electrochemical properties of minerals. Meanwhile, these studies did not take into account the galvanic interaction between arsenic and copper minerals which determines anodic oxidation and cathodic reduction on mineral surfaces when they are contacted.

Eh control during flotation exploits differences in the flotation response of arsenic and copper minerals at particular pulp potentials. A number of studies demonstrated that enargite flotation is strongly Eh dependent. However, as outlined by Ma and Bruckard (2009), there is a disagreement on enargite flotation at high pulp potential regions. Like Heyes and Trahar (1979), Kantar (2002) found that enargite flotation reached the maximum between 0.15 and 0.27 V (SHE), and then decreased significantly at lower or higher potential values. However, Guo and Yen (2005) and Senior et al. (2006) did not observe the strong depression of enargite at the higher Eh region. Ma and Bruckard (2009) indicated other significant disagreements on the effect of Eh on the flotation of chalcopyrite as well. Despite these disagreements, Eh control has been applied to separate arsenic from copper minerals. Smith et al. (2012) reported some case studies by using pulp potential control to separate copper and arsenic. In one case, tennantite was floated from the other non-tennantite copper minerals (bornite and chalcopyrite) between −200 and −130 mV (SHE). Arsenic recovery in this region was between 80% and 90% while the recovery of non-tennantite copper minerals was about 30%. In another case reported by Smith et al. (2012) there was little recovery of either arsenic (tetrahedrite/tennantite) or non-arsenic copper (chalcopyrite) minerals at reducing potentials. There was, however, a window at +400 mV to separate arsenic and non-arsenic copper minerals where 80% of the non-arsenic copper and only 25% of the arsenic were recovered.

Previous studies on either pre-oxidation of flotation pulp or Eh control during flotation reveal the complexity of selective separation of arsenic from non-arsenic copper minerals and a straightforward method to achieve the separation is not available. In this study, the flotation behaviour of arsenic and copper minerals was examined at Rosebery copper concentrator based on which methodologies may be developed to control the amount of arsenic into the final copper concentrate.

1.2. Rosebery copper concentrator

The Rosebery comminution circuit has three stages of crushing followed by two stages of closed circuit grinding, utilising mild steel grinding media. Classified slurry from the grinding circuit is dewatered in a flotation feed thickener from where feeds a three stage copper–lead–zinc sequential flotation circuit. The copper flotation section produces a copper concentrate through two stages of flotation as shown in Fig. 1. Flotation reagents are added through the conditioning tank, TKF2. Cytec's Aerofloat, a dithiophosphate, is used as a collector and Interfroth 63 is added as a frother. Sodium meta-bi-sulphite (SMBS) is added to control lead and zinc levels in copper concentrate. All reagents are added to the head of the rougher, there are no reagents added along either flotation bank. A single stage rougher-scavenger, (LF8), reports to a single stage cleaning circuit (LF13), while cleaner tails recirculate back to the head of the roughers via TKF2. There is no pH modification following grinding. Rougher flotation is carried out in the range of pH 8.0–8.5 which drops to 5.0–6.0 in the cleaner circuit.

From Woodcock (1980), the composition of "tetrahedrite" in the Rosebery ore is 4.4% Zn, 4.0% Fe, 36.4% Cu, 20.8% Sb, 5.7% As and 4.6% Ag. The silver content of this mineral poses a potential economic dilemma. Depression of the arsenic in tetrahedrite/tennantite will result in a loss of both copper and silver.

2. Experimental details

2.1. Plant survey

Flotation behaviour of arsenic and non-arsenic copper minerals was investigated through a complete survey conducted at the Rosebery copper circuit. Pulp and concentrate samples were taken from each cell. Concentrate samples were assayed for a variety of elements, including Cu and As. The pulp samples were used to measure the chemical conditions in the copper circuit, specifically pH, Eh and DO.

2.2. Laboratory grinding and flotation tests

Flotation behaviour of arsenic and non-arsenic copper minerals at finer sizes was investigated by grinding and flotation tests conducted in the on-site laboratory at Rosebery on samples taken from the copper rougher concentrate stream.

The average assay of the copper rougher concentrate was 9% Cu, 3600 ppm As and 1900 ppm Ag. The size distribution of the copper rougher concentrate is shown in Fig. 2. 80% of the particles were smaller than 30 μm.

The sample was filtered first and 300 g was ground in a sand mill using 200 g of 2 mm ceramic media. Grind establishment tests determined the time required to produce a P80 of 20 and 10 μm from the copper rougher concentrate at a P80 of 30 μm. The grind establishment determined that 15 and 45 min of grinding were required to produce the desired P80 of 20 and 10 μm, respectively.

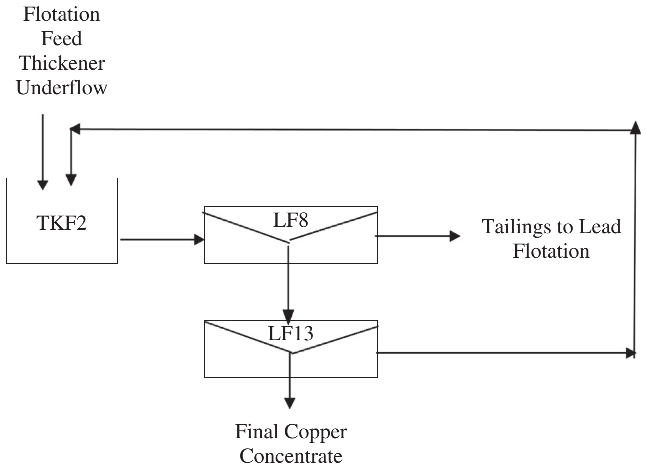

Fig. 1. A diagrammatical representation of the Rosebery copper flotation circuit.