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Mitigation negative effects of thiosulfate on flotation performance of a Cu-Pb-Zn sulfide ore

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ABSTRACT

Thiosulfate ions are formed during processing of sulfide ores. They have a detrimental effect on flotation resulting in recovery and selectivity problems. In this work, removal/management of thiosulfate ions during flotation of a Cu-Pb-Zn sulfide ore was investigated and discussed in detail. Batch scale flotation tests were performed by using synthetic water samples of different chemical composition. Evaluation of froth stability, metal recovery and selectivity showed that presence of thiosulfate ions resulted in depression of the sulfide minerals. Oxidation of thiosulfate by hydrogen peroxide (H_2O_2) was applied to remove/minimize the adverse effects on flotation. H_2O_2 was added to process water and concentration of thiosulfate ion was decreased down to acceptable levels for flotation. H_2O_2 oxidized majority of thiosulfate ions to sulfate form. Increase in sulfate ion concentration influenced froth stability, but not the flotation performance which was restored after water treatment.

1. Introduction

In the processing of sulfide ores, thiosalts are produced by the oxidation of sulfide group (e.g., pyrite, FeS_2 and pyrrhotite, FeS) by oxygen. They occur as partially oxidized sulfoxy anions like thiosulfate ($S_2O_3^{2-}$), trithionates ($S_3O_6^{2-}$), and tetrathionates ($S_4O_6^{2-}$), these anions are metastable species and oxidize or disproportionate to more stable sulfate (Williamson and Rimstidt, 1992; Rao, 2011).

Thiosalts represent a delayed acid producing capacity in mill effluents. They reduce pH and increase metal and solid concentration. As a results of that thiosalt anions hinder the action of mineral collector and act as depressant (Rao, 2006).

Shengo et al. (2014) reported that recovery of copper and cobalt in flotation of an oxidized ore decreased due to the presence of thiosulfate ions in recycled process water. Thiosulphate ions consume dissolved oxygen through oxidation to polythionates and sulphates (González-Lara et al., 2009). In sulphidization process, depletion of oxygen slows down the action of sulphidizing agent through generation of excess hydrogensulphide ions, which hinder collector adsorption. Thiosulphate ions are known as strong reducing agents reacting with the dissolved ions from the mineral surface and easily forming more stable complexes than those with metal xanthates (Bulatovic, 2007). The reduction in collector adsorption through competition with thiosulphate ions results in a decrease in mineral recovery.

It is clear that thiosalts influence surface characteristics of sulfide minerals and decrease flotation recovery. In this study, influence of thiosulfate ions on flotation performance of a Cu-Pb-Zn sulfide ore was investigated. In the first phase of the study, batch scale flotation tests were performed by using synthetic water samples of different chemical composition and effects of thiosalt on flotation performance was demonstrated. Mass pull, water recovery, grade and recoveries of Cu, Pb, Zn and pyrite were measured to show the effect of water constituents on flotation.

In the second phase, the process water was treated by hydrogen peroxide to decrease the thiosulfate level. Thiosalts can be oxidized to sulfate by oxidants such as hydrogen peroxide. Addition of H_2O_2 to water at a molar H_2O_2:S_2O_3 ratio of 1–1.5 removes thiosulfate to safe levels for flotation (Kuyucak, 2014). Flotation tests were also performed with treated process water to demonstrate influence of water treatment on flotation performance.

2. Materials and methods

2.1. Flotation tests

A Cu-Pb-Zn sulfide ore from Somincor (Neves Corvo, Portugal) with a chemical composition of 0.5% Cu, 1.2% Pb, 7% Zn, 32% Fe and 43% S was used. The ore sample is a massive sulfide ore containing chalcopyrite, galena, sphalerite and pyrite as the major sulfide minerals.

Batch scale kinetic flotation tests were performed to investigate

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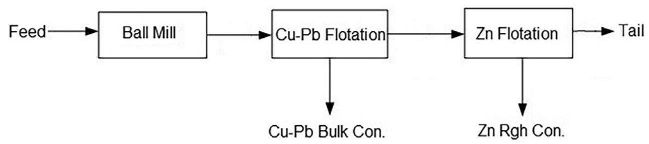

Fig. 1. Flowsheet of the batch scale flotation tests and water sampling points.

Table 1
Taguchi L9 (34) experimental design to test effects of process water on flotation performance.

Std	Run	Block 1	Ca (ppm)	SO_4 (ppm)	S_2O_3 (ppm)	Pb (ppm)
6	1	Block 1	1018.5	4000	0	0.3
5	2	Block 1	1018.5	2012	4000	0
4	3	Block 1	1018.5	24	2000	0.6
8	4	Block 1	2000	2012	0	0.6
1	5	Block 1	37	24	0	0
2	6	Block 1	37	2012	2000	0.3
9	7	Block 1	2000	4000	2000	0
7	8	Block 1	2000	24	4000	0.3
3	9	Block 1	37	4000	4000	0.6

Table 2
Variations in thiosulfate and sulfate concentrations with and without H_2O_2 treatment.

	No treatment (RUN-9)		H_2O_2 treatment (RUN-9 H_2O_2)	
	$S_2O_3{}^{2-}$ (mg/L)	$SO_4{}^{2-}$ (mg/L)	$S_2O_3{}^{2-}$ (mg/L)	$SO_4{}^{2-}$ (mg/L)
Synthetic water	3894	3906	4270	4311
1% H_2O_2 treatment			840	6044

Table 3
Statistical evaluation of the tested parameters on Cu-Pb bulk flotation performance (95% confidence level).

Response	Ca	SO_4	S_2O_3	Pb
GCu	NS	S	S	NS
GPb	NS	NS	NS	NS
GZn	NS	NS	S	NS
GPy	NS	NS	NS	NS
RCu	NS	NS	S	NS
RPb	NS	NS	S	NS
RZn	NS	NS	S	NS
RPy	NS	S	S	NS
Mass Pull	NS	S	S	NS
Water Rec.	NS	NS	S	NS

*S: Significant, NS: Not Significant.

Table 4
Statistical evaluation of the tested parameters on Zn flotation performance (95% confidence level).

Response	Ca	SO_4	S_2O_3	Pb
GCu	NS	NS	S	NS
GPb	NS	NS	S	NS
GZn	NS	NS	S	NS
GPy	NS	NS	NS	NS
RCu	NS	NS	NS	NS
RPb	NS	NS	NS	NS
RZn	NS	S	S	NS
RPy	NS	NS	S	NS
Mass Pull	NS	S	S	NS
Water Rec.	NS	S	S	NS

*S: Significant, NS: Not Significant.

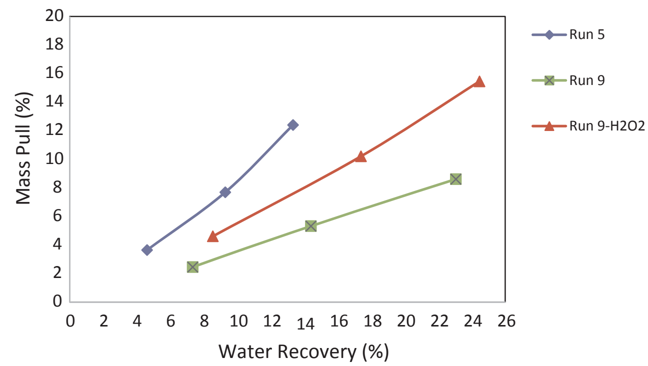

Fig. 2. Water recovery vs mass pull of Cu-Pb Rougher flotation with and without water treatment with H_2O_2 (Run 5: tap water).

influence of water chemistry on flotation performance. The flotation conditions were similar to that used in plant scale operation, in which Cu-Pb bulk flotation was followed by Zn flotation (Fig. 1).

4.5 L Denver flotation cell was used and the same flotation conditions were applied in all of the tests:

Cu-Pb Flotation: 500 g/t MBS to ball mill, grind size p80 = 60 µm, 10 min pre-aeration (pH 6.5–7), 30 g/t Aero3418A as collector (stage addition was applied), 25 g/t MIBC as frother, 6 min of total flotation time.

Zn Flotation: pH = 9.5 (lime), 600 g/t CuSO4 as activator, 90 g/t SIBX as collector (stage addition was applied), 20 g/t MIBC as frother, 10 min of total flotation time.

Mass pull, water recovery, grade and recoveries of Cu, Pb, Zn and Pyrite were the measured responses for both Cu-Pb bulk flotation and Zn flotation sections. Water samples from the flotation feed, Cu-Pb rougher flotation tail and final tail were taken and analyzed for cations and anions. ICP-OES (Thermo Elemental Iris Intrepid) and Ion Chromatography (Dionex ICS-3000) were used for cation and anion analysis, respectively.

2.2. Synthetic process water

$SO_4{}^{-2}$, $S_2O_3{}^{-2}$, Ca^{+2} and Pb^{+2} ions were found to be the major ions accumulated in process water based on the long term plant scale water chemistry measurements. Hence, their effects on flotation performance were investigated.

Taguchi experimental design technique was employed to investigate effects of accumulated ions at three levels (concentrations). Concentrations were determined based on the water chemistry analysis from Somincor mine site. The details of the experimental design are given in Table 1.

2.3. Removal of thiosulfate by hydrogen peroxide oxidation

Thiosalts occur as partially oxidized sulfoxy anions like thiosulfate ($S_2O_3{}^{2-}$), trithionates ($S_3O_6{}^{2-}$), and tetrathionates ($S_4O_6{}^{2-}$), as shown in reactions (1)–(4) (Rao, 2011):

$$2FeS_2 + 1/2O_2 + H_2O \rightarrow 2Fe^{2+} + 2OH^- + 4S^\circ \quad (1)$$

$$4S^\circ + 6OH^- \rightarrow 2S^{2-} + S_2O_3{}^{2-} + 3H_2O \quad (2)$$

$$3S_2O_3{}^{2-} + 2O_2 + H_2O \rightarrow 2S_3O_6{}^{2-} + 2OH^- \quad (3)$$

$$4S_2O_3{}^{2-} + O_2 + 2H_2O \rightarrow 2S_4O_6{}^{2-} + 4OH^- \quad (4)$$

These anions are metastable species and oxidize or disproportionate to more stable sulfate, as described by following reactions (5)–(7), (Rao, 2011):

$$S_2O_3{}^{2-} + 2O_2 + H_2O \rightarrow 2SO_4{}^{2-} + 2H^+ \quad (5)$$