



# Management of thiosalts in mill effluents by chemical oxidation or buffering in the lime neutralization process



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## ARTICLE INFO

### Article history:

Received 19 December 2013

Accepted 17 February 2014

Available online 12 March 2014

### Keywords:

Thiosalts

Sulphide ores

Mill effluents

Chemical oxidation

Carbonate and bicarbonate buffering

## ABSTRACT

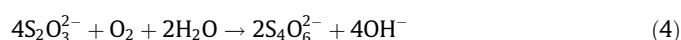
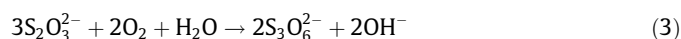
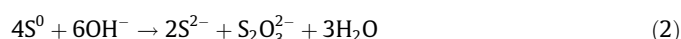
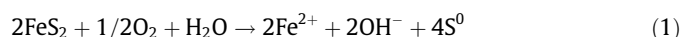
Laboratory studies were conducted to investigate the removal or management of thiosalts within the lime-neutralization process, to prevent or minimize the adverse effects of thiosalts that cause delayed acidity to downstream environment. The oxidizing reagent hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and the pH stabilizing (buffering) reagents carbon dioxide (CO<sub>2</sub>), sodium bicarbonate (NaHCO<sub>3</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) were examined for removal and management of thiosalts, respectively. Chemical oxygen demand (COD) was determined to be a proxy for thiosalts and was employed for their rapid assessment. The *Target Level* of thiosalts harmless to aquatic life was found to be 30 mg/L or less. The optimized lime-neutralization process required a pH level of 9.5–10 and aeration. Over-liming to pH levels >11 did not provide excess alkalinity, hardness, or a decrease in thiosalt levels.

Addition of H<sub>2</sub>O<sub>2</sub> to either the acid or lime-neutralized water at a molar H<sub>2</sub>O<sub>2</sub>:S<sub>2</sub>O<sub>3</sub> ratio of 1–1.5 removed thiosalts to safe levels. About 10–15 min. at room temperature was ample time low temperatures slowed down the process but the dosages were not affected. Removal of thiosalts from 170 to 30 mg/L caused a decrease in pH from 9.6 to 6.5. Among the buffering reagents studied, both NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> provided adequate buffering and a stable pH of 7 to the lime-neutralized water; whereas CO<sub>2</sub> resulted in poor buffering and an unstable pH that remained below 6. In cold temperatures, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> also outperformed CO<sub>2</sub> with higher alkalinity and hardness. Na<sub>2</sub>CO<sub>3</sub> addition to lime neutralized water at pH 9.5 was found to be the most cost-effective option. Other methods could have niche applications, depending on seasonal variations and temperature.

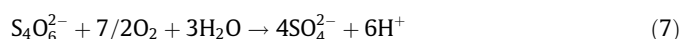
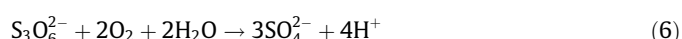
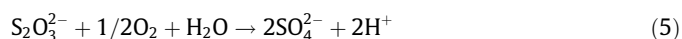
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## 1. Introduction

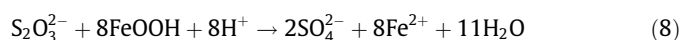
Grinding and flotation of sulphide ores containing pyrite (FeS<sub>2</sub>) and pyrrhotite (FeS) in alkaline conditions unavoidably generate thiosalts, viz. partially oxidized sulphur oxyanions including thiosulphate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>), trithionate (S<sub>3</sub>O<sub>6</sub><sup>2-</sup>) and tetrathionate (S<sub>4</sub>O<sub>6</sub><sup>2-</sup>) as shown by Eqs. (1)–(4) (Kuyucak and Toreci-Mubarek, 2012; Rao, 2011; Vongporm, 2008).



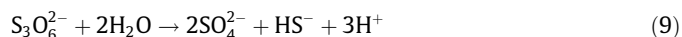
Thiosalts represent delayed acidity in effluents, with a potential to reduce pH to toxic levels in water resources as they produce H<sup>+</sup> ions (proton acidity) and sulphate (SO<sub>4</sub><sup>2-</sup>) upon oxidation or disproportionation as described by Eqs. (5)–(9) (Rao, 2011). Their presence in mill effluents or in tailings reclaim waters can threaten the aquatic life in downstream environment such as rivers, lakes and wetlands as well as the performance of flotation, as they lead to increased acidity and drop in pH (Buttler et al., 2003).



Or by iron oxyhydroxides (FeOOH):



Or simply by disproportionation:



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The pH, acid or alkaline conditions, temperature and catalysts play an important role on the stability, the oxidation rate and oxidation products of thiosalts (Vongporm, 2008). Complete oxidation of thiosalts by aeration is extremely slow at temperatures below 20 °C, in the absence of chemical or microbiological catalysts, strong oxidants and ultraviolet light from the sun (CANMET, 2007). Production of elemental sulphur from anaerobic degradation of thiosalts also was claimed (Boonstra et al., 2003).

Mining companies have to meet water quality standards set by the federal and provincial authorities for a number of parameters such as pH a between 5.5 and 9.0 and metal ions of Zn, Ni and Cu to below 0.5 mg/L, and aquatic toxicity tests before releasing effluents to the environment (CANMET, 2006, 2007). They use “natural oxidation/degradation” in tailings ponds where the mill effluents are retained for a prolonged time (e.g., several days to weeks) and exposed to air, bacteria and sunlight as a common method for removal and management of thiosalts (Kuyucak and Yaschyshyn, 2007; Rao, 2011). Because of seasonal and unpredictable performance of natural oxidation to breakdown thiosalts as well as the frothers and collectors in mill effluents, the use of other treatment processes such as biological (aerobic and anaerobic), chemical (destruction, oxidation), electrochemical (electrodialysis, electro-oxidation), reverse osmosis and activated carbon is required (CANMET, 2007). Oxidation of thiosalts is usually followed by a lime neutralization process for the ultimate treatment and recycling of the water. The present study aimed to investigate potential thiosalt management methods by incorporating in a lime-neutralization process. Bench-scale laboratory experiments conducted to evaluate removal by oxidation (e.g., hydrogen peroxide “H<sub>2</sub>O<sub>2</sub>”), and rendering the presence of thiosalts harmless by pH stabilization (e.g., using buffering reagents such as carbon dioxide “CO<sub>2</sub>”, sodium bicarbonate “NaHCO<sub>3</sub>” and sodium carbonate “Na<sub>2</sub>CO<sub>3</sub>”).

## 2. Materials and method

### 2.1. Wastewater

The waste (acid) water was sampled from a mine located in Ontario (Canada) that recovers Ni and Zn from pyrite ores. A tailings pond and a lime-neutralization water treatment plant (WTP) to manage tailings and the reclaim water before releasing the water to a nearby river. The samples were taken from the outlet of the tailings pond with the intention of incorporating a thiosalt management process to the site’s WTP. The treated water standards were set based on the Ontario (Canada) Municipal, Industrial Strategy for Abatement (MISA) regulations (Environmental Protection Act (Ontario), 2007). The pH, dissolved oxygen (DO), oxidation/reduction potential (ORP, Eh) and temperature of the samples at the time of acquisition were recorded. The water samples had an average pH of 3 and contained (in mg/L) average 3.8 Cu, 0.52 Pb, 66 Zn and 172 thiosalts ranging from 168 to 188. The water at the tailings pond inlet had average 250 mg/L thiosalts Table 1 gives detailed analysis of the raw water and the required effluent quality.

### 2.2. Chemical reagents

The chemicals included technical grade hydrated dry lime (Ca(OH)<sub>2</sub>), sodium carbonate (soda ash, Na<sub>2</sub>CO<sub>3</sub>), sodium bicarbonate (baking soda, NaHCO<sub>3</sub>), calcium chloride (CaCl<sub>2</sub>·2H<sub>2</sub>O), hydrogen peroxide (50 wt% aq. H<sub>2</sub>O<sub>2</sub>), flocculant polymer (Magnafloc E10, weak anionic polymer). They were obtained from CIBA chemicals (Montreal, QC) and stored in a dark, dry and well ventilated area. Their Materials Safety Data Sheet (MSDS) information was kept nearby within easy access.

**Table 1**

The quality of mill effluent and the target quality for the treated water according to a regulated standard (conc.s in mg/L).

Parameter	Raw (acid) water <sup>a</sup>	Target <sup>b</sup>
pH	3.08 2.6 ± 3.6	5.5–9
Alkalinity	<1	
Total cyanide (CN <sup>-</sup> )	<0.02	<1
Total suspended solids (TSS)	5 4 ± 7	<15
Copper	3.8 3.2 ± 4.4	<0.3
Lead	0.52	<0.2
Nickel/Nickel spiked	0.36/15.0 0.24 ± 0.48/15.0	<0.5
Zinc	66 59 ± 81	<0.5
Arsenic	<0.005	<0.5
Aluminum	21.6 18.1 ± 27.1	–
Iron	75.2 69.5 ± 81.9	–
Manganese	38.4 34.1 ± 45.7	–
Magnesium	288 269 ± 313	–
Calcium	565 498 ± 652	–
Hardness <sup>c</sup>	4300 4253 ± 4397	–
Sulphate (SO <sub>4</sub> <sup>2-</sup> )	2500 2439 ± 2659	–
Thiosalts (S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , S <sub>3</sub> O <sub>6</sub> <sup>2-</sup> , S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> )	172 168 ± 188	–

<sup>a</sup> Averaged over a year.

<sup>b</sup> Treated water quality required by Municipal, Industrial Strategy for Abatement (MISA), Ontario.

<sup>c</sup> Total hardness. min ± max: range. Thiosalts and pH measurements of 25 samples as other parameters from 10 samples.

### 2.3. Laboratory method

Three sets of tests were conducted. One set aimed to optimize the lime-neutralization process by investigating the effect of pH, aeration, mixing time, flocculation and temperature. The second set evaluated the effectiveness of buffering reagents CO<sub>2</sub>, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> in stabilising the pH at near neutral or alkaline conditions. The third set investigated the removal of thiosalts by H<sub>2</sub>O<sub>2</sub> from raw (acid) and lime-neutralized (alkaline) water samples. The parameters such as dosage, temperature and the required mixing time were evaluated.

#### 2.3.1. Lime neutralization tests

The lime neutralization experiments were performed in batch mode at room temperature (18–23 °C) on 1-L water samples contained in 2-L beakers (PYREX<sup>®</sup> Griffin beakers, Sigma–Aldrich Co., LLC). The water was mixed continuously with a magnetic stirrer (IKA 3810001) at 150 rpm. One set was aerated by sparging approximately 0.01 cfm air. Changes in pH, DO and Eh were continuously monitored with a multi parameter meter (Hack, HQ40d) equipped with appropriate probes (Intelli CAL pH101, CDC401, LDO101). Dry Ca(OH)<sub>2</sub> was added to the water until the desired pH level was attained and the consumption was deduced from the initial and final lime weights. The pH stabilized in about 0.5 h, while stabilization of Eh required about 2 h. After the pH stabilized, water samples were kept mixing for at least another hour. Then, the slurry was transferred to a graduated cylinder and left still on the bench for 2–4 h to allow settling and separation of the precipitates (i.e., the sludge). Flocculant (2 mL of 0.05%

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