MANAGING THIOSALTS IN MILL EFFLUENTS¹
“STUDIES CONDUCTED AT THE KIDD METALLURGICAL SITE”

Nural Kuyucak², David Yaschyshyn³

Abstract: Grinding and flotation of sulphide (S²⁻) ores containing pyrite (FeS₂) and pyrrhotite (FeS) in alkaline conditions produces a series of partially oxidized sulphur oxyanions (SₓOᵧ²⁻) with the most common being thiosulphate (S₂O₃²⁻), trithionate (S₃O₆²⁻) and tetrathionate (S₄O₆²⁻), which are collectively called “Thiosalts”. Oxidation of thiosalts continues in the solution pulp or effluent until the end product of sulphate (SO₄²⁻) is reached. Since oxidation reactions also produce proton (H⁺), thiosalts represent delayed acidity in effluents with the potential to cause a drop in pH within the treatment system and in the downstream environment. Thiosalts generation is site-specific and current processing technology has not been able to cost effectively prevent their production. As natural degradation in tailings ponds may not be sufficient to fully manage thiosalts oxidation, some sites may require implementation of additional measures due to the presence of site constraints or conditions such as short retention time and cold climate. Currently known best “thiosalts management” practices include: increasing retention time in tailings ponds; improving thiosalt oxidation rates through optimization of pond pH’s prior to discharge; increasing alkalinity and/or buffering capacity in effluents; and treating water using chemical or biological oxidation or biological (sulphate) reduction processes. Some sites practice addition of excess buffering/alkalinity in the treated water as a cost-effective option to delay and compensate for the acid generation. However, results can be variable during different times of the year and development and use of alternative methods are required. Hydrogen peroxide as a chemical oxidation method is often chosen due to its low capital cost, high reactivity and non-toxic by-product generation. The Xstrata Copper Canada, Kidd Metallurgical Site in Timmins, Ontario has investigated possible options to manage thiosalts by conducting laboratory tests and modeling studies. The studies conducted and the management methods implemented for the site are discussed.

Key Words: Thiosalts; sulphide ores processing; thiosalts management; mine mill effluents treatment; sulphide reduction; hydrogen peroxide chemical oxidation; bicarbonate buffering; natural oxidation; tailing reclaim water treatment; biological oxidation; acid generation.

Introduction

Thiosalts Formation: Grinding and flotation of sulphide (S²⁻) ores containing pyrite (FeS₂) and pyrrhotite (FeS) in alkaline conditions produce a series of partially oxidized sulphur oxyanions (SₓOᵧ²⁻) with the most common being thiosulphate (S₂O₃²⁻), trithionate (S₃O₆²⁻) and tetrathionate (S₄O₆²⁻) which are collectively called “Thiosalts” as shown below with Equation 1-4 (Environment Canada, 1987).

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² Golder Associates Ltd., 32 Steacie Drive, Kanata, Ontario Canada K2K 2A9 Tel: 613-592 9600; Fax: 613-592 9601; e-mail: nkuyucak@golder.com
³ Xstrata Copper Canada, Kidd Metallurgical Site, 10050 Highway 101 East, PO Bag 2002, Timmins, Ontario, P4N 7K1, Tel: (705) 235-8121 ext.7899; Fax: (705) 235-7355; e-mail: dyaschyshyn@kiddmet.xstratacopper.ca
FeS$_2$ + 2O$_2$ + H$_2$O $\rightarrow$ Fe$^{2+}$ + 2OH$^-$ + 2S$^0$  
Eq. 1
4S$^0$ + 6OH$^-$ $\rightarrow$ 2S$^{2-}$ + S$_2$O$_3^{2-}$ + 3H$_2$O  
Eq. 2
3S$_2$O$_3^{2-}$ + 2O$_2$ + H$_2$O $\rightarrow$ 2S$_2$S$_6^{2-}$ + 2OH$^-$  
Eq. 3
4S$_2$O$_3^{2-}$ + O$_2$ + 2H$_2$O $\rightarrow$ 2S$_2$O$_6^{2-}$ + 4OH$^-$  
Eq. 4

In oxidation reactions, the rate limiting step may vary for different conditions under which the pyrite/pyrrhotite oxidation proceeds. Thiosulphate is produced at about pH 9 and remains relatively stable. At pH 6 and lower, sulphate and polythionate formation prevails. Possibly, the Fe-S bond is broken before the S-S bonds releasing sulphur decomposition products from the pyrite surface which control the rate in the overall process. Pyrite oxidation by O$_2$ at about pH 7 is found to be first order making the O$_2$ concentration and the surface area of the pyrite grains important. Current processing technology has not been able to cost effectively prevent the production of thiosalts. The factors affecting thiosalts generation are site-specific and may include: sulphur content of the ore, grinding and floatation pH, mill water temperature, residence time in the mill and floatation circuits, pulp agitation rate, grind size, pulp density, and pulp, SO$_2$ gas rate and air available for flotation (Kuyucak et al., 2001).

**Consequences of Thiosalts:** Oxidation of thiosalts continues in the solution pulp or tailings waters until the end product of sulphate (SO$_4^{2-}$) is reached. Since oxidation reactions also produce protons (H$^+$) as explained below with Equations 5-9, thiosalts represent delayed acidity in tailings water/supernatants with the potential to cause a drop in pH within the treatment system and in the downstream environment such as in rivers, lakes and wetlands (Environment Canada 1987; Kuyucak 2001; Butler et al., 2002). Consequently, the potential exists for an increase in metal and dissolved salts concentrations.

S$_2$O$_3^{2-}$ + 1/2O$_2$ + H$_2$O $\rightarrow$ 2SO$_4^{2-}$ + 2H$^+$  
Eq. 5
S$_2$O$_6^{2-}$ + 2O$_2$ + 2H$_2$O $\rightarrow$ 3SO$_4^{2-}$ + 4H$^+$  
Eq. 6
S$_4$O$_6^{2-}$ + 7/2O$_2$ + a 3H$_2$O $\rightarrow$ 4SO$_4^{2-}$ + 6H$^+$  
Eq. 7
Or by iron oxyhydroxides (FeOOH):
S$_2$O$_3^{2-}$ + 8FeOOH + 8H$^+$ $\rightarrow$ 2SO$_4^{2-}$ + 8Fe$^{2+}$ + 11H$_2$O  
Eq. 8
Or simply disproportionate:
S$_2$O$_6^{2-}$ + H$_2$O $\rightarrow$ SO$_4^{2-}$ + HS$^-$ + H$^+$  
Eq. 9

**Acute and Sublethal Toxicity of Thiosalts:** Recent studies (Schwartz et al., 2006) by researchers at CANMET have determined the acute and sublethal toxicity of thiosalts to various biological test organisms regularly used in testing mine effluents. Their collective results are presented in Table 1.

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Test Organism</th>
<th>Thiosulphate</th>
<th>Tetrathionate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acute</td>
<td>Rainbow trout</td>
<td>LC50 &gt;800 ppm</td>
<td>LC50 &gt;800 ppm</td>
</tr>
<tr>
<td></td>
<td><em>Daphnia magna</em></td>
<td>LC50 ~300 ppm</td>
<td>LC50 ~750 ppm</td>
</tr>
<tr>
<td>Sublethal</td>
<td><em>Lemma minor</em></td>
<td>IC$_{25}^{dry, wt}$ = 498 ppm</td>
<td>IC$_{25}^{dry, wt}$ &gt;798 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IC$_{25}^{FC}$ = 525 ppm</td>
<td>IC$_{25}^{FC}$ &gt;798 ppm</td>
</tr>
<tr>
<td></td>
<td><em>Ceriodaphnia dubia</em></td>
<td>IC$_{25}$ = 59 ppm</td>
<td>IC$_{25}$ = 562 ppm</td>
</tr>
<tr>
<td></td>
<td>Fathead minnow</td>
<td>IC$_{25}$ = 665 ppm</td>
<td>IC$_{25}$ &gt;891 ppm</td>
</tr>
<tr>
<td></td>
<td><em>Selenastrum capricornutum</em></td>
<td>IC$_{50}$ &gt;2220 ppm</td>
<td>IC$_{50}$ &gt;2110 ppm</td>
</tr>
</tbody>
</table>

The data suggest that the most sensitive species would be *Daphnia magna* and *Ceriodaphnia dubia* and the least sensitive would be Rainbow trout and *Selenastrum capricornutum* for their respective test types. Data are useful as a screening level tool in toxicity identification testwork. In many cases, concentrations of thiosalts in the final effluents of Canadian mining companies are below levels likely to cause direct toxicity. However, indirect toxicity caused by pH depression from thiosalts oxidation over the test duration is more likely, especially for effluents with low alkalinity to buffer any proton generation.
**Factors Affecting Thiosalts Degradation:** Complete oxidation of thiosalts occurs extremely slowly at low temperatures and in the absence of catalysts and strong oxidants. Rapid oxidation observed in the natural environment in the presence of biological and/or chemical catalysts such as iron and ultraviolet (UV) radiation from sunlight suggest these are important degradation mechanisms (Tan and Rolia, 1985).

Alkaline conditions and elevated temperatures are favourable for the chemical breakdown of polythionates to S$_2$O$_3$ and sulphite. Oxidation to sulphuric acid could occur chemically and microbially by *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* at acidic conditions (Sampson, et al., 1985). In the temperature range of 15-45°C and pH 5.5-12, trithionate reacts with water to give S$_2$O$_3$ and SO$_4$. Thiosulphate is oxidized to SO$_4$ by dissolved oxygen in an alkaline solution (Kuyucak, 2001).

**Treatment Alternatives:** Methods available that have been evaluated in laboratory or pilot scale tests include (Wasserlauf et.al., 1988; Haque and Diberto, 1997; Vigneault et al., 2003; Bechard et al., 1996; Kuyucak et al., 2001; CANMET, 2003):

- Natural Oxidation in tailings ponds;
- Chemical Oxidation by hydrogen peroxide (H$_2$O$_2$), chloride (Cl$_2$) or ozone (O$_3$);
- Increasing Buffering Capacity by adding carbonate (CO$_3^{2-}$) and/or bicarbonate (HCO$_3^-$);
- Membrane and Electrochemical processes (e.g., reverse osmosis (RO), electrodialysis (ED) and electro-oxidation (EO));
- Air Oxidation (e.g., alkaline oxidation, Cu-catalyzed air oxidation and SO$_2$-air oxidation);
- Biological Oxidation using rotary biological contractors, rock filters and activated sludge;
- Biological Reduction to sulphide followed by precipitation of metal sulphides; and
- Other methods such as: adsorption and elution, and disposal of the concentrated thiosalts solution, reduction by metal (e.g., Fe) and sea disposal.

Many of above methods were found to be technically feasible, but expensive. The high cost for a biological process was mainly attributed to the cold climate in Canada (Wasserlauf et.al., 1988). The “natural degradation” process in tailings ponds having over several days to weeks from exposure to air and sunlight is the most common method. Also, organic compounds such as frothers and collectors contained in process effluents could also be degraded under these conditions (Kuyucak et al., 2001). Brunswick Mine in Canada reported a pH decrease from 7.5 to ≤ 4 after storing tailings water containing 850 - 1,200 mg/L thiosalts in rock-packed ponds for about four days, possibly due to bacterial and natural oxidation and sunlight (Butler, et al., 2003). While non-detectable levels (i.e., <10 mg/L) could be obtained during summer, the levels could be as much as 800 mg/L in the final effluent during winter.

Some sites practice the “increased buffering capacity” method in the treated waters by first increasing the pH to levels >10 to remove metal ions (e.g., Zn) and then, decreasing the pH in decant by adding carbon dioxide (CO$_2$) to ≤9 to meet regulatory discharge limits. This method may function satisfactorily for thiosalts concentrations <100 mg/L (Kuyucak et al., 2001). Similarly, the use of sodium bicarbonate (NaHCO$_3$) was also tested to increase buffering capacity in treated waters (Li and Boucher, 1999).

**Industry Consortium:** Mining companies and researchers in collaboration with CANMET’s Mining and Mineral Sciences Laboratories (CANMET-MMSL) have been conducting research since 1995 to understand the formation of thiosalts, developing appropriate technologies to reduce/remove thiosalts from mining effluents and providing a forum for technology exchange and transfer (CANMET, 2003; CANMET, 2007; Thiosalts Consortium reports: [http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/enviro/effluents/effthiosalts-e.htm](http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/enviro/effluents/effthiosalts-e.htm)).
**Studies at the Kidd Metallurgical Site**

**Site Overview:** Xstrata Copper Canada, Kidd Metallurgical Site (Kidd Metsite) located in Timmins, Ontario is an integrated, multi-plant facility for the mineral processing of base metal ores and for the metallurgical processing and refining of metals. The facility produces copper, zinc, cadmium, indium, and nickel concentrate, as well as several by-products such as lead/silver residue, precious metals slimes, sulphuric acid and liquid sulphur dioxide.

The Concentrator began operation in 1966. The Concentrator consists of: a railroad load-in, a custom ore receiving building, one fine crushing plant, three parallel Kidd ore grinding and flotation circuits (A, B, C Divisions), one custom ore grinding and flotation circuit (D Division), one concentrate handling circuit, one thickened tailings management area, and associated facilities for water supply, reagents, maintenance, and metallurgical testing. The main feed source is the massive sulphide copper-zinc ore from the Xstrata Copper, Kidd Mine located 30 km northeast of the site. The sulphide mineral is predominantly pyrite. In 2004, the custom ore circuit was re-commissioned to process a nickel copper ore from the Xstrata Nickel, Montcalm Mine. The sulphide mineral in the Montcalm ore is predominantly pyrrhotite. Current annual milling rates for Kidd Mine and Montcalm Mine ore in 2006 were 2.5 and 0.9 Mtonnes, respectively.

**Tailings and Water Management:** The Tailings Management Area (TMA) is 1,250 hectares in size and is located north of the plant site (Figure 1). It is used for the storage of tailings and metallurgical wastes. In the Concentrator, the overall tails conditioner is fed with flotation circuit tailings and wastewater from the Zinc and Copper Operations. A two-stage pumping system is used to pump the tailings through two 4.5 km tailings lines to the TMA. Conventional tailings discharge was upgraded to a Thickened Tailings Discharge method in 1973. The high-density thickened tailings are spigotted to form a conical shaped deposit with approximately 2% side slopes. The system was upgraded further in 1995 with the addition of the current high rate No.3 tailings thickener. Overflow water from the tailing thickener along with site drainage and precipitation is collected within the TMA in Ponds A and C, which are used for primary holding/settling. Water from Ponds A and C is treated with lime and flows into Pond D where low density sludge metal precipitates are allowed to settle. A portion of the treated water is recycled back to the plants while excess water flows to Pond E for further clarification. Following final pH adjustment with carbon dioxide the final effluent is discharged to the Porcupine River.

The final effluent is regulated under both Ontario Reg. 560 Metal Mining Sector - Effluent Monitoring and Effluent Limits and Federal Metal Mining Effluent Regulations that require monitoring for pH (6.0 – 9.5), TSS, metals (eg. Zinc <0.5 mg/L), and aquatic toxicity for *Daphnia magna* and Rainbow trout.

**Thiosalts Management Program:** Thiosalts have traditionally been managed by natural degradation in the TMA in combination with increased lime addition setpoints to offset pH declines after the lime treatment stations located at Ponds A and C. More recently, the site has experienced sporadic episodes of aquatic toxicity. Investigations revealed at least half of the failed lab toxicity tests were attributed to stress from low pH caused by thiosalts oxidation. In response, a Thiosalts Program was initiated in 2002 with the goal to consistently producing a quality final effluent with no indirect toxicity from thiosalts while reducing operating challenges in the water treatment system. The Program included the following tasks:

- Review existing water quality and toxicity monitoring data;
- Literature review of thiosalts formation, characteristics, treatment options, and ecotoxicity;
- Determine an alternative field parameter for rapid indication of thiosalts;
- Review existing monitoring program, implement any modifications;
- Assess and rank potential treatment options for thiosalts;
- Complete cost-benefit study on applicable treatment options;
• Select options for controlling thiosalts release to the TMA and receiving environment; and
• Implement selected management option(s).

Review Existing Water Quality Monitoring Data: For over a decade Kidd Metsite has been proactively monitoring thiosalts concentrations at various locations within the TMA. A snapshot of these data is presented in Figure 2. Temporal trends are evident during the warm summer periods, when natural degradation within the TMA is sufficient to produce a final effluent with a non-detectable level (<10 mg/L) of thiosalts. During winters when cold water temperatures prevail and ice covered ponds exist, natural degradation is less effective at reducing thiosalts in the final effluent.
Literature Review: Information regarding economically achievable technologies to manage thiosalts and practices used by other mining companies was reviewed to provide a solid understanding of thiosalts behaviour. The Kidd Metsite also became an active member of the Thiosalts Consortium in 2004.

Chemical Oxygen Demand as an Alternative Thiosalts Indicator: As part of an intensive monitoring program to identify all sources of thiosalts within the Concentrator and TMA, a separate study was initiated to find an alternative indicator that could be used as a rapid onsite correlation to thiosalts. The use of chemical oxygen demand (COD) was investigated as a relatively rapid and cost-effective analytical tool to monitor thiosalt levels, as reported by Kuyucak et al., (2001). At the time, thiosalts were being analyzed at an offsite commercial lab and results were typically being received within 2 to 4 weeks. Samples from 32 locations taken at four different intervals across the TMA were analyzed for thiosalts.
Freezing the sample is the preferred preservation method for thiosalts if the sample cannot be analyzed immediately by the laboratory.

After considering the possible effect of ferrous iron, sulphide species, chloride ions and remnant flotation reagents on COD values, the data from the various locations was reasonably consistent (Thiosalts_{TMA} = 1.106*COD_{TMA}, R^2 = 0.87). Further refinement of this alternative indicator was not pursued due to other program priorities.

**Review Existing Monitoring Program:** In order to develop a site-specific thiosalts degradation model, it was necessary to determine actual hydraulic retention times (HRT). Actual flow rates and HRT were measured in perimeter ditches and treatment ponds using a variety of methods including bathymetric surveys, submerged drogues (floats), flow meters, and an automatic pH sampler with lime injected as a tracer (Golder, 2003b). Actual HRT’s were in some instances less than half of the theoretically expected values revealing short-circuiting and the natural loss of storage capacity due to sedimentation.

**Assess and Rank Potential Treatment Options for Thiosalts:** This involved investigation of thiosalts degradation behaviour within the TMA, a ranking of available treatment options, and completion of laboratory testing to assess effectiveness of site specific opportunities to increase thiosalts degradation. Based on literature reviews and benchmarking studies, 16 among 24 identified thiosalts treatment options were first ranked based on experience-based judgment according to their technical feasibility, capital and operating costs, adverse environmental or safety effects, and practicality for the Kidd Metsite. Options with the highest ranking which were selected for further assessment with laboratory tests included:

- natural oxidation by increased retention time
- chemical oxidation with hydrogen peroxide
bi-carbonate buffering.

**Natural Oxidation by Increased Retention Time:** Thiosalt degradation follows the first order rate law as in Equation 10.

\[
C(t) = C_0 e^{kt} \quad \text{Eq. 10}
\]

where:
- \(C_0\) is the thiosalt concentration at any particular time (mg/L),
- \(C_0\) is the initial thiosalt concentration at the Concentrator (mg/L),
- \(k\) is the degradation rate constant (minutes\(^{-1}\)),
- \(e\) is the base for natural logarithms, and
- \(t\) is the time (minutes).

Actual monitoring data from the TMA were plotted against the HRT’s determined earlier. Site data exhibited a first order degradation behaviour as expected. Data were regressed to determine site degradation rate constants (Table 2). Degradation rate constants varied seasonally from a fast rate of 0.00042 min.\(^{-1}\) in summers to a slow rate of 0.00025 min.\(^{-1}\) in winters with an average rate of 0.00032 min.\(^{-1}\).

<table>
<thead>
<tr>
<th>Degradation Rate Constants</th>
<th>Slow</th>
<th>Average</th>
<th>Fast</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.00025 minutes(^{-1})</td>
<td>0.00032 minutes(^{-1})</td>
<td>0.00042 minutes(^{-1})</td>
</tr>
</tbody>
</table>

For first-order reactions, the use of a half-life rather than a rate constant is often more convenient. The half-life of a degrading substance is simply the time required for half of the amount originally present to degrade. The half-life is directly related to the rate constant for a first-order reaction. At Kidd Metsite, under average natural degradation conditions one half-life (1\(t_{(1/2)}\)), two half-lives (2\(t_{(1/2)}\)) and three half-lives (3\(t_{(1/2)}\)) for thiosalts are 2.2, 4.3 and 6.5 days, respectively.

These thiosalts degradation rate constants or kinetics were used in a site-specific Thiosalts Natural Degradation Model. The model allowed testing of various possible scenarios to increase natural oxidation within the TMA. Scenarios modelled included potential modification of the Thickener overflow collection box, so that upwards of 50% flow could be diverted to a South Route to utilize unused retention time. In addition, the potential for volume increases in Pond C to increase its holding capacity by dredging was also evaluated.

**Chemical Oxidation with Hydrogen Peroxide:** Bench scale lab tests were conducted to evaluate the possible use of hydrogen peroxide (H\(_2\)O\(_2\)) at the Kidd Metsite and verify consumption for cost estimating. According to chemical reactions shown in Equations 11-13 (CANMET, 2003), each mole of thiosalts as S\(_2\)O\(_3\)\(^{2-}\) equivalent (of S\(_4\)O\(_6\)\(^{2-}\)) could consume about 3.5 (14/4) moles of H\(_2\)O\(_2\) or about 0.00202, 0.00101, and 0.00176 mL of 50% H\(_2\)O\(_2\) solution per mg of thiosalts existing as thiosulphate, trithionate, and tetrathionate, respectively (Li, 2004).

Brunswick Mine found that 0.0028 ml of H\(_2\)O\(_2\) (34-37% solution) could destroy 1 mg of thiosalt from water containing about 850 mg/L thiosalts. A rapid drop in pH within the first 5 min indicated that a reaction time would be sufficient in a full-scale treatment plant. Treatment of 30,000 L/month containing about 172 mg/L thiosalts for a period of 8 weeks at the Brunswick site would cost about $375,000 with H\(_2\)O\(_2\) (Butler et al., 2002).

A likely dosage of 0.0017 ml 50% H\(_2\)O\(_2\) per mg of thiosalts and a constant overflow rate of 42,000 m\(^3\)/day and 125mg/L thiosalts were considered. H\(_2\)O\(_2\) delivered to the Kidd Metsite was quoted as $0.46/kg in 2003. The median annual reagent cost was estimated at C$2.1 million and C$1.2 million for year-round
operation or for a seven-month operation, respectively. The capital cost of reagent storage and dosing equipment installations for \(\text{H}_2\text{O}_2\) treatment was estimated to be in the order of $200,000-300,000 (Golder, 2003a) and possible rental or lease fees of about $12,000-20,000 per year. Clearly the cost of the \(\text{H}_2\text{O}_2\) reagent would be the major factor influencing the cost of treatment.

**Carbonate (CO\(_3^{2-}\)) and Bi-Carbonate (HCO\(_3^{-}\)) Buffering Addition:** Investigations were undertaken to determine if the dissolved alkalinity (buffering capacity) of the effluent could be increased, thus minimizing the pH depression due to oxidation of thiosalts. Soda ash (Na\(_2\text{CO}_3\)) and sodium bicarbonate (NaHCO\(_3\)) could be used, but Na\(_2\text{CO}_3\) would be a better choice because it would have twice as much NaHCO\(_3\) content on a per mole basis and half cost choice over NaHCO\(_3\). The buffering process is presented by Equations 14 to 16 (Li and Boucher, 1999).

\[
\begin{align*}
\text{NaHCO}_3 (\text{sodium bicarbonate}) & \rightarrow \text{Na}^+ + \text{HCO}_3^- \text{ (bicarbonate)} \quad (\text{Eq. 14}) \\
\text{HCO}_3^- + \text{H}^+ & \rightarrow \text{H}_2\text{CO}_3 \text{ (carbonic acid)} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (\text{Eq. 15}) \\
\text{Na}_2\text{CO}_3 (s) + \text{H}_2\text{O} + \text{CO}_2 (g) & \rightarrow 2\text{NaHCO}_3 \quad (\text{Eq. 16})
\end{align*}
\]

In addition to the flow rates and thiosalts concentrations to be treated, the need for over-dosing lime due to the release of Ca\(^{2+}\) ions, the concentration of Ca and Mg ions and handling CaCO\(_3\) precipitates would influence the cost estimate. Producing NaHCO\(_3\) on site from dry Na\(_2\text{CO}_3\) by sparging CO\(_2\) (Equation 18) would cost about $188/t in comparison to about $500/t for NaHCO\(_3\).

Neutralizing the tailings reclaim water (e.g., at the outlets of Pond C or Pond A) by adding lime to a pH of about 9.5, (instead of to a pH of about 11.0 as was the practiced at the site at the time), and adding NaHCO\(_3\) could decrease lime consumption and the formation of excessive CaCO\(_3\) precipitates. Assuming about 125 mg/L thiosulphates equivalent, about 45,000 m\(^3\)/day flow rate and the dosage of about 75% theoretical alkalinity demand, the cost of reagent would be about $533/d after subtracting lime credit of $660/day. The capital costs would be about $200,000 – $300,000 (Golder, 2003a).

**Cost-Benefit Analysis of Highest Ranked Methods:** As a result of desktop and laboratory studies, a cost-benefit analysis was conducted on the short listed methods. Enhanced “Natural Degradation by Increased Retention Time” was selected as the preferred option for controlling thiosalts and indirect toxicity that was attributed to thiosalts degradation. Although it had a large capital cost up front, operating would be easy with significantly lower costs, and without environmentally harmful reagents and by-products. The required dredging of Pond C was compatible with the Metsite’s ongoing maintenance program. Chemical oxidation with hydrogen peroxide would be considered as a future control method if Enhanced Natural Degradation by Increased Retention Time proved ineffective.

**Implement selected management option(s):** This task aimed at constructing new or modifying existing treatment methods within the TMA and modifying applicable operating procedures. Attention to pH behaviour caused by thiosalts degradation was increased to reduce the risk of having out of compliance final effluent samples for pH or acute toxicity. A set of standard operating procedures (SOP) has been developed and tailings operators were trained to respond in a timely, consistent, and appropriate manner.

**Conduct Pilot Tests for H\(_2\)O\(_2\) Oxidation for Full-Scale System Implementation:** Pilot tests are currently being conducted this summer and fall of 2007. The pilot test is evaluating in a designed experiment the dosage rate, application points at the Tailings Thickener overflow, resulting percent destruction of thiosalts, and effect on acute toxicity. This information will be used in the detail design stage for scale up purposes of the full-scale plant. It is projected that about 13,000 USG 50% H\(_2\)O\(_2\) would be stored for an average usage of 20 tpd or peak period usage of about 36 tpd. Early testwork has determined that iron levels in the Tailings Thickener overflow water is very important to catalyze the
oxidation reaction. After Boliden Apirsa Mine in 2001 and Brunswick Mine in 2005, Kidd Metsite will be the third site in the world using a chemical ($\text{H}_2\text{O}_2$) oxidation method for controlling thiosalts.

**Conclusion**

The main objectives of the Thiosalts Program were to identify the major sources of thiosalts released to the TMA, identify effective options to control thiosalts concentrations released from the TMA and implement cost effective treatment options. “Natural Oxidation by Increased Retention Time” was selected by the Kidd Metsite as the preferred treatment option for controlling thiosalts in the TMA. Retention time was increased through the completion of hydraulic retention time studies in the TMA, hydraulic dredging of treatment ponds, and the installation of Tailings Thickener overflow diversion gates. Investigation into alternative treatments has lead to the development of a hydrogen peroxide treatment plant. Pilot plant studies and detailed design of the plant are currently on-going.

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