“Managing Thiosalts at Xstrata Copper - Kidd Operations”
by: David Yaschyshyn
17th Annual BC MEND ML/ARD Workshop

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Xstrata Copper – diverse copper assets and projects
Kidd Operations

- Located in Timmins, Ontario
- Kidd Mine and Kidd Concentrator
- Copper/zinc mined since 1966
- Production reached 9,200 feet (2,800m) in 2009, making the operation the deepest base metal mine in the world
- Projected mine life to 2017
- Ore processed at Kidd Concentrator using conventional flotation techniques
- Copper and zinc concentrates dewatered and shipped for further refinement in Canada
• Conventional slurry tailings discharge started in 1966
• Thickened tailings discharge since 1973
• Lime Treatment at Pond A and C
• Settling Pond D, water recycled for milling
• Polishing Pond E
• Treated Final Effluent discharged to Porcupine River
Where/When Thiosalts Occur?

- Typically during grinding or flotation of sulphide ores containing pyrite and pyrrhotite in alkaline conditions:

\[
\text{FeS}_2 + 2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + 2\text{S}^0
\]

\[
4\text{S}^0 + 6\text{OH}^- \rightarrow 2\text{S}^{2-} + \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}
\]

\[
3\text{S}_2\text{O}_3^{2-} + 2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{S}_3\text{O}_6^{2-} + 2\text{OH}^-
\]

\[
4\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{S}_4\text{O}_6^{2-} + 4\text{OH}^-
\]

- Thiosalts are a series of partially oxidized sulphur oxyanions \((\text{S}_x\text{O}_y^{2-})\)

- Thiosalts generation tends to be site-specific

Thiosulphate \((\text{S}_2\text{O}_3^{2-})\)

Trithionate ion \((\text{S}_3\text{O}_6^{2-})\)

Tetrathionate ion \((\text{S}_4\text{O}_6^{2-})\)
Thiosalts Speciation (2009-2010)
Why Thiosalts May Require Management?

- They typically oxidize until end product sulphate (SO$_4^{2-}$) is reached

- During oxidation reactions, proton (H+) is produced. This represents delayed acidity with potential to drop pH in treatment ponds, and effluents which could cause aquatic toxicity

\[
\begin{align*}
S_2O_3^{2-} + 2O_2 + H_2O & \rightarrow 2H^+ + 2SO_4^{2-} \\
S_3O_6^{2-} + 2O_2 + 2H_2O & \rightarrow 4H^+ + 3SO_4^{2-} \\
S_4O_6^{2-} + 7/2O_2 + 3H_2O & \rightarrow 6H^+ + 4SO_4^{2-}
\end{align*}
\]

or by iron oxyhydroxides (FeOOH):
\[
S_2O_3^{2-} + 8FeOOH + 8H^+ \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 11H_2O
\]

or simply disproportionate:
\[
S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + HS^- + H^+
\]
Thiosalts Monitoring and Receiving Environment pH

- Monitoring thiosalts within treatment system for 11 years
- Seasonal trend evident, peaks lowered, more periods when final effluent at 0 mg/L

- Receiving environment pH monitoring since 1970’s
- No significant pH depression observed downstream
The Kidd Experience

- Natural thiosalt oxidation in the Tailings Management Area (TMA) created the following issues:
  - Drops in pH after lime addition points
  - Lime addition set-points increased to compensate for pH reduction
  - Increased lime costs and sludge generation
  - Risks to Final Effluent compliance for pH and Acute Toxicity
  - Indirect toxicity in acute lab samples for *Daphnia magna* and Rainbow Trout, downstream monitoring has confirmed no effects

- Assessed Potential Treatment Options in 2004
- Highest Ranked Options included
  - Increased/Enhanced Natural Degradation (first-order rate)
  - Chemical Oxidation with Hydrogen Peroxide ($H_2O_2$)
  - Buffering addition using sodium carbonate ($CO_3^{2-}$) and/or sodium bicarbonate ($HCO_3^-$)
Acute Toxicity Testing, Variation in Lab pH

Extended Rainbow Trout testing

![Graph showing variation in Lab pH over days with and without thiosalts]

- **Lab pH (units)**
  - 10
  - 9
  - 8
  - 7
  - 6
  - 5
  - 4
  - 3

- **Day 0**
- **Day 1**
- **Day 2**
- **Day 3**
- **Day 4**
- **Day 5**
- **Day 6**
- **Day 7**
- **Day 8**

- **Containing Thiosalts**
- **No Thiosalts**
Hydrogen Peroxide Pilot Plant Studies in 2007

- Trials investigated peroxide dosage rates, dosing locations at No.2 Tailings Thickener Overflow which is <1 mg/L iron, ferric iron as catalyst, % thiosalts degradation, acute toxicity.
Hydrogen Peroxide Pilot Plant Studies + Ferric Sulphate

- Discovered iron concentrations in the 15-30 mg/L range resulted in complete thiosalt destruction within minutes of peroxide addition.

- Repeated pilot trial with $\text{H}_2\text{O}_2$ and Ferric Sulphate $\text{Fe}_2(\text{SO}_4)_3$.

- Achieved 100% thiosalt destruction in <5 minutes downstream of peroxide addition point.

- Maximum $\text{H}_2\text{O}_2$ requirement with $\text{Fe}_2(\text{SO}_4)_3$ determined to be only 50% of the theoretical requirement.
Chemistry of Iron Catalyzed Peroxide Oxidation

“Modified” Fenton’s Reagent (from FMC Environmental Solutions website)

- Chemical oxidation is a proven water treatment technology
- Hydrogen peroxide is a powerful oxidant, but at low concentrations reaction kinetics maybe too slow to degrade many contaminants of concern
- Addition of ferrous (II) or ferric (III) iron dramatically increases the oxidative strength of peroxide. This increase is attributed to the production of hydroxyl radicals (OH*) and initiation of a chain reaction causing the formation of new radicals
- The reaction of iron catalyzed peroxide oxidation at pH 3-5 is called “Fenton’s Chemistry” after its discoverer H.J.H. Fenton. The iron/peroxide combination is known as “Fenton’s Reagent.” If the pH is less than 5, the iron (III) is reconverted to iron (II), via a side cyclic reaction, and the iron remains in solution to sustain the initiation of hydroxyl radical production.
- The basic reaction for the application of Fenton’s Reagent is:
  
  **Radical initiation**
  \[
  \text{H}_2\text{O}_2 + \text{Fe}^{+2} \rightarrow \text{Fe}^{+3} + \text{OH}^- + \text{OH}^*
  \]
  
  **Radical Propagation**
  \[
  \text{OH}^* + \text{RH} \rightarrow \text{R}^* + \text{OH}^-
  \]
  \[
  \text{R}^* + \text{H}_2\text{O}_2 \rightarrow \text{ROH} + \text{OH}^*
  \]
Thiosalt Treatment System Design Criteria (2008)

- Thiosalt concentration = 217 mg/L at No. 2 tailings thickener

- Flow rate = 44,000 m³/day at No. 2 tailings thickener

- H₂O₂ addition rate = 0.00105 mL H₂O₂/mg thiosalts
  - 50% of theoretical requirement from reaction stoichiometry

- Fe₂(SO₄)₃ addition rate = 0.09 mL 55% Fe₂(SO₄)₃/L No. 2 thickener O/F
  - Theoretical requirement to achieve a minimum concentration of 20 mg/L Fe in the No. 2 thickener overflow
Thiosalt Treatment Plant (2009)

- One all weather safety shower and eyewash station
- One 40 m³ fibreglass ferric sulphate storage tank
- 3 ferric sulphate metering pumps housed in an 8’ x 8’ building
  - Owned by Kidd
- One 50 m³ stainless steel H₂O₂ storage tank
- 4 H₂O₂ metering pumps housed in a 15’ x 8’ sea container
  - Leased from Arkema
Thiosalt Treatment System

Ferric sulphate metering pumps (2 operating 1 spare)

Hydrogen peroxide metering pumps (2 operating 2 spare)
Thiosalt Treatment System Control

- Hydrogen peroxide and ferric sulphate addition rates automatically controlled by the PLC
  - Adjusted continuously based on the calculated No. 2 thickener overflow rate

- Operator is only required to enter a “pre-treatment” thiosalt concentration once per day, which is obtained from a sample of the No. 2 thickener overflow that is submitted to our onsite Analytical Lab each morning

- Pre-A, Pre-C, and Pre-D samples also collected daily to determine treatment effectiveness

- Opportunity identified to optimize reagent addition rates by incorporating natural degradation within existing system
In 2009, hydrogen peroxide and ferric sulphate made up 19% of the site total water treatment reagent costs.
## Hydrogen Peroxide Consumption Optimization

<table>
<thead>
<tr>
<th>Season</th>
<th>Average % Natural Thiosalt Degradation</th>
<th>Natural Thiosalt Degradation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td>35.0</td>
<td>0.35</td>
</tr>
<tr>
<td>Spring</td>
<td>50.0</td>
<td>0.50</td>
</tr>
<tr>
<td>Summer</td>
<td>85.0</td>
<td>0.85</td>
</tr>
<tr>
<td>Fall</td>
<td>75.0</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Hydrogen Peroxide Consumption 2009 & 2010 After Optimization
The Kidd Experience (Now)

- Optimization has reduced consumption and costs for peroxide
- No further drops in pH after lime additions points
- Lime addition set-points have now been lowered
- Sludge generation has decreased
- Reduced re-circulating load of thiosalts in recycle water
- No need for non-routine addition of neutralizing agents, safety
- Final effluent in compliance, no pH issues.
- Carbon dioxide consumption has dropped, lower incoming pH’s
- No more sporadic acute toxicity tests at the lab for past 2 years
- Reduced residual process reagents (ie: xanthate) in effluent
# Other H$_2$O$_2$ Treatment Plants for Oxidation of Thiosalts

<table>
<thead>
<tr>
<th>Location</th>
<th>Ore Type</th>
<th>Install Date</th>
<th>Vendor</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apirsa Mine Seville, Spain</td>
<td>Zinc, Lead, Copper</td>
<td>2001</td>
<td>Degussa</td>
<td>50% H$_2$O$_2$, 13000 USG Storage, 750-800 m$^3$/h flow rate with 500 mg/L thiosalts, 13 tpd average</td>
</tr>
<tr>
<td>Brunswick Mine Bathurst, NB, Canada</td>
<td>Zinc, Lead, Copper, Silver</td>
<td>2004</td>
<td>Degussa</td>
<td>50% H$_2$O$_2$, 9500 USG Storage, 10 tpd average in spring, 30 tpd peak</td>
</tr>
<tr>
<td>Kidd Met. Site Timmins, ON, Canada</td>
<td>Zinc, Copper, Silver</td>
<td>2009</td>
<td>Arkema</td>
<td>50% H$_2$O$_2$, 13000 USG Storage, 20 tpd average, 36 tpd peak</td>
</tr>
<tr>
<td>Voisey’s Bay Mine &amp; Mill Site, NL, Canada</td>
<td>Nickel, Copper, Cobalt</td>
<td>2010</td>
<td>TBD</td>
<td>TBD</td>
</tr>
</tbody>
</table>
Knowledge Sharing

**Sudbury 2007 Mining & Environment Conference** – Managing Thiosalts in Mill Effluents “Studies Conducted at the Kidd Metallurgical Site” by Nural Kuyucak, David Yaschyshyn

**2009 Xstrata Copper Canada Sustainable Development Report** – Case Study “Sharing innovative solutions in water treatment with the industry”

**42nd Annual CMP Conference (Ottawa) January 2010** – “Development of a Thiosalt Treatment System at Xstrata Copper Kidd Metallurgical Site” by Andréa Lagacé

**17th Annual BC/MEND Metal Leaching/Acid Rock Drainage Workshop**, Vancouver December 2010 – “Managing Thiosalts at Xstrata Copper, Kidd Operations” by David Yaschyshyn
Knowledge Sharing

CANMET MMSL Thiosalts Consortium 2009 Annual Meeting – held at Kidd Metallurgical Site with field tour of peroxide plant
Acknowledgements

Thiosalt Treatment Project Team
- Dave Scott, Concentrator Manager
- Andréa Lagacé, Engineer in Training
- Tim Miller, Tailings Metallurgist
- Leah Fedat, Environmental Coordinator
- Brian Raittinen, Project Engineer
- Porcupine Engineering Services
- Arkema (Hydrogen Peroxide)
- Kemira (Ferric Sulphate)

Treatment Optimization
- Juzer Tayabally, Engineer in Training
Thank You. Questions? (dyaschyshyn@xstratacopper.ca)