Managing Thiosalts in Mill Effluents

"Studies Conducted at the Kidd Metallurgical Site"

Mining and the Environment IV

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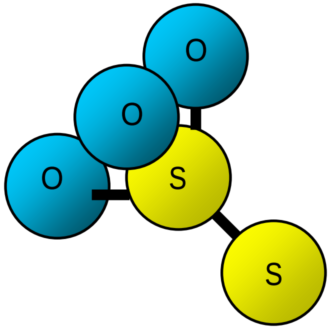
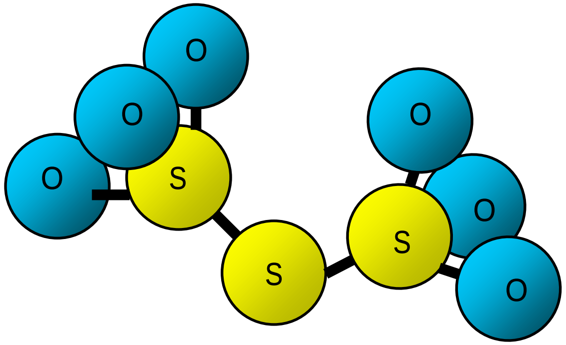
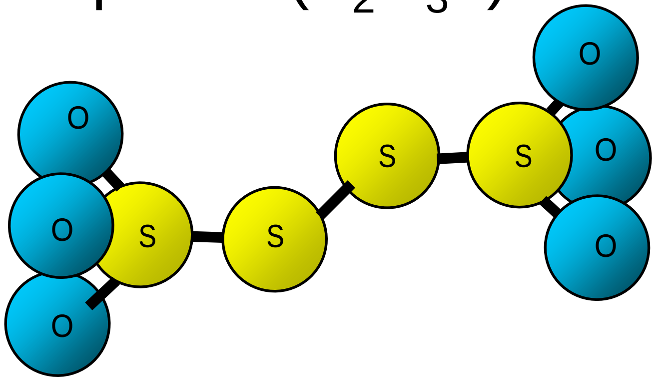
What are Thiosalts?



Thiosulphate ($S_2O_3^{2-}$)



Trithionate ion ($S_3O_6^{2-}$)



Tetrathionate ion ($S_4O_6^{2-}$)

Speciation at Kidd Met. Site

No.2 Tailings Thickener (2007)

180 mg/L as S_2O_3
<2 mg/L as S_3O_6
30 mg/L as S_4O_6

- A series of partially oxidized sulphur oxyanions ($S_xO_y^{2-}$)

Where/When “Thiosalts” occur?

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

$FeS_2 + 2O_2 + H_2O \rightarrow Fe^{2+} + 2OH^- + 2S^0$

$4S^0 + 6OH^- \rightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$

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

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

- Generation of thiosalts tends to be site-specific

Why Thiosalts require removal/reduction?

- Oxidize until end product sulphate (SO_4^{2-}) is reached
- Oxidation reactions produce proton (H^+) i.e., delayed acidity with potential to drop pH in treatment ponds, and effluents which could cause aquatic toxicity

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2H^+ + 2SO_4^{2-}$$

$$S_3O_6^{2-} + 2O_2 + 2H_2O \rightarrow 4H^+ + 3SO_4^{2-}$$

$$S_4O_6^{2-} + 7/2O_2 + 3H_2O \rightarrow 6H^+ + 4SO_4^{2-}$$

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 Generation at the Source

Grinding Circuit

Generation = *f* (ore type, % sulphide, pyrite vs. pyrrhotite, pH adjustment level, lime vs. soda ash use, ball vs. rod mill, grind time, oxygen exposure, quality and quantity of reclaim water)

Flotation Circuit

Generation = *f* (sulphur dioxide dosage, residence time, pH, water temperature, pulp agitation rate, sulphur content of the ore, fineness of the grind)

- As thiosalts formation in the concentrator cannot be economically eliminated, treatment is required.

How do Thiosalts Degrade?

- By reaching their final oxidation state
- Degradation is affected by pH, alkalinity, water temp. (e.g., slow at low temp.), retention time, UV
- Other methods or catalysts such as:
  - chemical (hydrogen peroxide, ozone, enhanced air oxidation, SO_2-Air oxidation, and HRT)
  - biological (*Thiobacillus ferroxidans* and *Thiobacillus thiooxidans* under acidic & aerated conditions, in biological contactors*)*
  - photodegradation (natural or artificial UV radiation)

Toxicity Thresholds of Thiosalts Species

Source: (Schwartz, Vigneault, McGeer, 2006)

Test Type	Test Organism	Thiosulphate	Tetrathionate
Acute	Rainbow trout	LC50 >800 ppm	LC50 >800 ppm
	Daphnia magna	LC50 ~300 ppm	LC50 ~750 ppm
Sublethal	*Lemna minor*	$IC25_{dry\ wt}$ = 498 ppm $IC25_{FC}$ = 525 ppm	$IC25_{dry\ wt}$ >798 ppm $IC25_{FC}$ >798 ppm
	Ceriodaphnia dubia	IC25 = 59 ppm	IC25 = 562 ppm
	Fathead minnow	IC25 = 665 ppm	IC25 >891 ppm
	Selanastrum capricornutum	IC50 >2220 ppm	IC50 >2110 ppm

- *Daphnia magna* more sensitive than Rainbow trout
- Data beneficial for toxicity identification evaluations

Thiosalts Consortium (est. 1995)

For Further Information Contact:

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BLUE NOTE CARIBOU MINES

BREAKWATER RESOURCES LTD

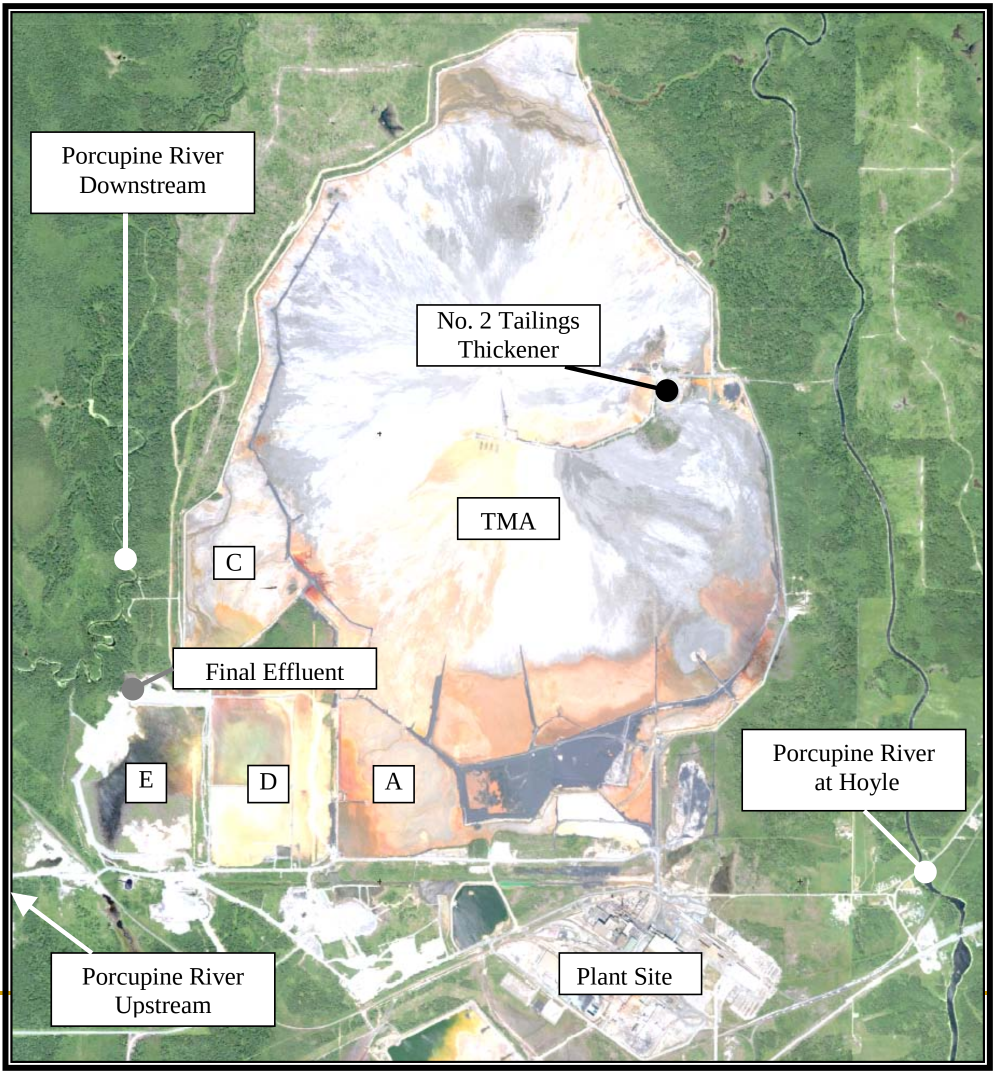
xstrata copper

HBMS

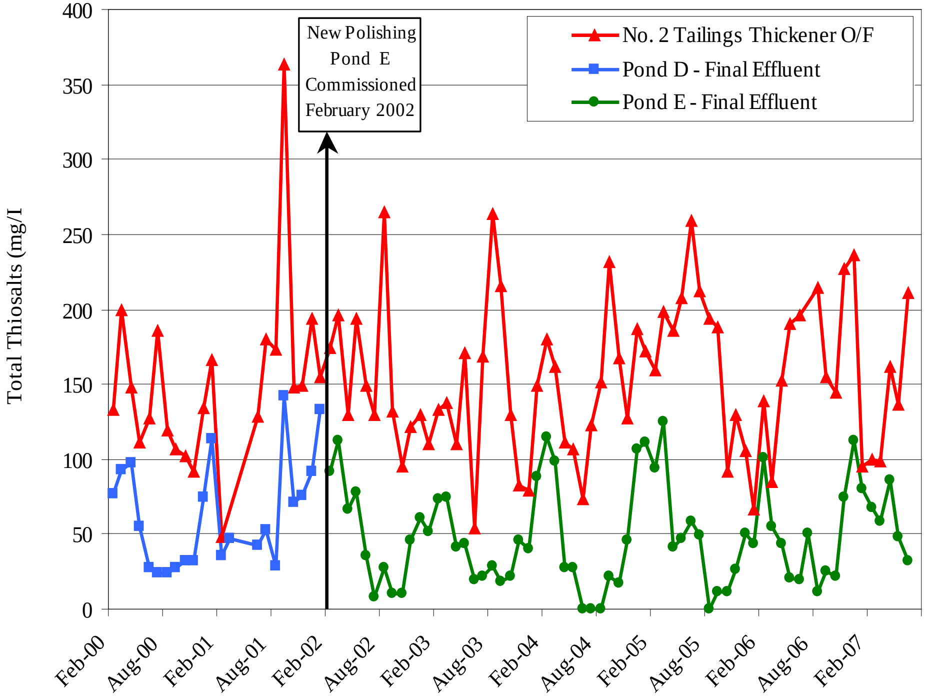
xstrata zinc

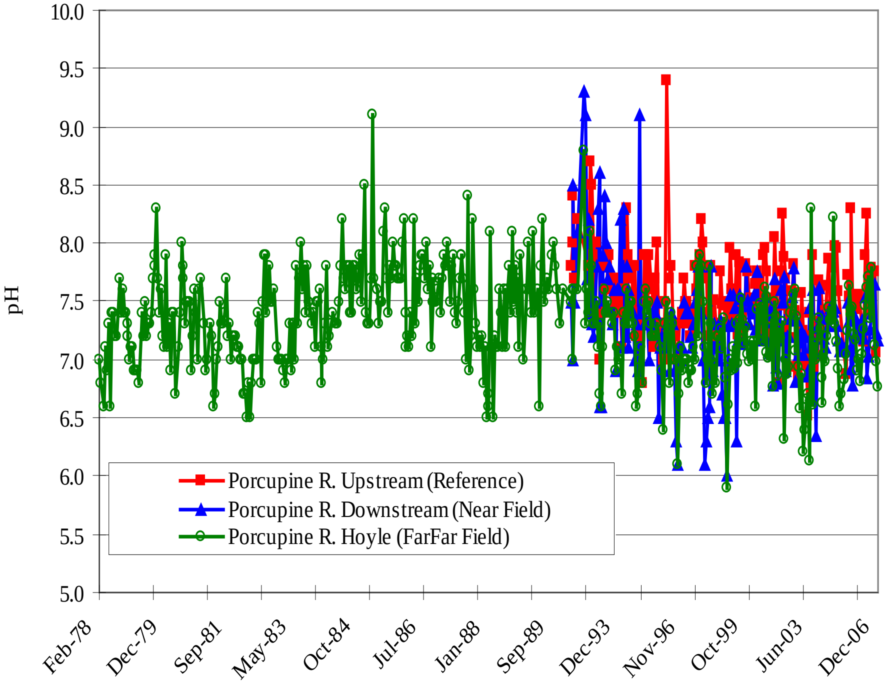
Xstrata Copper, Kidd Metallurgical Site - Timmins, Ontario

- Established 1966
- Integrated facility (Concentrator, Zn & Cu Operations)
- Thickened tailings discharge in 1973
- Lime Treatment at Pond A and C
- Settling Pond D
- Polishing Pond E
- Final Effluent to Porcupine River



Thiosalts Management at Kidd Metsite



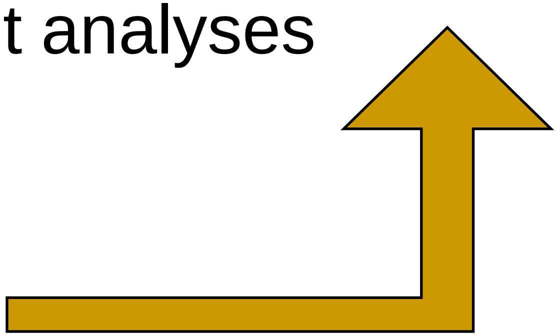


- Monitoring thiosalts for 10 years
- Seasonal trend evident in Final Effluent

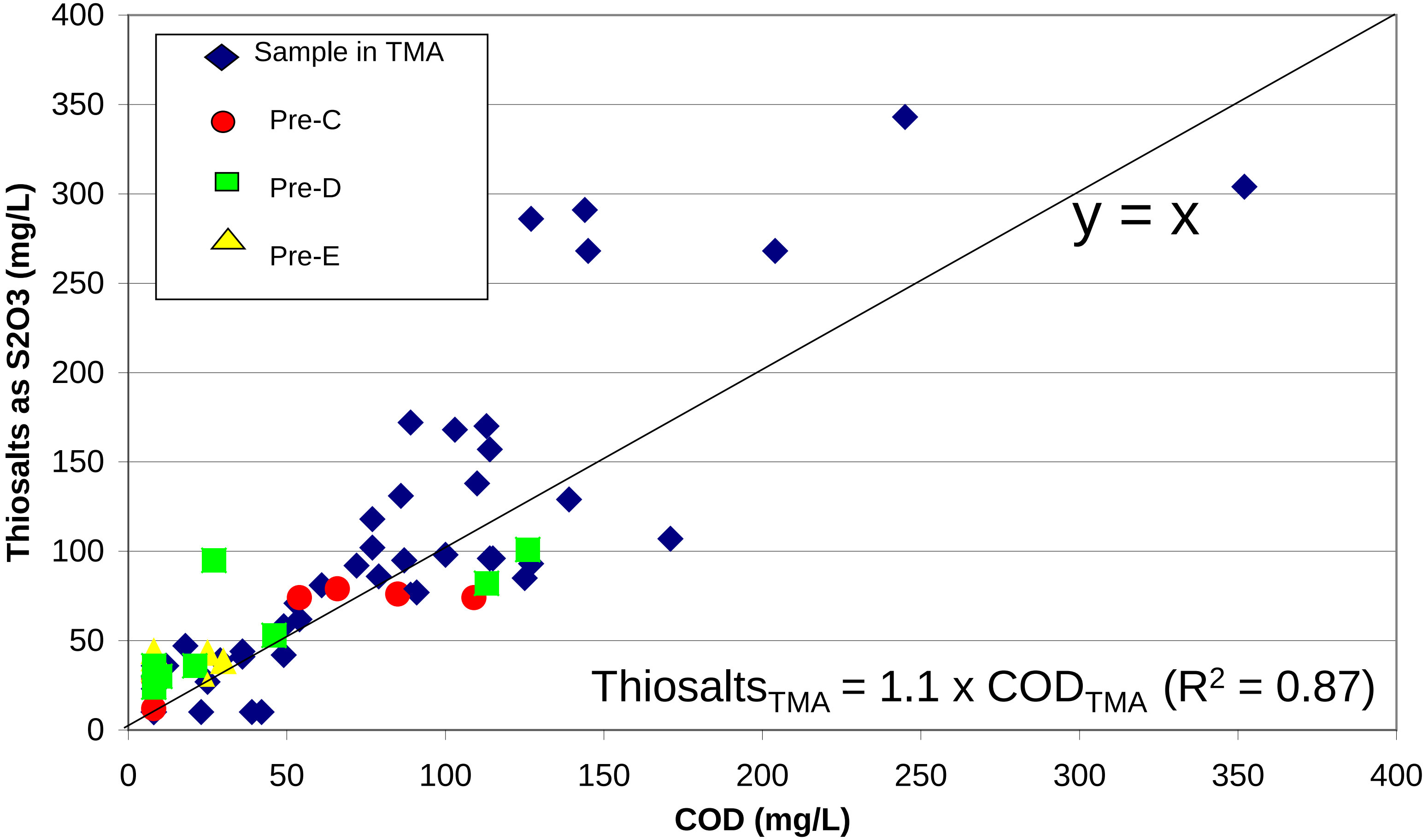
- Receiving environment pH monitoring since 1970’s
- No significant pH depression observed in the Near or Far Field downstream locations

Thiosalts Management Program

- Monitoring data review
- Literature review
- Determine alternate indicator parameter for thiosalts
- Developed site-specific natural degradation model
- Enhanced monitoring program
- Assess and rank possible options to reduce thiosalts
- Conduct lab studies and cost-benefit analyses
- Select cost-effective option(s)
- Conduct demonstration tests
- Implement the selected option(s)



Chemical Oxygen Demand (COD) as Alternative Thiosalts Indicator



Assess and Rank Potential Treatment Options

- Options ranked against the following criteria:
  - Technical feasibility
  - Capital and Operating costs
  - Environmental Impact
  - Safety
  - Practicality at Kidd Metsite
- Highest ranked options identified for assessment:
  - Increased Natural Degradation (first-order rate)
  - Chemical Oxidation with H_2O_2
  - Buffering addition using CO_3 and HCO_3

H_2O_2 Treatment Demonstration Trials

Peroxide Tanker

Dosing System

Dosing Location (North Overflow Collection Box)

- Trials in 2007 investigating peroxide dosage rate, dosing locations at No.2 Tailings Thickener Overflow, ferric iron as catalyst, % thiosalts degradation, acute toxicity

H_2O_2 Treatment Plants for Thiosalts

Location	**Ore Type**	**Install Date**	**Vendor**	**Capacity**
Apirsa Mine Seville, Spain	Zinc, Lead, Copper	2001	Degussa	50% H_2O_2, 13000 USG Storage, 750-800 m^3/h flow rate with 500 mg/L thiosalts, 13 tpd average
Brunswick Mine Bathurst, NB, Canada	Zinc, Lead, Copper Silver	2004	Degussa	50% H_2O_2, 9500 USG Storage, 10 tpd average in spring, 30 tpd peak
Kidd Met. Site Timmins, ON, Canada	Zinc, Copper, Silver	2007-08	Arkema	50% H_2O_2, 13000 USG Storage, 20 tpd average, 36 tpd peak

Acknowledgments

Xstrata Copper, Kidd Metallurgical Site

- Michael Patterson, Manager Environment & Hygiene
- Dave Scott, Manager Concentrator

Golder

- Ken Bocking, Principal

Thank You – Questions?