Effluent Treatment Experience with Proprietary Organosulfide Reagents

December 4, 2014

Presentation Overview

- Context: BATEA Study
- Proprietary Organosulfide Reagents
    - What are they?
    - How do they work?
    - Why are they used in mine effluent treatment?
- CCWWTP
    - Nalmet 1689
    - MetClear™ MR2405
- Whistle Mine WWTS
    - MetClear™ MR2404

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Study to Identify BATEA for the Management and Control of Effluent Quality from Mines

Study Purpose

- Provide reference information regarding (sub)sector water management, effluent treatment applicable BAT
  - BAT: Best Available Technology
- Establish water management and effluent treatment models for each (sub)sector
- Identify BATEA to *augment* effluent treatment systems utilized by Canadian mining (sub)sectors to improve effluent quality for current and proposed *MMER* parameters
  - BATEA: Best Available Technology Economically Achievable

Base Metal Sector BATEA

- BATEA was defined as sulfide precipitation with proprietary polymeric organosulfide chemicals for dissolved metal polishing
  - selected based on bounds of study design, with outstanding questions and concerns

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What are Proprietary Polymeric Organosulfide Reagents?

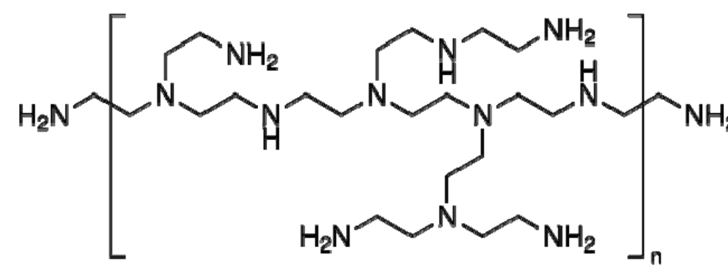
"Second generation" organosulfides

Proprietary formulations

- Ethlylene dichloride-ammonia polymers (polyamines, polyimines)
- Modified with carbon disulfide to make dithiocarbamate functional groups
- Sodium hydroxide matrix

Polymeric chemicals

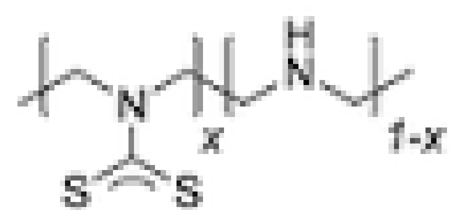
Anionic sulfur-containing functional groups



MP Biomedicals Polyethyleneimine Solution

Dithiocarbamate (DTC) salt

KP1



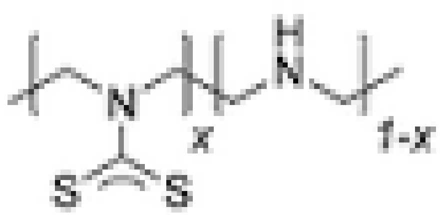
PEI-DTC

J. Mater. Chem., 2011, 21, 4371-4376

How do Proprietary Polymeric Organosulfide Reagents Work?

$Me^{2+} + S^{2-} \leftrightarrow MeS(s)$

$Me^{2+} + HS^{-} \leftrightarrow MeS(s) + H^{+}$



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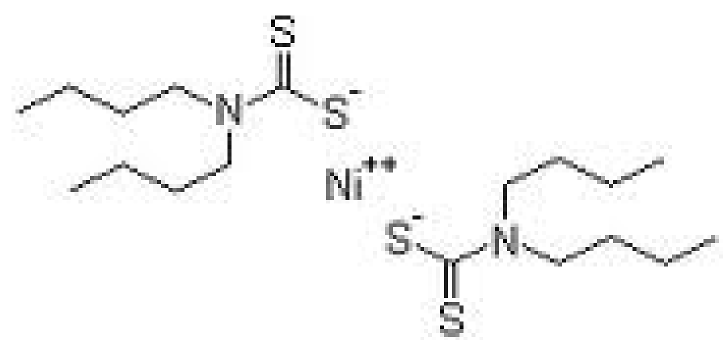

Chemical Book CAS No. 13927-77-0

Why Use Proprietary Polymeric Organosulfide Reagents?

As compared to hydroxide precipitation:

Advantages

- Solubility MeS << solubility $Me(OH)_2$ over a wide pH range
- Effective in presence of metal chelants
- Offset potential for coagulant, flocculant and/or post-pH adjustment reagents
- Residuals more stable under pH variation

Disadvantages

- Expensive – often limited to polishing
- Residues more difficult to settle and dewater (risk of carryover)
- Residuals less stable under oxidative conditions
- Risk of oxidation in storage or downstream (COD)
- Deactivated by acidity ($pH < 4$) and soluble oils and non-metallic suspended solids which adsorb onto surface
- Risk of H_2S and CS_2 evolution
- Risk of aquatic toxicity
- Difficult to measure residuals and diagnose toxicity root cause

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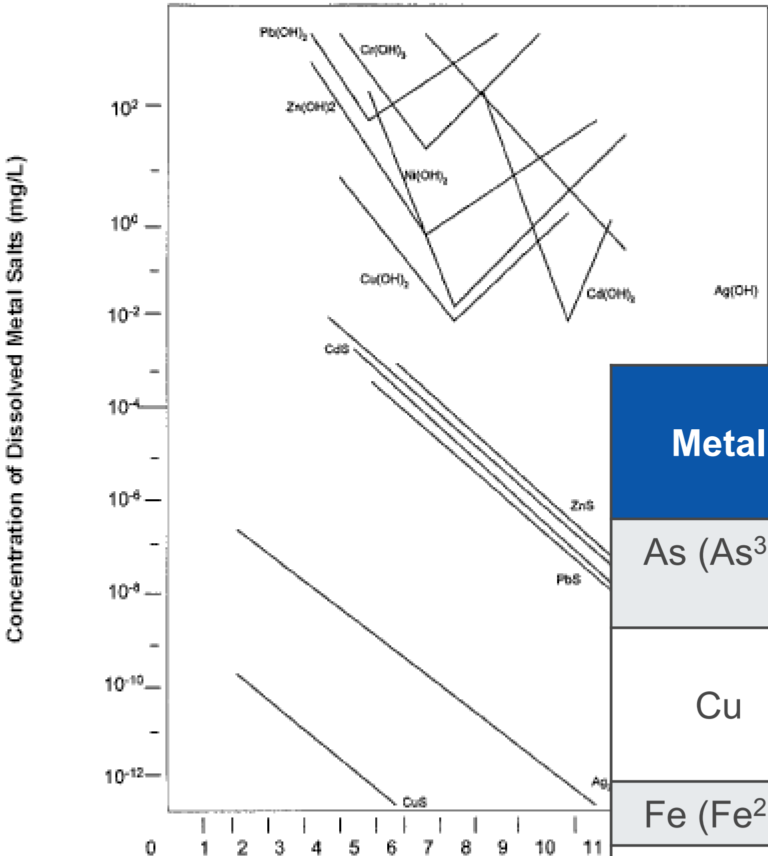
Why Use Proprietary Polymeric Organosulfide reagents? (cont'd)



EPA, 1983

Metal	Hydroxide Precipitation mg/L	Organosulfide Precipitation mg/L	Site Data Exceptions mg/L
As (As^{3+})	~5	<0.05	
Cu	<0.07	<0.03	<0.005 (+ filtration) <0.05 (jar tests + filtration) 3.16 to <0.35
Fe (Fe^{2+})	<0.1 (total)	<0.30	
Mn (Mn^{2+})		<0.05	
Ni	<0.20	<0.05	<0.20 14.55 to <0.35
Pb	<0.04	<0.05	<0.12
Se		<0.05	
Zn	<0.40	<0.02	<0.17

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Who Uses Proprietary Polymeric Organosulfide Reagents?

Ontario

- Base Metal - MetClear™ MR2405 to overcome organic chelation
- Base Metal - MetClear™ MR2405 to polish metals
- Base Metal - MetClear™ MR2405 to polish metals
- Closed Base Metal Site - MetClear™ MR2404 (MR2404 is non-polymeric)

New Brunswick

- Base Metal - Hydrex® 6909 to overcome ammonia chelation and obtain extremely low copper concentrations.

Alberta/British Columbia

- Coal – batch application of NALMET 1689 to remove mercury

United States

- Base Metal - Michigan - Hydrex® 6909 to remove mercury

Many applications in other industries (power generation/FGD, refineries, battery, metal plating, ceramics) to polish metals.

Copper Cliff Waste Water Treatment Plant (CCWWTP)

- Double clarifier, lime hydroxide precipitation
- Final pH adjustment with H_2SO_4
- Treatment Plant Design Capacity: 9,460m^3/hr or 227,040m^3/day
- Treats water from:
  - 4 Mines
  - Mill and Tailings Impoundment
  - Smelter Complex
  - Nickel Refinery
  - Sewage Treatment Plant (municipal)
  - Municipal Drainage



CCWWTP: Background on Reagent Use

- Proprietary polymeric organosulfide reagents used seasonally to supplement treatment processes
  - DETA used at the upstream mill creates chelating conditions during winter months
  - Lime-based precipitation found to be less effective at removing complexed Cu, Ni under these conditions

Winter Season	Reagent Used
2007-2010	Nalmet (Trials)
2010/2011, 2011/2012	Nalmet 1689
2012/2013	MetClear™ MR2405
2013/2014	None (No DETA)

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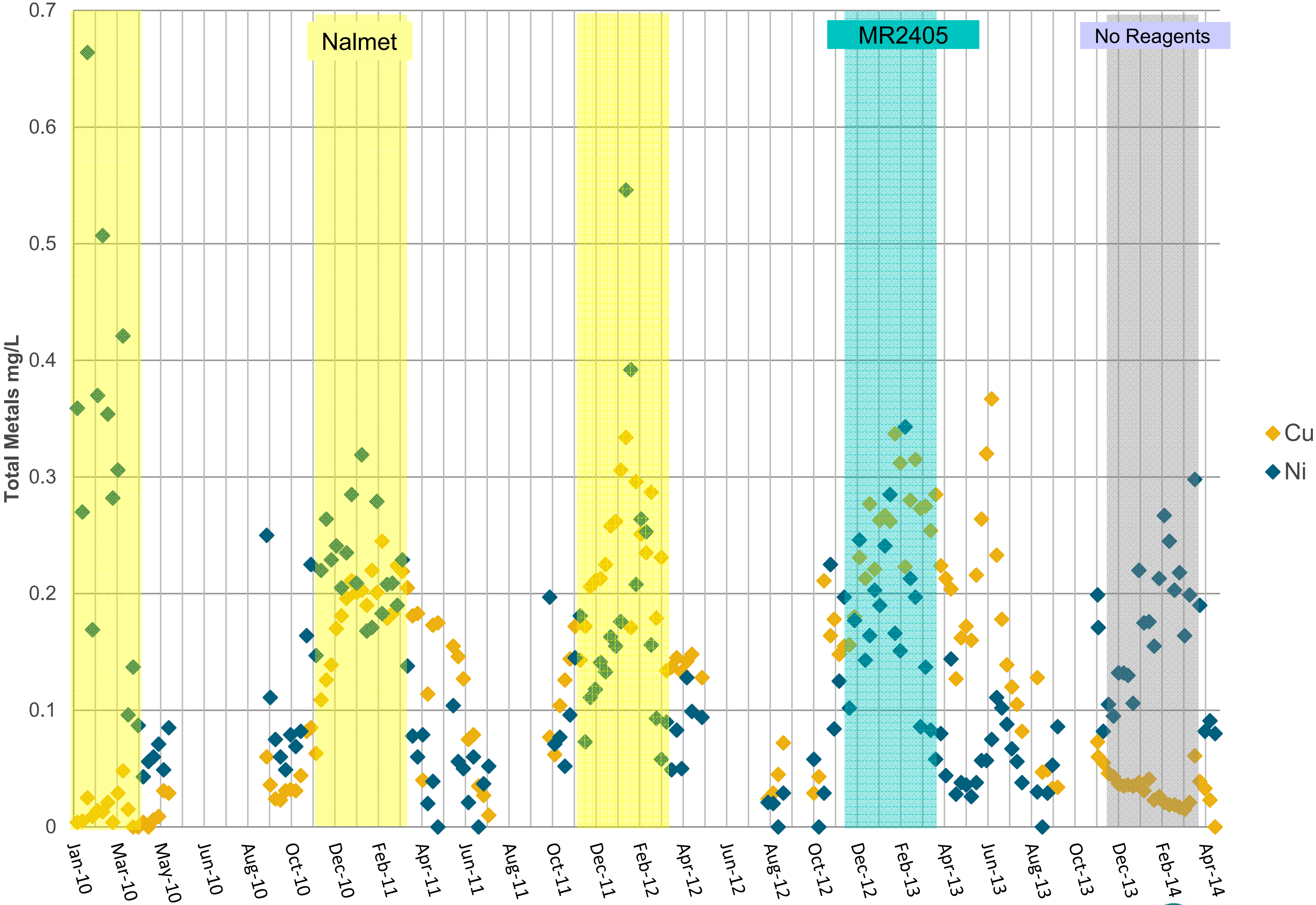
CCWWTP: Reagent Performance

Achievable Concentrations BATEA Report ← Jar Test Results ← Actual Performance

NALMET 1689	Cu (mg/L)	Ni (mg/L)
BATEA Report	<0.03*	<0.05*
Effluent Mean 2010/2011	**0.1761**	**0.2233**
Effluent Mean 2011/2012	**0.2404**	**0.1988**
MetClear™ MR2405	**Cu (mg/L)**	**Ni (mg/L)**
BATEA Report	<0.03*	<0.05*
Jar Test Results	0.06-0.11	0.11-0.21
Effluent Mean 2012/2013	**0.2540**	**0.1938**
No Reagents	**Cu (mg/L)**	**Ni (mg/L)**
Effluent Mean 2013/2014	**0.0291**	**0.1754**

CC Performance with Proprietary Organosulfide Reagents



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CCWWTP: Reagent Toxicity and the Receiving Environment

	LC50 RBT mg/L	LC50 DM mg/L	Proposed Dosage per mg/L Ni	Proposed Dosage per mg/L Cu
Nalmet 1689	74	73	16.8	15.4
MR2405	8	240	10	10

Example:

- Influent [Ni] 15mg/L = 150mg/L MR2405
  = 252mg/L Nalmet 1689
- Influent [Cu] 1.5mg/L = 15 mg/L MR2405
  = 23.1 mg/L Nalmet 1689

CCWWTP: Reagent Toxicity and the Receiving Environment

NALCO

SAFETY DATA SHEET

PRODUCT

NALMET® 1689

EMERGENCY TELEPHONE NUMBER(S)

(800) 424-9300 (24 Hours) CHEMTREC

6. ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS :
Restrict access to area as appropriate until clean-up operations are complete. Use personal protective equipment recommended in Section 8 (Exposure Controls/Personal Protection). Stop or reduce any leaks if it is safe to do so. Keep people away from and upwind of spill/leak. Ventilate spill area if possible. Remove sources of ignition. Ensure clean-up is conducted by trained personnel only. Do not touch spilled material. Have emergency equipment (for fires, spills, leaks, etc.) readily available. Notify appropriate government, occupational health and safety and environmental authorities.

METHODS FOR CLEANING UP :
SMALL SPILLS: Soak up spill with absorbent material. Place residues in a suitable, covered, properly labeled container. Wash affected area. LARGE SPILLS: Contain liquid using absorbent material, by digging trenches or by diking. Reclaim into recovery or salvage drums or tank truck for proper disposal. Clean contaminated surfaces with water or aqueous cleaning agents. Contact an approved waste hauler for disposal of contaminated recovered material. Dispose of material in compliance with regulations indicated in Section 13 (Disposal Considerations).

ENVIRONMENTAL PRECAUTIONS :
Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment., Prevent material from entering sewers or waterways., If drains, streams, soil or sewers become contaminated, notify local authority.

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Whistle Mine Waste Water Treatment System

- Pond based system with small treatment plant
- Treats water from a decommissioned open pit mine
- Intermittent discharger, 1000-2000m^3/day
- Hydroxide precipitation aided by proprietary reagents – MR2404, Klaraid
  - Remote location and limited pond capacity
  - Reagents allow metal removal a lower pH

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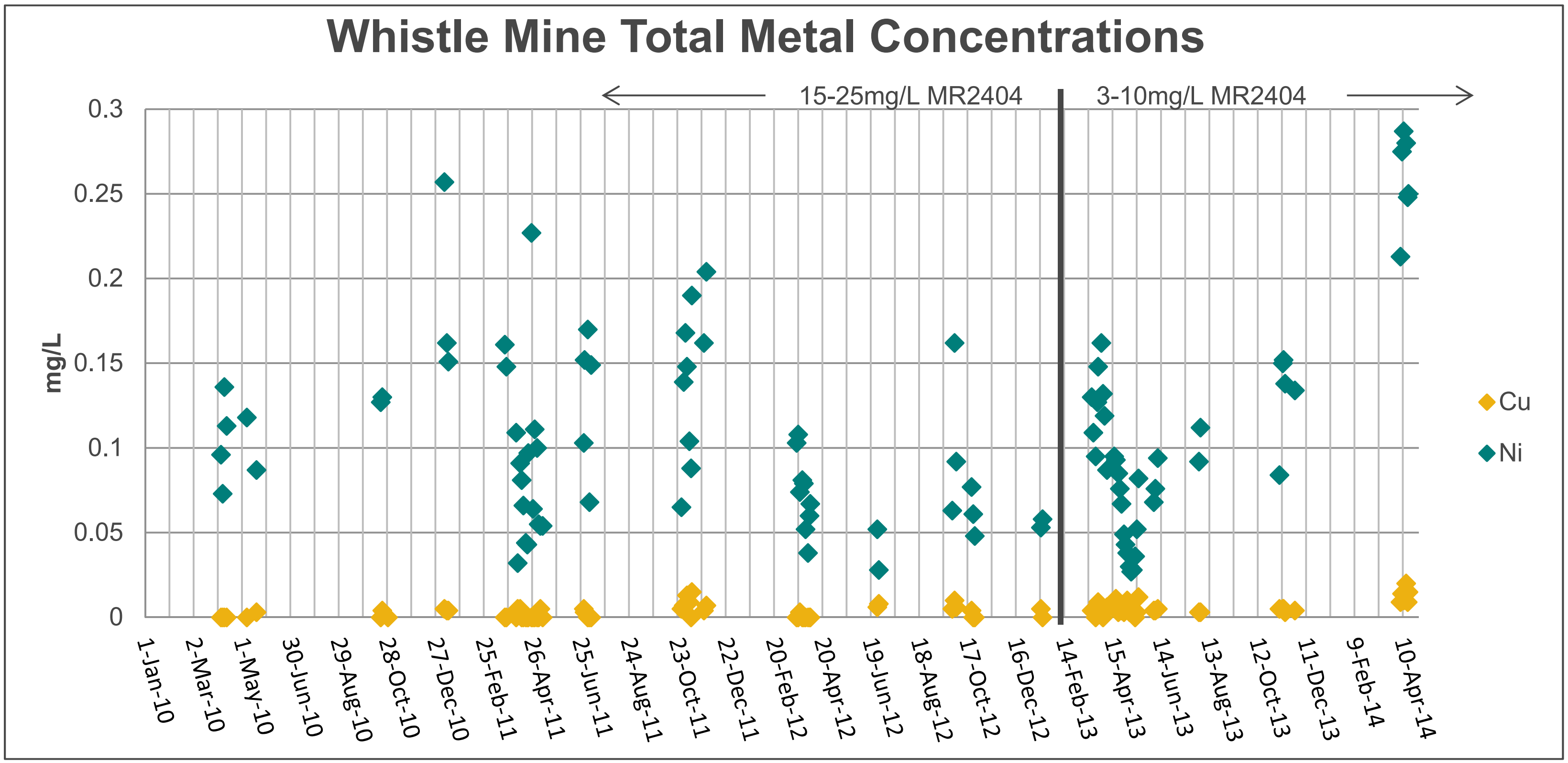
Whistle Mine WWTS: MR2404 Reagent Performance

- Jar testing by GE Betz initially recommended target dosage of 15-25mg/L
- Revised dosage range 3-10mg/L MR2404 based on influent Nickel concentrations of 1-9mg/L
  - Results: 0.061-0.295mg/L Ni



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Whistle Mine WWTS: MR2404 Toxicity Concerns

- Single item listed on the MSDS: sodium dimethyldithiocarbamate
    - Metal precipitant
    - Biocide

- LC50 Rainbow Trout: 0.85mg/L
- LC50 *Daphnia magna*: 0.03mg/L

Whistle Mine WWTS: MR2404 Toxicity Concerns

- Acute toxicity test failure in January 2013 attributed to excess concentrations of MR2404 in effluent and treatment ponds
    - Recommended dosage rate + recirculation

- Two lines of corrective action investigation
    - Treatment to remove MR2404
    - Development of test method for sole ingredient listed on MSDS

- Throughout investigation, Vendor was present but could not provide information on product make-up, fate and behaviour in the environment, constraints on biodegradation, etc.

Overarching Concerns

Realized Treatment Capabilities

Toxicity

Proprietary Nature

Long Term Fate in Environment

Vendor Control of Treatment Costs

Unanswered Questions

Are vendors willing to disclose formulations?

Are residuals stable in the long term under typical mining storage conditions?

- How does polymeric nature influence residuals stability?

Are vendors willing to work with government, academia, and industry to:

- provide sufficient evidence to satisfy regulators and communities that these reagents are safe?
- develop residual reagent monitoring methodologies?
- assess long term stability of residuals?
- develop best practices for reagent use? e.g., dosage optimization, solid/liquid separation, water management, residuals disposal

Is any party developing alternative formulations to reduce toxicity while still achieving quality?

Path Forward

- MAC reached out to Environment Canada and Natural Resources Canada
  - MEND/CANMET, potentially in cooperation with Environment Canada, would be well placed to address the issues of process monitoring and control, fate and behaviour in the environment, and the long term stability of residues

- Increased discussion, data sharing and outreach

Thank You

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