# Thiosalt in Mining and Metal Processing

Thiosalt Group:

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# Outline

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- Thiosalts Overview
- Research Objectives
- Literature Background
- Past/Current Work
- Path Forward

# Overview

- Thiosalts are sulphur oxyanions that include thiosulphate ($S_2O_3^{2-}$) and polythionates ($S_xO_6^{2-}$ where $3 \le x \le 10$)
- Result of oxidation of sulphide minerals during milling, grinding, and flotation of sulphide ores or in the hydrometallurgical processing of the concentrate to recover metals
  - In pyritic Cu-Zn and Cu-Ni pyrrhotite ores approximately 17% of the total thiosalts present in the pond influent are present in the dry feed prior to milling
  - Average 15%, 32%, and 36% are generated in the grinding, aeration, and copper circuit respectively (Negeri et al., 1999 and Dinardo and Salley, 1998)
- Thiosalts typically end up in the effluent ponds and/or AMD

# Environmental Concerns

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- The chemical/biological oxidation of thiosalts in natural waters results in pH depression that can harm aquatic organisms

- Additional thiosalt impacts on natural waters are:
  - sediment metal leaching, and
  - reduction of dissolved oxygen and of buffering capacity

- These impacts can be mitigated by proper design of wastewater treatment management
  - Treatment systems
  - Pond design

# Thiosalts and Wastewater Management

- “Typical” methods to manage thiosalts pH control, accelerated oxidation, and/or biological degradation
  - Biological has shown limited success, especially in northern climates
  - Addition of chemical based on simplified mass balance as the reactivity of thiosalts is poorly understood
  - Thiosalts fluctuate between different species due to; pH, temperature, and reactions with each other or other oxidants/catalysts in the pond/AMD
- Lack of method to differentiate between species quickly (on-site) and accurately

# Thiosalts and Wastewater Management

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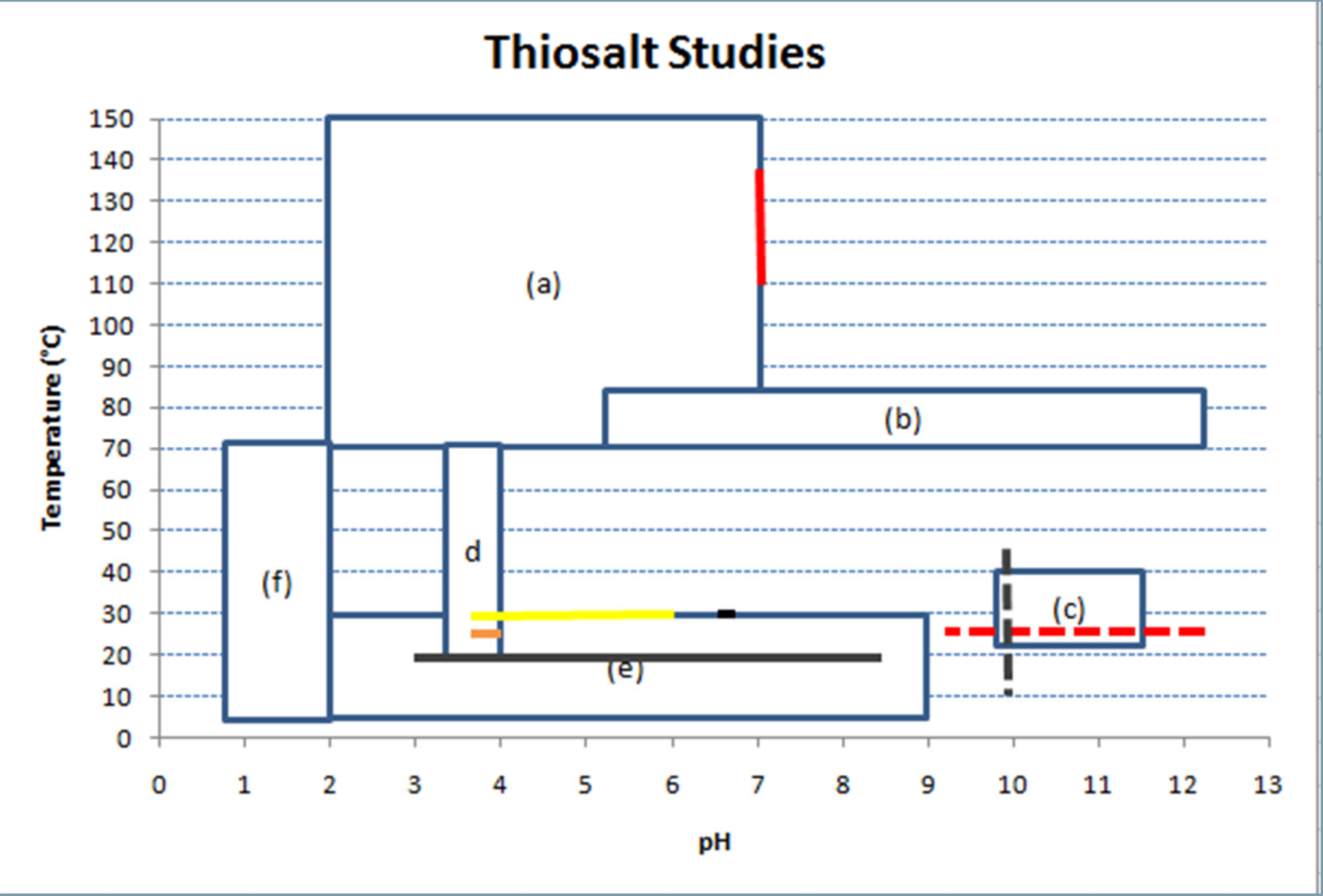
- Under or over prediction of thiosalt levels may result in flawed wastewater management systems (treatment, pond design)
- Knowledge of overall reaction rates and impacts of catalysts (metals, microbes) result in more effective thiosalt management methods and minimize environmental impacts.
- Critical to the development of wastewater management methodologies for both operating and abandoned mines where sulphide ore processed

# Research Objective

- Better understanding of the reaction rates
- Impact of catalysts (chemical and biological) in the pond/AMD
- Develop a methodology to minimize thiosalt formation and/or treatment
- Research in this area tended to focus on higher temperatures, limited range of pH, and/or species of thiosalt

# pH and Temp Conditions of past studies




a – Mizoguchi et al 1972

b – Rolia and Chakrabarti 1982

c – Zhang and Dreisinger 2002

d – Meyer and Ospina 1982

e – Vongporm 2008

f – Druschell 2003

Rolia and Chakrabarti 1982

Bernier and Warren 2007

Wentzien et al 1994

Chanda 1987

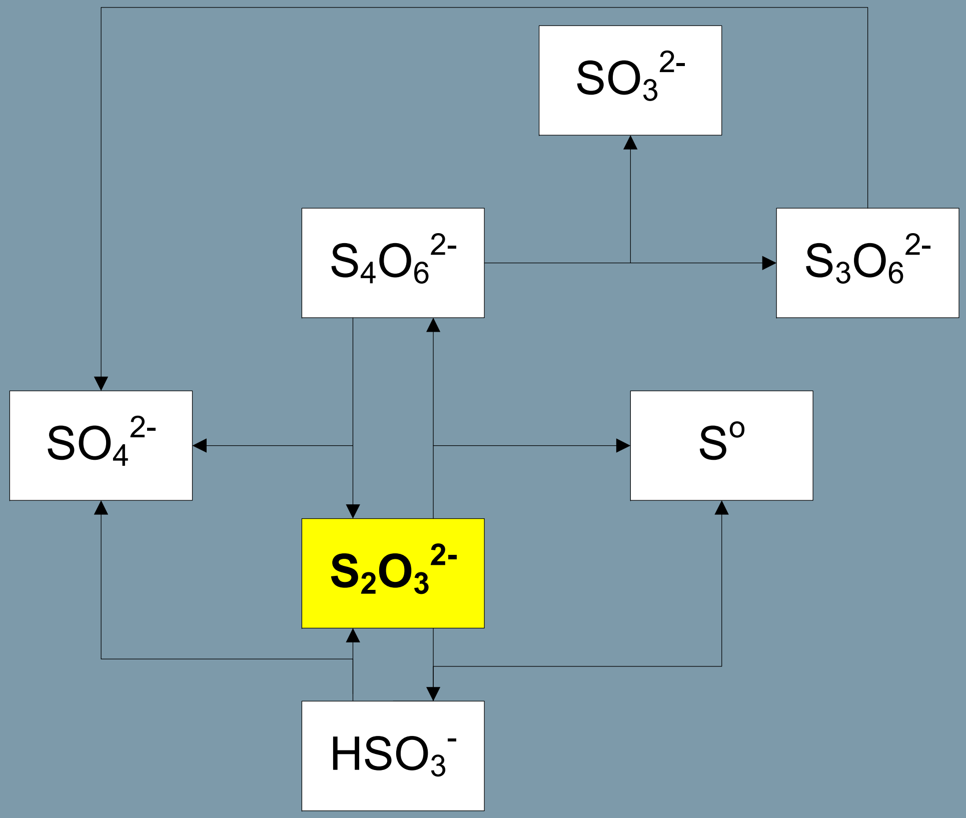
Rolia and Chakrabarti 1982

Varga and Horvath 2007

Xu and Schoonen 1995

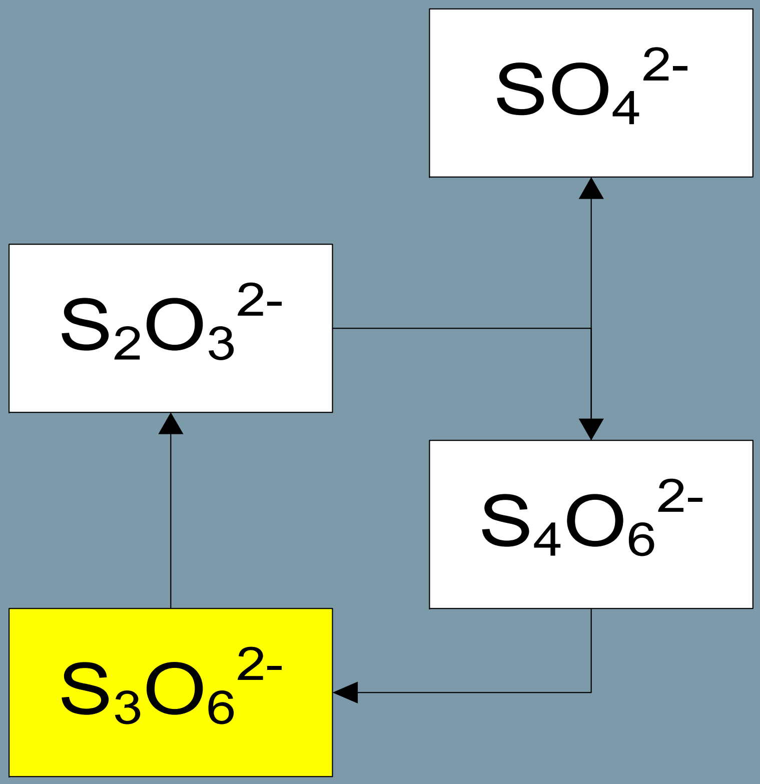
# Thiosulphate

- Highly reactive at low pH (<4)
- Pyrite, Cu, Fe and microbes accelerate the reaction
- Main product of reaction is tetrathionate
- Reactivity at basic conditions restricted to at high temperature (<70°C)



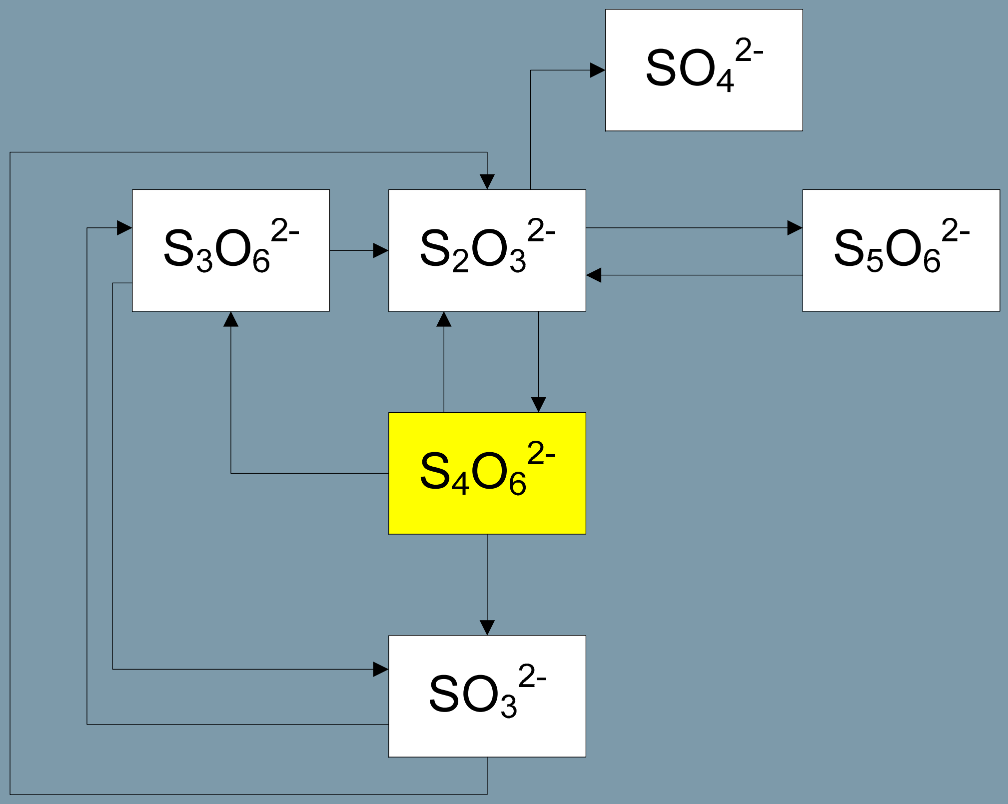
# Trithionate

- Stable in neutral and acid conditions
- $Fe^{3+}$ enhance the oxidation in the presence of oxygen.
- Limited reactivity in the presence of $H_2O_2$ which is improved with the presence of the Fenton reagent.
- Main products of reaction are thiosulphate and sulphate
- Limited reactivity in the presence of Cu



# Tetrathionate

- Highly stable in acid and near neutral conditions except at high temperatures (>70°C)
- Thiosulphate shown to act as a catalyst of tetrathionate oxidation
- Limited reactivity in the presence of $H_2O_2$ which is improved with the presence of the Fenton reagent.
- Main products of oxidation are thiosulphate and sulphite



# Research Strategy

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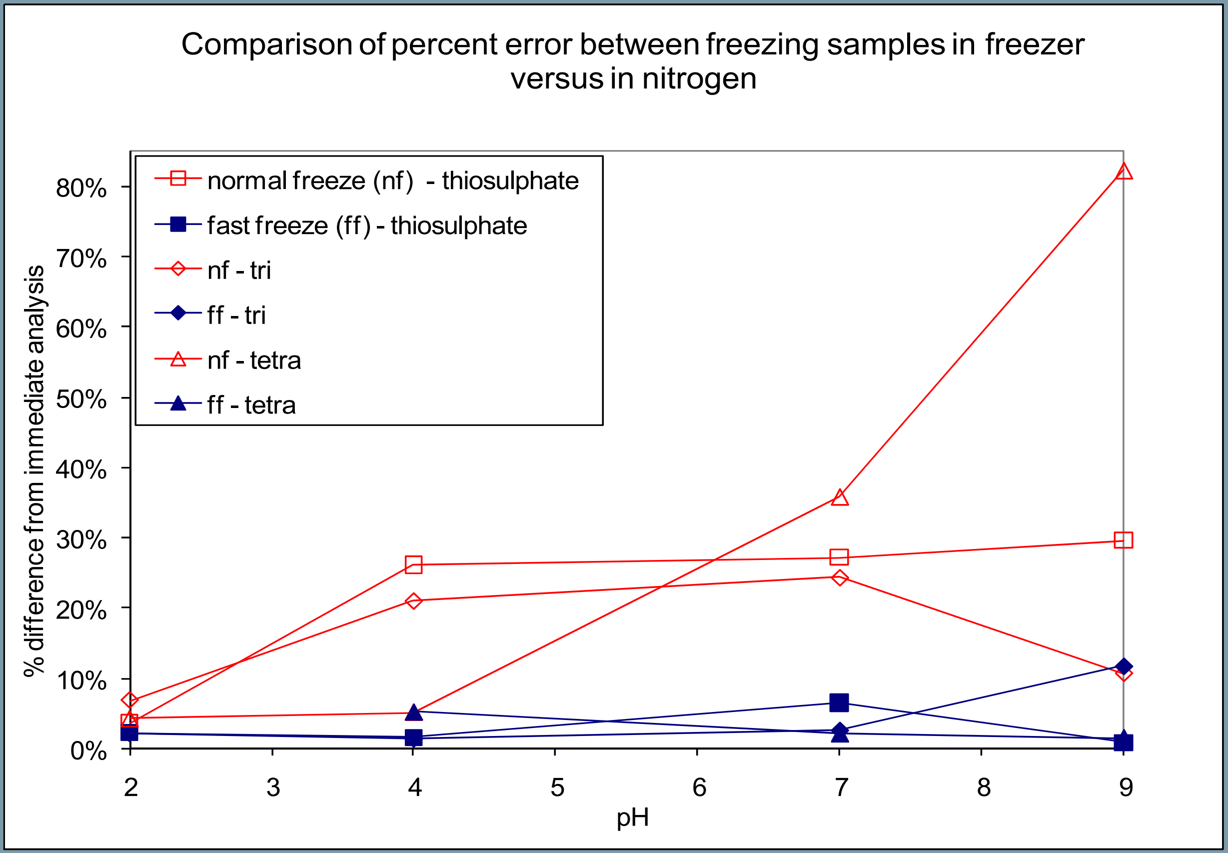
- Kinetic model and global reaction mechanisms for major species (pure and in the presence of reagents)
- Development of analytical techniques (CE)
- Treatment technology evaluation and risk assessment analysis

| Variable | Levels |
|---|---|
| Thiosalt | • Thiosulphate, trithionate and tetrathionate |
| pH | • Acid to Basic (2, 4, 7 and 9) |
| Temperature | • 4, 15 and 30 °C |
| Reagents | • $Fe^{3+}$, $Pb^{2+}$, $Cu^{2+}$<br>• $H_2O_2$<br>• Pyrite<br>• Thiobacillus ferroxidans<br>• Acidithiobacillus thioxidans |

# Preliminary Results

## Sampling



# Preliminary Results

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## Reactive conditions according to speciation

| | Temp= 4°C | Temp= 15°C | Temp= 30°C |
|---|---|---|---|
| pH=2 | Thiosulphate | Thiosulphate | Thiosulphate<br>Trithionate |
| pH=4 | | Trithionate | Trithionate |
| pH=7 | | Trithionate | Trithionate |
| pH=9 | Tetrathionate | Tetrathionate | Thiosulphate<br>Trithionate<br>Tetrathionate |

# Preliminary Results

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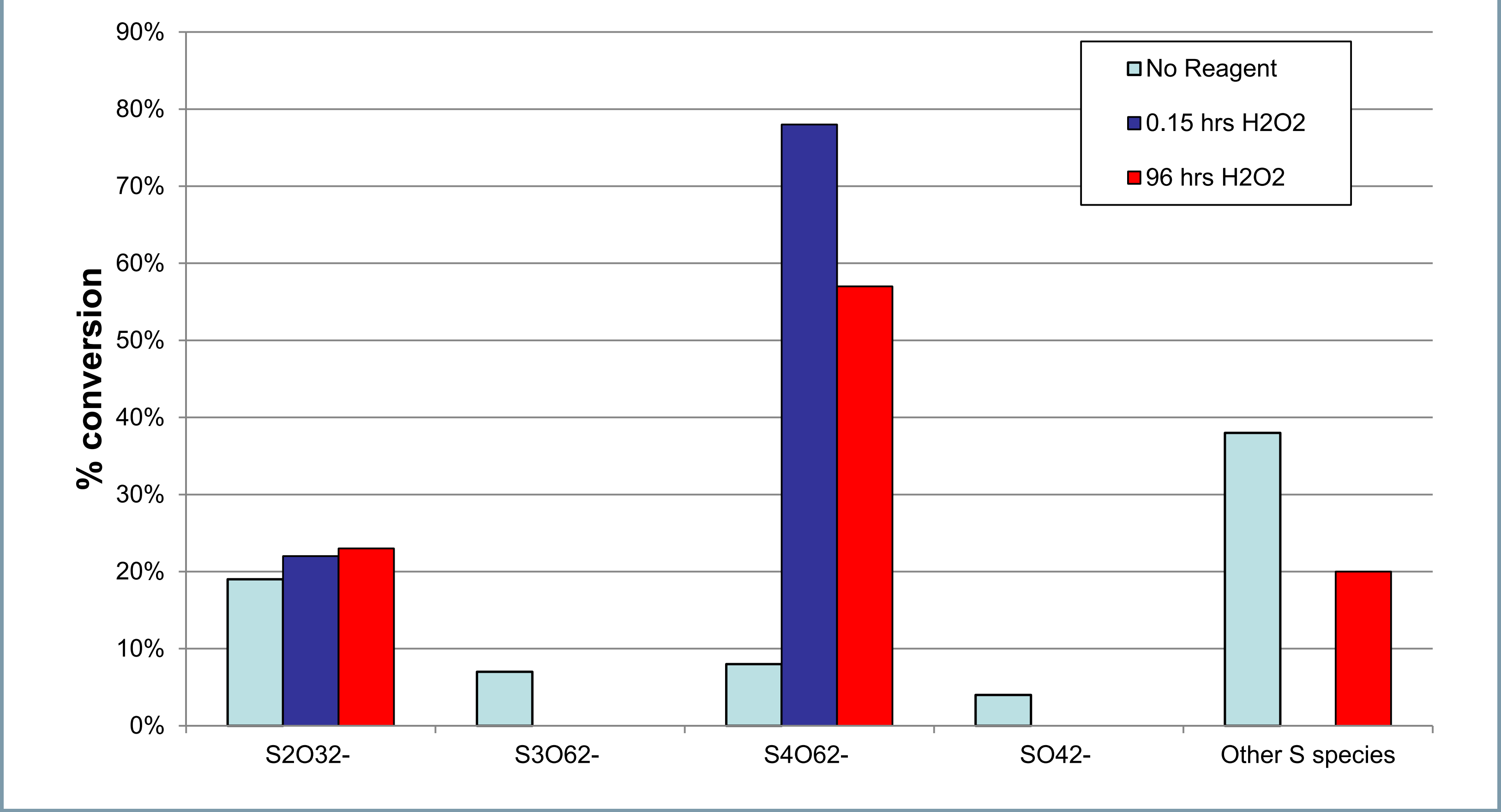
Thiosulphate experimental at pH=2 after 72 hrs

| | 4 °C | 15 °C | 30 °C |
|---|---|---|---|
| $S_2O_3^{2-}$ | 61% | 30% | 19% |
| $S_3O_6^{2-}$ | 5% | 5% | 7% |
| $S_4O_6^{2-}$ | 0% | 7% | 8% |
| $SO_4^{2-}$ | 3% | 3% | 4% |
| S° and other S species | 30% | 56% | 62% |

Thiosulphate experimental results at pH=2 after 10 min with $H_2O_2$ treatment

| | 4 °C | 15 °C | 30 °C |
|---|---|---|---|
| $S_2O_3^{2-}$ | 1% | 14% | 22% |
| $S_3O_6^{2-}$ | 0 | 0 | 0 |
| $S_4O_6^{2-}$ | 99% | 86% | 78% |
| $SO_4^{2-}$ | 0 | 0 | 0 |
| S° and other S species | 0 | 0 | 0 |

# Preliminary Results



# Preliminary Results

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Treatment results with $H_2O_2$ for thiosulphate at different pH

| | pH = 4 | | | pH = 7 | | | pH =9 | | |
|---|---|---|---|---|---|---|---|---|---|
| | 4 °C | 15 °C | 30 °C | 4 °C | 15 °C | 30 °C | 4 °C | 15 °C | 30 °C |
| $S_2O_3^{2-}$ | 0 | 6% | 7% | 31% | n/a | 39% | 70% | 63% | 63% |
| $S_3O_6^{2-}$ | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| $S_4O_6^{2-}$ | 100% | 94% | 87% | 56% | n/a | 31% | 0 | 0 | 0 |
| $SO_4^{2-}$ | 0 | 0 | 0 | 0 | n/a | 0 | 0 | 0 | 0 |
| S° and other S species | 0 | 0 | 6% | 13% | n/a | 29% | 30% | 37% | 37% |

# General Observations

- Sulphur formation in low pH experiments with thiosulphate
- Thiosulphate and trithionate produce $H_2S$ with $H_2O_2$ treatment at low pH
- Sampling protocol is critical as the thiosalts may speciate which impacts treatment approach
- Thiosalts management must not only include pH and temperature but the species of thiosalts present

# General Observations

- Wastewaters/groundwater containing thiosalts may not respond to remediation alternatives in the same way as sulphate containing waters.

    Reactions could undo neutralization step and result in more neutralizing agent addition, driving up treatment costs and sludge generation and even possibly affecting dissolved metal concentrations.

- These stability issues complicates development of wastewater management methodologies and a systematic analysis of these many factors is required to optimize and improve management

# General Observations

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- Presence, formation, and degradation of thiosalts complicate management mine waste.

# Path Forward

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- Optimize CE method
- Continue with the analysis with other reagents
- Develop kinetic model and global reaction mechanisms (sensitivity analysis)
- Develop risk assessment
- Apply model to real samples from mines

# Thanks to

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NSERC
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VALE

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CONACYT

Natural Resources Canada
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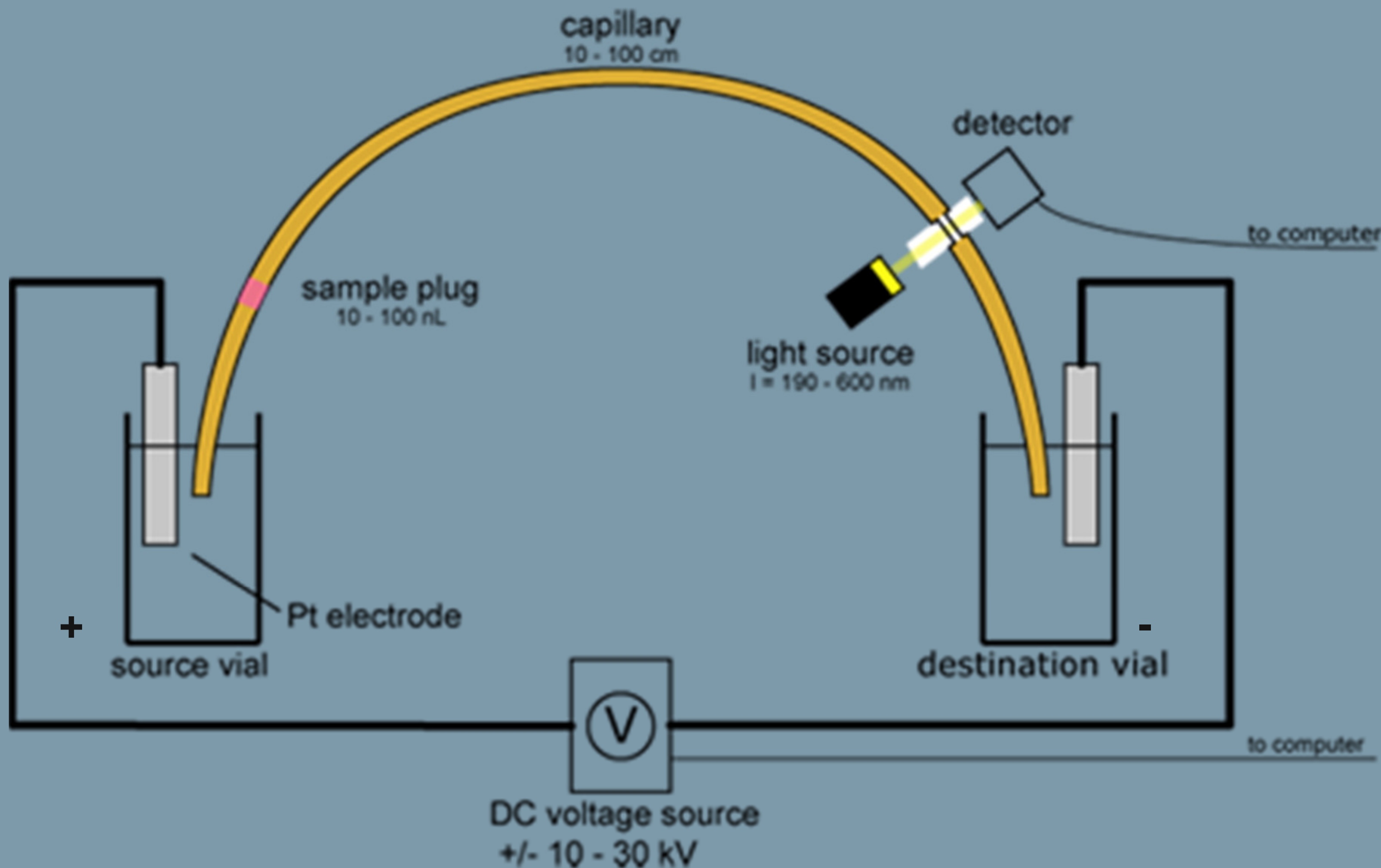
# END OF PRESENTATION

# Capillary Electrophoresis






http://www.richardcarbonaro.com/projects/CE.html