

Thiosalts in the Mining Industry — A Review of the Projects Funded by the Thiosalts Consortium

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Abstract

The Thiosalts Consortium is an industry and government group, formed in 1995, to provide a forum for participants to fund projects aimed at reducing the environmental effect of thiosalt-contaminated mining effluents. The goals of the Consortium are as follows:

- Fund research into practical solutions to environmental problems related to thiosalts;
- Provide a forum for technology exchange and transfer;
- Raise the awareness of the mining industry with respect to environmental problems;
- Provide a technical basis for codes, standards and regulations;
- Keep abreast of new environmental regulations; and
- Establish a core group with expertise on thiosalts.

In the past seven years, the Thiosalts Consortium has funded fourteen projects. This paper is a review of nine projects completed since 1998. These projects are as follows: (1) inter-laboratory measurement testing program for total thiosalts; (2) investigation of the SO₂-air mixtures for thiosalts destruction from metal mining effluents, (3) thiosalt treatment by bicarbonate addition, (4) characterization of thiosalt generation during milling of sulphide ores, (5) co-precipitation of thiosalts with ferric salts, (6) acute toxicity of thiosalts to *Daphnia magna* and *Selenastrum capricornutum*, (7) direct photolytic process for the removal of thiosalts from mine effluent (8) evaluation of thiosalts oxidation by ultrasonic irradiation, and (9) photocatalysed singlet oxygen oxidation of thiosalts.

Keywords: thiosalt, treatment, generation, analysis, bicarbonate, sulphur dioxide, toxicity, consortium, oxidation, mercuric chloride, ferric, co-precipitation, ultrasonic, ultraviolet, photosensitiser.

Introduction

During the milling of sulphide-rich ores, part of the sulphide content is oxidised to sulphate in the grinding, aeration and flotation circuits. In addition to sulphate, partially oxidised sulphur oxyanions such as S₂O₃²⁻, S₃O₆²⁻, and S₄O₆²⁻ are formed. These oxyanions are collectively known as thiosalts.

The resulting seasonal acidification of thiosalt-contaminated watercourses is an ongoing environmental problem at some mining operations in Canada. The acid produced when species of *Thiobacillus* bacteria consume thiosalts, downstream, has the potential to cause harm to the environment (AQUAMIN, 1996). Significant adverse effects on fish and benthic biota arise if the degree of acidification exceeds the tolerance of those organisms.

At present, natural microbial oxidation of thiosalts in effluent treatment ponds is the accepted practice for thiosalt removal. This method is cost-effective, simple and environmentally friendly because no chemical agents are introduced into the effluent. The acid produced by the oxidation of thiosalts is neutralised by lime addition before the effluent is discharged. However, microbial oxidation in a biostabilisation ponds is not reliable for year round operation in Canada. The efficiency of biological removal of thiosalt decreases to near zero during winter.

This paper is to review the projects funded by the Thiosalts Consortium. The majority of projects focused on investigation of technologies to remove thiosalts. Other projects studied the toxicities of thiosalt species, reliability of the mercuric chloride acidimetric method for determination of total thiosalts and the generation of thiosalts from two sulphide ores.

Inter-Laboratory Measurement Program for Thiosalts

CANMET's Mining and Mineral Sciences Laboratories (CANMET-MMSL) organized a workshop to train technicians on proper sample handling, storage and thiosalt analysis to improve the accuracy of total thiosalts analysis at laboratories participating in the workshop. The workshop had two objectives as follows: 1) establish and document a protocol for sample storage, sample stability and accuracy of the analytical method and train personnel on the application of the mercuric chloride acidimetric titration method for measuring total thiosalts and 2) conduct an inter-laboratory measurement program to assess the effectiveness of the training by testing the sample handling protocol and evaluate the accuracy and precision of the mercuric chloride acidimetric titration (Graham, 1998).

The inter-laboratory measurement program produced relatively reliable results for total thiosalt concentration, sufficient for routine analysis. The result indicates no problem with sample stability as long as the sample is packed in ice immediately after taking the sample, and kept frozen until analysed.

Investigation of the SO₂-Air Process

The oxidation of thiosalts with mixtures of SO₂-air would not result in other contaminants being introduced into the effluent. The SO₂ added to the effluent would be converted to H₂SO₄, and finally precipitated with lime as gypsum. Iron added to catalyse the reaction would also be precipitated as hydroxide.

Lakefield Research Limited evaluated SO₂-air mixtures for the oxidation of thiosalts (Ferron *et al.*, 1998). The initial tests were conducted on a synthetic solution that contained relatively low thiosalt concentrations of 150 mg/L S₂O₃²⁻ and 50 mg/L S₄O₆²⁻.

The test results indicated that complete thiosalt destruction was achieved during SO₂/air oxidation process in the presence of Fe²⁺/Fe³⁺ at 20°C. The final treated effluent after pH adjustment to 7.5 - 9.0 level contained less than 5 mg/L total thiosalts (including S₂O₃²⁻, S₄O₆²⁻ and S₃O₆²⁻) and ~1.5 g/L SO₄²⁻. The oxidation was completed after one hour of agitation.

The same test conditions applied to a synthetic solution at 5 °C resulted in a build-up of lower polythionates such as S₃O₆²⁻ and S₄O₆²⁻. SO₂/air oxidation without iron additions resulted in the conversion of S₂O₃²⁻ and S₄O₆²⁻ species into S₃O₆²⁻. Similarly, addition of Cu²⁺ as a catalyst did not appear to prevent conversion to S₃O₆²⁻.

Other tests were conducted with mill effluent containing thiosalt concentrations of 600 mg/L S₂O₃²⁻, 300 mg/l S₃O₆²⁻ and 55mg/L S₄O₆²⁻ (Ferron *et al.*, 1999). The tests were conducted at 20 °C, natural pH, with a pH adjustment to 7.0 -7.5 at the end of the tests.

Complete thiosalt destruction was achieved with SO₂/air oxidation in the presence of 5 g/L Fe³⁺. Ferric ion concentrations of less than 0.5 g/L Fe³⁺ did not destroy the thiosalt species. S₂O₃²⁻ was converted to S₄O₆²⁻, which was stable under conditions tested.

The large amount of iron needed in the reaction and an effluent temperature of 20°C would limit the practical application of this process.

Bicarbonate Addition as a Buffering Agent

Noranda Technology Centre, evaluated thiosalt treatment by bicarbonate addition (Li, 1999). The objective of this study was to assess, on a laboratory scale, the technical feasibility of adding bicarbonate to the effluent to increase the buffering capacity required to maintain a near-neutral pH in the watercourse.

The test results showed that bicarbonate addition to an effluent is effective in preventing pH depression. A near-neutral solution pH was maintained before, during and after bacterial oxidation. Acute toxicity tests using rainbow trout demonstrated that the addition of up to 0.91 g/L sodium bicarbonate to the effluent was non-toxic. However, additions of sodium bicarbonate caused severe depressions in dissolved oxygen concentration in some tests for a limited time. Further study is required to determine if low dissolved oxygen concentration would occur under field conditions.

Preliminary economic analysis based on typical thiosalt treatment requirements indicates that the unit treatment cost corresponds to 9 to 20 ¢ per m³ of effluent, with the capital cost amortised over 15 years of operating life at 12%.

Characterization Of Thiosalt Generation During Milling Of Sulphide Ores

A study conducted by CANMET-MMSL on a pyritic Cu-Zn ore and pyrrhotite-rich Cu-Ni ore showed that some of the thiosalts in a mill circuit comes with the feed in dry form (Negeri and Paktunc, 1999). Approximately 17% of the overall thiosalts produced originated from the feed, whereas grinding, aeration and copper circuit flotation contributed 15, 32 and 36% respectively.

The stainless steel grinding media produced more thiosalts than mild steel, but regardless of the grinding media, the pyritic ore was oxidized faster than the pyrrhotitic ore during grinding. Other differences between the two ores, which affects thiosalt generation, are their sensitivity to

temperature, pH, and residence time. In particular, the pyrrhotitic ore appears to be more sensitive to pulp temperature, whereas the pyritic ore is more sensitive to changes in pH. Pulp residence time significantly increased thiosalt generation during processing of the pyrrhotitic ore, but not the pyritic ore. Flotation of the pyrrhotitic ore produced more thiosalts than the pyritic ore at pH values typical for flotation.

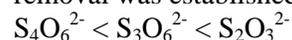
Semi-batch testing results on the pyritic ore indicated that grinding contributed approximately one-third of the total thiosalts generated. Copper rougher/scavenger/cleaner circuit produced 23 per cent of the total thiosalts generated; Cu cleaning stage being responsible for approximately half of this amount and zinc rougher/flotation/cleaner produced 26 per cent of the total thiosalts.

Semi-batch testing results of the pyrrhotitic ore indicated that conditioning the collector (xanthate) contributed the highest amount of thiosalts generated in the circuit, followed by the regrinding of flotation products in the pyrrhotite rejection circuit. The amount of thiosalts in the pulp solution increased with higher dosage of the collector.

Removal of Thiosalts from Solution by Co-Precipitation with Ferric Salts

Ferric oxyhydroxides have strong adsorption and coagulating properties. In the mining industry, ferric salts are used to remove arsenic, molybdenum and selenium from effluents (Denning, 1996). CANMET-MMSL conducted a preliminary evaluation of the feasibility of using Fe(III) salts to co-precipitate thiosalts from solution (Riveros and Chaulk, 2000).

In general, thiosalts are can be removed by co-precipitation with Fe(III) oxyhydroxides. The efficiency depends on the thiosalt species, pH and the Fe(III)/thiosalt molar ratio. Under the best experimental conditions, 64.4 % of the thiosalts were removed at pH 4.4 and Fe(III)/thiosalt molar ratio of 12/1. The order of removal was established as follows:



Ferric salts are inexpensive coagulants, however for thiosalts removal, high Fe(III)/ thiosalt molar ratio and effluent pH adjustment to ~pH 4.5 may be required to achieve high removal of thiosalts. The high iron would result in an increase in sludge production and high operational costs.

The Acute Toxicity of Sulphur Oxyanions to *Daphnia magna* and *Selenastrum capricornutum*

Toxicity experiments were conducted at CANMET-MMSL on the relative acute toxicities of three species of thiosalts (thiosulphate, trithionate and tetrathionate) as well as the toxic nature of their mixtures, whether antagonistic, additive or synergistic (MacGeer *et al.*, 2000).

Experiments showed that *Selenastrum capricornutum* and *Daphnia magna* have very different responses to these three thiosalt species and in general, algae are more resistant. The IC50 values for algae were well above *Daphnia* EC50 concentrations for both thiosulphate and tetrathionate. Thiosulphate was most toxic to *Daphnia magna* followed by tetrathionate and trithionate.

The trend of greater toxicity for *Daphnia* did not hold for trithionate, but this was likely the result of an inability to control test solution pH in the standardized microwell plate assay for algae. A 1,000 mg/L trithionate solution produced 75% mortality of *Daphnia* when pH was not maintained, but when pH was maintained at 7.5 the rate was only 15%. The acidification associated with trithionate solutions also illustrated that for *Daphnia*, the toxicity associated with the production of H⁺ is greater than the toxicity of the thiosalt anion by itself.

Mixtures of thiosalts proved to be much less toxic to *Daphnia* than the individual anions themselves illustrating that thiosalts pairs are antagonistic (less than additive) in terms of toxicity.

Direct Photolytic Process For the Removal of Thiosalts

TechNet Consulting carried out a study of the Direct Photolytic Process (DPP) for the destruction of thiosalts (Sridhar and Dinardo, 2001). DPP does not employ any photocatalysts, oxidizers or other chemical additives to enhance the process, and the destruction of thiosalts is dependent on the direct absorption of UV irradiation by the thiosalts.

Experiments were conducted with synthetic thiosulphate solutions in a bench-scale UV photochemical reactor over a pH range of 2 to 10 and over a temperatures range of 6 to 15 °C. Under proper operating conditions, the thiosulphate and the polythionates such as tri- and tetrathionates can be converted predominantly to sulphate, sulphite and acid production. At pH 11 and above, the efficiency of destruction decreases.

The study shows that although the destruction of thiosalts by DPP is technically feasible, a preliminary cost estimate indicates that the cost of the process could be prohibitive.

Evaluation of Thiosalts Oxidation by Ultrasonic Irradiation

Ultrasonic liquid treatment uses high frequency (20 kHz to 10 MHz) energy to cause vibration in liquids, thereby producing physical or chemical changes as a result of cavitation. Cavitation is the formation, expansion, and implosion of microscopic gas bubbles in liquid. Within the cavitation bubble temperatures range from 2000 to 5000°C, and pressure reaches 1800 atmospheres. These extreme temperatures and pressures last only microseconds, however the localized temperature and pressure can increase chemical reactivity, and production of chemical free-radical (Innovative Environmental Solutions Inc., 1998). Current applications include emulsification, dispersion, disruption of biological cells, removal of trapped gases, cleaning of microscopic contamination, and acceleration of chemical reactions.

The evaluation of ultrasonic oxidation of thiosalts in synthetically prepared solutions was conducted at CANMET-MMSL (Pawlak, 2000).

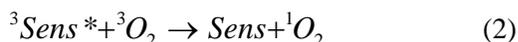
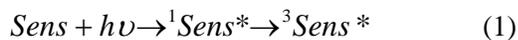
Following 60 minutes of sonication, the concentration of thiosalt species decreased by 2.5% at pH 10 for thiosulphate, and 10% and 25% at pH 3 for trithionate and tetrathionate, respectively. Addition of ferrous iron had no catalytic effect on the oxidation of thiosulphate, and only a small effect on trithionate and tetrathionate. In the absence of ferrous iron, an initial pH 10 produced the highest degradation rates. Throughout all sonication experiments, a pungent odour was noted suggesting the formation of hydrogen sulphide.

Based on the results from the 0.2 L lab scale setup, the power consumption calculation for treatment of 1.0 m³ of effluent resulted in high costs. At present, large capacity flow-through units are available and power consumption for a 27.8 m³/m unit requires 206 kW/hr based on 24 hours/day operation. (Innovative Environmental Solutions, 1998).

Investigation of the Photosensitiser ZnPc(COOH)₄ on the Oxidation of Thiosalts

Singlet oxygen oxidation of thiosalts (SOOT) was tested at Carleton University (MacLean and Crutchley, 2002). Zinc tetracarboxylate-phthalocyanine was used as a benchmark photosensitiser to provide photosensitiser properties that will be necessary to make the singlet oxygen treatment of mining effluent economical.

The absorption of visible light by a substance (photosensitiser) can initiate the production of energy-rich active oxygen or singlet oxygen (¹O₂). Ground state triplet oxygen (³O₂) can be photosensitised to an excited singlet state by energy transferred from a long-lived triplet excited state of zinc tetracarboxylatephthalocyanine (³Sens*) (Iliev *et al.* 1995, 2000).



Iliev *et al.* noted that singlet oxygen is far more reactive than ground state triplet oxygen in oxidising thiosulphate, but offered no further

suggestion as to the possible mechanism of thiosulphate oxidation.

MacLean and Crutchley reported that singlet oxygen oxidation of thiosulphate can occur between 0 and 14 °C with percent conversion of thiosulphate to sulphate of 24 to 48%, respectively, over a twelve-hour period of irradiation at pH 10 to 11. However, the tendency for ZnPc(COOH)₄ to dimerize in aqueous solution and photobleaching of the photosensitiser by Cu(II) ions severely limits its usefulness for practical applications. Finding photosensitisers that do not dimerize or immobilizing the photosensitiser on a support are possible solutions.

In order to achieve 40% conversion of a 1000 mg/L thiosulphate solution (8.93 mM), a 5.7 μM photosensitiser solution must have a turnover number of at least 600 (8.93 mM/5.7 μM x 40%).

Assuming turnover number of 1000 for the ZnPc(COOH)₄ photosensitiser and a photosensitiser cost of \$10/mole, for a 1000 mg/L thiosalt effluent, a photosensitiser concentration of 8.93 mmole/m³ corresponds to 8.93 μM. The amount of photosensitiser required to achieve this concentration in the holding pond would be added gradually to a holding pond.

The extra costs associated with a photosensitiser oxidation process are aeration of the holding ponds and construction of holding ponds, if required. The holding ponds should remain alkaline during the photosensitiser process and this will require the addition of base.

Conclusions

Up until now, most mining sites have conducted acute toxicity testing for trout at times when low thiosalt levels were discharged and it is unclear if the monthly requirement for absence of acute toxicity will be met in periods of high thiosalt levels.

Starting in December 2002, the new Metal Mining Effluent Regulations (MMER) will

require the absence of acute lethality of effluents to rainbow trout and the monitoring of acute lethality to *Daphnia magna*. The MMER also includes an Environmental Effects Monitoring (EEM) program requiring the monitoring of sub-lethal toxicity of the effluents twice a year. Sub-lethal toxicity tests must be conducted on a fish species, an invertebrate species, a plant species and an algal species beginning in June 2003 (Canada Gazette, 2002).

Thiosalts can potentially contribute to the observed toxicity by means of pH depression in the exposure solutions. Effective management of thiosalt levels could become an important, albeit indirect, issue under the new MMER. These new regulations require significant further reductions in acidifying effluent emissions to fully protect all Canadian ecosystems.

The members of the Thiosalts Consortium have signed a new agreement to extend the consortium to November 2004. The annual membership fee is \$5,000. The focus for the group will be on exchanging ideas among members on approaches to management of thiosalts at mill sites. New members would have access to past research and on analytical techniques.

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