TREATMENT OF THIOSALTS
IN MILLING EFFLUENTS:
A REVIEW OF TREATMENT PROCESSES

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MINING AND MINERAL SCIENCES LABORATORIES
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Cambior Inc., Noranda Mining and Exploration Inc., Rio Algom Ltd., Voisey's Bay Nickel
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EXECUTIVE SUMMARY

Thiosalts are incompletely oxidized sulphur compounds formed by the oxidation of the sulphide ores in milling and flotation circuits. These sulphur compounds are not considered toxic and thus, are not regulated. However, the presence of species such as $S_2O_3^{2-}$, $S_3O_6^{2-}$ and $S_4O_6^{2-}$ in milling effluents can indirectly impact on the environment. Thiosalts pass through conventional effluent treatment processes (i.e., lime additions) mostly unaffected and are discharged to the receiving waters. In the presence of bacteria, thiosalts are oxidized to form sulphuric acid. This acid can cause pH drops affecting fish and benthic organisms; the severity depends on the concentration of thiosalts, dilution and flow rates. In addition to pH drop, other effects may include oxygen depletion, depletion of the buffering capacity of the water and dissolution of metals from the sediment.

The Thiosalts Consortium - Phase II was formed to stimulate discussion with respect to thiosalts formed during processing of sulphide ores and to provide practical and economically feasible solutions for the removal of thiosalts from milling effluents. The members of this Consortium are: Cambior Inc., Noranda Mining and Exploration Inc. (Brunswick Mining Division), Rio Algom Ltd., Voisey's Bay Nickel Company Ltd., Aur Ressources Inc., Falconbridge Ltd. and CANMET-Mining and Mineral Sciences Laboratories.

As a first step the Thiosalts Consortium commissioned a study to provide executives in the mining industry with a synopsis of the current status of effluent treatment technologies applicable to thiosalts removal. This report is an update of the treatment technologies evaluated in the 1985 report “Techno-Economic Evaluation of Thiosalts Treatment Process” by Wasserlauf and co-workers including new treatment technologies developed since 1985. Details are provided on process principles, applications, advantages, limitations, patents and development status (i.e., commercially available, demonstrated at pilot scale, laboratory scale or conceptual stage).

Several treatment processes are capable of achieving complete thiosalts removal; either as distinct unit processes or in combination of unit processes given site specific needs. Previous work found that chlorination, ozonation, hydrogen peroxide, $SO_2$-air, chalcopyrite catalysis, alkaline pressure oxidation and reduction by iron achieved complete thiosalts removal and almost complete removal in the case of biological oxidation. Although these methods are technically feasible, there is a high degree of uncertainty regarding the effectiveness of these technologies to treat large volumes of effluent on a continuous basis. This uncertainty is largely due to limited testwork done.
Only biological oxidation has been investigated at pilot scale, using a rock-packed pond and rock-packed columns. Almost complete oxidation of thiosalts was achieved over a period of nine months at temperatures as low as 1.0°C and thiosalts loads varying from 400 to 1,200 mg/L. Compared to thirteen thiosalt treatment processes reviewed in this study, the general opinion is that biological oxidation using packed bioreactors is the most economically feasible process.

There will be occasions when biological oxidation may not achieve the target thiosalts concentration in the treated effluent and a secondary chemical oxidation process is needed as a polishing step. Hydrogen peroxide and chlorine are reliable and effective oxidants for thiosalts. Both oxidants can reduce thiosalts concentrations below 10 mg/L. Although chlorine may have a cost advantage, hydrogen peroxide is a much safer oxidant for storing and handling. Furthermore, residual hydrogen peroxide decomposes quickly to form water without producing toxic by-products.

Economic factors are the principal barriers to application of these treatment processes. Specific technologies for thiosalts removal will achieve acceptance if the expected benefits are greater than the incremental cost of thiosalt removal or if regulations impose limits on thiosalts concentration in milling effluents that are discharged to the environment.

The Management Committee selected the following methods for economic evaluation:

- Biological Oxidation in rock-packed reactors;
- Biological Oxidation in rock-packed reactors combined with hydrogen peroxide as a polishing step; and
- Hydrogen Peroxide alone.

Three effluent cases were considered:

- Noranda Mining and Exploration, Brunswick Mining Division with an effluent flow of 1,380 m³/h and 9,936 kg/d thiosalts discharge;
- Bouchard-Hébert Mine with an effluent flow of 408 m³/h and 4,602 kg/d thiosalts discharge; and
- Aur Louvicourt Mine with an effluent flow of 160 m³/h and 230 kg/d thiosalts discharge.
The economic evaluation is discussed in Part B of this report. The capital and operating costs derived in 1985 and 1997 are presented in Table 14 [page 84]. As shown, the capital costs in 1997 dollars for Case 1997A vary from $7.0 million to $12.3 million and operating costs vary from $2.0 million to $11.8 million for an operation treating 1,380 m$^3$/h effluent and 9,936 kg/d thiosalts discharge. The capital costs for Case 1997C vary from $733,000 to $1.3 million for an operation treating 160 m$^3$/h effluent and 230 kg/d thiosalts discharge. The total costs for the capitalization and operation of a thiosalts treatment facility range from $12.6 million to $18.8 million per year for Case 1997A and from $1.3 million to $2.0 million per year for Case 1997C. Based on these estimates, biological oxidation is the lowest cost option of the three processes evaluated.

As a result of this investigation, the following recommendations are made for future projects to develop further thiosalts treatment processes:

1. Conduct more rigorous pilot testing of biological oxidation of thiosalts using packed bed reactors to determine:
   - performance at low temperatures, scale up parameters;
   - flow rates (particularly at high flow and at low concentrations); and
   - develop technical expertise and operational experience.

1. Investigate biological oxidation at low temperatures to define the optimum values of operating parameters.

2. As a long term objective investigate the potential of using technologies such as bio-augmentation, genetic engineering and microbial entrapment to improve the performance and robustness of biological oxidation.

3. Investigate a thiosalt treatment process based on a combination of bacterial oxidation for bulk removal of thiosalts followed by hydrogen peroxide as a polishing step and as a backup treatment system.

4. Investigate advanced oxidation processes using hydrogen peroxide (e.g., ULTROX® process) as a means of achieving higher oxidation efficiency and faster reaction rates.

5. Conduct further investigation into the SO$_2$-air process to better define process variables and their optimum values.
6. Conduct further investigation into a chalcopyrite catalyst system with the goal of achieving efficient thiosalts oxidation in the temperature range of 2° to 30°C.
ACKNOWLEDGMENTS

The authors wish to acknowledge the support of the following members of the Thiosalts Consortium - Phase II: Cambior Inc., Noranda Mining and Exploration Inc. (Brunswick Mining Division), Rio Algom Ltd., Voisey's Bay Nickel Company Ltd., Aur Ressources Inc., Falconbridge Ltd. and CANMET-Mining and Mineral Sciences Laboratories.

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Thanks are also extended to Doug Gould, Geneviève Béchard, David Koren, and Jim Skeaff for their comments.
PART A - REVIEW OF TREATMENT PROCESSES

INTRODUCTION

Background

Oxidation of thiosalts produced during the processing of sulphide ores have been documented as the indirect cause of the acidification of surface waters which receive milling effluents. Acidification of these waters can cause significant impact on the downstream environment. Therefore, although thiosalts have relatively low toxicity and their release in receiving waters is not regulated, sulphuric acid formed by thiosalts oxidation can cause impairment to fish and benthic invertebrate communities. Other effects of thiosalts on the receiving waters include depletion of dissolved oxygen, reduced buffering capacity and dissolution of metals from the sediment.

AQUAMIN in its final report “Assessment of the Aquatic Effects of Mining in Canada” recommended that current research efforts to identify and develop treatment technologies for thiosalts should continue [1]. Previous investigations [2, 3] concluded that the best available technologies including chemical/physical methods and biological oxidation could achieve a target concentration of <100 mg/L thiosalts in the treated milling effluents. These methods, though technically feasible, were all uneconomical. Currently, natural degradation is a widely-used method to treat thiosalts in milling effluents; however, it is not an effective method as a year-round operation in northern climates.

The environmental impact of thiosalts is a concern to mining companies. Treatment of dilute solutions of thiosalts in large flows of effluent represents a challenge for existing treatment technologies. Accordingly, six mining companies and CANMET formed the Thiosalts Consortium, with its main goal to develop and identify new technologies for managing thiosalt levels in milling effluents. Currently, the consortium members are as follows: Cambior Inc., Aur Ressources Inc., Falconbridge Ltd., Voisey's Bay Nickel Co. Ltd., Mining and Exploration Inc. (Brunswick Mining Division), Rio Algom Ltd. and CANMET-Mining and Mineral Sciences Laboratories.
What are Thiosalts?

Thiosalts can be viewed as aqueous anionic intermediate products in the oxidation of sulphur to sulphate. The prefix “thio” indicates that the sulphur atom has been substituted for an oxygen atom in the progression from S²⁻ to SO₄²⁻. In the case of the thiosulphate ion, the substitution is in the sulphate ion:

- sulphate ion: SO₄²⁻
- thiosulphate ion: S₂O₃²⁻

Polythionates are partially oxidized sulphur-chain oxyanions with the general formula SₙO₆²⁻ where 3 ≤ n ≤ 10. These sulphur compounds are collectively known as “thiosalts.” The processing of base metal sulphide ores often results in the generation of thiosalts in the grinding and flotation circuits. Usually, the main thiosalts formed during processing are thiosulphate, trithionate (S₃O₆²⁻) and tetrathionate (S₄O₆²⁻) [2, 4] with the higher polythionates occurring at very low concentrations.

The amount of thiosalts produced is influenced by the type of sulphide minerals in the ore, grinding conditions, pulp densities, and chemical conditioning of the flotation operation (i.e., reagents, temperature, aeration).

Impact of Thiosalts on Metal Recovery

With good water management and recycling of milling water, it is possible to reduce the amount of thiosalts discharged. However, thiosalt levels in the recycle water must be adjusted, otherwise it can affect metal recoveries. The effect of thiosalts on the response of sulphide mineral flotation is not well understood and it is difficult to isolate the effect of individual thiosalt species in the process water. Laboratory studies have demonstrated that thiosulphate, in combination with calcium ions at high concentrations, can depress pyrite and sphalerite in flotation cells under certain conditions and thiosulphate can have especially strong detrimental effects on the selectivity and efficiency of the zinc blende flotation [5, 6].

Behaviour of Thiosalts in Milling Effluents

Thiosalts are not oxidized to form SO₄²⁻ by conventional lime neutralization treatment of milling effluents. They pass virtually unaltered into the receiving waters where they may be oxidized by Thiobacillus bacteria, generating sulphuric acid and lowering the pH. This decrease in pH may affect changes in downstream environments. Whether or not thiosalts cause
impairment of biotic communities in the receiving waters is dependent on a number of variables, including the rate of thiosalt oxidation, temperature and the quality/volume of the receiving waters.

The high acidity in the receiving waters can be a seasonal occurrence. During the warm summer months, thiosalts are generally completely oxidized in the tailings pond if the retention time is sufficiently long. As bacterial activity decreases during autumn, relative to decreasing water temperature, the thiosalts concentration in the effluent increases, reaching a maximum in winter. This process is reversed in the spring. As water temperature increases, thiosalts concentration gradually decreases to zero by summer. This cycle results in a distinct pH drop in the receiving water during autumn and spring.

The Thiosalt Consortium placed a high priority on updating the 1985 report “Techno-Economic Evaluation of Thiosalts Treatment Processes” [3]. Thirteen treatment processes listed in Appendix A were evaluated and appeared clearly uneconomic. Even with potential technological advances, some of the oxidation processes would still be uneconomic based on high reagent and energy requirements of the processes. Furthermore, the report concluded that none of the technologies evaluated were proven to be consistently effective on a continuous basis for large-scale treatment of milling effluents.

As a first step, the Consortium agreed to review the status of potential thiosalt treatment processes and identify new treatment options that should be investigated.

Objectives

One of the goals of the Thiosalts Consortium is to find an affordable and effective treatment process for thiosalts removal from mill effluents. This report is a first step toward this goal by providing mining executives with current information on existing effluent treatment technologies. The objectives of this report are:

2. Identify new treatment technologies.
3. Recommend treatment processes for economic evaluation in Part B of this project.
Criteria Used in Comparing Thiosalt Treatment Processes

The criteria used to select the treatment processes for economic evaluation in Phase II are as follows:

- Capital and operating costs of the treatment process;
- Must technically achieve less than 10 mg/L total thiosalts in the treated effluent;
- Commercially available;
- Tested at pilot-scale or laboratory-scale; and
- Potential environmental impact and safety of the process.

In Part B of this project, capital and operating cost estimates were calculated by CANMET for selected process flowsheets developed by Wasserlauf and co-workers [3]. The cost estimates are based on three cases shown in Table 1. The Noranda Mining and Exploration Inc. (Brunswick Mining Division) case considers a high flow with 300 mg/L thiosalts. Secondly, the Bouchard-Hébert Mine case considers medium flow with 470 mg/L thiosalts. Finally, the Louvicourt Mine case considers low flow at 60 mg/L thiosalts.

The estimated capital and operating costs for the thirteen processes in the report by Wasserlauf and co-workers are summarized in Appendix A. These costs were calculated in 1985 in Canadian dollars and were based on the treatment of 720 m³/h effluent containing 24,500 kg/d \( \text{S}_2\text{O}_3^{2-} \), (1,400 mg/L \( \text{S}_2\text{O}_3^{2-} \)).

<table>
<thead>
<tr>
<th>Cases</th>
<th>Ore Milled (t/d)</th>
<th>Sulfide in Ore (wt%)</th>
<th>Average Thiosalts in outflow (mg/L ( \text{S}_2\text{O}_3^{2-} ))</th>
<th>Average Effluent Flow (m³/h)</th>
<th>Effluent Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Noranda Mining and Exploration Inc. (Brunswick Mining Division)</td>
<td>9,000</td>
<td>80</td>
<td>300</td>
<td>1380</td>
<td></td>
</tr>
<tr>
<td>2. Bouchard-Hébert Mine</td>
<td>2,800</td>
<td>40</td>
<td>470</td>
<td>408</td>
<td></td>
</tr>
<tr>
<td>3. Louvicourt Mine</td>
<td>4,500</td>
<td>40</td>
<td>60</td>
<td>160</td>
<td></td>
</tr>
</tbody>
</table>

* Average 1996 values
PROCESS USED FOR THE LITERATURE REVIEW

Methodology

Multiple on-line searches of the open literature were conducted on twelve computerized databases. These commercial databases have index entries as recent as two weeks after publication and are assumed to have the most up-to-date information on effluent treatment technologies available from the open literature. Descriptions of the databases are given in Appendix B. Disciplines covered by these databases include: pollution, wastewater treatment, environmental engineering, technology, science and patents. The search covered the period from 1984-1997.

Several search strategies were used in combination with key words listed in Table 2. Each search strategy was tailored to extract information related to specific topics relevant to effluent treatment and only citations designated as English text were reviewed. Multiple databases were searched with each search strategy. Combination of key words were used to reduce the number of hits in the range of 100 to 200. After screening for duplicates and non-English papers, the number of unique citations identified ranged from 30 to 100. Overall, 650 titles with abstracts were printed and examined. Approximately 15 percent of the abstracts were judged to be relevant, and subsequently the complete texts were obtained.

All the collected articles were reviewed for information on the following topics:

• application of technology to milling effluents;
• capital and operating costs;
• status of the technology (commercially available, pilot-scale, laboratory-scale and conceptual stage);
• potential hazards;
• effectiveness in removing thiosalts; and
• ease of integration into mill effluent treatment process systems.
Table 2 - Databases and keywords used for the literature search

<table>
<thead>
<tr>
<th>Databases</th>
<th>Keywords</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Abstracts</td>
<td>electro?</td>
</tr>
<tr>
<td>Derwent World Patents Index</td>
<td>equipment</td>
</tr>
<tr>
<td>Energy SciTech</td>
<td>generation</td>
</tr>
<tr>
<td>Enviroline</td>
<td>hazard</td>
</tr>
<tr>
<td>Environmental Bibliography</td>
<td>hydrogen peroxide</td>
</tr>
<tr>
<td>Metadex (Metal Sciences)</td>
<td>installation</td>
</tr>
<tr>
<td>Mineral Processing Database</td>
<td>ion exchange</td>
</tr>
<tr>
<td></td>
<td>membrane</td>
</tr>
<tr>
<td></td>
<td>oxidation</td>
</tr>
<tr>
<td></td>
<td>ozone</td>
</tr>
<tr>
<td>Mining Technology Database</td>
<td>pressure oxidation</td>
</tr>
<tr>
<td>National Technical Information Service (NTIS)</td>
<td>purification</td>
</tr>
<tr>
<td>Pollution Abstracts</td>
<td>reduction</td>
</tr>
<tr>
<td>SciSearch</td>
<td>reverse osmosis</td>
</tr>
<tr>
<td>Water Resources Abstracts</td>
<td>risk</td>
</tr>
<tr>
<td>Waternet</td>
<td>sulphur?#</td>
</tr>
<tr>
<td></td>
<td>sulphur# dioxide</td>
</tr>
<tr>
<td></td>
<td>thio?</td>
</tr>
<tr>
<td></td>
<td>ultraviolet light</td>
</tr>
<tr>
<td></td>
<td>waste?</td>
</tr>
</tbody>
</table>

1.  ? represents one or more subsequent letters to allow for related derivatives
2.  # allows for alternate spelling

### BIOLOGICAL OXIDATION OF THIOSALTS

The oxidation of thiosalts, in particular thiosulphate, by bacteria of the genus *Thiobacillus* has been studied extensively over the past 40 years [7, 8, 9, 10, 11]. Several theories have been proposed for the reaction pathways of thiosalt oxidation. Vesniac [7] proposed that oxidation of thiosulphate by *Thiobacillus thioparus* produces tetrathionate with subsequent production of trithionate ($S_3O_6^{2-}$) and dithionate ($S_2O_6^{2-}$) and finally sulphate. Other researchers [10, 12, 13] have proposed many other pathways depending on the bacterial species and experimental conditions. In summary, the reaction pathways of thiosalts biooxidation are complex and dependent on environmental conditions; however, the general tendency is towards a decrease in pH of the system.
Oxidation of thiosalts by bacteria may produce elemental sulphur, polythionates and sulphate depending on the environmental conditions. However, under suitable environmental conditions, sulphate is the sole end-product according to the following equation:

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

(1)

This equation indicates that one mole of thiosulphate produces two moles of hydrogen ions, resulting in a significant decrease in pH as low as 2.0.

Several studies indicate that indigenous *Thiobacillus* species can oxidize thiosalts at pH 2. At these extreme acidic conditions, it is quite probable that only a few species are able to survive and grow and thus dominate the catalytic oxidation of thiosalts. Among the genus *Thiobacillus*, the species most likely involved in the oxidation of thiosalts are shown in Table 3.

<table>
<thead>
<tr>
<th>Name</th>
<th>Substrates Utilized</th>
<th>pH Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Thiobacillus</em> thiooxidans</td>
<td>sulphur tetrathionate thiosulphate</td>
<td>optimum 2.0 - 3.0 range 1.0 - 6.0</td>
</tr>
<tr>
<td><em>Thiobacillus</em> thioparus</td>
<td>sulphur trithionate tetrathionate dithionate thiosulphate</td>
<td>optimum near neutrality</td>
</tr>
<tr>
<td><em>Thiobacillus</em> neapolitanus</td>
<td>sulphur thiosulphate</td>
<td>optimum 7.0 range 4.5 - 7.8</td>
</tr>
<tr>
<td><em>Thiobacillus</em> novellus</td>
<td>thiosulphate organics</td>
<td>optimum 7.0 range 5 - 9.5</td>
</tr>
<tr>
<td><em>Thiobacillus</em> denitrificans</td>
<td>sulphur thiosulphate dithionate tetrathionate sulphide</td>
<td>range 6 - 8</td>
</tr>
</tbody>
</table>

Biological oxidation of thiosalts appears to have many environmental and economic advantages over conventional treatment processes. Used alone or in conjunction with other treatment technologies, biooxidation may provide a cost effective process for treatment of milling effluents. However, application of biotechnology to effluent treatment in the mining industry is almost non-existent even though many laboratory-scale and pilot-scale studies indicate that biologically engineered systems for effluent treatment, in many cases, are among the lowest cost processes.
Experience has shown that bacterial oxidation of thiosalts can be relatively effective in existing effluent treatment ponds during summer operation. As expected, temperature is a limiting parameter in the kinetics of biooxidation. Conditions could be improved that would extend the effective summer period (i.e., aeration, mixing, substrate), but in practice it is impossible to maintain temperatures conducive to microbial growth in a large open-pond biological reactor in northern climates. Higher degrees of control over parameters necessary to promote microbial activity could be achieved in packed bed reactors. And while increased process control in tank reactors can decrease treatment time, they do result in increased capital and operating costs. Up to now, this potential for biooxidation of thiosalts has not been fully exploited. More effective application of biooxidation is possible and should be investigated further. Successful application of biooxidation to the removal of thiosalts will require the extensive collaboration of microbiologists, chemists and engineers. Further pilot testing of this technology can provide operational experience required to gain confidence in the process as well as demonstrate the robustness of the process for year-round operation and the economics of the process.

Types of Biological Reactors

Rotating Biological Contactor: The RBC reactor is essentially a rotating shaft supporting closely spaced disks which are partially immersed in the effluent being treated (Figure 1). A layer of microbes growing on the surface of the disks degrade the pollutants in the effluent. Effluent and air are channeled through the space between the disks to increase the contact time between the microbes and the effluent. The RBC offers a number of advantages: (1) low energy requirements, (2) simplicity of operation, (3) low maintenance requirements, (4) excellent oxygen transfer and (5) resistance to shock loads. The possible disadvantages in the application to thiosalts oxidation is corrosion due to the acidic effluent and precipitation of calcium on the disks.

Aerated Packed Column and Tank Reactors: The packed column and packed tank reactors consist of a large receptacle (i.e., tube or tank) filled with a material to which the microbes
Figure 1 - Rotating Biological Contactor System - Schematic Design
adhere. The effluent and air flow through the packing material provides maximum contact with the microbes. The fluidized bed reactor is a variation of the packed tower reactor; the packing material is kept suspended, (fluidized), by the upward flow of the effluent.

The packed column and packed tank reactors may be less efficient in terms of oxygen transfer and effluent contact with the microbes compared to the RBC, but they are simple to control and operate [14].

**Packed Bed Reactors:** Packed bed reactors consist of an aerated packed-bed using a high surface area material as a carrier for the microorganisms. The reactor consists of several compartments, in series, to model a plug flow pattern in the reactor. Moreover, completely different populations of bacteria can reside in each compartment, which takes advantage of the natural ability of different species of microorganisms to thrive under different growing conditions (i.e., pH, temperature, dissolved metal concentration and substrate concentration). Water and air flow concurrently upwards through the compartments.

BIOPUR [15] is a patented biofilm reactor system consisting of an aerated, packed-bed reactor using reticulated polyurethane (PUR) as a carrier material for a thin film of microorganisms. The polyurethane foam has a very open structure with a large surface area (500 m²/m³). High biomass concentrations can be achieved. Advantages of biofilm reactors include:

- longer biomass retention time compared to suspended sludge reactors;
- good control in each reactor unit to achieve process conditions for optimum microbial growth and thiosalt oxidation;
- compact design of the reactor; and
- low maintenance cost because there are no moving parts.

The first full-scale application of the biofilm reactor was in 1989 for the treatment of groundwater containing a mixture of organics. Table 4 compares the cost of a biofilm reactor to other treatment systems for the treatment of groundwater contaminated with hydrocarbons. The estimate includes installation, maintenance and addition of nutrients. In this specific application, the biofilm reactor was more cost effective than activated carbon and rotating biological contactor.
Table 4 - Estimation of the costs of groundwater treatment systems

<table>
<thead>
<tr>
<th>Treatment System</th>
<th>Capacity (m³/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Stripper + activated carbon</td>
<td>0.61</td>
</tr>
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<td>BIOPUR biofilm reactor</td>
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* adapted from Marsman et al. [15], costs estimates are in 1993 U.S. dollars

**Applications for Biological Reactors to Thiosalts Removal:** Laboratory studies by B.C. Research [16] evaluated bench-scale Rotating Biological Contactor (RBC) units using a synthetic feed containing 800 to 4,000 mg/L thiosalts. The RBC was operated in a continuous mode with nutrients added to the effluent (i.e., (NH₄)₂SO₄ and KH₂PO₄) for bacterial growth. Thiosalts oxidation rates achieved by the RBC were 267 mg/ft²/h at ambient temperature and 146 mg/ft²/h at 8°C for an effluent flow rate of 120 L/h. Complete oxidation of thiosalts was achieved at 30°C and an effluent with thiosalts concentration <200 mg/L thiosalts was produced at 8°C.

Environment Canada [17] carried out tests utilizing pilot-scale RBC units on milling effluents at Brunswick Mining and Smelting Co. Ltd. The thiosalts concentration in the feed was 1.7 to 2.7 g/L as S₂O₃. Oxidation rates were as high as 760 mg/L/h for flow rates of 100 to 400 L/day and thiosalt levels of 200 mg/L in the treated effluent were realized at 22°C or higher. At 2°C the thiosalts concentration in the treated effluent was significantly higher than 200 mg/L. Sludge accumulation in the reactor was negligible with an effluent suspended solids concentration consistently less than 10 mg/L. Based on the results of these studies, capital cost estimates were calculated by Environment Canada for an RBC facility treating 2.3 million gal/day of effluent containing 1250 mg/L thiosalts. Capital cost was estimated at $1.66 million and operating cost of $428,000/yr in 1980 Canadian dollars.

Extensive corrosion problems were encountered during pilot testing and dependable continuous operation proved difficult to maintain. RBC units are also prone to mechanical failure, in particular the rotating shaft. The corrosive nature of the treated milling effluent would dictate the use of corrosion-resistant materials in the construction of RBC. Additionally, the complexity of the system requires close supervision of the process during operation resulting in
increased operational costs. These results suggest that RBC would not achieve a target thiosalt concentration of <10 mg/L when treating the effluent at low temperature.

**Thiosalts Oxidation in Aerated Packed Column and Packed Tank Reactors:** Wasserlauf and co-workers [18] investigated biological oxidation of thiosalts using mill tailings and thickener overflows as the feed for continuous bench-scale tests on site at Brunswick Mining and Smelting. Successful thiosalt oxidation was achieved in two hours (about 500 mg/L/h) using rock-packed columns and tank reactors at temperatures as low as 3°C and as high as 29°C. With feed levels of 650 to 2450 mg/L S\(_2\)O\(_3\)\(^2-\), the thiosalt concentration in the treated effluent was less than 100 mg/L S\(_2\)O\(_3\)\(^2-\). Lowering the temperature to 2.6°C resulted in an oxidation rate decrease of 50%.

During optimal continuous operation, the average pH of the treated effluent was pH 2.0. It was observed that packed columns were less sensitive to changes in feed composition compared to the simple aerated tank reactor. This is attributed to greater stability in the microbial concentration. The rocks provide a surface for microbial adhesion and thus maintain a high microbial to thiosalts ratio compared to suspended bacterial reactors. The highest oxidation rates achieved in the rock-packed column reactor was 1,000 mg/L/h. This higher oxidation rate was probably due to better air utilization and mixing in the columns. High oxidation rates (1,000 mg/L/h thiosulphate as sulphur) was also reported by Aullenback and Heukelekian [19] using activated sludge in a batch column reactor.

The Noranda Research Centre [3] conducted further on-site tests at Brunswick Mining and Smelting Corp. using thickener overflow as the feed for pilot-scale rock-packed columns. The flowsheet for the Noranda pilot plant is shown in Figure 2. Although the operation of the columns was besieged with technical, operational and labour problems during the pilot study, the short continuous operations of the rock-packed columns achieved oxidation rates as high as 160 mg/L/h compared to 70 mg/L/h for the rock-packed pond at ambient temperature [18]. Despite difficult operating conditions, packed column reactors reduced thiosalts levels to less than 100 mg/L for feed concentration varying from 400 to 1,200 mg/L. These results show that packed columns holds promise as a method for thiosalt oxidation and should be investigated further.
Figure 2 - Flowsheet of the Noranda Research Thiosalt Pilot Plant
A large microbial concentration is needed to achieve high oxidation rates. DeMillano et al. [20] found that the nutrient to microorganisms ratio was a determinant parameter in the conversion of thiosulphate to sulphate. At a thiosulphate to microorganisms ratio below 0.53 mg $S_2O_3^{2-}$ as S/mg M LVSS (mixed liquor volatile suspended solids) more than 92% of the initial thiosulphate was converted to sulphate. About one million bacteria of the genus *Thiobacillus* were present per milliliter of solution in the mixed activated sludge unit. Whereas, another study, reported concentrations exceeding $1.6 \times 10^8$ bacteria per mL for flask tests, regardless of pH [21].

Kreye et al. [22, 23] reported that the concentration of phosphorous was an important parameter in the biooxidation of thiosulphate to sulphate. Initially thiosulphate transformed to tetrathionate with low COD removal. However, when the phosphorous concentration in the influent was increased, the conversion of thiosulphate to sulphate was almost complete at concentrations in the range of 400 to 2,200 mg/L thiosulphate as sulphur. Silver and Dinardo [10] reported that concentrations of more than 2 mg/L ammonium and 1 mg/L phosphate achieved the highest oxidation rate of thiosulphate.

At the same time as Noranda Research Centre conducted pilot tests of rock-packed columns, a series of pilot tests were conducted on treating thickener overflow in a 29,000 gal aerated rock-packed pond. A flowsheet for the rock-packed pond is presented in Figure 2. The maximum thiosalts oxidation rate achieved in the aerated rock-packed pond was 70 mg/L/h. These pilot tests were beset with many technical problems (i.e., frozen water lines, broken pumps, poor operation of the thickener resulting in high suspended solids and dissolved metals in the feed that prevented extended run operation of the rock pond. However, the results of one successful continuous run from early March to mid-December is shown in Figure 3. Almost complete removal of thiosalts was observed at water temperatures as low as 1.0°C with feed thiosalts concentration ranging from 400 to 1,200 mg/L $S_2O_3^{2-}$ and 80 hours retention. Cessation of nutrient addition did not noticeably affect performance.

According to Mueller [6], it is practically impossible to decrease thiosalts levels to zero in a continuous operation mode without auxiliary means. A low thiosalt concentration will always be present; this is about 10 mg $S_2O_3^{2-}$/L. Restarting the process in the rock-packed pond after an interruption was difficult. On average, one to two months was needed to establish efficient operation, whereas, experience with other biological effluent treatment systems indicates that the
Aerated Rock Pond - 1984 Pilot Test Results

Retention time, h

Feed Temp °C

Thiosalts OS S\textsubscript{4}\textsubscript{3-} mg/L

Additions of nutrients halted

Feed

Treated effluent

Figure 3 - Aerated Rock Pond - 1984 Pilot Test Results
process can be started in two weeks [24]. Despite the problems encountered with the pilot tests conducted by the Noranda Research Centre, the results confirm the technical feasibility and robustness of biological oxidation of thiosalts. Near zero thiosalts levels can be attained using a simple rock-packed pond at temperatures as low as 1.0°C.

Based on the results of pilot tests at Brunswick Mining and Smelting, the Noranda Research Centre proposed a biological oxidation process shown in Figure 4. Mill tailings decant combined with thickener overflow are sent to a settling pond to remove the solids. Subsequently, the effluent from the settling pond is passed through aerated rock-packed ponds. The ponds have a total retention time of three days. Phosphate and ammonium ion nutrients are added for optimal microbial growth. A hydrogen peroxide oxidation system is provided to supplement biological oxidation in the event of process failure and as a polishing step. Lime is added to neutralize the acid and the clean overflow from the clarifier is discharged to the receiving waters. It was estimated that an average temperature of 5°C could be maintained in the rock-packed pond with combined tailings and warm thickener overflow during winter operation. The capital and operating costs for this biological oxidation process with $\text{H}_2\text{O}_2$ post-treatment was estimated at $15.6$ million and $7.1$ million respectively. These costs are for a complete effluent treatment system.

Bio-engineered reactors could improve the performance and robustness of the biooxidation treatment. An effective effluent equalization system can minimize short-term shock loading and thus, reduce stress on the biotreatment process. Reactors operated in parallel would provide flexibility in the process where one reactor could be drained for modification or repairs and the flow from the reactor being modified could be distributed to the other reactors. Furthermore, oxidation rates approaching 200 mg/L/h reported for packed-columns [6] could be realized by increasing microbial concentration, effluent contact time, aeration and improved mixing.

The rock-packed pond used in the pilot tests was not technically advanced yet, the results are exceptionally good and hold promise that a biological oxidation process for thiosalts could be developed to a full-scale process. Of thirteen processes evaluated in 1985, biological oxidation was the most cost-effective treatment process, based on capital and operational costs [3]. Upfront capital investments are high, but, operational and maintenance costs are low. Only marine discharge had lower operational and maintenance costs. There is still a high degree of
Figure 4 - Biological Oxidation
uncertainty regarding low temperature operation of a biooxidation process. More studies are needed to determine the optimum values for parameters at low temperature operation.

**THIOPAQ® Sulphate Reducing Bacteria Process**

Paques Inc. is a company involved in the development and installation of treatment systems based on biological processes. Recently, the company installed its patented biological process for the removal of sulphur compounds and dissolved metals from contaminated ground water at the Budelco Zinc Refinery in the Netherlands [24, 25, 26, 27]. Figure 5 shows a simplified process diagram of the metal and sulphate-reducing plant at Budelco. The system uses two biological steps:

1. Sulphate reducing bacteria converts sulphate to hydrogen sulphide (H₂S). The hydrogen sulphide reacts with the dissolved metals to form insoluble metal sulphide precipitates.
2. Sulphide oxidizing bacteria convert excess H₂S to elemental sulphur.

This system has been operating since 1992, treating a flow of 5,000 m³/day. The sulphate concentration is decreased from 1,200 to less than 160 mg/L in the treated effluent.

Paques has built seven full-scale installations which uses THIOPAQ® technology. In 1995 a pilot-scale THIOPAQ® process was operated at a lead mine. The sulphide concentration in the outflow was consistently reduced to below 1.0 mg/L at very short effluent retention times in the reactor [24]. This technology has proven to be robust and of minimal complexity.

THIOPAQ® technology could be adapted to thiosalts removal in milling effluent. Thiosulphate is oxidized to sulphate and elemental sulphur without the formation of acid as shown in the following equation:

\[
S_2O_3^{2-} + 1/2O_2 \rightarrow S^* + SO_4^{2-} \quad (2)
\]

Paques claims that this process has the following advantages:

- production of a non-oxygen demand effluent, in which the pH will remain unchanged;
- the biological reactor can be easily added to the existing treatment system;
- the sulphur can be removed in existing clarifier in conjunction with the metal and calcium precipitates;
- the microorganism selected by Paques is active at low temperature and high pH; and
- no extra lime addition is required with thiosulphate removal.
Figure 5 - Simplified THIOPAQ Process Diagram Metal and Sulphate Reducing Plant at Budeco
Béchard and co-workers investigated the reduction of thiosalts by sulphate reducing bacteria (SRB) [28]. The results of shake flask tests are consistent with the hypothesis that thiosalts reduction is sequential (trithionate>thiosulphate) and are not reduced to H₂S. Tetrathionate and trithionate concentrations decreased to less than 5 mg/L and thiosulphate decreased to less than 10 mg/L.

Figure 6 shows a simplified flowsheet diagram of a pilot plant proposed by Paques Inc. applying THIOPAQ® technology to remove thiosalts at Noranda Mining and Exploration Brunswick Mining Division. The estimated cost of the pilot plant is $800,000 Canadian.

Bio-augmentation

Bio-augmentation is an enabling biotechnology that can powerfully improve the performance of engineered biological effluent treatment systems. The purpose of bacterial augmentation is to eliminate or reduce portions of the population that do not contribute to a new biological activity and also, to exploit induced mutations beneficial to the new activity [29]. Subjecting indigenous microorganisms to strong selective pressure can enrich for new activities. An organism, arising from natural recombination and random mutations can be isolated using bio-augmentation techniques [30] and cultured in the laboratory. The biological reactor is inoculated with this improved strain. This is in contrast to biostimulation which is defined as the addition of nutrients or alterations of the microbial environment to increase the activity of native bacteria. Biostimulation of thiosalts oxidizing bacteria was in fact used in pilot-scale studies discussed earlier, the native population present in a pond. This may serve to increase non-working bacteria which would competitively inhibit thiosalts oxidizers.

Bio-augmentation techniques can be an effective tool in increasing the reaction rate of the microbial oxidation of pollutants. For example decomposition of ferrocyanide is known to occur naturally in many bacteria and fungi [31]. Thompson and Gertis [32] applied bio-augmentation techniques on a mixed population of native bacteria from a sulphide ore residue and subcultured for cyanide tolerance and degradation. A comparison between native bacteria and biologically augmented bacterial populations for cyanide decomposition is shown in Figure 7. The augmented population achieved 98% ferrocyanide decomposition compared to about 10% for the native bacteria. Similarly, Figure 8 shows the improved ability of an augmented strain of bacteria to remove dissolved metals from a solution compared to native bacteria [32, 33, 34].
Figure 6 - Simplified Flow Diagram Thiosulphate Oxidation Using THIOPAQÔ Technology
**Native bacteria vs augmented bacteria**

<table>
<thead>
<tr>
<th></th>
<th>Native bacteria</th>
<th>Augmented bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control treatment</td>
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<td>0.5</td>
</tr>
<tr>
<td>population #1</td>
<td>8</td>
<td>87.4</td>
</tr>
<tr>
<td>population #2</td>
<td>10.2</td>
<td>98.2</td>
</tr>
</tbody>
</table>

**Note:** All tests were run using a synthetic ferrocyanide solution which contained >150 mg/L at a pH of 9.5

---

Figure 7 - Bioaugmentation Applied to the Decomposition of Ferrocyanide
**Native bacteria vs augmented bacteria**

![Bar chart showing percent metal removal for Cu, Zn, Ni, Pb, and Co in native and augmented bacteria.](image)

**Percent Metal Removal**

Metals in standard = >125mg/L total

<table>
<thead>
<tr>
<th></th>
<th>Native bacteria</th>
<th>Augmented bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>30</td>
<td>97</td>
</tr>
<tr>
<td>Pb</td>
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</tr>
<tr>
<td>Co</td>
<td>1</td>
<td>74</td>
</tr>
</tbody>
</table>

**Note:** Bacteria were immobilized on an inert support matrix and batch tested with synthetic metal solutions.

**Figure 8 - Bioaugmentation Applied to Metal Sequestering**

CANMET-MMSL Report 97-060(CR)
Bio-augmentation can select bacteria that are more active at low temperature, have higher tolerance to toxic metal and have good substrate adhesion [35]. Improved strains could effectively compete with native species in a reactor and become the dominant species. Augmented bacterial strains would be less susceptible to change in the effluent feed. Overall, bio-augmentation could improve the efficiency and reliability of biological oxidation of thiosalts.

**Genetically Modified Bacteria**

Beneficial traits of microorganisms to carry out specific biological reactions have been improved by mutation and selection for decades. Genetic modification and bio-augmentation are technologies used to develop new bacterial strains. While bio-augmentation depends on the quirks of nature to cause desired mutations in a bacteria, genetic modification takes a more direct approach and creates the needed change in the genes of the bacteria. Recently, modern mutagens such as transposons and gene cloning have come into use. These methods can change genes to bring about desirable characteristics in microorganisms [36]. Genetic modification of *Thibacilli* could improve the following characteristics:

- increased resistance to toxic and inhibiting ionic species such as metals and chlorides;
- increased activity at cold temperatures;
- increased enzyme production for higher reaction rates for higher conversions; and
- better adhesion of the bacteria to the substrate.

Application of genetic engineering to thiosalts oxidation requires detailed knowledge of the metabolic pathway and the genes encoding the enzymes responsible for biodegradation of thiosalts. In general, the genetics of *Thiobacillus* species remain essentially uncharacterized. The few investigations into the genetics of this group of bacteria were directed at improving their resistance to toxic ions and to enhance their growth rates [37]. Transferring genes from one organism to another is one approach to creating a superior strain of bacteria to oxidize thiosalts [38].

Application of genetic engineering in the mining industry has focused mainly on biological leaching of ores [39, 40]. For example, one of the problems associated with the combusting of coal is the emission of SO$_2$ during its direct combustion. A cost-effective method for desulphurization of coal is needed. In one study, Clark [40] used genetically modified bacteria to remove sulphur from natural coal. Recent work on genetic engineering in Canada was
conducted at the Biotechnology Research Institute in Montreal [39]. A number of areas have been investigated including mineral leaching, cyanide degradation and sulphate reduction.

The main issues concerning genetically modified bacteria are the impact on the environment and human health associated with the release of these microorganisms. There are strong perceptions of risk associated with the use of genetically modified organisms. Regulations affecting the application of genetically modified organisms require extensive testing before allowing their use in effluent treatment processes.

The pace of development in genetics has increased with the availability of powerful analytical tools. It is conceivable that in the future, genetic modification techniques could customize microbial processes for the destruction of pollutants in effluents. Innovative technologies such as genetic modification could eventually provide the means to develop a low cost process for thiosalts oxidation.

**Immobilized Microorganisms**

Immobilized cells may be defined as cells that are physically confined with retention of their catalytic activities. In addition, immobilization in a matrix keeps active cells within a reactor system and prevents their entry into the mobile liquid phase thus preventing washout of the cells. Immobilization can be accomplished by adsorption, entrapment in three dimensional polymer network, covalent coupling and physical entrapment in a porous material. The most common approach is by a process known as ionotropic gelation. In this process, precultured cell suspension is mixed with a long-chain polymer and the mixture is then dropped into a solution of counterions. The resulting microporous network traps the cells in the matrix. The diffusion of oxidisable substrate and reaction products is fast, resulting in high oxidation activity. Matrices used to entrap the cells include acrylamide, polyurethane, collagen, agar alginate and chitosan [41].

This technique for immobilizing bacterial cells is not new. The pharmaceutical and cosmetic industries have used immobilized superior strains of bacteria to manufacture many products. However, the application of immobilized bacteria to treat effluents is new. Work done to date shows that immobilized bacteria holds promise for effluent treatment.

Application of immobilized cell technology to environmental problems is limited. In a study by Lewandowski [42] immobilized bacteria were used to carry out denitrification. Another study [43] reported that the biodegradation rate of 2-chlorophenol was 40 times greater for
immobilized fungus cells compared to free cells. Sofer and co-workers [44] showed that bacteria immobilized in alginate beads were able to withstand higher concentrations of 2-chlorophenol. In addition, the immobilized bacteria coped better with toxic shock loads and sudden changes in pH compared to free cells.

Lin et al. [45] investigated the treatment of food processing wastewater using entrapped mixed microbial cell process (EMMC). High removal rates of COD and BOD were achieved. He states that based on studies on wastewater treatment it is expected that EMMC process can provide the following advantages: 1) less land area, 2) less starting-up period, 3) simple to operate and maintain, 4) less sludge production, and 5) no bulking/rinsing sludge problems.

The advantages of this biotechnique over conventional free cell reactors include a much higher cell density resulting in high rates of biodegradation; easy separation of the immobilized cells from the liquid phase; greater operational flexibility; and more resistance to high concentrations of toxic chemicals because the microbes are protected by the matrix.

Bacteria entrapped in beads can overcome bulk washout. This is a major problem with fluidized biological reactors. Bacteria entrapped in small beads could improve the performance of fluidized bed reactor by providing a high surface area of biofilm per unit volume of reactor and high oxygen transfer rates [46].

Development of immobilized bacteria and genetically modified bacteria should be considered as long-term objectives to improve the efficiency and robustness of biological reactors. Studies in these areas should be undertaken only after the limitations of biological oxidation of thiosalts in conventional reactors are clearly defined.

**Advantages of Biological Oxidation of Thiosalts**

- biological oxidation of thiosalts was evaluated as the most cost-effective process;
- produces non toxic by-products;
- biological oxidation of thiosalts is inherently safe (environmental and worker);
- under optimum conditions thiosalts concentration can be reduced to less than 10 mg/L; and
- low energy requirement.

**Disadvantages of Biological Oxidation of Thiosalts**

- process is not efficient at low temperatures;
- the mining industry is not familiar with the operation of biological reactors; and
biological processes are prone to process upset due to short term changes in effluent feed.

TRANSITION METAL CATALYZED AIR OXIDATION

Air oxidation of thiosalts under normal pressures and temperatures is a very slow process and not practical for thiosalts oxidation from large volumes of effluent. Solutions of thiosulphate and polythionates were aerated at pH 7 for four months under sterile conditions with minimal changes in thiosalts concentration (<10% was oxidized) [47]. O'Brien and Birkner [48] studied the kinetics of reduced sulphur oxidation by molecular oxygen in simulated natural water environments at 25°C and pH 7.5. Thiosulphate was a stable reaction product with little oxidation occurring over a 72-hour period. The rate for thiosalts oxidation was best described by a zero order expression with respect to O₂.

Several researchers have investigated catalyzed air oxidation of thiosalts. Catalysts containing metals such as copper, manganese, nickel, cobalt, tungsten, zirconium, and titanium, either in a soluble form or in a supported or complexed form, are all mentioned in the literature as effective catalysts in oxidizing sulphur compounds contained in effluents [49].

Bull [50] describes a patent process for the oxidation of low-valence sulphur compounds such as thiosulphate in an aqueous medium. Hydrogen peroxide and a solid catalyst consisting of copper, iron or manganese supported on a metal oxide base are contacted with the effluent medium at a temperature of 10° to 80°C. Yan [51] describes a process for the removal of concentrated thiosulphate solutions with a catalyst composed of copper on a zeolite substrate. Catalytic oxidation occurs at temperatures from about 10° to 200°C. Sodium thiosulphate was reduced from 158 to 28 g/L and with three times stoichiometric requirements of oxygen at 88°C. The sulphate produced in the reaction are precipitated as Na₂SO₄ (Glaubers salt).

Chanda et al. [52, 53] reported that poly (4-vinyl pyridine)-Cu(II) [PVP-Cu(II)] complexes had superior stability and superior catalytic activity over other types of ligands in oxidizing thiosalts. Further enhancements were made to the stability and catalytic activity of the PVP-Cu(II) complex by crosslinking the residual free pyridine units in the complex by means of quarternization [54]. Continuous slurry reactor operation of two to four weeks duration were carried out for catalyzed air oxidation of thiosalts using poly (4-vinyl pyridine)-Cu(II) and quarternized poly (4-vinyl pyridine-Cu(II)) [QPVP-Cu(II)] catalysts. Thiosalts levels were
reduced to less than 100 mg/L during continuous operations of one month when operating at 20°
to 30°C. The PVP-Cu(II) and QPVP-Cu(II) catalyst systems have optimum activity for thiosalts
effluent streams of <1,000 mg/L thiosalts.

PVP-Cu(II) catalyst required regeneration and desorption of thiosalts after 7 days of
continuous operation to maintain a thiosalt level of <100 mg/L in the treated effluent. Similarly,
the QPVP-Cu(II) catalyst required desorption after 7 days and regeneration after six months [55,
56]. Batch thiosalts oxidation tests were also done using polythiosemicarbazide-Cu(II) complex.
This catalyst had higher stability compared to PVP-Cu(II), however, the catalytic activity of
polythiosemicarbazide was significantly slower than PVP-Cu(II) [56]. The work on QPVP-
Cu(II), PVP-Cu(II) and polythiosemicarbazide-Cu(II) identified some serious practical problems
associated with catalyst regeneration and catalyst life that would have to be resolved prior to any
commercial application of this approach.

In a patent assigned to the University of Waterloo, Rampel et al. [57] describes a process
that uses sulphur-bonded copper as a catalyst in the oxidation of thiosalts by molecular oxygen.
Several sulphur-bonded copper compounds are suitable catalysts including CuS, Cu2S or
naturally-occurring chalcopyrite (CuFeS2). The oxidation of thiosalts can be affected in a slurry
of sulphur bonded copper compound over a temperature range of 20° to 90°C and pH 3 to 6. The
process was operated over a period of one month without any loss of catalytic activity of the
copper compound. Some activity variation was observed between sources of the chalcopyrite
concentrates, Opemiska and Bethlehem chalcopyrite concentrate had the highest catalytic
activity. A feed of 450 mg/L thiosulphate was completely oxidized to SO\(_4^{2-}\) by air oxidation with
a 15% (w/v) slurry of Opemiska chalcopyrite in 24 hours at 30°C. A chalcopyrite catalyst holds
promise as a method for removing thiosalts in particular thiosalts in warm thickener overflow.

Iron compounds have also been investigated as a catalyst for the oxidation of sulphide
compounds. Johnson et al. [58] describes a process where polyionic additives in the presence of
iron catalysts and O\(_2\) or H\(_2\)O\(_2\) as the oxidizing agent can promote oxidation of water soluble
sulphide compounds.

Gillespie [59] describes a method for treating an aqueous stream containing a water-
soluble inorganic sulphur compounds using iron or cobalt phthalocyanine supported on activated
carbon. The stream is contacted with oxygen in a thermal non-catalytic conversion zone to
convert inorganic sulphide compound to sulphate and thiosulphate. The catalytic oxidation of
thiosulphate to sulphate is carried out at temperatures from 100° to 160°C, pH values greater than
12 and pressures of 1 to 1,000 psig with oxygen. Greater than 90 weight percent thiosulphate to sulphate conversion rates was reported.

Several improvements are claimed in a patent issued to Eastman Kodak Company [60]. The process uses a catalytic anion ion exchange resin to oxidize thiosalts in aqueous solutions while maintaining a temperature of 55°C and pH below 8 in the solution. The protonated ion exchange resins tested were polyvinyl pyridine and phenol formaldehyde. The copper catalyst is physically contained in the resin.

A particularly effective resin for the process is sold under the trade name Amberlite™ IRA-68, manufactured by Rohm and Haas Company. Laboratory batch-scale tests conducted by the authors using Amberlite IRA-68 silver sulphide complex demonstrated good catalytic activity in decreasing thiosulphate in concentrated photographic solutions at 55°C and pH 3. Periodic regeneration of the catalyst is needed to maintain high activity.

Based on the results of the studies conducted by Chanda and Rampel, the Noranda Research Centre developed a flowsheet for a process using PVP-Cu(II) catalyzed air oxidation. The flowsheet is shown in Figure 9 [3].

Thiosalts in mill tailings decant and the warm thickener overflows are catalytically oxidized in aerated earthen basins with 2% PVP-Cu resin slurry. Heat is added to maintain water temperatures in the pond at 30°C and lime is added to maintain optimum pH. Since the resin becomes deactivated due to loss of copper, 10% of the resin will be sent continuously for regeneration. The capital and annual cost for catalyzed air oxidation process were estimated at $32.2 and $26 million respectively.
Figure 9 - PVP-Cu Catalyzed Air Oxidation
Advantages of Metal Catalyzed Air Oxidation

- Potentially low cost method for removal of thiosalts;
- Sulphur bonded copper catalysts has good long term catalytic activity and is inexpensive (i.e., natural chalcopyrite);
- Process does not require reagents and does not produce toxic by-products; and
- Complete oxidation of thiosalts.

Disadvantages of Metal Catalyzed Air Oxidation

- Catalysts are not effective at low temperatures;
- Most catalyst require frequent regeneration resulting in high operational costs;
- Precipitation of gypsum on the catalyst may reduce the active surface;
- Catalysts for thiosalts require further development; and
- An effective catalyst would require several years to develop.

ELECTROCHEMICAL OXIDATION

Direct electrochemical oxidation of thiosalts is interesting from a technical standpoint because of the simplicity in concept, safety and flexibility of the process. Although electrooxidation of thiosalts is technically feasible the economic feasibility is not proven. At the present time, electrochemical treatment of effluent is generally limited to specific streams with low flows and high concentrations. Studies on direct electrolytic oxidation of thiosalts indicate that the anodic reactions are complex with the formation of many polythionates. Figure 10 [4] outlines the main anodic reactions occurring during electrooxidation of thiosalts in neutral, and alkaline solutions.
Figure 10 - Anodic Reactions Occurring During Electrooxidation of Thiosalts
Yokosuka and co-workers [61] reported that regardless of the pH during the electrolytic oxidation of an aqueous solution of sodium thiosulphate, the ultimate products were sulphate and dithionate ($\text{S}_2\text{O}_2^-\text{S}_3^-$) and dithionate could not be oxidized by electrochemical means. Laboratory-scale tests conducted by Bartels [62] and Noranda Research Centre [3, 63] reported a buildup of dithionate with 80 percent of the thiosalts oxidized to $\text{SO}_4^{2-}$ and 20 percent converted to dithionate. The effect of dithionate on the receiving waters has not been studied but it is reasonable to postulate that over a long reaction time, dithionate will oxidize and generate acid.

In the same study, Bartels reported a significant drop in current efficiency at concentrations below 500 mg/L thiosalts. Cotton and Johnson [63] reported that the oxidation of 1.0 pound of thiosalts requires 14-36 kWh of electricity. Current efficiencies could be influenced by solution concentration and composition (i.e., thiosalts concentration, dissolved metals, and organics). Additionally, side reactions involving ionic species other than thiosalts decreases oxidation rate of thiosalts [64].

Electrochemical processes have been technically successful in the treatment of domestic wastewater mixed with seawater [65, 66]. Electrochemical treatment of a wastewater-seawater mixture resulted in a high rate of elimination of ammonia. Szpyrkowicz and Zilio Grandi [67] reported that graphite and steel electrode successfully removed all of $\text{NH}_4^+$ from biologically treated wastewaters. Carbon fibre electrodes gave much lower efficiency but the results were not reproducible.

Recently, Haque and Dinardo [68] conducted laboratory-scale tests on the oxidation of thiosalts in milling effluents using chloride mediated electrooxidation. This process is based on the generation of elemental chlorine by electrolysis of a brine solution containing thiosalts. The chlorine hydrolyzes into hypochlorous acid (HOCl) which in turn oxidizes thiosalts. The main product of the reaction are $\text{SO}_4^{2-}$ and $\text{Cl}^-$. The chloride ion can be oxidized once again at the anode to generate more chlorine. Chlorine mediated electrooxidation decreased thiosalts concentration to less than 10 mg/L and for all practical purposes, dithionate was completely oxidized [69, 70, 71]. Where available, seawater which may be regarded as a slightly alkaline solution of 3% sodium chloride could be mixed with milling effluent, thus, eliminating the need to add sodium chloride [72].

Conceptually, catalysts could be combined with electrooxidation to improve the efficiency of the cell to oxidize thiosalts and reduce power requirement. In a recent study, Franklin and co-workers [73] bonded copper(II) and bismuth(III) to the surface of the anode with polystyrene. It
was shown that copper(II) oxide bonded to the anode catalyzed the oxidation of organic compounds in a manner similar to powdered copper oxide suspended in an aqueous system. The polystyrene increased the oxidation potential allowing the copper(II) to be oxidized to copper(III). The copper(III) ions could affect electro-catalytic oxidation of organic species. Electrode surfaces modified with copper catalysts could achieve high reaction rates, greater selectivity for thiosalts and lower electrical energy requirements. These advantages would improve the feasibility of large-scale electrooxidation of thiosalts.

A flowsheet of a potential electrochemical process for thiosalts is presented in Figure 11 [3]. The combined effluents from the settling pond and thickener are passed through a sand filter to remove solids. Subsequently, the effluent is sent to the electrolytic cells. The electrochemical reactor consists of standard modular electrolytic cells. Lime is added to neutralize the acid followed by addition of a polymer to aid settling of the solids in a clarifier. The final effluent is discharged to the receiving waters and the sludge is disposed in a sludge pond. The capital and operating costs for this conceptual electrochemical process was estimated at $79 million and $32.9 million respectively.

Advantages of Electrochemical Oxidation

- Chloride mediated electrooxidation can reduce thiosalts to concentrations less than 10 mg/L;
- Does not require handling and storage of chemical oxidants;
- Chloride mediated electrooxidation can oxidize dithionate to form sulphate;
- Higher current efficiency for chloride mediated electrooxidation [71];
- Electrooxidation is more cost-effective for concentrated thiosalts solutions;
- Complete automation of the electrolytic process is technically possible;
- Process can be easily controlled from a remote location; and
- Mixture of seawater and effluent could be used instead of NaCl.

Disadvantages of Electrochemical Oxidation

- Treatment of high effluent flows and low thiosalts concentrations is not proven cost-effective;
- Needs routine cleaning of the electrodes to remove precipitates;
Figure 11 - Electrochemical Oxidation
Electrooxidation using carbon fibre electrodes may generate chlorocarbons;
Not proven efficient at low temperatures;
Toxicity of the treated effluent on fish is not known;
High power requirements;
Establishing an exact electrolytic process for complex mill effluent is difficult; and
Direct electrooxidation of thiosalts generates dithionate which cannot be further oxidized.

OZONE OXIDATION

There is no question that kinetically and ecologically ozone is the superior oxidant. Its high reactivity, lack of residue after reaction, simplicity of application and safety also favours ozone over other oxidants for solving many effluent treatment problems. Ozone is used in many different applications such as water treatment, waste treatment, disinfection and oxygenation. It is gradually replacing the very problematic chlorination process in the pulp and paper industry. Despite these advantages, ozone has found relatively little application in mining and industrial effluent treatment as an end-of-pipe treatment technology.

Ozone is a very powerful oxidant; it has the ability to oxidize materials further than do the other oxidants or to oxidize the same substrate at a faster rate than do other oxidants. Table 5 lists the oxidation potential of common oxidants. Only fluorine, atomic oxygen and hydroxyl radicals have a high oxidation potential than ozone.

Table 5 - Relative oxidation power of oxidizing species*

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxidation potential (volts)</th>
<th>Relative oxidation power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine (F₂)</td>
<td>3.06</td>
<td>2.25</td>
</tr>
<tr>
<td>Hydroxyl radical (HO')</td>
<td>2.80</td>
<td>2.05</td>
</tr>
<tr>
<td>Atomic oxygen</td>
<td>2.42</td>
<td>1.78</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>2.07</td>
<td>1.52</td>
</tr>
<tr>
<td>Hydrogen peroxide (H₂O₂)</td>
<td>1.77</td>
<td>1.30</td>
</tr>
<tr>
<td>Hydroperoxyl radical (HO₂⁻)</td>
<td>1.70</td>
<td>1.25</td>
</tr>
<tr>
<td>Hypochlorous acid (HOCl)</td>
<td>1.49</td>
<td>1.10</td>
</tr>
<tr>
<td>Chlorine (Cl₂)</td>
<td>1.36</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*Rice, R.G. [74]
When molecular ozone dissolves in water the molecules can remain as $O_3$ or they can decompose by a variety of mechanisms ultimately producing free radicals ($OH^+$, $HO_2^+$). These radicals are themselves strong oxidizing agents which react very quickly to oxidize organic and inorganic compounds present in water [75]. The dominant reaction of ozone depends on the reactor condition and the chemical composition of the wastewater. For example natural alkalinity anions (carbonate and bicarbonate) destroy hydroxyl radicals and will assure the absence of hydroxyl radicals and stabilization of ozone levels. Increasing the pH (above 7), temperature or addition of $H_2O_2$ will promote the formation of hydroxyl radicals [76].

Ozone is generated by high voltage or high frequency electrical equipment capable of producing a corona discharge through an oxygen-containing gas; usually dry air or pure oxygen [76, 77]. Since ozone is an unstable gas it must be generated and applied at its point of use. Additionally, an ozonation system should always have extra capacity to handle flow variation in the treatment plant. A minimum of 50% standby capacity is generally recommended for both the feed-gas preparation and ozone generation systems. Turnkey ozone generation systems from 1 lb/day to 5,000+ lb/day are commercially available from several manufacturers. For comparison, the ozone system required to treat 24,000 kg/d thiosalts would produce 26,000 kg/d ozone assuming an $O_3$ to $S_2O_3$ weight requirement of 1.1 to 1.

The selection of air or oxygen as the gas feed affects the performance of the ozone generator [3, 75, 77]. Commercial units have typical outputs of 2 to 6 wt% ozone using air as the feed gas compared to a maximum 2 wt% with dry air as the feed gas. Ozone generation is not an energy-efficient process. Nearly 80% of the electrical energy supplied to the generator is converted to heat. Consumption of between 15 and 26 kWh/kg $O_3$ is common for an air-fed generator.

There are many publications describing laboratory studies in which ozonation was apparently technically successful in effluent treatment. However, adoption of ozonation as a full-scale effluent treatment process is not extensive. Some examples of full-scale effluent treatment applications involving ozone are as follows:

- recycling marine aquaria waters (organic matter);
- cyanide destruction from electroplating effluents;
- electronic chip manufacture (recycle/reuse of rinse waters);
- textile industry (dechlorination);
- petroleum refineries (organic destruction);
- pulp bleaching plants;
- drinking water treatment; and
- photo processing.

Extensive use of ozone is made in the treatment and recycling of artificial brines in marine mammal aquaria. The treatment process involves ammonia removal, ozonation, dual media filtration and return to exhibit tanks. Chlorine dioxide is used as a backup in the event of ozone equipment failure [76]. In 1992 it was estimated at least 35 marine aquaria in the United States and Canada were using ozone treatment and new aquaria are being designed with ozone treatment [76, 78]. This treatment process allows 100% recycle of wastewater and permits the animals to thrive in a chlorine-free environment.

Sukes et al. [79] described the ozone installation at the Cadillac Motor Car Division of General Motors Corporation in Detroit for the full-scale destruction of cyanide containing metal finishing effluent. Cyanide levels in the effluent of less than 1 mg/L has been achieved consistently. The ozone system installed requires 24.9 kWh/Kg ozone produced with air as a feed gas. Typically 60 to 80% of the operating and maintenance cost for ozone treatment systems is electrical cost. Based on 1985 power costs of $0.056/kWh, the cost per kg of cyanide treated was $3.00. This cost includes operation of turbine contactors and other auxiliaries. Compared to alkaline chlorination process, the cost of ozonation was estimated to be much higher.

In a pilot plant study, Munter and co-workers [80] compared the cost of ozonation with other treatment methods. Wastewater from an oil shale ash dump was treated using the following methods; 1) aerobic biooxidation, 2) anaerobic biooxidation, 3) hydrogen peroxide, and 4) granular activated carbon adsorption (GAC). Table 6 shows the relative costs of these processes.

In this particular application ozonation and aerobic biooxidation have similar costs, while anaerobic biotreatment is about 40 percent cheaper. However, biological treatment could only remove about 50% of the phenolic constituents. Munter concluded that the most cost effective method to achieve complete removal of phenols was by a combination of biooxidation followed by ozonation.
Table 6 - Relative expenses of oil shale wastewater purification

<table>
<thead>
<tr>
<th>Purification process</th>
<th>Relative costs of initial concentration of phenols</th>
<th>500 mg/L</th>
<th>50 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerobic biooxidation</td>
<td></td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Anaerobic biooxidation</td>
<td></td>
<td>0.38</td>
<td>0.68</td>
</tr>
<tr>
<td>Ozonation</td>
<td></td>
<td>0.98</td>
<td>1.13</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td></td>
<td>0.30</td>
<td>3.85</td>
</tr>
<tr>
<td>GAC adsorption</td>
<td></td>
<td>8.00</td>
<td>1.25</td>
</tr>
</tbody>
</table>

In a more recent study, Tozer [81] compared treatment systems using ozone, chlorine and activated carbon for the removal of colour from paper mill wastewaters. Table 7 shows a summary of these comparisons. He concluded that capital and operating costs are high for ozone treatment.

Table 7 - Comparison of treatment process for the removal of colour from paper mill wastewaters

<table>
<thead>
<tr>
<th>Process</th>
<th>Sludge generation</th>
<th>Relative capital cost</th>
<th>Relative operating cost</th>
<th>Aquatic toxicity test</th>
<th>Process control issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powdered activated carbon</td>
<td>very high</td>
<td>moderate to high</td>
<td>very high</td>
<td>not tested</td>
<td>difficult to completely remove from treated water</td>
</tr>
<tr>
<td>Chlorine oxidation</td>
<td>none</td>
<td>low to moderate</td>
<td>low</td>
<td>low with pH neutralization</td>
<td>easy to control but requires dechlorination</td>
</tr>
<tr>
<td>Ozone oxidation</td>
<td>high</td>
<td>low to moderate</td>
<td>low</td>
<td></td>
<td>easy to control</td>
</tr>
</tbody>
</table>

Presently there is limited use of ozone in the pulp and paper industry. The high organic content of the effluent and the oxidation resistant halogenated compounds produced during chlorine bleach require large amounts of ozone make the process uneconomical. However, there is a move toward a totally chlorine-free bleaching of paper pulp with a total recycle of process water.
The Union Camp Corporation Franklin paper mill in the state of Virginia, installed proprietary high-consistency ozone treatment process in its pulp bleaching process. This mill is located near a small river where no discharge is allowed for eight months of the year. Ozone is generated from oxygen at about 14% by weight and is applied under proprietary conditions in a reactor. Oxygen-rich off-gases are recycled back to the ozone generator [82, 83].

Leachate from landfill are also successfully treated using a combination of biooxidation and ozonation. Friedrich [84] described an ozonation process followed by aerobic biooxidation of leachate from a landfill. The treatment process installed in 1993 is commercially successful and is now offered as a service to treat other leachates. Another successful treatment process was installed in 1994 at a chemical manufacturing plant near Dresden, Germany. Ozonation followed by biological treatment is used to oxidize various organics [84]. Toffani and Richard [85] reported that an ozone treatment process was successfully integrated into a conventional treatment plant for combined municipal/industrial wastewater.

In 1994, an ozone treatment system was installed to treat 1,000 gpm effluent from an active lead and zinc mine in Colorado [86]. Ozone was selected because of its ability to destroy toxic organics, precipitate heavy metal complexes, destroy cyanide and oxidize ammonia. Thus, all treatment objectives for the site could be satisfied by one treatment system as well as meet Whole Effluent Toxicity (WET) test limits. As shown in the flowsheet in Figure 12, the ozone treatment system was installed directly downstream of the existing tailings pond and sand filter. An additional filter was installed after the ozone system to remove metals oxidized by ozone.

Pure oxygen from storage tanks is fed to two ozone generators rated at 300 pounds O₃ per day at 4% concentration. The effluent is fed to three stainless steel contactors connected in series. Ozone transfer efficiencies in the contactors are in the order of 99% compared to 90% for mixed tanks reactors and fine bubble diffusers [77].

Removal of heavy metals by ozone is an added advantage. Netzer and Bowers [87] showed that after the bulk of heavy metals is removed by lime adjustment to alkaline conditions the remaining dissolved metals are precipitated by ozone with greater than 99.5 percent removal.
Figure 12 - Ozone Treatment System
Ozone oxidation of thiosalts in mill effluents was investigated by Environment Canada, Wastewater Technology Centre [88, 89, 90]. The following reactions were proposed:

\[
2 \text{S}_2\text{O}_3^{2-} + 5\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 4 \text{SO}_4^{2-} + 3.5 \text{O}_2 + 4\text{H}^+ \quad (3)
\]

\[
5 \text{S}_2\text{O}_3^{2-} + 2\text{O}_3 + 7\text{O}_2 + 5\text{H}_2\text{O} \rightarrow 10 \text{SO}_4^{2-} + 10 \text{H}^+ \quad (4)
\]

Tan and Rolia [91] conducted exploratory ozonation tests on synthetic thiosulphate solutions. With oxygen as the feed gas, thiosulphate was rapidly oxidized to sulphate. At lower ozonation rates with air as the feed gas some H\(_2\)S was formed. In view of these results, molecular oxygen may compete with ozone in the oxidation of some reaction intermediates such as sulphide species which are more amenable to oxidation by oxygen than thiosalts. Takizawa et al. [92] also reported that pH dependent side reactions were observed with a low ozone supply rate. Ozone requirements were twice as much for air compared to oxygen as the O\(_3\) generator gas. The average ozone consumption for milling effluent was 3 mol O\(_3\)/mol S\(_2\)O\(_3^{2-}\). There was indication that sulphur oxidation occurred at higher pH values.

The process flowsheet shown in Figure 13 for ozone oxidation of thiosalts [3] is based on the laboratory-scale tests conducted at Environment Canada [89], CANMET’s Mineral Sciences Laboratories and Noranda Research Centre [93].

Ozone treatment of mill tailings decant and thickener overflow would occur in agitated ozone reactors operated in series with a total retention time of 60 minutes. The pH in the reactors is maintained at pH 9 with lime. Following ozonation, a polymer is added to the effluent and is sent for solid/liquid separation. The clean overflow is discharged to the receiving waters. Oxygen produced at a liquefaction plant is fed to the ozone generators. Subsequently, a mixture of 4% O\(_3\) and 10% O\(_2\) is fed into the reactors. Residual ozone and oxygen gas leaving the reactors is fed to an ozone destruction unit and the oxygen is returned to the ozone generators. The estimated capital cost for the plant was $50.5 million plus $18.5 million in annual operating costs [3, 93].
Figure 13 - Ozone Oxidation
A very large ozone generation plant would be needed to treat milling effluents; 5,000 lb/day is considered a large plant. The high capital investment in oxygen and ozone generation plants and the high operating costs limits ozone to special applications. The size of the plant could be reduced if ozone is used as a polishing step following bulk removal of thiosalts by biological oxidation.

**Advantages of Ozone Oxidation**

- Ozone is produced on-site, thus eliminating transportation and storage requirements;
- Does not produce toxic by-products;
- Application of ozone is simple and safe;
- Can be used as a year-round operation;
- Improved performance of biooxidation in combination with O$_3$;
- Residual ozone decomposes into oxygen very quickly thus, eliminating downstream environmental effects;
- Ozone is a very strong oxidizer that can achieve complete removal of thiosalts;
- More flexibility in recycling thiosalt-free water to mill processes;
- Fast reaction rate with short retention time;
- Pilot studies indicate reduced polymer requirement for coagulation [94];
- Extensive experience in the use of ozone for industrial wastewater and municipal drinking water treatment; and
- Ozone combined with lime can decrease lime requirement and the amount of sludge formed [81].

**Disadvantages of Ozone Oxidation**

- High capital investment mainly due to on-site oxygen and ozone generation facilities;
- High electrical energy requirement to generate oxygen and ozone;
- Need for stand-by capacity to provide sufficient ozone to meet peak load requirements and varying flows;
- Ozone cannot be stored and must be generated and applied at its point of use;
- Requires stand-by supply of other oxidants in the event of equipment failure; and
- Complex system requiring skilled workers.
CHLORINE OXIDATION

Chlorine is one of the chemical elements noted for its great power as an oxidizing agent. When dissolved in water, free chlorine attacks everything it touches producing chemical by-products (combined chlorine) with every reaction and some of these by-products retain some oxidizing power. Because of this residual oxidizing power of chlorine it is the most common treatment method for sterilizing drinking water and wastewater.

Chlorine is relatively inexpensive and on a cost basis it is a good choice for thiosalts oxidation. Reaction kinetics are fast and, the oxidation of thiosalts is essentially complete in 30 minutes at temperatures ranging from 5°C to 25°C. Chlorination requires simple equipment that can be easily integrated into an existing treatment process. Despite these advantages, the use of chlorine in effluent treatment is problematic.

Chlorine is a very toxic substance that poses challenges to its safe use as an oxidant. Stringent safety regulation requires construction of high cost scrubbers and containment systems. Emergency response plans in the event of a chlorine spill including evacuation plans and cost effective mitigation measures are needed. Furthermore, plant personnel would require training in the event of a spill and in the safe handling of chlorine. All the above would add to the cost of a chlorination process. These safety requirements coupled with the impact of chlorine and combined chlorine by-products to the biota in the receiving waters makes chlorine less attractive as an oxidant for effluent treatment.

Reaction of chlorine with thiosalts under neutral conditions involves the formation of the active component HOCl by hydrolysis of Cl₂ [2] as shown in the following reaction:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{Cl}^- + \text{H}^+ \] (5)

which then reacts with S₂O₃²⁻:

\[ 4\text{HOCl} + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 4\text{Cl}^- + 6\text{H}^+ \] (6)

Overall the reaction can be expressed as:

\[ \text{S}_2\text{O}_3^{2-} + 4 \text{Cl}_2 + 5 \text{H}_2\text{O} \rightarrow 2 \text{SO}_4^{2-} + 10\text{H}^+ + 8 \text{Cl}^- \] (7)

Oxidation of one mole of thiosalts requires four moles of Cl₂ and generates four equivalents of acid per mole of S₂O₃²⁻.
In addition to the acid that is generated, chlorination requires significantly more lime when compared to the other oxidants because of the initial formation of hypochlorite:

\[ 2\text{Cl}_2 + \text{Ca(OH)}_2 \rightarrow \text{Ca (OCl}_2) + 2\text{HCl} \quad (8) \]

\[ \text{Ca(OH)}_2 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} \quad (9) \]

Based on stoichiometric prediction, each kilogram of thiosalts oxidized requires 2.54 kg \( \text{Cl}_2 \) and 2.64 kg \( \text{Ca(OH)}_2 \) [2, 3]. Sulphides will also react with chlorine to yield hydrochloric acid and elemental sulphur. However, in the presence of enough chlorine, the reaction will produce hydrochloric acid and sulphuric acid [95]. Naturally, these side reactions will increase the overall chlorine demand. Compared to other oxidants chlorine could generate greater quantities of acid; consequently, lime requirement will be high.

Chlorine is the “number one toxic pollutant” to many environmental activists these days. The pulp and paper industry knows only too well the cost that can result from public and political perception about chlorine and combined chlorine by-products. The industry has spent more than $1 billion dollars to eliminate dioxins in its products and eliminate the use of elemental chlorine in its bleaching process. Chirat and co-workers [96] and Rounsaville and Rice [97] reported on recent trends in the paper pulp industry towards a totally chlorine-free bleaching of paper pulps. The authors point out that the issue of organic halogens in pulp and paper effluents and residual chlorine have forced current changes in the bleaching process. The current opinion is that chlorine will no longer be used for bleaching and that ozone and hydrogen peroxide, in combination, offer good prospects for a zero effluent discharge paper mill [96]. The pulp and paper industry in central Europe have followed a similar trend. Many mills have abandoned chlorine for bleaching due mainly to a more stringent water protection and industrial development policy [98].

In Canada, there are no recommended levels for chloride ions in water but it is expected that the generation of chloride ions from thiosalts treatment will be high; approximately 2.5 g Cl\(^-\) for every gram of \( S_2\text{O}_3^{2-} \) oxidized. However, both British Columbia and Newfoundland regulate chlorine concentration at 0.5-1.0 mg/L and 1.0 mg/L respectively [1]. Environment Canada [99] conducted an ecological assessment of chlorine added to effluents and released to the Canadian environment. In-situ testing and biological surveys downstream from the discharge point demonstrated that chlorinated effluents caused lethality to fish and changes to benthic invertebrate communities up to 500 m from the discharge point. These effects generally occurred when total residual chlorine levels exceeded 0.02 mg/L. Dechlorination of the effluents prior to discharge eliminated or significantly reduced the observed effects.
One by-product of chlorine reactions is trihalomethanes (THMs). THMs form when chlorine reacts with naturally occurring organic matter in water, like leaves. THMs have been classified as possible carcinogens by the U.S. Environmental Protection Agency and furthermore, research indicates that many other volatile organic chemicals are often present in water that have been treated with chlorine.

Rolia and Barbeau [100] conducted laboratory tests using chlorine to oxidize synthetic solutions containing $\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$ and $\text{S}_4\text{O}_6^{2-}$. They found that the oxidation rate depends on the rate of chlorine addition and each mole of thiosalt sulphur requires two moles of chlorine.

Batch and continuous laboratory-scale tests done at Noranda Research Centre and CANMET using mill effluent found that chlorine requirements were 70% higher than stoichiometric prediction and lime demand at pH 7 was roughly 5.5 g Ca(OH)$_2$/g S$_2$O$_3^{2-}$ [3, 101]. In other bench-scale tests chlorination was essentially a stoichiometric reaction with the effluent containing 1,050 mg/L thiosalts.

A flowsheet of chlorine treatment for milling effluents is shown in Figure 14 [3]. Effluents from the tailings pond and the thickener are treated in three stirred tank reactors operated in series with a total retention time of 45 minutes. Chlorine gas is injected into the reactors with lime added to maintain the pH at 7. The overflows from the tank reactors are combined and polymer is added in a flash mixing reactor to improve solid/liquid separation. From the flash mixer, the effluent is sent to a clarifier where part of the underflow sludge is limed and recycled to the reactors to promote densification of sludge; the rest is sent for disposal in a sludge pond. The treated effluent is discharged to the receiving water. The estimated capital and annual costs for this chlorination process was $10 million and $20.4 million respectively [3].

**Advantages of Chlorine Oxidation**

- Chlorination is a well known technology that can be easily integrated in existing effluent treatment systems;
- Comparatively chlorination requires low initial capital investment;
- A full-scale facility, based on current available data could be constructed;
Figure 14 - Chlorine Oxidation
• Very fast reaction rates;
• High degree of certainty that thiosalts can be completely oxidized;
• Dose can be varied to meet changing thiosalts concentrations and effluent flow; and
• Chlorination is effective as a year-round operation.

Disadvantages of Chlorine Oxidation
• Residual chlorine carry-over into downstream processes;
• Chlorine and combined chlorine remains as residual concentration for a long time;
• Toxic combined chlorine by-products would require further treatment;
• High chlorine requirement due to side reaction with sulphide minerals and organic reagents;
• Need for storage tanks and space at a distance from the mill to meet safety requirements;
• Compared to other oxidants, chlorine generates more acid (H₂SO₄ and HCl) and consequently more lime is consumed;
• Chlorine is very toxic and requires training of employees and implementation of safety measures;
• Need for special gas handling, and contacting equipment;
• Chlorinated compounds can affect invertebrate communities in the receiving waters; and
• Dechlorination is required to meet discharge limit of chlorine residual in the effluent.

HYDROGEN PEROXIDE OXIDATION

Hydrogen peroxide is one of the most powerful oxidizers known, even stronger than chlorine. Through iron catalysis, H₂O₂ can be converted into hydroxyl radicals (OH⁻) with reactivity second only to fluorine. This powerful oxidizer that looks like water in its chemical formula, appearance and reaction products is widely used in the treatment of contaminated waters; a powerful yet versatile oxidant that is both safe and effective for effluent treatment [76, 102]. Commercially, this product is available in bulk in strength from 35-70% (w/w), with 50% H₂O₂ being the most common for effluent treatment applications. Hydrogen peroxide can be stored on site for thiosalts oxidation in a continuous year-round operation and unlike chlorine, leaks from bulk storage tanks are less toxic.
Hydrogen peroxide reacts differently with thiosalts depending on the pH of the effluent [103, 104]. In alkaline pH, hydrogen peroxide reacts with thiosalts as shown in the following reactions:

\[
\begin{align*}
S_{2}O_{3}^{2-} + 4H_{2}O_{2} & \rightarrow 2 SO_{4}^{2-} + 2H^{+} + 3 H_{2}O \quad (10) \\
S_{2}O_{6}^{2-} + 4H_{2}O_{2} & \rightarrow 3 SO_{4}^{2-} + 4H^{+} + 2 H_{2}O \quad (11) \\
S_{4}O_{6}^{2-} + 7H_{2}O_{2} & \rightarrow 4 SO_{4}^{2-} + 6H^{+} + 4 H_{2}O \quad (12)
\end{align*}
\]

The reactions described above are not very rapid. If the reaction is too slow $H_{2}O_{2}$ will decompose and is thus wasted as indicated by the following reaction [104, 105].

\[
2H_{2}O_{2} \rightarrow O_{2} + 2 H_{2}O \quad (13)
\]

Reasonable rates of complete oxidation of thiosalts to sulphate at ambient temperatures are obtained only in acidic media. However, in the presence of a metal catalyst such as ferrous ions reaction time can be greatly reduced to a few minutes. With ferrous ions present in a solution, hydrogen peroxide can undergo a series of reactions which generate perhydroxyl ($HO_{2}^{•}$) and hydroxyl ($OH^{•}$) radicals as follows:

\[
\begin{align*}
Fe^{2+} + H_{2}O_{2} & \rightarrow Fe^{3+} + OH^{-} + OH^{•} \quad (14) \\
OH^{•} + H_{2}O_{2} & \rightarrow HO_{2}^{•} + H_{2}O \quad (15) \\
HO^{•} + H_{2}O_{2} & \rightarrow O_{2} + H_{2}O + OH^{•} \quad (16)
\end{align*}
\]

These radicals are the chain carriers in the conversion of $H_{2}O_{2}$ into hydroxyl radicals. The perhydroxyl and especially the hydroxyl radicals are strong oxidants due to their high electron affinities. Weaker catalytic activities of other heavy metal ions follow similar reaction mechanisms. Reactions 10 to 12 indicate that complete oxidation of thiosalts will result in high $H_{2}O_{2}$ and lime consumption. Table 8 shows the $H_{2}O_{2}$ requirements for the complete oxidation of various thiosalts species [103].
Table 8 - The calculated H₂O₂ requirements for the oxidation of thiosalt species expressed as moles of thiosulphate

<table>
<thead>
<tr>
<th>Thiosalt species</th>
<th>Concentration (mol of S₂O₃²⁻)</th>
<th>Oxidation (mol H₂O₂)</th>
<th>Oxidation (mol ratio) (H₂O₂/S₂O₃²⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₂O₃²⁻</td>
<td>1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>S₂O₆²⁻</td>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>S₄O₆²⁻</td>
<td>2</td>
<td>7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Cost is clearly an important factor when choosing an oxidant for effluent treatment. Table 9 compares the relative chemical costs for H₂O₂ at a facility using 1,200 lbs/day of gaseous chlorine to treat 200 lbs/day H₂S. The unit costs for Cl₂ were based on information provided by municipal treatment facilities and H₂O₂ cost was based on list prices in bulk in 1985 [106]. A difference of $36.00 per day in this example is not significant if environmental, safety, and storage requirements needed for chlorine are factored into the cost.

Table 9 - Cost comparison for treatment of 200 lb/day H₂S

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Average Oxidant Weight Ratio (100% Basis)</th>
<th>Unit Cost</th>
<th>lb-gal per day</th>
<th>Cost per day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂ (gas)</td>
<td>6:1</td>
<td>$400/ton</td>
<td>1,200 lb</td>
<td>$240</td>
</tr>
<tr>
<td>H₂O₂ (50%)</td>
<td>2:1</td>
<td>$3.45/gal</td>
<td>80 gal</td>
<td>$276</td>
</tr>
</tbody>
</table>

Ohtami and co-workers [105] reported that 0.1 to 10 mg/L of iron was required to catalyze the reaction of S₂O₃²⁻ to higher polythiosalts in an industrial effluent containing 10,000 mg/L NaS₂O₃. Concentrations greater than 10 mg/L slowed down the reaction rate. A previous study [103] indicated that oxidation of thiosalts in milling effluent at pH 6 to 7 was extremely slow. This was attributed to precipitation of heavy metal ion catalyst from solution. Under these conditions, the amount of ferrous ion required to catalyze the reaction was very much in excess of the amounts recommended by Ohtami et al. for the partial oxidation of thiosulphate to polythionates.

Rolia and Tan [107] investigated oxidation of synthetic solution of thiosalts using H₂O₂ at constant pH 11 in the absence of a catalyst. They achieved complete oxidation of thiosalts [91]. The reaction was slightly faster than corresponding reactions in neutral or weakly acidic solutions.
but significantly slower than Fe\(^{2+}\) catalyzed oxidation in moderately acidic media reported by Rolia. However, no real economic improvement can be achieved at high pH over Fe\(^{2+}\) catalyzed oxidation in moderately acid media [103].

Batch and continuous laboratory tests at the Noranda Research Centre and CANMET using milling effluent indicate that oxidation of thiosalts by H\(_2\)O\(_2\) with Fe\(^{2+}\) catalysis in weakly acidic media is technically possible as a year-round operation. These tests showed that optimum dosage of about 1 g H\(_2\)O\(_2\)/g S\(_2\)O\(_3\) at pH 7 reduced thiosalts concentration to below the target concentration of 100 mg/L in 5 minutes at 25\(^\circ\)C and 50 minutes at 5\(^\circ\)C. The milling effluent used in the tests contained enough Fe\(^{2+}\) for catalysis and thus did not require addition of ferrous ions [103, 108].

Other heavy metals have also been tested as a catalyst in combination with H\(_2\)O\(_2\). Kibbel [49] reports that solutions of molybdenum, tungsten, titanium, zirconium can catalyze thiosulphate oxidation in neutral or weak acidic solutions, however, the rates of catalyzed oxidation in acid solution are in the order of uncatalyzed reactions under alkaline conditions.

In a patent assigned to Interox America Inc., Walton [109] describes a process which uses soluble copper ions with H\(_2\)O\(_2\) to enhance the removal of thiosulphate from effluents at a pH 8 or higher. In another patent, sulphur compounds are oxidized with H\(_2\)O\(_2\) at pH 6.5 by adding soluble copper salt as a catalyst [110]. Copper significantly improved the rate of reaction and extent of removal of thiosulphate. As in the case with ferrous ion catalysis, copper must be added continuously to the effluent. Furthermore, the copper must be removed by precipitation as hydroxide before discharging the effluent. Continuous addition of copper or other metal catalyst is undesirable because of the possibility of secondary pollution problems due to the added metals, high metal reagent costs and increased lime requirement.

As previously mentioned, Bull and McManamon [111] reported that thiosulphate can be oxidatively destroyed with H\(_2\)O\(_2\) in combination with a supported metal catalyst system such as iron supported on mordenite and copper supported on synthetic zeolite. Experimentation demonstrated the effectiveness of these heterogeneous catalysts in oxidizing thiosulphate and the large catalytic particles used permitted recovery of the metal catalyst from a packed bed reactor. The practical pH operating range was from 4 to 12 but it depends on the chemistry of the effluent.

The INMET Winston Lake Mine is presently conducting laboratory testwork to determine the optimum conditions for the oxidation of thiosalts using hydrogen peroxide. At 1.5 to 2 times stoichiometric quantities approximately 80% of the thiosalts are oxidized in an effluent with a high suspended solid content. Contrary to what is reported in the literature, test results indicate that
hydrogen peroxide is persistent in the treated effluent. More laboratory-scale tests are planned to determine the effect of suspended solids on the oxidation of thiosalts by hydrogen peroxide [112].

The flowsheet for a hydrogen peroxide oxidation process is presented in Figure 15 [3]. Tailings decant is mixed with thickener overflows and sent for treatment in three reactors. Ferrous sulphate is added to convert H$_2$O$_2$ into hydroxyl radicals at an optimal pH value of 7.0. Based on laboratory tests the reagent requirements are 1.15 g H$_2$O$_2$/g S$_2$O$_3^{2-}$ and 65 mg/L Fe.

Following oxidation, the effluent is sent for neutralization to pH 9 and solid/liquid separation. Some of the sludge is limed and returned to the reactor for sludge densification. The clean overflow is then discharged to the receiving waters and the solids are disposed in a sludge pond. The estimated capital and operating costs for the flowsheet shown in Figure 15 using FeSO$_4$ as the catalyst ranged from $8.9 to $16.7 million respectively.

Advantages of Hydrogen Peroxide Oxidation

- Hydrogen peroxide technology is familiar to mill operators and easily integrated into existing effluent treatment;
- A full-scale facility, based on current available data could be installed with a high degree of certainty of successful operation;
- H$_2$O$_2$ and Cl$_2$ are economically comparative oxidants as shown in Table 9;
- No toxic by-products are generated the only by-products are SO$_4^{2-}$ and H$_2$O;
- The process adds dissolved oxygen to the effluent which helps to maintain aerobic conditions for microbial oxidation of thiosalts;
- The process is simple and effective as a year-round operation;
- More selective oxidant compared to chlorine (less tendency to react with organics);
- Dosage can be regulated according to process demand; and
- Lower risk due to spills compared to chlorine.

Disadvantages of Hydrogen Peroxide Oxidation

- Soluble heavy metal catalysts cannot be reused and must be removed by precipitation;
- High cost of FeSO$_4$ catalyst (supported metal catalyst would reduce reagent costs);
- Side reactions with other sulphur compounds can increase H$_2$O$_2$ requirement; and
- H$_2$O$_2$ is not economical for the removal of the bulk of thiosalts (should be considered only as a polishing step and as a backup system for biooxidation treatment).
Figure 15 - Hydrogen Peroxide Oxidation
SO₂ - AIR OXIDATION

The Inco SO₂/air process [113] is used in many gold mill operations for continuous cyanide removal from effluents. This process uses SO₂ (gas, or sulphite salt or solution) in combination with air as an oxidant and copper as a catalyst to achieve low total cyanide concentrations. Cyanide oxidation is achieved at temperatures from 5° to 60°C and pH from 8 to 10. The reaction works best at an SO₂ to air ratio at or below 2 vol.% [114]. This process uses inexpensive reagents and equipment and has a low energy requirement.

The oxidation of thiosalts by SO₂ and air and neutralization of acids produced from the reaction probably occurs as follows [88]:

1. Formation of Caro's acid:
   \[ \text{H}_2\text{O} + \text{SO}_2 + \text{O}_2 \rightarrow \text{H}_2\text{SO}_5 \]  
   (17)

2. Oxidation of thiosulphate by Caro's acid:
   \[ \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} + 4 \text{H}_2\text{SO}_5 + 2\text{H}^+ \rightarrow 6\text{H}_2\text{SO}_4 \]  
   (18)

3. Neutralization of acid generated:
   \[ \text{H}_2\text{SO}_4 + \text{Ca(OH)}_2 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \]  
   (19)

In equations (17) and (18) all the SO₂ is converted to H₂SO₄ thus greatly increasing lime requirements compared to chemical oxidants.

In Table 10 the comparative cost data for cyanide destruction is shown for three processes [115]. The SO₂-air process is compared to the Homestake biotechnology process and the hydrogen peroxide process. These comparisons are based on data from commercial scale operations. In applications for the removal of CN⁻ from gold milling effluents the SO₂-air process has the cost advantage compared to hydrogen peroxide.
Table 10 - Comparative cost data for cyanide destruction in effluents

<table>
<thead>
<tr>
<th>Process</th>
<th>Capacity + ore/day</th>
<th>Capital Costs Millions U.S.$</th>
<th>Operating Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>U.S./CN</td>
<td>U.S./m^3 Soln.</td>
</tr>
<tr>
<td>Homestake Biodegradation</td>
<td>6,000</td>
<td>10.0</td>
<td>15,000</td>
</tr>
<tr>
<td>Inco SO₂-air</td>
<td>3,000</td>
<td>2.3-2.8</td>
<td>3,800-4,900</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>3,000</td>
<td>2.3-2.9</td>
<td>10,300-11,400</td>
</tr>
</tbody>
</table>

* Adapted from R.W. Lawrence and R. Poulin [115].

Oxidation of thiosalts using SO₂-air was investigated by Inco, Noranda Research Centre and CANMET in the early 1980s. Results of preliminary tests conducted by Inco to evaluate thiosalts oxidation using SO₂ were inconclusive [88]. Rolia and Barbeau [100] evaluated the oxidation of thiosalts by SO₂ and air. Tests carried out without copper catalysis showed minimal changes in thiosalts concentration after a period of 48 hours. Ferrous ion was added as a catalyst but had no effect on the results.

The Noranda Research Centre [3, 116] conducted tests using mill effluent at various conditions (pH 2 to 9, 100 mg/L Cu) and SO₂/S₂O₃ ratios up to 11 times stoichiometric requirement. No significant decrease of thiosalts levels was observed. However, later tests were done using fresh milling effluent. Complete removal of thiosalts was achieved at a retention time of one hour, but results were not consistent.

Depending on the conditions used in the tests SO₂ can either act as a reducing or oxidizing agent and the ratio of SO₂:air is an important parameter which may determine the rate of thiosalts oxidation [117]. It appears that optimum reaction kinetics requires careful balance of the relationships between all process variables. Further experimentation is needed to determine the right balance of these process variables.

Experimentation done at Inco determined that by applying all process variables at their respective optimum values, did not produce maximum reaction kinetics for cyanide destruction. All process variables are interdependent; some more important than others, some are limiting. The ability to optimize conditions required complex testwork and careful balancing of the relationships between all process variables. Once the balanced values of the variables are determined maximum reaction kinetics for cyanide oxidation could always be achieved.
Based on the limited test results using milling effluent from Brunswick Mining and Smelting, a flowsheet was developed for oxidation of thiosalts using \( \text{SO}_4/\text{air} \) oxidation and Cu catalysis. The flowsheet is shown in Figure 16 [3]. The effluent is treated in three stirred reactor tanks operated in series. The \( \text{SO}_2 \) is injected into the reactors at a volumetric ratio of 1:20 and pH is maintained at 8.5 to 9. Flocculant is added to the third reactor overflows and sent to a solid/liquid separator. The underflow sludge is sent to the tailings pond and the overflow is discharged to the receiving waters.

Several estimates for the \( \text{SO}_2 \) air process were prepared assuming alternate sources of \( \text{SO}_2 \) gas and lime. The option of burning sulphur for \( \text{SO}_2 \) generation and purchasing quicklime for acid neutralization was the more cost-effective option at $13.3 million for capital costs and $11.3 million in annual operating costs.

**Advantages of \( \text{SO}_2 \) - Air Oxidation**
- Process is commercially available;
- Low reagent cost because roaster gas can be used as oxidant where available or low cost; elemental sulphur can be burned to generate \( \text{SO}_2 \); and
- \( \text{SO}_2/\text{air} \) process is effective as a year-round operation.

**Disadvantages of \( \text{SO}_2 \) - Air Oxidation**
- Requires high Cu addition for catalysis;
- All \( \text{SO}_2 \) is converted to \( \text{H}_2\text{SO}_4 \) resulting in high lime requirement; and
- Requires implementation of safety measures and worker training programs to ensure the safe application of toxic \( \text{SO}_2 \).
Figure 16 - SO₂ - Air Oxidation
ADVANCED OXIDATION PROCESSES

Advanced oxidation processes (AOP) use combinations of O_3/H_2O_2, UV light/O_3, ozone/elution, photocatalytic degradation, UV light/H_2O_2, UV light/H_2O_2/Fe(II) to promote the formation of hydroxyl radicals (OH•) and hydroperoxyl radical (HO_2•). The recent development of AOPs is an attempt to take advantage of the rapid non-selective reactivity of hydroxyl radicals. Advanced oxidation processes have mainly found application in removing relatively refractory organic contaminants from wastewater especially for dilute pollutants. These refractory organics are difficult to degrade by conventional chemical oxidation processes.

Hulsey and co-workers [118] evaluated several combinations of biological and AOP treatments on aqueous petroleum wastewater to meet discharge limits. Post biological treatment with O_3/H_2O_2 decreased concentrations of COD and TOC. However, the dosages for ozone and hydrogen peroxide required to eliminate the toxicity of the effluent were very high for these concentrated effluents. In one study researchers successfully treated bleach process effluents from a pulp and paper mill with combinations of O_3/H_2O_2 [119].

Although water treatment units based on AOP's have been commercially available since the early seventies, the complex chemistry of such processes has only recently been elucidated to allow modelling. Payton [120] has developed a stoichiometric model for AOPs. The usefulness of the model in understanding the application of AOPs has been verified for complex organic contaminants systems in predicting hydroxyl radical production and the type of reaction that can occur with the contaminants.

Castrantas and Gibilisco [121] reported the results of the destruction of phenols by UV/H_2O_2, without iron catalysis. They point out that this approach is somewhat simpler than methods using soluble additives (e.g. Fenton's reagent) and is more effective under a wider pH range. Compared to UV alone the UV/H_2O_2 system gives almost a factor of 20 increase in reaction rate.

Over the past 7 years, Ultrox International has demonstrated the effectiveness of UV/ozone or UV/hydrogen peroxide in treating halogenated compounds [122]. The ULTROX®
oxidation system is shown in Figure 17. This system consists of an oxidant, either ozone or hydrogen peroxide feed and UV radiation as the promoter for hydroxyl radical formation. The UV light used in this system generates radical species in large quantities producing a highly oxidative environment. Ultralux International hold a patent on this process. The economics of the ULTROX® oxidation system was evaluated at the U.S. EPA Superfund Innovative Technology Evaluation Program (SITE). Pilot plant studies have been conducted at more than 21 sites treating a large variety of effluents, contaminated groundwater and drinking water. Commercial systems are available to treat flows from 10,000 to 1.4 million gallons per day. The direct maintenance and operating costs for eight installation range from $0.10/1,000 gal to $1.90/1,000 gal in 1990 U.S. dollars. The capital costs for an ULTROX® oxidation system to treat 5 mg/L cyanide at a flow rate of 72,000 gpd was $400,000.

Some advantages of the Ultrox system are as follows:

- has very few moving parts;
- requires a minimum of maintenance;
- operates full-time or intermittently; in either continuous or batch treatment mode;
- utilizes efficient low temperature, long life UV lamps;
- employs the use of a microprocessor to control and automate the treatment process;
- and
- rapid reaction kinetics and lower reagent requirement.

When used as a polishing treatment process a UV/H₂O₂ process could be more cost effective than H₂O₂ alone. The test results at Winston Lake Mine indicates that some of the H₂O₂ remains as residual in the effluent or if the reaction is too slow H₂O₂ will decompose to form oxygen and water. The efficient production of HO• radicals from the decomposition of H₂O₂ in the ULTROX® process could decrease the quantity of H₂O₂ needed to oxidize thiosalts. This technology offers advantages over conventional treatment processes and it is worth investigating to determine its feasibility to treatment of thiosalts containing effluents.

As mentioned earlier ferrous ions acts as a catalyst to convert H₂O₂ into hydroxyl radicals. Sofarzadeh-Amiri and co-workers [123] investigated a new photooxidation process using light/ferrioxalate/H₂O₂ which is a Fenton-like reagent. Ferrioxalate is very efficient at
Figure 17 - Ultrl Ox System Flow Diagram
capturing light energy and utilizing about 18% of the incident radiation energy [124]. The best known catalyst for solar photo-oxidation is the anatase crystal of titanium dioxide, (TiO$_2$), [125, 126]. This compound can utilize about 0.12% of the incident solar radiation energy. Thus, the ferrioxalate/H$_2$O$_2$ system could theoretically be about 120 times more efficient than the TiO$_2$ photocatalyst in utilizing solar energy [123].

Other sources of radiation can be used to replace light radiation in enhancing hydroxyl radical formation in water. Gehringer and Eschweiler [127] used a combination of electron beam radiation and ozone to treat water spiked with pollutants. The action of ionizing radiation on ozone added to an effluent has two outstanding features among AOPs; (1) the whole radiation energy is adsorbed by the water and (2) irradiation initiates two different OH$^-$ generation processes at the same time. Compared to other AOPs, these actions result in higher OH$^-$ concentration that can achieve lower residual pollutants concentration and lower ozone requirement. Furthermore, at low pH values the ozone/electron beam process is much more efficient than other ozone based AOPs. The experiments were run in a prototype down-scaled model of a full size plant capable of treating up to 1,000 m$^3$/h [128].

**Advantages of Advanced Oxidation Processes**

- Fast reaction rate;
- Low oxidant dose can be used for the destruction of dilute contaminants resulting in more efficient operation;
- Small reactors can treat large flows; and
- May be more cost effective than conventional chemical treatment as a polishing step.

**Disadvantages of Advanced Oxidation Processes**

- Plant installation could be costly; and
- Not tested on thiosalts in milling effluents.
REVERSE OSMOSIS

Reverse osmosis is the flow of solvent from a concentrated solution to a more dilute one across a suitable membrane by applying hydraulic pressure greater than the osmotic pressure to the concentrated side of the membrane system. The permeate is the solution which passes through the membrane thereby having a lower concentration of solutes than that of the feed. The remaining feed (solute) on the pressurized side of the membrane is enriched with dissolved material by trapping them on one side of the membrane [129, 130].

Reverse osmosis uses three types of membrane configurations: 1) tubular, 2) spiral-wound, and 3) hollow-fiber membrane. Tubular membrane consists of tubes inserted into casings with porous walls. This type can be cleaned easily and can process dirty effluent feed. Unfortunately, these membranes are very expensive [129].

Spiral-wound membrane consist of a planar membrane sandwiching a porous supporting material. This sandwich configuration is wrapped around a central tube and inserted into a metal casing. Low cost and compactness are this system's main advantages; however, spiral-wound membranes are very prone to clogging and difficult to clean.

The hollow fiber membrane consists of filament bundles arranged in a U-shaped form. Low cost and compactness are this system's advantages but this type of membrane is impossible to clean.

Reverse osmosis is not a cheap process and is not without problems. Consequently, its adoption in effluent treatment has been slow. Fouling of the membrane by bacterial growth and scaling problems from calcium precipitation precludes the use of these technologies in separating thiosalts from the effluent. Application of this technology to treatment of milling effluents would be costly in terms of energy requirements, membrane replacement, cleaning and labour.

Reverse osmosis is essentially non-selective and would concentrate all the dissolved species. This concentrated stream requires further treatment and this would impose an additional cost on the treatment of thiosalts by reverse osmosis. Treatment alternatives for the concentrated lime solutions can include alkaline pressure oxidation, and electrooxidation or biological oxidation.

The U.S. EPA conducted pilot tests using reverse osmosis to treat acid mine drainage. Reverse osmosis produced an exceptionally clean permeate; however, severe scaling due to calcium sulphate precipitation occurred at 85% permeate recovery. Along with the scaling problem, bacteria oxidized ferrous ions precipitation compounded the problem of fouling [131].

Several studies indicate that reverse osmosis can be successfully applied to the treatment of landfill leachate and industrial effluents [132, 133, 134, 135]. In particular, tubular reverse osmosis units are successfully applied to the treatment of municipal leachate [133, 136]. Schoeman and co-
workers [134] evaluated reverse osmosis and physical/chemical processes for the treatment of neutralized acid effluent containing high concentration of calcium. Frequent cleaning of the membrane was necessary to maintain flux.

The estimated capital costs given by Schoeman et al. for a 600,000 L/d reverse osmosis process was $3,500,000 in 1996 U.S. dollars. Operational costs for clarifier/thickener softening, reverse osmosis, and hydrogen peroxide oxidation were estimated at $0.47/kl, $0.47/kl and $0.50/kl respectively.

PCI Membrane Systems in collaboration with Haase Energietechnik [137] has installed a landfill leachate treatment system in Germany incorporating, pre-filtration, biological treatment with ultrafiltration, reverse osmosis and evaporation. The leachate is prefiltered before undergoing biological treatment. Following biological treatment the biomass is removed by ultrafiltration and the ultrafiltration permeate is concentrated by two-stage reverse osmosis process. Despite these prefiltration steps, the reverse osmosis membrane required chemical cleaning once a week to maintain optimum operation.

In a pilot plant study by Canepa and co-workers [138] 80,000 litres of wastewater from olive mills was treated by combined membrane processes including ultrafiltration, absorbing polymers and reverse osmosis membranes. Daily washing was needed to maintain best performance of the ultrafiltration and reverse osmosis membranes. An economic evaluation was made for wastewater treatment from a plant processing 10,000 tons olives/year working 300 days/year. The treatment cost provided by Canepa was $0.33 U.S./L of treated effluent.

Ridgway and co-workers [139] reported that among a number of technologies tested at a pilot plant scale, reverse osmosis emerged as the least expensive. Pilot plant tests evaluated the following technologies; to treat secondary municipal effluent; reverse electrodialysis, ion exchange, evaporation and reverse osmosis to treatment of secondary municipal effluent. This effluent had undergone extensive chemical and biological pretreatment. Reverse osmosis produced a high purity permeate that met the U.S. Environmental Protection Agency drinking water standards and emerged as one of the least expensive and most practical method, but gradual fouling of the membrane by chemical and biological contaminants reduced the energy efficiency and cost effectiveness. Chlorine added to the water to prevent bacterial growth on the membrane caused structural damage to the membrane.

On a larger scale, Sikora and co-workers [140] reported on the full-scale plant operation treating 3.8 million gallons per day mine drainage. Spiral wound reverse osmosis membranes contained in more than 500 pressure vessels recover 2.6 million gallons per day of drinking water
and process water. A complex pretreatment process is used to prevents fouling of the membrane. The pretreatment included the following steps:

- storage of the feed in retention tanks for algicide dosing;
- disinfection and chlorination;
- flocculation and pH adjustment;
- sedimentation with polymer dosing;
- dual media filtration (sand-anthacite and granular activated carbon); and
- thickening and disposal of sludge.

The cost of the entire desalination plant was about $60 million U.S. dollars. Part of this cost could be recovered by the sale of valuable by-products from the solute. Based on the sale of these valuable products payback is estimated at 10 years and is considered to be quite good for an environmental project.

There are very few reports in the literature on the application of reverse osmosis for thiosalts removal. Sastri [141] and Dutrizac [142] conducted preliminary evaluation of reverse osmosis using synthetic and milling effluent. These investigations confirmed the technical feasibility of separating water and thiosalts. However, an initial calcium removal step was needed to prevent precipitation on the membrane.

Based on the limited test work done by Sastri and Dutrizac, a flowsheet for a reverse osmosis process was developed and is illustrated in Figure 18 [3]. The effluent is passed through a two-step solid/liquid separation to minimize membrane fouling and phosphonate is added prior to reverse osmosis treatment to prevent scale formation. The permeate (which is expected to have less than 10 mg/L thiosalts) is discharged to the receiving stream or can be all recycled to mill processes or used to adjust thiosalt concentration in the water recycled to the milling circuit.

The concentrated solute generated by reverse osmosis could be treated using electrochemical oxidation, alkaline oxidation and evaporation. The estimated capital and annual costs for the conceptual flowsheet was lowest for reverse osmosis combined with evaporation at $22.2 million and $15.1 million respectively.
Figure 18 - Treatment by Reverse Osmosis
Advantages of Reverse Osmosis

- Only limited data known;
- Technically proven to remove thiosalts from synthetic solutions;
- Produces a clean permeate that can be all recycled to the mill; and
- Potentially metal values could be recovered from the concentrated solute.

Disadvantages of Reverse Osmosis

- Prone to fouling due to fine solids, bacterial growth and scale formation;
- Extensive pretreatment is required to prevent membrane fouling;
- Operational and maintenance costs are high; and
- Produces a concentrated waste stream that needs further treatment.

ACTIVATED CARBON

Activated carbon adsorption is currently the most widely applied technology for removing organic compounds from effluents. This method is non-destructive and only transfers the compound between phases. Thiosalts and other compounds which accumulates at the surface of the carbon by adsorption could be removed by thermal or chemical methods to regenerate the carbon. Thermal decomposition in kilns at 950°C would involve a three-step process as follows:

- drying;
- decomposition of thiosalts to SO₂; and
- solubilization and treatment of SO₂ and other contaminants.

The energy required to dry the activated carbon and decompose the thiosalts at 950°C would be very high. Recently, a new technology developed by Ontario Hydro Technologies [143] uses microwaves to regenerate the carbon. This technology is cost-effective compared to kiln regeneration. Significant energy savings and reduced carbon losses can be realized through thermal regeneration using microwave technology. Sodium hydroxide can also be used to dissolve the thiosalts from the activated carbons. However, the resulting alkali solution would require treatment to oxidize the thiosalts. Activated carbon is a good solid support for bacterial growth. It is likely
that in a reactor biological oxidation would remove the thiosalts adsorbed on the carbon. This could extend the period between carbon regeneration.

Laboratory-scale tests conducted by Rolia [100] investigated the removal of thiosalts species in synthetic solutions by activated charcoal in a range of conditions (pH 6 to 12 and temperatures from 20° to 65°C). Essentially, no adsorption occurred.

The Noranda Research Centre [144, 145] conducted laboratory-scale tests of a number of adsorbents including activated carbon, bone charcoal, bituminous coal, peat, alumina, diatomaceous earth, and clay. Only activated carbon Calgon Filtrasorb 200 was able to retain significant quantities of thiosalts. The highest loading capacity was 10 lb thiosalts /100 lb of carbon in batch tests. Based on these test results it was estimated that 1,600,000 lb of carbon is required to treat 3,000 imp.gal./min. milling effluent containing 800 mg/L thiosalts.

Others [146] reported successful removal of sulphide entrained in a gas stream and sulphite in aqueous solutions using rice bran activated carbon. Aside from the work done at CANMET and Noranda Technology Centre, no other study was found on thiosalts removal by activated carbon in the published literature. Calgon Carbon [147] was consulted concerning the application of activated carbon to the removal of thiosalts from effluents. The technical opinion was that activated carbon would achieve limited success at best. Secondly, the application to wastewater will make the probability of success drop even further. In one study done at Calgon Inc. some success was achieved at oxidizing sulphite to sulphate in a trickle-bed reactor.

There are new developments in activated carbon technology that may have application to thiosalts removal. Certainly, the variety of activated carbon is large and only a few have been tested for application to thiosalts removal. Calgon Corporation [148] has developed a new line of activated carbon under the trade name of Centour TM. The company claims that this is new activated carbon technology which offers dramatic advances combining highly developed catalytic properties with an optimized pore structure. The Centour process technology changes the surface properties of granular activated carbon. As a result, without chemicals or metal catalyst impregnated on the carbon dramatic increases in reaction rates of 10 to 100 times are achieved compared to standard carbons. These reaction rates may be further increased by using a metal catalyst impregnated [59]. Smaller adsorption equipment and less activated carbon are required because of the faster reaction rates.
Figures 19 and 20 [3] shows the process flowsheets for thiosalts removal from milling effluents using activated carbon and the processes for carbon regeneration. These flowsheets are based on the limited test results reported by Noranda Research Centre. The effluent flows through the activated carbon columns that are operated in parallel. Depending on the effectiveness of removal of thiosalts and metal contaminants by the carbon, the effluent from the columns may be discharged directly to the receiving waters without additional treatment. Regeneration of the activated carbon can be accomplished by thermal or chemical methods as described in previous sections. Operating costs for thermal regeneration are very high ($33 to $65 million/year) mainly due to furnace operation and carbon make-up charges. The most cost-effective method was alkaline carbon regeneration with alkaline pressure oxidation of the concentrated thiosalts solution ($12.7 to $19 million). Capital and annual costs of the activated carbon process were estimated at $19.1 and $11.7 million respectively [3].

Advantages of Activated Carbon

- Carbon adsorption is a well developed technology used in gold milling operations;
- Produces a clean effluent for direct discharge or recycle; and
- Carbon adsorption is an inherently safe process.

Disadvantages of Activated Carbon

- Limited practical data is available on the removal of thiosalts from effluent with activated carbon;
- Unlikely to consistently achieve a target concentration of <10 mg/L thiosalts in the treated effluent;
- Carbon absorption is not selective;
- High energy requirement to regenerate the carbon;
- Process is semi-continuous;
- High degree of technical uncertainty;
- Carbon adsorption is sensitive to suspended solids, bacterial growth, oils and grease;
- Spent carbon needs to be disposed or regenerated;
- Carbon fines may difficult to remove from the treated effluent; and
- Potentially high attrition of the carbon.
Figure 19 - Activated Carbon Adsorption with Thermal Regeneration
Figure 20 - Activated Carbon Adsorption with Electrochemical and Alkaline Pressure Oxidation
NATURAL DEGRADATION OF THIOSALTS

Natural degradation in the effluent treatment ponds is the conventional method used to treat thiosalts in milling effluents. This method uses a long retention period in the pond system allowing time for bacterial oxidation to take place. Natural oxidation is the least costly process to implement in an existing effluent treatment system. However, in northern climates, natural degradation is not effective as a year-round operation. Experience at milling operations indicates that thiosalts are rapidly oxidized during the summer and as expected, the rate of oxidation decreases during autumn and winter as the temperature drops. Low water temperature, short circuiting, low dissolved oxygen and short retention time are the more important parameters that limit natural oxidation in the ponds. Johnson [149] reported evidence of stratification in a biostabilization pond. At lower depth in the pond, the pH, dissolved oxygen, heavy metals and conductivity were lower than near surface values. The bacterial concentration and thiosalts levels were higher at the bottom compared to near surface values. These observations were consistent with the hypothesis that low levels of dissolved oxygen and poor mixing at lower depths decreases the rate of thiosalts biooxidation.

Oko [90] has stated that six weeks retention in the summers was sufficient to convert all thiosulphate at a Falconbridge operation in northern Ontario. Experience at Flin Flon [150] and Noranda Mining and Exploration Brunswick Mining Division supports this; approximately two weeks are required in mid-summer [151].

For effective natural oxidation, the effluent should have a retention time of at least one year [2]. The cost of the earthworks for an extensive pond system to hold the effluent over a period of one year would be very costly.

Practically speaking, good control over biological processes in large ponds is not possible and clearly, this option will have a high degree of uncertainty in achieving target levels of thiosalts in the treated effluent.

The flowsheet in Figure 21 [3] shows a natural degradation pond system. The estimated capital and annual costs were $12.4 million and $4.1 million respectively.
Advantages of Natural Degradation of Thiosalts

- Evaluated as the least expensive treatment system for thiosalt oxidation;
- Easily integrated into existing treatment ponds system; and
- Works relatively well during the summer.

Disadvantages of Natural Degradation of Thiosalts

- Requires extensive pond system and land area which may not be available;
- Earthworks may be very expensive depending on topography of the mill site;
- Requires lengthy tests to determine retention time requirements;
- Not effective in oxidizing all of the thiosalts during cold weather; and
- Requires chemical polishing step to decrease thiosalts concentration to less than 10 mg/L.

OCEAN DISCHARGE OF THIOSALTS

Ocean disposal involves the transport of milling effluents through a pipeline to an ocean outfall. Discharge of wastewater to the ocean is presently considered an acceptable disposal technique for treated industrial, municipal, and mining effluents. Many cities in the eastern and western seabords discharge treated municipal effluent and sludge into the ocean [152]. Recently, this method of effluent disposal has come under increased regulatory pressure in some jurisdictions, especially in areas of sensitive marine environments [153]. Ocean disposal of milling effluents would involve careful control of the discharge over a sufficiently large area to ensure adequate dilution to cause negligible changes in the ambient marine water concentration.

From an economic, environmental and regulatory perspective ocean discharge is an attractive option for milling operations located close to the coast. This method of thiosalt disposal is simple and has a high degree of certainty for continued successful operation [154].

Scale formation in the pipeline may be a problem and the use of scale inhibiting agents would need to be evaluated. Also there is the potential of corrosion due to acid generation in the requiring plastic pipe for the pipeline.
Figure 21 - Natural Degradation
Advantages of Ocean Discharge

- Technically simple process;
- High degree of success and long term operation;
- Less need for construction of large ponds; and
- Comparatively safe process.

Disadvantages of Ocean Discharge

- Environmental risks due to pipe rupture;
- High cost of buried pipeline;
- Public opinion;
- Obtaining right of way may be difficult;
- Future land use could be affected;
- Generation of acid in the pipeline by bacterial oxidation can result in corrosion problems;
- Booster stations would have to be constructed and maintained; and
- Evaluation of potential environmental impact on marine environment.

REDUCTION BY IRON

Rolia [155] investigated reactions between metals and synthetic thiosalts solutions at temperature from 80° to 100°C. In preliminary tests thiosalts were completely destroyed in 24 hours in the presence of iron or nickel powders; iron achieved faster reaction rates. Qualitative test thiosalts reacted with excess iron to form H₂S and FeS and colloids of Fe₂O₄ and FeO.

The high energy requirement to heat the water to 100°C limits the application of this process to treating small volumes of concentrated solutions such as those generated by reverse osmosis and activated carbon. Heat exchangers and a steam generating plant accounts for approximately 50% of capital cost for an iron reduction process.

Based on the limited test results from Rolia's work, Wasserlauf and co-workers developed the process flowsheet shown in Figure 22 [3]. The combined tailings decant and thickener overflow are heated in a heat exchanger. Subsequently, the effluent is passed through four mixed tank reactors operated in series at 100°C. Iron powder produced from scrap iron in a mill is added to the reactor to catalyze the reduction of thiosalts. The H₂S gas produced in the reactors is collected and is either reacted with H₂O₂ or converted to elemental sulphur using the Claus
Figure 22 - Thiosalt Reduction by Iron
process. The treated effluent is passed through a clarifier for solid/liquid separation. The unreacted iron underflow is recycled in the process and the overflow is discharged after passing through a heat exchanger for heat recovery. At Fe/S\(_2\)O\(_3\) weight ratio of 2 to 1 it would cost $2.5 million annually to treat 24,000 kg/d thiosalts at $140/tonne U.S. for shredded scrap iron [156]. The capital and annual costs of iron reduction was estimated at $13.4 million and $17.4 respectively.

**Advantages of Reduction by Iron**

- No acid is produced in the reaction between iron and thiosalts; and
- \(\text{H}_2\text{S}\) may react with dissolved metals and precipitate as sulphides.

**Disadvantages of Reduction by Iron**

- High cost of iron powder;
- \(\text{H}_2\text{S}\) gas has to be collected and treated;
- Evolution of \(\text{H}_2\text{S}\) gas make the process hazardous to operate and requires a \(\text{H}_2\text{S}\) destruction process; and
- High energy requirement due to the heating of the effluent to 100\(^\circ\)C.

**ALKALINE PRESSURE OXIDATION**

Autoclaves have been used commercially in the mining industry since the early 1950’s to extract metals from refractory ores. Operational experience has made rapid progress and the result is a much more reliable and safer autoclave operation. Advances in new corrosion resistant materials combined with sophisticated instrumentation allows greater safety and less down-time. As a consequence, operating costs and maintenance costs have decreased. Greater reliability has gone hand-in-hand with greater acceptance of this technology in the mining industry.

Experimentation at CANMET [157] has shown that all thiosalts species are rapidly oxidized in a few minutes with mixtures of Ca(OH)\(_2\) and NaOH at a temperature of 100\(^\circ\)C and oxygen pressures of 2,000 kPa [158]. Mixtures of lime and sodium hydroxide are added to
neutralize the acid formed. Experimentations showed that NaOH is needed for complete oxidation of thiosalts.

Thiosalts oxidation based on a pressure autoclave process is capital intensive. The major capital items include on-site oxygen generations, autoclaves and steam plant. Energy requirements for heating the effluent to 100°C would contribute the most to annual operation costs and this limits the application of this process to low volumes of concentrated solutions. Furthermore the high level of operator training and increased safety requirements needed to work with pressurized equipment at elevated temperatures would increase operating costs of this process.

Figure 23 [3] shows a flowsheet for the oxidation of thiosalts by pressure oxidation. The combined tailings and thickener overflows are pre-heated in a heat exchanger and subsequently sent to two autoclaves for thiosalts oxidation. From the autoclaves the effluent is passed to an expansion tank to reduce pressure to atmospheric pressure and is then passed through a heat exchanger to warm incoming effluent. Polymers are added to the cooled effluent to promote settling in the clarifier. The sludge is sent to a disposal pond and the clean overflow is discharged following pH adjustments. The capital and annual operating costs were estimated at $23.7 million and $17.3 million respectively.

Advantages Alkaline Pressure Oxidation
- Economically feasible for small volume of concentrated solutions;
- Complete removal of thiosalts; and
- Fast reaction rates.

Disadvantages of Alkaline Pressure Oxidation
- Process has a high energy requirement;
- High maintenance cost;
- Complex system (oxygen generation, steam plant and autoclaves); and
- High degree of uncertainty of future energy cost.
Figure 23 - Alkaline Pressure Oxidation
CONCEPTUAL METHODS FOR THIOSALTS REMOVAL

Over the past year, the Thiosalts Consortium has received proposals incorporating new ideas and new technologies for the destruction of thiosalts. These new concepts are as follows:

1. Addition of Sodium Bicarbonate (NaHCO₃) to Milling Effluent

   Proposed by Michael Li, Noranda Technology Centre

   Stoichiometric amounts of sodium bicarbonate are added to the treated milling effluent prior to discharge during the spring and fall periods. Sodium bicarbonate would not increase the pH of the treated effluent but instead would act as a buffer to maintain a pH above 6.0 in the receiving waters.

2. Pre-concentration of Thiosalts Using Ion Exchange

   Proposed by Patricio Riveros, CANMET

   Since thiosalts are anionic species, they should be extracted by resins having amino groups. The thiosalts could be eluted with a suitable solution to produce a concentrated thiosalts solution for chloride mediated electrooxidation, or iron reduction. The solution could be recycled for elution.

3. Catalytic Oxidation of Aqueous Thiosalts

   Proposed by Jim Skeaff, CANMET

   Investigate the oxidation of thiosalts by aerating the solution over a high surface area catalyst such as can be made by decomposition of nickel carbonyl.

4. Removal of Thiosalts by Reaction with Phenolic Type Compounds

   Proposed by Doug Gould, CANMET
Dihydric phenols and quinones would likely react with thiosalts to form stable relatively non-toxic products. Conduct preliminary tests to verify this concept using commercial preparations of benzoquinone, humic acid, fulvic acid and activated peat moss.

5. Biological Oxidation of Thiosulphate to Sulphate and Elemental Sulphur

Proposed by Paques Inc., Netherlands

Paques Inc. would conduct a laboratory study to verify the application and design criteria of a biological oxidation process developed by Paques. Following this study, on-site pilot tests will be conducted. The estimated capital cost for this project is $800,000 Cdn.

6. Thiosalts Reduction by Reaction with Wood Waste

Proposed by Diane Germain, Hydrogéochem Environment Inc.

Investigate the feasibility of thiosalts reduction by bacteria using waste wood as a nutrient source and substrate in a packed reactor. Test results with acid mine drainage indicates a decrease in $SO_4^{2-}$ concentration and an increase in pH.
PART B - ECONOMIC EVALUATION OF THIOSALTS TREATMENT PROCESSES

The 1985 Economic Evaluation of Thiosalts Treatment Processes report consisted in developing methods for the destruction of thiosalts in mill effluents. Since available cost estimates lacked a uniform basis, a base case of an effluent flow of 720 m$^3$/h and 24,500 kg/d thiosalt discharge was used for the 1985 report.

This report provides costing for three treatment options which are described earlier in this report. Included are the cost estimates of the original base case and estimates for three new cases, given in Canadian dollars (1997 3rd Quarter) with an accuracy of ±40%. The economic evaluation was done using the cost indexes of 1985, the original year of the report, and those of 1997. The assumptions and data needed for the economic evaluation are listed. The format for the economic evaluation is the same as that used in the 1985 report by Wasserlauf et al. to allow a comparison between the reports.

The Management Committee of the Thiosalts Consortium selected the following three treatment options for costing and three new base cases, which are described in Tables 11 and 12:

- Biological Oxidation using rock-packed reactors;
- Biological Oxidation in rock-packed reactors combined with Hydrogen Peroxide as a polishing step; and
- Hydrogen Peroxide alone.

Table 11 - Parameters of the selected base cases for 1997 economic evaluation

<table>
<thead>
<tr>
<th>Base Cases</th>
<th>Ore Milled (t/d)</th>
<th>Sulfide in Ore (wt.)</th>
<th>Average Thiosalts in Outflow (mg/l $S_2O_3^{2-}$)</th>
<th>Average Effluent Flow (m$^3$/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Brunswick Mining</td>
<td>9,000</td>
<td>80</td>
<td>300</td>
<td>1,380</td>
</tr>
<tr>
<td>B Bouchard-Hébert Mine</td>
<td>2,800</td>
<td>40</td>
<td>470</td>
<td>408</td>
</tr>
<tr>
<td>C Louvicourt Mine</td>
<td>4,500</td>
<td>40</td>
<td>60</td>
<td>160</td>
</tr>
</tbody>
</table>
Table 12 - Summary of base cases for 1997 economic evaluation

<table>
<thead>
<tr>
<th>Base Cases</th>
<th>Effluent Flow m³/h</th>
<th>Thiosalt Concentration mg/L</th>
<th>kg/h</th>
<th>kg/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1985</td>
<td>720</td>
<td>1,400</td>
<td>1,008</td>
<td>24,192</td>
</tr>
<tr>
<td>1997 A</td>
<td>1,380</td>
<td>300</td>
<td>414</td>
<td>9,936</td>
</tr>
<tr>
<td>1997 B</td>
<td>408</td>
<td>470</td>
<td>192</td>
<td>4,602</td>
</tr>
<tr>
<td>1997 C</td>
<td>160</td>
<td>60</td>
<td>10</td>
<td>230</td>
</tr>
</tbody>
</table>

Capital Cost Estimate Approach

The original assumptions for capital and operating costs were kept. Assuming that the thiosalt treatment facility was an add-on installation to handle the milling effluents of an existing mine/mill complex, the derived capital cost estimates considered and excluded for the purpose of the study are summarized in Table 13. It was also assumed that the utility main lines (electricity, water) and all service facilities would be adequate to handle the increased load.

For costing purposes, the process flowsheets were subdivided into process modules (e.g. settling basins, thiosalt oxidation, lime neutralization). Cost estimates of equipment in each module were derived using two methods. In most cases, individual equipment was sized and priced using either suppliers' quotations or recent literature, and the sixth-tenths factor rule was used to generate costs at other than given equipment ratings. In some cases, correlation's relating capital cost to process throughput was utilized. All original equipment costs were based on mid-1984 values, with the Marshall and Swift index used where necessary, for updating earlier costs. The resulting capital charge for the module was the sum of individual process unit costs.

The bare equipment cost was the sum of all process units in the primary (Thiosalts destruction) module. Settling basin and lime neutralization modules were priced separately.

Operating and Maintenance Estimate Approach

The following parameters contributing to operating and maintenance costs were considered (see Table 13):

- Reagents (lime, etc.)
- Utilities (electricity, steam, fuel)
- Operating man-power
- Replacement of components
For each alternative, reagent and utility requirements were based on process conditions. Mid-1984 reagent costs were considered, assuming delivery to northeastern New Brunswick. Electricity rates quoted were those paid by Brunswick Mining and Smelting during 1984. Costs for maintenance, taxes and insurance were taken as 4.5% of the overall total capital costs. Although by-products may be generated in some of the schemes, no credits were considered against operating costs.

### Table 13 - Summary of battery limits cost components

<table>
<thead>
<tr>
<th>Includes the cost of:</th>
<th>Excludes the cost of:</th>
</tr>
</thead>
<tbody>
<tr>
<td>All process equipment.</td>
<td>Land, site preparation, fencing, access roads and paving, Loading and unloading facilities.</td>
</tr>
<tr>
<td>All material and labour to connect and make operable the process equipment, including control rooms, buildings within the battery limits.</td>
<td>Off-site utilities and piping to/from the battery limits from such services.</td>
</tr>
<tr>
<td>Indirect field expense, engineering, construction supervision fees.</td>
<td>Support facilities such as the administration building, laboratory, cafeteria, gatehouse, maintenance shops, fire-fighting equipment, and communications systems and safety equipment.</td>
</tr>
</tbody>
</table>

### Economic Evaluation

The estimate was carried out on the capital and operating costs only and these are summarized in Table 14.

### Table 14 - Summary of capital and operating cost

<table>
<thead>
<tr>
<th>Cost</th>
<th>1985 ($ '000)</th>
<th>1997 A ($ '000)</th>
<th>1997 B ($ '000)</th>
<th>1997 C ($ '000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biological Oxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital</td>
<td>13,460.16</td>
<td>10,590.32</td>
<td>6,673.65</td>
<td>1,106.81</td>
</tr>
<tr>
<td>Operating</td>
<td>2,523.71</td>
<td>1,985.63</td>
<td>1,251.27</td>
<td>207.52</td>
</tr>
<tr>
<td>Biological Oxidation with Polishing Step</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital</td>
<td>15,588.29</td>
<td>12,264.71</td>
<td>7,728.80</td>
<td>1,281.80</td>
</tr>
<tr>
<td>Operating</td>
<td>3,945.47</td>
<td>3,104.26</td>
<td>1,956.20</td>
<td>324.43</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital</td>
<td>8,917.08</td>
<td>7,015.86</td>
<td>4,421.16</td>
<td>733.24</td>
</tr>
<tr>
<td>Peroxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital</td>
<td>14,934.27</td>
<td>11,750.13</td>
<td>7,404.53</td>
<td>1,228.02</td>
</tr>
<tr>
<td>Operating</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The original estimates were based on higher concentrations and effluents rates than those used in the 1997 base cases. Since the effluent flows varied from 160 to 1,380 m$^3$/h and thiosalts concentration also varied from 60 to 1,400 mg/L, a base line or reference point was needed so that a comparison could be made between the different processes. The thiosalt loading (kg/d) was used as the reference point. This was done because the thiosalt loading is a factor of both flow rate and concentration in all three processes.

The factors used to adjust costs, the Marshall and Swift Index (M&S Index), Thiosalt Factor, 6th Factor rule and Equipment Cost Index, are summarized in Table 15. Marshall and Swift Indexes [159], which are used to update equipment costs, were obtained from published data (Chemical Engineering magazine, January 1998, p. 162). The other three factors were calculated. The Equipment Cost Index was calculated by dividing the 1997 M&S Index by the 1985 M&S Index.

Table 15 - Summary of factors used

<table>
<thead>
<tr>
<th>Base Cases</th>
<th>M &amp; S Index</th>
<th>Thiosalt Factor</th>
<th>6th Factor rule</th>
<th>Equip. Cost Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 85</td>
<td>789.6</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>Case 97 A</td>
<td>1059.6</td>
<td>0.4107</td>
<td>0.5863</td>
<td>1.3419</td>
</tr>
<tr>
<td>Case 97 B</td>
<td>1059.6</td>
<td>0.1902</td>
<td>0.3695</td>
<td>1.3419</td>
</tr>
<tr>
<td>Case 97 C</td>
<td>1059.6</td>
<td>0.0095</td>
<td>0.0613</td>
<td>1.3419</td>
</tr>
</tbody>
</table>

The Six-tenths-Factor-Rule or the Order-Of-Magnitude Estimate was used to adjust for the loading. This is a method of calculating cost which is inexpensive but has the least accuracy when finished. According to this rule, if the cost of a given unit at one capacity is known, the cost of a similar unit with X times the capacity of the first is approximately (X)$^{0.6}$ times the cost of the initial unit. This is an oversimplification of a valuable cost concept since the actual values of the cost capacity factor vary from less than 0.2 to greater than 1.0. This does not completely give an accurate picture since some chemicals and power costs might have changed considerably, some higher and some lower. One such example is the cost of hydrogen peroxide, whose price in 1997 is nearly half of what was quoted in 1985. Another example is the cost of electrical power: the 1985 cost estimates used a price of 0.035 $/kwh while in 1997 the price quoted is between .04 to .05 $/kwh.

The thiosalts factor was also required to adjust for loading. It was calculated by dividing the 1997 loading by the 1985 loading.
Example of a New Price Calculation

Using the Biological Oxidation Process overall total capital cost for 1985 as an example, $13,460.16 million; the following shows how the indexes were calculated and how an estimated cost was obtained for 1997 Case A. The new price is $10,590.32 million.

\[
\text{New Price} = \text{Original Price} \times \text{Equipment Cost Index} \times 6^{\text{th}} \text{ Factor Rule}
\]

\[
(13,460.16) \times (1.3419) \times (0.5863) = 10,590.32
\]

M & S Indexes:

1985 = 789.6

1997 (3\text{rd Quarter}) = 1059.6

Equipment Cost Index:

\[
1059.6 / 789.6 = 1.3419
\]

Thiosalts Factor:

\[
9,936 \text{ (kg/d)} / 24,192 \text{ (kg/d)} = 0.4107
\]

6\text{th} Factor rule:

\[
(\text{Thiosalt Factor})^{0.6} = (0.4107)^{0.6} = 0.5863
\]

The 1985 Biological Oxidation Process capital cost was estimated at $13.5 million dollars and the operating cost was $2.5 million dollars. The 1997 Case A Biological Oxidation Process capital cost is $10.6 million dollars and with an operating cost of $2.0 million dollars. Although the 1997 Case A flow rate was nearly twice the 1985 flow rate and the thiosalts concentration of 1985 was nearly three times that of the 1997 Case A concentration, the price for the process was nearly $3.0 million dollars less than the 1985 price.

Table 16 shows the detailed costs for all modules for the four cases using the Biological Oxidation Process. Table 17 shows the costs for the Biological Oxidation Process with a Polishing Step and Table 18 is for the Hydrogen Peroxide Process.
Table 16 - Biological oxidation process

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$'000</td>
<td>$'000</td>
<td>$'000</td>
<td>$'000</td>
</tr>
<tr>
<td>Bare Equipment Items</td>
<td>529.00</td>
<td>416.21</td>
<td>262.28</td>
<td>43.50</td>
</tr>
<tr>
<td>Misc. Unspecified items (15% of 1)</td>
<td>79.35</td>
<td>62.43</td>
<td>39.34</td>
<td>6.52</td>
</tr>
<tr>
<td>Subtotal Bare Equipment</td>
<td>608.35</td>
<td>478.64</td>
<td>301.62</td>
<td>50.02</td>
</tr>
<tr>
<td>Installed Cost (Bare Equipment x 1.45)</td>
<td>882.11</td>
<td>694.03</td>
<td>437.36</td>
<td>72.53</td>
</tr>
<tr>
<td>Other Items – Installed Cost</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Subtotal Installed Equipment</strong></td>
<td><strong>882.11</strong></td>
<td><strong>694.03</strong></td>
<td><strong>437.36</strong></td>
<td><strong>72.53</strong></td>
</tr>
<tr>
<td>Services:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical 15%</td>
<td>132.32</td>
<td>104.10</td>
<td>65.60</td>
<td>10.88</td>
</tr>
<tr>
<td>Instruments 10%</td>
<td>88.21</td>
<td>69.40</td>
<td>43.74</td>
<td>7.25</td>
</tr>
<tr>
<td>Service Piping 10%</td>
<td>88.21</td>
<td>69.40</td>
<td>43.74</td>
<td>7.25</td>
</tr>
<tr>
<td>Other Services 5%</td>
<td>44.11</td>
<td>34.70</td>
<td>21.87</td>
<td>3.63</td>
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<tr>
<td><strong>Total Services</strong></td>
<td><strong>352.84</strong></td>
<td><strong>277.61</strong></td>
<td><strong>174.94</strong></td>
<td><strong>29.01</strong></td>
</tr>
<tr>
<td>Building 3,250.00, 2,500.00, 2,500.00</td>
<td>56.00</td>
<td>44.06</td>
<td>27.77</td>
<td>4.60</td>
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<tr>
<td>Earthworks and Concrete</td>
<td>1,642.00</td>
<td>1,291.91</td>
<td>814.12</td>
<td>135.02</td>
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<td>Total Primary Module Cost (A)</td>
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<td>1,454.18</td>
<td>241.17</td>
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<td>Settling Basin Cost (B)</td>
<td>150.00</td>
<td>118.02</td>
<td>74.37</td>
<td>12.33</td>
</tr>
<tr>
<td>Lime Module Cost (C)</td>
<td>3,580.00</td>
<td>2,816.71</td>
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<tr>
<td><strong>Total Cost of Module (A+B+C)</strong></td>
<td><strong>6,662.95</strong></td>
<td><strong>5,242.34</strong></td>
<td><strong>3,303.54</strong></td>
<td><strong>547.88</strong></td>
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<td>Engineering &amp; Construction (25% of A+B+C)</td>
<td>1,665.74</td>
<td>1,310.59</td>
<td>825.89</td>
<td>136.97</td>
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<td><strong>6,552.93</strong></td>
<td><strong>4,129.43</strong></td>
<td><strong>684.85</strong></td>
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<tr>
<td>Contingency (40% Subtotal)</td>
<td>3,331.48</td>
<td>2,621.17</td>
<td>1,651.77</td>
<td>273.94</td>
</tr>
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<td>Washed Rocks (incl. 20% Contingency)</td>
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<td>892.45</td>
<td>148.01</td>
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<td><strong>13,460.16</strong></td>
<td><strong>10,590.32</strong></td>
<td><strong>6,673.65</strong></td>
<td><strong>1,106.81</strong></td>
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<td>Operating Cost:</td>
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<td></td>
</tr>
<tr>
<td>Materials, Supplies, Utilities &amp; Labour</td>
<td>918.00</td>
<td>722.27</td>
<td>455.15</td>
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<td>495.81</td>
<td>82.23</td>
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<tr>
<td>Maintenance, Taxes &amp; Insurance (4.5% of Tot. Cap.)</td>
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<td>476.56</td>
<td>300.31</td>
<td>49.81</td>
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<td><strong>Total Operating Cost</strong></td>
<td><strong>2,523.71</strong></td>
<td><strong>1,985.63</strong></td>
<td><strong>1,251.27</strong></td>
<td><strong>207.52</strong></td>
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</table>
Table 17 - Biological oxidation with polishing step process

<table>
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<td></td>
<td>$'000</td>
<td>$'000</td>
<td>$'000</td>
<td>$'000</td>
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<tr>
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<td>879.00</td>
<td>691.59</td>
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<td>Misc. Unspecified items (15% of 1)</td>
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<td>103.74</td>
<td>65.37</td>
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<td>Subtotal Bare Equipment</td>
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<td>795.33</td>
<td>501.19</td>
<td>83.12</td>
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<tr>
<td>Installed Cost (Bare Equipment x 1.45)</td>
<td>1,465.73</td>
<td>1,153.22</td>
<td>726.72</td>
<td>120.52</td>
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<tr>
<td>Other Items – Installed Cost</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>Subtotal Installed Equipment</td>
<td>1,465.73</td>
<td>1,153.22</td>
<td>726.72</td>
<td>120.52</td>
</tr>
</tbody>
</table>

Services:

|                                |       |       |       |       |
| Electrical 15%                 | 219.86| 172.98| 109.01| 18.08 |
| Instruments 10%                | 146.57| 115.32| 72.67 | 12.05 |
| Service Piping 10%             | 146.57| 115.32| 72.67 | 12.05 |
| Other Services 5%              | 73.29 | 57.66 | 36.34 | 6.03  |
| Total Services                 | 586.29| 461.29| 290.69| 48.21 |

Building 3,250.00, 2,500.00, 2,500.00 |

|                                |       |       |       |       |
| Earthworks and Concrete        | 1,642.00| 1,291.91| 814.12| 135.02 |

Total Primary Module Cost (A)   |

|                                |       |       |       |       |
| Settling Basin Cost (B)        | 150.00| 118.02| 74.37 | 12.33 |
| Lime Module Cost (C)           | 3,580.00| 2,816.71| 1,774.99| 294.38 |
| Total Cost of Module (A+B+C)   | 7,879.03| 6,199.14| 3,906.48| 647.88 |
| Engineering & Construction (25% of A+B+C) | 1,969.76| 1,549.78| 976.62| 161.97 |
| Subtotal                       | 9,848.78| 7,748.92| 4,883.10| 809.85 |

Contingency (40% Subtotal)      |

|                                |       |       |       |       |
| Washed Rocks (incl. 20% Contingency) | 1,800.00| 1,416.22| 892.45| 148.01 |

Overall Total Capital Cost      |

|                                |       |       |       |       |
| Operating Cost:                |       |       |       |       |
| Materials, Supplies, Utilities & Labour | 2,244.00| 1,765.56| 1,112.59| 184.52 |
| Lime                           | 1,000.00| 786.79| 495.81| 82.23 |
| Maintenance, Taxes & Insurance (4.5% of Tot. Cap.) | 701.47| 551.91| 347.80| 57.68 |
| Total Operating Cost           | 3,945.47| 3,104.26| 1,956.20| 324.43 |
### Table 18 - Hydrogen peroxide process

<table>
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<td></td>
<td>$'000</td>
<td>$'000</td>
<td>$'000</td>
<td>$'000</td>
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<tr>
<td>Bare Equipment Items</td>
<td>405.00</td>
<td>318.65</td>
<td>200.80</td>
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<tr>
<td>Misc. Unspecified items (15% of 1)</td>
<td>60.75</td>
<td>47.80</td>
<td>30.12</td>
<td>5.00</td>
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<td>Subtotal Bare Equipment</td>
<td>465.75</td>
<td>366.45</td>
<td>230.92</td>
<td>38.30</td>
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<tr>
<td>Installed Cost (Bare Equipment x 1.45)</td>
<td>675.34</td>
<td>531.35</td>
<td>334.84</td>
<td>55.53</td>
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<tr>
<td>Other Items - Installed Cost</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Subtotal Installed Equipment</strong></td>
<td><strong>675.34</strong></td>
<td><strong>531.35</strong></td>
<td><strong>334.84</strong></td>
<td><strong>55.53</strong></td>
</tr>
<tr>
<td>Services:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical 15%</td>
<td>101.30</td>
<td>79.70</td>
<td>50.23</td>
<td>8.33</td>
</tr>
<tr>
<td>Instruments 10%</td>
<td>67.53</td>
<td>53.13</td>
<td>33.48</td>
<td>5.55</td>
</tr>
<tr>
<td>Service Piping 10%</td>
<td>67.53</td>
<td>53.13</td>
<td>33.48</td>
<td>5.55</td>
</tr>
<tr>
<td>Other Services 5%</td>
<td>33.77</td>
<td>26.57</td>
<td>16.74</td>
<td>2.78</td>
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<tr>
<td><strong>Total Services</strong></td>
<td><strong>270.14</strong></td>
<td><strong>212.54</strong></td>
<td><strong>133.94</strong></td>
<td><strong>22.21</strong></td>
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<tr>
<td>Building 3,250.00, 2,500.00, 2,500.00</td>
<td>420.00</td>
<td>330.45</td>
<td>208.24</td>
<td>34.54</td>
</tr>
<tr>
<td>Earthworks and Concrete</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Total Primary Module Cost (A)</strong></td>
<td><strong>1,365.47</strong></td>
<td><strong>1,074.34</strong></td>
<td><strong>677.01</strong></td>
<td><strong>112.28</strong></td>
</tr>
<tr>
<td>Settling Basin Cost (B)</td>
<td>150.00</td>
<td>118.02</td>
<td>74.37</td>
<td>12.33</td>
</tr>
<tr>
<td>Lime Module Cost (C)</td>
<td>3,580.00</td>
<td>2,816.71</td>
<td>1,774.99</td>
<td>294.38</td>
</tr>
<tr>
<td><strong>Total Cost of Module (A+B+C)</strong></td>
<td><strong>5,095.47</strong></td>
<td><strong>4,009.07</strong></td>
<td><strong>2,526.37</strong></td>
<td><strong>418.99</strong></td>
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<tr>
<td>Engineering &amp; Construction (25% of A+B+C)</td>
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<td>1,002.27</td>
<td>631.59</td>
<td>104.75</td>
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<td><strong>Subtotal</strong></td>
<td><strong>6,369.34</strong></td>
<td><strong>5,011.33</strong></td>
<td><strong>3,157.97</strong></td>
<td><strong>523.74</strong></td>
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<tr>
<td>Contingency (40% Subtotal)</td>
<td>2,547.74</td>
<td>2,004.53</td>
<td>1,263.19</td>
<td>209.50</td>
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<tr>
<td>Washed Rocks (incl. 20% Contingency)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Overall Total Capital Cost</strong></td>
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<td><strong>7,015.86</strong></td>
<td><strong>4,421.16</strong></td>
<td><strong>733.24</strong></td>
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<td>Operating Cost:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Materials, Supplies, Utilities &amp; Labour</td>
<td>13,533.00</td>
<td>10,647.63</td>
<td>6,709.77</td>
<td>1,112.80</td>
</tr>
<tr>
<td>Lime</td>
<td>1,000.00</td>
<td>786.79</td>
<td>495.81</td>
<td>82.23</td>
</tr>
<tr>
<td>Maintenance, Taxes &amp; Insurance (4.5% of Tot. Cap.)</td>
<td>401.27</td>
<td>315.71</td>
<td>198.95</td>
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</tr>
<tr>
<td><strong>Total Operating Cost</strong></td>
<td><strong>14,934.27</strong></td>
<td><strong>11,750.13</strong></td>
<td><strong>7,404.53</strong></td>
<td><strong>1,228.02</strong></td>
</tr>
</tbody>
</table>
CONCLUSIONS

Several effluent treatment processes are technically capable of achieving complete thiosalts removal from milling effluents. Previous work reported that ozonation, chlorination, hydrogen peroxide, SO$_2$-air, chalcopyrite catalysis, reverse osmosis, iron reduction and alkaline pressure oxidation achieved complete thiosalts removal or almost complete removal in the case of biological oxidation.

Applications of these processes would add significant costs to treating milling effluents and it appears that technological advances made since 1985 would not significantly improve the economic feasibility of these processes.

Among all the processes investigated, biooxidation of thiosalts has the best prospect to develop into a commercially viable process. Pilot tests using rock-packed biooxidation pond achieved almost complete oxidation of thiosalts over a 9-month period at temperatures as low as 1.0°C. Certainly, these results indicate a good likelihood that biooxidation could potentially treat thiosalts in milling effluents as a year-round operation using engineered biological reactors. Furthermore, the evaluation of thirteen treatment processes conducted in 1985, reported that biological oxidation was more cost-effective than chemical or physical processes; only natural degradation in the effluent ponds was less costly.

Improved performance of biooxidation process could be realized by using packed tank reactors. Tank reactors allow greater control over process variables to achieve optimal values. Technologies such as genetic manipulation, bio-augmentation, and microbial entrapment could potentially improve the reliability and economics of biological reactors. A process based on biological treatment in combination with chemical oxidation as polishing step and as a backup process appears to be the best strategy in decreasing thiosalts concentration to less than 10 mg/L in milling effluent. More laboratory studies and pilot tests are needed to define operational parameters at low temperatures and develop expertise and operational experience with biological oxidation of thiosalts contained in milling effluents.

Chemical oxidation processes, though reliable, effective and easily integrated into existing treatment processes are costly if used as a stand-alone process. Practically, chemical processes should be considered only as a backup system or as a polishing step for the more cost-effective biological oxidation process.
Chlorine is the least expensive oxidant. However, unlike ozone and hydrogen peroxide, chlorine can generate combined chlorine compounds which could have environmental impacts.

The SO$_2$-air oxidation successfully oxidized thiosalts in one test but other test results were inconclusive. This process needs careful balancing of the process variables to achieve oxidation. Further experimentation is needed to determine the optimum values of the process variables and their interrelationship.

Reverse osmosis can technically remove all of the thiosalts from milling effluents. However, scaling, iron precipitation and microbial growth can quickly degrade their performance. Reverse osmosis membranes are difficult to clean and expensive to replace. Furthermore, this process does not destroy thiosalts. The concentrated thiosalts solution generated by reverse osmosis would need further treatment.

Potentially, metal catalysis of thiosalts oxidation could be cost-effective. Several studies have shown that supported copper catalysts are effective in degrading thiosalts at ambient temperature or higher. Complete thiosalts oxidation was achieved using chalcopyrite concentrate as a catalyst over a temperature range of 20° to 90°C. No loss of catalytic activity was observed over a period of one month. Further studies are needed to develop catalysts that are effective over a temperature range of 5° to 30°C.

Mediated electro-oxidation can technically reduce thiosalts levels to less than 10 mg/L S$_2$O$_3$$_2^-$ without generating dithionate. However, test results indicate that power requirements would be high due to side reactions. Furthermore, optimizing cell parameters would require extensive testing due to the complex chemistry of mill effluents.

Conceptually, a combination of electrooxidation with copper catalysis could increase oxidation rates and increase cell efficiency. The copper catalyst can be fixed on the electrode surface to enhance the oxidation of activated thiosalts intermediates.

Iron reduction and alkaline pressure oxidation can achieve complete destruction of thiosalts at elevated temperatures. In practice, heating the large volumes of effluent to 100°C limits this processes to treatment of concentrated thiosalts solutions.

Natural degradation is the most widespread method used for thiosalts removal. However, in northern climates, this method is not effective as a year-round operation.

Marine discharge of thiosalts containing milling effluents is similar to the common practice of discharging lime-treated effluent into a lake or river. The advantage of marine discharge is that the high dilution potential in the sea can dissipate large quantities of thiosalts.
Recently, this method of effluent discharge has come under increased regulatory pressure in some jurisdictions. Marine disposal of thiosalts is a feasible option and has a high degree of certainty for long term successful operations. However, this option is only available to mining operations located in coastal areas.

The Management Committee selected the following methods for economic evaluation:

- Biological Oxidation in rock-packed reactors;
- Biological Oxidation in rock-packed reactors combined with hydrogen peroxide as a polishing step; and
- Hydrogen Peroxide alone.

Three effluent cases were considered:

- Noranda Mining and Exploration, Brunswick Mining Division with an effluent flow of 1,380 m$^3$/h and 9,936 kg/d thiosalts discharge;
- Bouchard-Hébert Mine with an effluent flow of 408 m$^3$/h and 4,602 kg/d thiosalts discharge; and
- Aur Louvicourt Mine with an effluent flow of 160 m$^3$/h and 230 kg/d thiosalts discharge.

The costs discussed in Part B of this report are estimates with an accuracy of ±40%. The capital and operating costs derived in 1985 and 1997 are presented in Table 14. As shown, the capital costs in 1997 for Case 1997A vary from $7.0 million to $12.3 million and operating costs vary from $2.0 million to $11.8 million for an operation treating 1,380 m$^3$/h effluent and 9,936 kg/d thiosalts discharge. The capital costs for Case 1997C, vary from $733,000 to $1.3 million for an operation treating 160 m$^3$/h effluent and 230 kg/d thiosalts discharge. The total costs for the capitalization and operation of a thiosalts treatment facility range from $12.6 million to $18.8 million per year for Case 1997A and from $1.3 million to $2.0 million per year for Case 1997C. Based on these estimates, biological oxidation is the lowest cost option of the three processes evaluated.
RECOMMENDATIONS

As a result of this investigation, the following recommendations are made for future projects to develop further thiosalts treatment processes:

1. Conduct more rigorous pilot testing of biological oxidation of thiosalts using packed bed reactors to determine:
   - performance at low temperatures, scale up parameters;
   - flow rates (particularly at high flow and at low concentrations); and
   - develop technical expertise and operational experience.

1. Investigate biological oxidation at low temperatures to define the optimum values of operating parameters.

2. As a long term objective investigate the potential of using technologies such as bio-augmentation, genetic engineering and microbial entrapment to improve the performance and robustness of biological oxidation.

3. Investigate a thiosalt treatment process based on a combination of bacterial oxidation for bulk removal of thiosalts followed by hydrogen peroxide as a polishing step and as a backup treatment system.

4. Investigate advanced oxidation processes using hydrogen peroxide (e.g., ULTROX® process) as a means of achieving higher oxidation efficiency and faster reaction rates.

5. Conduct further investigation into the SO₂-air process to better define process variables and their optimum values and determine their effective balance to achieving fast reaction rates.

6. Conduct further investigation into a chalcopyrite catalyst system with the goal of achieving efficient thiosalts oxidation in the temperature range of 2° to 30°C.
REFERENCES


120. Noranda Research Centre; (1984) confidential progress report.


147. Dinardo, O.; (1997) personal communication with the technical staff at Calgon Carbon Inc.
151. Presentation: Thiosalts Workshop, Montreal, June 5, 1996.
APPENDIX A

Summaries of Effluent Parameters and Costs for the 1985 Techno-Economic Evaluation of Thiosalts Treatment Processes
## Summaries of the Costs for the 1985 Techno-Economic Evaluation of Thiosalts Treatment Processes

<table>
<thead>
<tr>
<th>Treatment Process</th>
<th>Overall capital (millions $)</th>
<th>Overall annual costs (capitalization, operating, maintenance) (millions $)</th>
</tr>
</thead>
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<tr>
<td><strong>Biological air oxidation</strong></td>
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<td></td>
</tr>
<tr>
<td>1.1 Without post-treatment</td>
<td>13.5</td>
<td>5.2</td>
</tr>
<tr>
<td>1.2 With H₂O₂ post-treatment</td>
<td>15.6</td>
<td>7.1</td>
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<td><strong>Catalyzed air oxidation</strong></td>
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</tr>
<tr>
<td>2.1 With polyvinyl pyridine</td>
<td>32.2</td>
<td>26.0</td>
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<td>2.2 With converter white metal (copper)</td>
<td>14.8</td>
<td>7.2</td>
</tr>
<tr>
<td><strong>H₂O₂ oxidation</strong></td>
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<td><strong>Ozone oxidation</strong></td>
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<tr>
<td><strong>Chlorine oxidation</strong></td>
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<td>5.1 Purchased lime</td>
<td>8.9</td>
<td>16.7</td>
</tr>
<tr>
<td>5.2 On-site lime production</td>
<td>50.5</td>
<td>18.5</td>
</tr>
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<td><strong>SO₂-air oxidation</strong></td>
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<td>6.1 Sulphur/purchased lime</td>
<td>13.3</td>
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<td>6.2 Sulphur/on-site lime production</td>
<td>22.0</td>
<td>10.2</td>
</tr>
<tr>
<td>6.3 Pyrite/purchased lime</td>
<td>15.5</td>
<td>10.4</td>
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<td>6.4 Pyrite/on-site lime production</td>
<td>24.2</td>
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<td><strong>Electrochemical oxidation</strong></td>
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<td><strong>Reverse osmosis</strong></td>
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<td>8.1 Brine treatment by evaporation</td>
<td>79.0</td>
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<td>8.2 Electrochemical brine treatment</td>
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<td>8.3 Alkaline pressure oxidation brine treatment</td>
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<td><strong>Reduction by iron</strong></td>
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<td>10.1 With H₂O₂ treatment for H₂S</td>
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<tr>
<td>10.2 With Claus reactor</td>
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<td>16.9</td>
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<tr>
<td><strong>Activated carbon adsorption</strong></td>
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<td>11.1 Thermal carbon regeneration</td>
<td>37.0</td>
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</tr>
<tr>
<td>11.2 Alkaline carbon regeneration/electrochemical oxidation of alkali</td>
<td>23.6</td>
<td>13.8</td>
</tr>
<tr>
<td>11.3 Alkaline carbon regeneration/Alkaline pressure oxidation of alkali</td>
<td>19.1</td>
<td>11.7</td>
</tr>
<tr>
<td><strong>Disposal to sea (pipeline)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Natural degradation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28.9</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>12.4</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>
## Techno-economic Study Effluent Parameters

(mg/L except pH, temperature)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Combined Effluent*</th>
<th>Final Effluent†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total thiosalts</td>
<td>1400</td>
<td>≤100</td>
</tr>
<tr>
<td>Thiosulphate</td>
<td>700</td>
<td>≤50</td>
</tr>
<tr>
<td>Tri-tetrathionate</td>
<td>700</td>
<td>≤50</td>
</tr>
<tr>
<td>Fe</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>Pb</td>
<td>5-10</td>
<td>0.2</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca</td>
<td>600</td>
<td>800</td>
</tr>
<tr>
<td>SO₄</td>
<td>2,000</td>
<td>2,000</td>
</tr>
<tr>
<td>Na</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>K and Mg</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>pH</td>
<td>7</td>
<td>9.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>15°C winter</td>
<td>variable</td>
</tr>
<tr>
<td></td>
<td>30°C summer</td>
<td>with treatment</td>
</tr>
</tbody>
</table>

* 720m³/h flow, 24 tonne/d thiosalts, 1,390 mg/L
† Quality of final effluent expected following thiosalt treatment and pH adjustment.
APPENDIX B

Description of the Computerized Databases Searched for Effluent Treatment Technologies
CA SEARCH®: Chemical Abstracts®

Coverage: 1967 to date
Updates: Weekly
Data Type: Bibliographic

CA RESEARCH: Chemical Abstracts contains over 12 million citations to the worldwide literature of chemistry and its applications. About 500,000 new documents are added each year. CA SEARCH contains bibliographic data and indexing from the print version of Chemical Abstracts. In addition, in April 1995, CAS® began adding electronic-only documents to CA SEARCH. These include journals, conferences at which researchers are invited to submit papers, and individually posted papers.

Derwent World Patents Index

Coverage: 1963 to date
Updates: Weekly
Data Type: Bibliographic

Derwent World Patents Index contains data from over 7.5 million inventions represented in more than 14 million patent documents from 40 patent issuing authorities around the world.

Records include images, consisting of intellectually selected drawings for electrical or mechanical technologies (beginning in 1988) and chemical structures (beginning in 1992). Equivalent patents are grouped together by patent family in the basic patent record. Special chemical indexing is available to Derwent subscribers, including manual and fragmentation codes and polymer indexing. Coverage of all chemical patents began in 1970; coverage of all patents irrespective of subject began in 1974.
Enviroline

Coverage: 1975 to date
Updates: Monthly
Data Type: Bibliographic

Enviroline provides indexing and abstracting coverage of more than 5,000 international primary and secondary source publications reporting on the technical, scientific, socioeconomic, and policy aspects of a wide range of environmental subjects.

Included are such fields as management, technology, planning, law, political science, economics, geology, biology, and chemistry, as they relate to environmental issues. Literature covered includes periodicals, government documents, industry reports, proceedings of meetings, newspaper articles, films, and monographs.

Environmental Bibliography

Coverage: 1973 to date
Updates: Monthly
Data Type: Bibliography

Environment Bibliography provides access to article references for every environmental research need. It covers the fields of general human ecology, atmospheric studies, energy, land and water resources, and nutrition and health. The database indexes almost 500 periodicals dealing with water, air, soil, and noise pollution; solid waste management; health hazards; urban planning; global warming, and many other environmental topics. Environmental Bibliography is Knight-Ridder Information’s online version of the Environmental Periodicals Bibliography database.

METADEX®: Metals Science

Coverage: 1966 to date (see below)
Updates: DIALOG: every two weeks DataStar: Monthly
Data Type: Bibliographic

METADEX: Metals Science provides the most comprehensive coverage of international literature on the science and practice of metallurgy. Each month about 3,500 new documents related to metals technology are scanned and abstracted for METADEX, with intensive coverage given to appropriate conference papers, reviews, technical reports, and books.

NTIS: National Technical Information Service

Coverage: DIALOG: 1964 to date/
DataStar: 1970 to date
Updates: Every two weeks
Data Type: Bibliographic

The NTS database is a comprehensive abstract collection and index of the results of U.S. government-sponsored research, development, and engineering, plus analyses prepared by federal agencies, their contractors, or grantees. It is the means through which unclassified, publicly available, unlimited distribution reports are made available for sale from agencies such as NASA, DDC, DOE, HUD, DOT, Department of Commerce, and some 600 other agencies. In addition, some state and local government agencies contribute their reports to the database.

Pollution Abstracts

Coverage: 1970 to date
Updates: Monthly
Data Type: Bibliographic

Pollution Abstracts is a leading resource for references to environmental-related international literature on pollution, its sources, and its control. Among the subjects covered by the database are air, water, land, and noise pollution; sewage and wastewater treatment; waste management; environmental quality; pesticides; radiation; and solid wastes.

SciSearch®

Coverage: 1974 to present
Updates: Weekly
Data Type: Bibliographic

SciSearch® is a multidisciplinary index to the literature of science and technology prepared by the Institute for Scientific Information (ISI); it contains all records published in Science Citation Index (SCI®) and additional records from the Current Contents series of publications that are not included in the print version of SCI. SciSearch is distinguished by two important and unique characteristics. First, journals indexed are carefully selected on the basis of several criteria, including citation analysis, resulting in the inclusion of 90 percent of the world’s significant scientific and technical literature. Second, citation indexing is provided, which allows retrieval of newly published articles through the subject relationships established by an author’s reference to prior articles. SciSearch covers every area of the pure and applied sciences.
WATERNET®

Coverage: 1971 to present
Updates: Every two months
Data Type: Bibliographic

WATERNET® provides a comprehensive index of premier publications relating to water and wastewater. Information sources include international coverage of books, journal articles, U.S. government reports, conference proceedings, handbooks, manuals and selected technical reports, in addition to all American Water Works Association and American Water Works Association Research Foundation materials.