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THE CHEMISTRY, GENERATION AND TREATMENT OF THIOSALTS IN MILLING EFFLUENTS - A NON-CRITICAL SUMMARY OF CANMET INVESTIGATIONS 1976-1982

M. WASSERLAUF AND J.E. DUTRIZAC

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THE CHEMISTRY, GENERATION AND TREATMENT OF THIOSALTS IN MILLING EFFLUENTS - A NON-CRITICAL SUMMARY OF CANMET INVESTIGATIONS 1976-1982

by

M. Wasserlauf* and J.E. Dutrizac**

ABSTRACT

CANMET's thiosalt program, as well as the relevant open literature on thiosalts, is reviewed in a non-critical manner. Prior to this program, very little was known about thiosalts or their behaviour in milling effluents. Analytical techniques previously available usually had been tested only on pure synthetic solutions often with only one thiosalt species present. Adequate sampling and storage procedures were not available. Virtually nothing was known about thiosalt generation in milling circuits. Some studies had been made on the chemistry of thiosalts, especially thiosulphate, and although many of the early studies suffered from analytical uncertainties, they indicated that thiosalt destruction might be achieved by a variety of unevaluated techniques.

During CANMET's thiosalt program it was found that thiosalt solutions were somewhat unstable at room temperature; freezing of solutions appeared to be the best method of sample preservation. Colorimetric analytical methods based on selective cyanolysis of thiosulphate, trithionate and tetrathionate contained in mill effluents were developed and evaluated. Titrimetric methods, based on EDTA back titration of barium remaining after selective oxidation of the individual thiosalts to SO_4, were developed. The Noranda mercuric chloride total thiosalt titration method was perfected. Methods were tried to permit the determination of low (<50 ppm) thiosalt levels, but these were subject to large uncertainties. As part of the general analytical work, the infrared and ultraviolet spectra of the dissolved thiosalts were measured; the crystal structures of trithionate and tetrathionate were determined; the crystal structures of trithionate and tetrathionate were accurately measured. The factors affecting thiosalt generation in milling circuits were determined, and the principal ones were grinding pH, sulphide content of the ore, residence time and temperature. Mass balances were conducted at two operating mills to define the importance of the various unit operations. Fourteen methods of thiosalt destruction were

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evaluated on technical and economic grounds. Although some methods such as electrodialysis were the subject of paper studies only, most of the techniques were extensively examined at the laboratory level and those such as biological oxidation, were tested at pilot scale. When all aspects of the treatment are considered, thiosalt destruction costs become very high; furthermore, none of the methods has yet been proved to be continuously effective for the large-scale treatment of actual thiosalt effluents.

LA CHIMIE, LA FORMATION ET LE TRAITEMENT DES THIO-SELS DANS LES EFFLUENTS PROVENANT DES USINES DE TRAITEMENT; UN SOMMAIRE NON CRITIQUE DES RECHERCHES DU CANMET DE 1976 à 1982.

par

M. Wasserlauf* et J.E. Dutrizac**

RÉSUMÉ

On examine ici sans en faire la critique le programme du CANMET sur les thio-sels, de même que la documentation pertinente à ces derniers. Avant ce programme, les thio-sels et leur comportement dans les effluents des usines de traitement étaient très peu connus. Les techniques analytiques disponibles auparavant n'avaient été étudiées que sur des solutions synthétiques pures, où on ne retrouvait souvent qu'une seule espèce de thio-sel. Il n'y avait aucun procédé d'échantillonage et d'entreposage satisfaisant. On ne savait pratiquement rien de la formation des thio-sels dans les circuits de traitement. Certaines études avaient été effectuées sur leur chimie, particulièrement sur celle du thio-sulphate, et bien que plusieurs des plus récentes études aient présenté des incertitudes analytiques, elles indiquèrent que la destruction des thio-sels était possible au moyen de diverses techniques non évaluées.

Pendant la durée du programme du CANMET sur les thio-sels, il fut découvert que les solutions de thio-sel étaient assez instables lorsques laissées à la température ambiante; le gel des solutions semblait être la meilleure façon de préserver les échantillons. Des méthodes d'analyse colorimétrique basées sur la cyanolyse sélective du thio-sulphate, du trithionate et du tetrathionate contenus dans les effluents d'usines de traitement furent développées et évaluées. Des modes opératoires par titration, basés sur la titration de type EDTA de l'excédent de barium qui demeure après l'oxidation sélective des thio-sels individuels au SO_4, furent développés. La méthode Noranda de titration par bichlorure de mercure pour obtenir le total des thio-sels fut perfectionnée. On a essayé des méthodes permettant de déterminer de faibles niveaux de thio-sels (<50 ppm), mais elles présentaient de grandes incertitudes. Les travaux analytiques généraux comprenaient la mesure à l'infra-rouge et à l'ultra-violet des spectres des thio-sels dissous; les structures cristallines du trithionate et du tétrathionate furent mesurées de façon exacte. Les facteurs influençant la formation du thio-sel dans les circuits de traitement furent déterminés, les principaux étant: le pH de broyage, le contenu en sulfure du minerai, le temps de résidence et la tempéraute. On a dressé des bilans matière à deux des usines en opération, afin de déterminer l'importance des diverses unités de l'opération. On a évalué du point de vue économique et technique quatorze méthodes pour la destruction des thio-sels. Bien que certaines méthodes, dont la méthode par électrodialyse, n'aient été étudiées que sur papier, la plupart des techniques furent examinées longuement et soigneusement en laboratoire, et d'autres, comme

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la méthode par oxydation biologique, furent étudiées à l'échelle pilote. Lorsqu'on considère tous les aspects du traitement, le coût de la destruction des thio-sels s'avère très élevé. De plus, aucune des méthodes n'a encore été prouvée continuellement efficace pour le traitement à grande échelle des effluents industriels de thio-sels.

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INTRODUCTION

During the milling of sulphide ores, part of the sulphide content is oxidized by oxygen dissolved in the processing streams. The oxidation is especially severe when dealing with massive sulphide ores such as those found in northeastern New Brunswick. Although the thermodynamics of the oxidation process suggest that only sulphate should be produced, kinetic limitations result in the formation of partially oxidized sulphur oxyanions such as $S_2O_3^{2-}$, $S_3O_6^{2-}$ and $S_4O_6^{2-}$. These species are collectively known as "thiosalts", and their presence in milling effluents can create serious environmental problems in receiving watercourses. The thiosalts pass through conventional effluent treatment operations (lime additions) largely unaffected, and enter river systems where they are oxidized, in the presence of bacteria, to sulphuric acid. The acid thus produced can be very injurious to the environment depending on the concentration of the thiosalts, the nature of the river bottoms, the distance from the sea, etc. Within the framework of our current knowledge, the problem appears to be associated only with the generated acid and not with the thiosalt species themselves.

In 1976, CANMET became involved with the thiosalt problem and developed a program to assist with its resolution. The program, as it developed, tackled four general topics. From the beginning it was apparent that difficulties were associated with sampling and sample storage; also, the analytical techniques then available were cumbersome and largely unproved, especially on actual mill effluents. There were great uncertainties concerning the mode of generation of thiosalts in milling circuits and whether simple modifications to the processing circuit could eliminate or greatly reduce the thiosalt problem. In the same vein, it was unclear why some mines had serious thiosalt problems while others did not. The third area of concern, of course, was thiosalt removal supposing that mere process modifications could not solve the thiosalt problem. Many possible removal options existed that required evaluation to ascertain their technical and economic viability. Much of the previous work in the removal area was either incomplete or suffered from sampling and/or analytical problems. Lastly, there was the question of the complex chemistry of thiosalts and its elucidation. Many of the existing chemical data were questionable because of uncertainties with analyses and sample storage, and one of the legitimate goals of the CANMET effort was to try to improve our understanding of the fundamental chemistry of these complex compounds. Although the basic chemistry sometimes emerged as a separate project entity, more often, the fundamental investigations were carried out in support of some more applied objective. The above four general areas of study constitute CANMET's thiosalt program which has as its ultimate objective to develop an economically acceptable solution to the thiosalt problem that would be applicable in the Canadian climate.

The program enjoyed many successes concerning both the elucidation of the problem and its ultimate resolution. Adequate sampling procedures were evolved and simple but accurate analytical methods were developed. Sampling campaigns were carried out to ascertain where and how thiosalts were produced in operating mills. Many methods of thiosalt destruction were evaluated and three of the more promising were tested on a mini-plant scale; bacterial oxidation is being evaluated on a pilot scale by an associated corporate participant. Costing studies were done on several of the removal techniques, and all have been shown to be relatively expensive when required pre- and post-treatment steps are considered.

Part of the success of the program can be attributed to the close involvement of industrial and university laboratories. These external groups have made significant contributions to the general resolution of the thiosalt problem and have materially strengthened the CANMET program. A list of external participants in the program is given in Appendix 4.

During the six-year study of the thiosalt problem, numerous reports, technical memoranda and other documents were issued and distributed within CANMET and to external participants. The various CANMET documents produced during the course of the program are given in Appendix 3. Several of the external bodies also issued reports covering their own investigations into thiosalts, and generously authorized their distribution as part of the general thiosalt program. Also, a large body of information from the open literature was assembled, examined and utilized in the current investigations. The successes of CANMET's thiosalt program ensure that the information generated will be of interest to the mining-metallurgical industry both now and for years to come. The great number and diversity of documents involved, however, make it difficult to obtain a simple, comprehensive idea of the activities and to assess the overall impact of the program. Hence, it was decided to issue a non-critical summary of all the documents produced as part of the program and to include a comprehensive bibliography of them. The Noranda Research Centre was contracted to prepare this document in conjunction with CANMET staff, and this report is the fruit of that cooperative endeavour.

PART I

LITERATURE REVIEW

LITERATURE REVIEW CONCLUSIONS

ANALYTICAL

Most of the analytical procedures published prior to the start of the CANMET thiosalt program were developed for the analysis of solutions containing the individual pure polythionates or their simple mixtures, and were not applied or demonstrated to be applicable to the analysis of industrial or mining waste waters. The information available with respect to mining effluents was limited to the experience of Noranda (6) and Wolkoff and Larose (28). The results given by Wolkoff and Larose indicated that the amount of trithionate, pentathionate and hexathionate in mill effluents was less than 30 to 60 ppm each. Trithionate, thiosulphate and tetrathionate concentrations were in the range 100 to 1000 ppm.

This suggested that it was necessary to investigate analytical methods for only thiosulphate, trithionate and tetrathionate because the other polythionates are virtually non-existent. Simple titrimetric or colorimetric methods would appear to be applicable because the concentrations of the species sought are moderately high. Noranda's procedures, for example, are able to cope with 50 to 5000 mg/L total thiosalts as $S_2O_3^{2-}$, but are unable to distinguish between individual polythionates. These methods are satisfactory for certain control purposes and have the advantage of being simple and relatively rapid. Some difficulties may arise if carbonate, sulphide or sulphite are present. When it is desired to distinguish between trithionate, tetrathionate and thiosulphate, the colorimetric methods should be investigated; e.g., that proposed by Mizoguchi and Okabe (19). The iodometric titration methods for sulphite and thiosulphate can also be employed, and the thiosulphate concentrations obtained by each can be compared.

Polarographic procedures, if applicable, would be more specific than either titrimetric or colorimetric methods and perhaps more sensitive, an advantage in the event lower concentrations need to be determined. These methods may not be suitable, however, if the sample solutions give rise to ill-defined polarographic waves or if they do not exhibit the same polarographic behaviour as solutions of the pure thiosalts. The presence of flotation agents, inhibitors or other surface active agents as well as trace elements, for example, may all have some adverse effect on polarographic behaviour. Other relevant points to consider in the analysis of thiosalt samples are:

(a) Due regard must be taken to prevent the oxidation of acidic samples and standard solutions by thiobacteria in the samples or the laboratory environment.

(b) The possibility of chemical degradation of samples and standard solutions of polythionates at alkaline pH must be considered.

(c) Storage of samples and standard solutions at low temperatures (ideally below freezing) would appear to decrease the amount of degradation due to either (a) or (b).

(d) The presence of catalysts must be considered in the analysis of thiosalt solutions. Thiosulphate catalyzes the alkaline degradation of higher polythionates. Sulphite, sulphide, arsenite, etc. are also degradation reagents. Copper catalyzes the oxidation of thiosulphate to tetrathionate.

(e) The possibility of incomplete oxidation with some nominally strong chemical oxidants; e.g., hydrogen peroxide, must be considered in the use of analytical methods requiring stoichiometric oxidation of thiosalts to sulphate.

(f) The use of heat in analytical procedures designed to differentiate between various polythionate/thiosulphate /sulphide /sulphate species must be considered with caution. Elevated temperatures could enhance the deleterious effects of (a), (b), and (d) above. Trithionate, for example, is quite stable at normal temperatures but is thermally unstable in the region of 70°C.

(g) The possibility of shifting polythionate equilibria when formaldehyde is used as a complexing agent for sulphite must be considered in the application of analytical methods whereby the various polythionate species are to be distinguished. Also, the formaldehyde should be neutral and not contain acidic substances such as formic acid.

AQUEOUS CHEMISTRY

Aqueous solutions of sulphur oxyanions form a complex equilibrium system, thus the chemistry of one component may not be treated independently of the others. Alternative and sometimes conflicting pathways may occur simultaneously. The pathways of decomposition and formation are probably best described in terms of linked cycles.

Some general trends are summarized below:

(1) Polythionates are thermodynamically unstable in alkaline solution, decomposing to elemental sulphur, thiosulphate and sulphite. Sulphite may decompose to sulphate in the presence of air. Thiosulphate may also be produced by secondary reaction between elemental sulphur and sulphite. Thiosulphate is apparently quite stable under alkaline conditions (pH > about 9), in the absence of strong oxidants or catalysts. The rates of decomposition of the polythionates increase with pH and temperature, and in the presence of degrading nucleophiles such as sulphite and sulphide. The rates of decomposition are in the order $S_6O_6^{2-} > S_5O_6^{2-} > S_4O_6^{2-} > S_3O_6^{2-}$. Consequently, build-up of lower polythionates, particularly trithionate and thiosulphate may be expected during reaction.

(2) Polythionates are relatively stable in mild to moderately strong acid solutions, the relative order of stabilities being: $S_xO_6^{2-}$, where $x = 4 > 3 > 5 > 6$. Stabilities decrease with increasing temperature and markedly so for trithionate. Under acidic conditions, thiosulphate may decompose chemically via diverse chemical pathways to yield sulphur, sulphate, trithionate or tetrathionate and may produce, consume, or utilize no acid, depending on the relative rates of the competing reactions.

In very mildly alkaline to moderately acidic solutions, thiobacteria can catalyze the aerobic oxidation of thiosalts to produce sulphuric acid. The efficiency of the oxidation is dependent on the nature of the bacteria, pH, temperature, and the presence of bacterial toxicants.

The maximum amount of acid which can be produced when thiosalts undergo complete oxidation (to sulphate) under mildly acidic conditions is predicted to be 6, 4, and 2 mol respectively, per mole of $S_4O_6^{2-}$, $S_3O_6^{2-}$ and $S_2O_3^{2-}$. Incomplete oxidation leads to lesser quantities of acid.

(3) With regard to possible treatment processes for thiosalt effluents, alkaline conditions and elevated temperatures favour the chemical breakdown of polythionates to thiosulphate and sulphite. Aerobic conditions cause the oxidation of sulphite to sulphate. Bacterial oxidation is not favoured. Acidic conditions result in the oxidation of thiosulphate to sulphuric acid chemically and bacteriologically. Aerobic conditions are required for complete bacteriological oxidation of the thiosalts. Anaerobic conditions result in only partial degradation of polythionates to sulphate and thiosulphate. Cold temperatures will inhibit thiosalt breakdown by any route.

ANALYTICAL DETERMINATION OF THIOSALTS

The following literature review was carried out by Smith and Hitchen in 1976, and thus does not include any information published since (1,2).

The analytical methods available for thiosalts can be grouped as follows:

TITRIMETRIC METHODS

Acidimetric Titrations

A titrimetric procedure based on the oxidation of thiosulphate and polythionates with mercuric chloride was originally proposed by Feld (3) and later underwent various modifications by Kurtenacker and Bittner (4) and Jay (5). Noranda Research Centre modified the method to improve its reliability (6).

The method is based on the fact that polythionates ($S_xO_6^{2-}$, where x = 3,4,5,6) react quantitatively with mercuric chloride to release acid according to the following:

$$2S_xO_6^{2-} + 3HgCl_2 + 4H_2O \rightarrow HgCl_2.2HgS + 8H^+ + 4Cl^- + 4SO_4^{2-} + (2x-6)S^\circ \qquad \text{Eq 1}$$

Thiosulphate reacts in a similar manner:

$$2S_2O_3^{2-} + 3HgCl_2 + 2H_2O \rightarrow HgCl_2.2HgS + 4H^+ + 4Cl^- + 2SO_4^{2-} \qquad \text{Eq 2}$$

In practice a titration with standard sulphuric acid is first made to pH 4.3 to neutralize the basic sample solution. After the addition of mercuric chloride, a second titration is made to pH 4.3 using standard sodium hydroxide to neutralize the acid produced. From the results of the second titration the sum of the species $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$ is calculated and expressed as $S_2O_3^{2-}$. If sulphite is present, it will interfere and high results will be obtained. The interference of sulphite can be partly overcome by the addition of formaldehyde but more accurate results are obtained by pretitration of the sulphite with an iodine solution after the sample has been neutralized to pH 4.3 with the standard sulphuric acid solution. The iodine will also titrate the thiosulphate to tetrathionate but this will not alter the subsequent results after addition of mercuric chloride because the amount of acid produced by the tetrathionate is equivalent to the amount of thiosulphate originally present.

The sample size is determined by the thiosalt concentration. A correction is applied for the alkalinity obtained on a blank titration. The latter correction depends on the age and concentration of the mercuric chloride stock solution. The titrations are performed using a pH meter to detect the end-point.

A modified method developed by Noranda for mill samples is simpler and faster and yields results within 10% of the true value in the 50 to 5000 mg/L concentration range (6). The solutions are titrated to pH 4.3, and no correction is made for the acid consumption by mercuric chloride. The results are calculated in terms of $S_2O_3^{2-}$ because the method does not distinguish between the various forms of sulphur.

Interference may be caused by a number of components existing in the mill waters. Sulphide ions, if present, will react with mercuric chloride to produce acid. This interference is unlikely to be significant in alkaline solutions if polythionates are also present because they react with sulphide to form thiosulphate and elemental sulphur (7). If sulphide is present, the solution is acidified and the sulphide is removed under vacuum. Samples containing suspended sulphide ore are filtered. Ferrous ion leads to high results but the interference may be eliminated by the addition of soda ash and titrating to pH 4.3 end-point. Sulphite will interfere and it can be overcome by a pretitration with iodine as mentioned previously. Substances which introduce a buffering effect; e.g., acetate, will interfere at pH 4.3. In this case the titrations should be made to pH 8.2 end-point rather than pH 4.3, but this type of interference is unlikely to occur in mill samples.

IODOMETRIC TITRATIONS

Thiosulphate and sulphite can be determined by the classical iodometric methods (7). Two titrations are made: in the absence of formaldehyde to determine the sum of thiosulphate and sulphite and after addition of formaldehyde to mask the sulphite, to determine only the thiosulphate. The sulphite is calculated by difference. Polythionates are not titrated and do not interfere. Sulphide would interfere but it is apparently not present in significant amounts especially if excess sulphite is present. Precautions should be taken to avoid air-oxidation of the sulphite, especially in alkaline solutions, if accurate results are desired.

Kurtenacker and Goldbach devised a procedure for the analysis of polythionates, thiosulphate, sulphite and sulphide in the presence of one another by analyzing five individual aliquots of a solution which is free of elemental sulphur

(8). Since sulphide and sulphite are usually not present together, the procedures are given for a sulphide-free solution. Sulphide, if present, is removed by treatment with zinc carbonate suspension prior to the determination of the other components and can be determined in the precipitate by iodometric titration.

Polythionates do not react with iodine and the sum of sulphite and thiosulphate can be determined in the first aliquot iodometrically. In a second aliquot the sulphite is masked by formaldehyde and the thiosulphate determined iodometrically. Sodium sulphite is added in excess to a third aliquot and the solution is neutralized. The tetra-, penta- and hexathionates react according to:

$$S_xO_6^{2-} + (x-3)\ SO_3^{2-} \rightarrow S_3O_6^{2-} + (x-3)\ S_2O_3^{2-} \qquad \text{Eq 3}$$

The excess sulphite is masked with formaldehyde and the thiosulphate is titrated with standard iodine solution. A fourth aliquot is titrated with iodine solution. The solution is then diluted and treated with potassium cyanide. In this case, the tetra-, penta- and hexathionates react with the cyanide:

$$S_xO_6^{2-} + (x-1)CN^- + H_2O \rightarrow S_2O_3^{2-} + 2HCN + SO_4^{2-} + (x-3)SCN^- \qquad \text{Eq 4}$$

and 1 mole of thiosulphate is formed per mole of polythionate. Trithionate reacts with cyanide only very slowly. The excess of cyanide is masked with formaldehyde and the thiosulphate formed in the above reaction is titrated with iodine solution. From the titration results of the third and fourth aliquots the sum of tetra- and pentathionate can be calculated. A fifth aliquot is required to determine trithionate. This aliquot is boiled with sodium sulphide solution and the excess sulphide is removed with zinc carbonate suspension. The precipitate is filtered off and the thiosulphate in the filtrate is determined iodometrically.

$$S_xO_6^{2-} + S^{2-} \rightarrow 2S_2O_3^{2-} + (x-3)S^\circ \qquad \text{Eq 5}$$

The trithionate reacts in two steps:

$$S_3O_6^{2-} + S^{2-} \rightarrow S_2O_3^{2-} + SO_3^{2-} + S^\circ \qquad \text{Eq 6}$$

$$SO_3^{2-} + S^\circ \rightarrow S_2O_3^{2-} \qquad \text{Eq 7}$$

If the second step does not go to completion, excess iodine is required in the titration because sulphite is titrated rather than thiosulphate. From the results of the five titrations, the amounts of all the components can be calculated. Details of the methods and the necessary calculations are also given by Kolthoff and Belcher (7).

The results are usually said to be high. According to Kolthoff and Belcher the trithionate-sulphide reaction is not exactly stoichiometric because some sulphite is also liberated (7). Moreover, the sodium sulphide used in the determination of trithionate nearly always contains thiosulphate and other sulphur compounds thus leading to positive errors. There are several points to remember in this scheme of analysis as well as other sources of error. In the event an excess of sulphide is present in the original samples, it is unlikely that tetra-, penta- and hexathionate will be present because they react rapidly at room temperature to form thiosulphate and elemental sulphur (as per Eq 5). Trithionate reacts only slowly at room temperature but reacts quantitatively at the boiling point (Eq 6,7). Any elemental sulphur formed will have to be removed. If sulphite is also present several reactions may take place depending on the concentration of the various species and whether the solution is acid or alkaline; e.g., in alkaline solutuon:

$$SO_3^{2-} + S^\circ \rightarrow S_2O_3^{2-} \qquad \text{Eq 8}$$

in acid solution:

$$4H^+ + 2HS^- + 4SO_3^{2-} \rightarrow 3S_2O_3^{2-} + 3H_2O \qquad \text{Eq 9}$$

If a large amount of zinc carbonate suspension is required to remove the sulphide, errors will occur if the solution is merely diluted to a known volume and filtered aliquots taken for analysis because of the volume occupied by the precipitates (9). Further errors can occur if air oxidation of the sulphide in the solution takes place; thus an oxygen-free atmosphere should be used throughout the determination.

For the determination of hexathionate Goehring et al. treated a sixth aliquot with alkali (10). The tetra-, penta- and hexathionate react with diluted alkali at room temperature to give thiosulphate:

$$S_6O_6^{2-} \rightarrow S_5O_6^{2-} + S° \qquad \text{Eq 10}$$

$$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \qquad \text{Eq 11}$$

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad \text{Eq 12}$$

At high alkali concentrations the trithionate also reacts:

$$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \qquad \text{Eq 13}$$

The thiosulphate so formed is titrated iodometrically. Hydrolysis of the elemental sulphur which is formed from the hexathionate takes place and can cause interference; e.g.:

$$4S° + 3H_2O \rightarrow S_2O_3^{2-} + 2H_2S + 2H^+ \qquad \text{Eq 14}$$

This reaction occurs rapidly in alkaline solution.

SPECTROPHOTOMETRIC METHODS

Based on Formation of Thiocyanate

Most spectrophotometric methods for polythionates and thiosulphate have been based on measuring the amount of thiocyanate produced after addition of suitable reagents. The thiocyanate is then determined as its iron(III) complex. In one method Utsumi (11) added solid silver thiocyanate to solutions of thiosulphate and in another he used mercury(II) thiocyanate (12). The equations for the reactions are:

$$mAgSCN + nS_2O_3^{2-} \rightarrow Ag_m(S_2O_3)_n^{(2n-m)} + mSCN^- \qquad \text{Eq 15}$$

and

$$2S_2O_3^{2-} + 3Hg(SCN)_2 + 2H_2O \rightarrow Hg(SCN)_2.2HgS + 4H^+ + 4SCN^- + 2SO_4^{2-} \qquad \text{Eq 16}$$

Note the similarity of Eq 16 to Eq 2 for the acidimetric titration of thiosulphate.

Schoon later investigated the silver thiocyanate method for thiosulphate using silver thiocyanate labelled with ^{110}Ag (13,14). The silver thiocyanate is soluble in the thiosulphate solution and the radioactivity of the solution can be measured. Schoon also utilized the reaction between p-benzoquinone and thiosulphate as the basis for a colorimetric method for thiosulphate in the presence of polythionates and bisulphite (14).

Robinson (15) proposed a method for the determination of tetrathionate that was based on the cyanolysis of the polythionates according to the procedure of Kurtenacker and Goldbach (8), as given by Eq 7 above. The method was modified by Nietzel and DeSesa to improve its sensitivity to determine concentrations of tetrathionate as low as 5 mg/L in the presence of about 30 g/L sulphate (16). These workers found that the colour of the ferric thiocyanate complex rapidly faded when exposed to daylight and they prevented this by developing the colour in black-coated mixing cylinders. The blank absorbance was decreased by employing ferric nitrate and nitric acid rather than ferric chloride and hydrochloric acid in the colour development step.

Subsequently this method was investigated and proposed, with modifications, for the determination of thiosulphate (17,18,19), trithionate (18,19,20) as well as higher polythionates (18,19,21). For the determination of thiosulphate it is necessary to add cupric ion as a catalyst. Advantage is taken of the fact that trithionate reacts only slowly with cyanide at room temperature. Urban, for example, took two aliquots of a trithionate-polythionate solution and cyanolysed one sample for 2 min and the other for 16 h; he then determined the thiocyanate formed colorimetrically in each aliquot (20). From the difference in the amounts of thiocyanate formed, the trithionate was calculated. Kelly et al. used a similar procedure but heated the solution for 45 min to hasten the reaction of the trithionate with cyanide (18). By using this technique and employing cupric sulphate as a catalyst for the thiosulphate reaction, these workers were able to determine the sum of trithionate, thiosulphate and tetrathionate in one aliquot of sample. A second aliquot of sample was cyanolysed at 5°C and at pH 9.65 in the absence of the cupric sulphate catalyst to determine only the tetrathionate. A third aliquot was cyanolysed at 5°C and at pH 7.35 in the presence of the cupric sulphate catalyst to determine the sum of the tetrathionate and thiosulphate. By appropriate calculations the individual amounts of trithionate, thiosulphate and tetrathionate were estimated in mixtures of the compounds.

The results for trithionate appeared to be satisfactory, but the results for tetrathionate were generally high and the results for thiosulphate were correspondingly low. The discrepancy was found only when mixtures were analyzed; for the individual compounds, the recoveries were close to the theoretical values. It was postulated that the error was due to some interaction of the cyanide with a thiosulphate-tetrathionate association complex. If true, other cyanolytic methods for determining thiosulphate and polythionates would be subject to similar errors.

Mizoguchi and Okabe (19) investigated the methods proposed by Kelly et al. (18) and suggested a simpler explanation for the high recoveries of tetrathionate. Unlike Kelly, they found that significant cyanolysis of trithionate and thiosulphate took place under the conditions employed by Kelly for the determination of tetrathionate. By adding acetone to the reaction mixture they were able to depress the cyanolysis of trithionate and thiosulphate to less than 1%. The error due to partial cyanolysis of thiosulphate was eliminated by converting the thiosulphate to thiocyanate in the presence of a cupric catalyst, and the sum of tetrathionate and thiosulphate was therefore determined. These workers also proposed a modified method in which thiosulphate was determined directly instead of by difference as was done by Kelly et al. In their method, Mizoguchi and Okabe cyanolysed the thiosulphate at 20°C or less and at pH 4.5 using a cupric catalyst. By operating at pH 4.5 the cyanolysis of tetrathionate was prevented. Significant cyanolysis of the tetrathionate did not occur unless the pH was greater than 5. The sum of thiosulphate, tetrathionate and trithionate was determined in a third aliquot by a procedure similar to that of Kelly et al. The results of analyses of mixtures of the three compounds agreed with the expected values with a maximum discrepancy of 3%. The behaviour of polythionates higher than tetrathionate was not investigated.

For the determination of ultra-micro amounts of tetra-, penta- and hexathionate Koh, Saito and Iwasaki developed a spectrophotometric method based on cyanolysis and solvent extraction of the resulting thiocyanate as a methylene blue complex (22). This reportedly improved the sensitivity of the method for polythionates by about sixtyfold. The effects of cyanide concentration, pH, temperature and time on the reactions were studied. Formaldehyde was used to mask the excess cyanide which otherwise interfered. Copper(II), sulphide, bromide, iodide, perchlorate and nitrate seriously interfered. Amounts of zinc, manganese, iron and aluminum at 100 ppm and thiosulphate at 1 ppm did not interfere with polythionates at the 10^{-5} to 10^{-7} M level. The procedure, however, does not distinguish between the various species of polythionates if they are present in mixtures. Under carefully controlled conditions the tetrathionate cyanolysis required at least 4.5 h to proceed to completion. The other polythionates required only slightly less. No attempt was made to apply the procedure to industrial-type solutions, effluents, etc.

Based on Formation of Thiosulphate

The cyanolysis reactions of polythionates and thiosulphate mentioned above are the basis of another method for the analysis of mixtures of polythionates, thiosulphate and sulphite. The procedures are analogous to the iodometric titration procedures discussed previously. In this case, Koh and Taniguchi employed a spectrophotometric measurement of the excess of iodine used to determine the thiosulphate equivalent to the polythionates (23). Thiosulphate was determined on aliquots of solution not subjected to cyanolysis and formaldehyde was added to mask any sulphite. The sum of thiosulphate and sulphite was determined on other aliquots in the absence of formaldehyde. Trithionate was not investigated. The method does not distinguish between tetra-, penta- and hexathionates, but by suitable calculations the total polythionates, thiosulphate and sulphite may be estimated.

HIGH-VOLTAGE IONOPHORETIC SEPARATION METHODS

Blasius and Munch described a technique using high-voltage ionophoretic separation of the polythionates $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$ on thinly coated foils (24). The method is said to combine the advantages of both paper and thin-layer ionophoresis for the determination of microgram amounts of these compounds. The separations are carried out in a special temperature controlled chamber developed for high-voltage paper ionophoresis. From the illustrations given in their paper the separations appeared to be clear cut. The apparatus required, however, is complex and was applied only to relatively pure solutions. The behaviour of mine or industrial effluents under similar conditions is unknown and many difficulties can be anticipated.

ANION EXCHANGE LIQUID CHROMATOGRAPHY METHODS

Anion exchange columns have been used for the separation of polythionates, but according to Szekeres the results have not been accurate (25). For example, Pollard and his co-workers used De-Acidite FF, 2% DVB cross-linkage resin to separate thiosulphate, sulphite, trithionate, tetrathionate and pentathionate (26). The various sulphur compounds were dissolved in a solution of 2 M potassium hydrogen phthalate at pH 4 and loaded on to the column of resin. The thiosulphate and sulphite passed through the column together and appeared in the effluent. An intermediate buffered wash solution of sodium acetate-hydrochloric acid at pH 4 was then used to remove the phthalate to avoid precipitation of phthalic acid in the subsequent steps. Successive batch elutions with 3 M, 6 M and 9 M hydrochloric acid separated the trithionate, tetrathionate and pentathionate in that order.

The thiosulphate and sulphite were estimated by the conventional iodine titration method. Sulphite was complexed with formaldehyde and the thiosulphate determined alone. The sum of thiosulphate and sulphite was titrated in the absence of formaldehyde and the sulphite value was obtained by difference. The individual polythionates were determined by titration with potassium iodate solution in the presence of 6 M hydrochloric acid. At the 0.04 mM level the recovery of trithionate, tetrathionate and pentathionate was said to be quantitative within ±2%. The observations with respect to sulphite and thiosulphate appear to be more qualitative than quantitative, and supporting data are lacking. In view of the nature of the separation it is unlikely that the determination of sulphite will be accurate or reproducible because of the likelihood of air oxidation or losses by volatilization. The procedure dealt only with the pure compounds and the practical application of the method has not been investigated.

More recently, methods for the separation of thiosulphate and polythionates by high-speed anion exchange chromatography have been developed by Chapman and Beard (27) and by Wolkoff and Larose (28). The latter applied their method to tailings pond effluents from the mining and milling industry. The detection limit is said to be 0.3 ppm. The procedure of Wolkoff and Larose involves passing a sample through a column of Permaphase AAX exchanger to separate the various species. The polythionates in the column effluent fractions are reacted with sodium hydroxide to produce thiosulphate which is then oxidized with cerium(IV) sulphate. The cerium(III) produced is continuously detected fluorometrically. Since only one species is detected fluorometrically; i.e., cerium(III), the detection system is considerably simplified. Only about 20 to 200 µL of sample is required and the time for a complete analysis is about 20 min. The instrumentation required, however, is complex and expensive.

POLAROGRAPHIC METHODS

Furness investigated the polarographic behaviour of dithionite, trithionate, thiosulphate and sulphide, and estimated their concentrations in commercial dithionite compounds (29). In an electrolyte composed of 0.5 M diammonium hydrogen phosphate plus 1 M ammonium hydroxide the dithionite and trithionate gave waves at half-wave potentials of -0.43 and -1.4 V vs SCE, respectively. The thiosulphate gave an anodic wave at -0.15 V vs SCE in a neutral 0.1 N potassium nitrate solution containing formaldehyde to mask the dithionite. Sulphide was determined in an electrolyte of 0.1 M disodium hydrogen phosphate containing formaldehyde to mask dithionite. The sulphide wave occurred at a half-wave potential of -0.65 V vs SCE. In a later paper, Furness and Davies used an electrolyte of 1.0 M ammonium dihydrogen phosphate at pH 4.0 to determine tetrathionate and trithionate (30).

Zezula studied the polarography of dithionate and trithionate (31), tetrathionate (32), pentathionate and other polythionates (33) and later investigated their behaviour by means of coulometry to establish the nature of the reactions (34). In the earlier work it was found that dithionate was polarographically inactive but trithionate gave useful waves in 0.2 M potassium chloride, 0.2 M barium chloride, and 0.2 M cesium chloride at half-wave potentials of about -1.6, -1.2 and -1.3 V vs SCE, respectively. Tetrathionate gives a wave in a number of supporting electrolytes and is characterized by the appearance of a minimum on the wave. The minimum can be eliminated by the addition of gelatin. The best waves are obtained in electrolytes composed of 0.2 M cesium chloride, 0.01 M lanthanum acetate, and 0.05 M barium chloride at half-wave potentials of -0.3 V vs SCE in each electrolyte. Pentathionate was found to give waves in Britton-Robinson buffer solutions containing 0.2 M sodium. The half-wave potential varied linearly with pH over the range pH 1 to 7. Pentathionate also gives a wave in 0.2 M potassium chloride. Well separated waves were found for trithionate and tetrathionate in an electrolyte of 0.05 M barium chloride at half-wave potentials of -1.2 and -0.3 V vs SCE, respectively. A slight maximum on the tetrathionate wave appeared at a concentration of 5×10^{-4} M, and this became greatly pronounced at 1×10^{-3} M. The trithionate wave was unaffected.

Murayama also reported the polarographic behaviour of trithionate in potassium chloride and barium chloride solutions (35). The polarography of trithionate in potassium iodide, potassium chloride and hydrochloric acid solutions with various additions of ethanol and different buffers was described by Subrahmanya (36). Tetra- and pentathionate were successfully determined in a solution of 50% ethanol and 50% 2 N hydrochloric acid. Trithionate does not give a wave in this medium.

The behaviour of tri-, tetra-, penta- and hexathionates in an electrolyte composed of 0.5% Rochelle salt plus 0.1 M barium chloride with 0.01% gelatin as a maximum suppressor was studied by Cavallaro et al. (37). They found that the compounds gave waves at half-wave potentials of -1.21, -0.15, -0.27 and -0.66 V, respectively. The half-wave potentials of the tetrathionate and pentathionate were too close to permit an estimation of their individual concentrations.

Schmidt and Sand undertook to determine the physical characteristics of tri-, tetra-, penta- and hexathionate by means of cathode-ray and alternating current polarography using 1 N sulphuric acid electrolyte (38). The alternating current technique permitted the determination of the pure polythionates but not their mixtures because of the small difference in their peak potentials. The analysis of mixtures was said to be possible by cathode-ray polarography but only within closely defined limits of concentration. Even so, the half-wave potentials observed in solutions containing mixtures of the polythionates were shifted from those obtained with the individual polythionates. In addition, the half-wave potential depended on the concentration of the polythionate. The analysis was made more difficult because each of the polythionates gave rise to two peaks and the second peak of one compound overlapped or merged with the first of another compound.

Alternating current polarography was also employed by Renard, Kubes and Bolker to determine various sulphur compounds in paper pulping liquors (39). In an acid medium of sodium acetate plus acetic acid buffered to pH 4.7, thiosulphate, sulphide and bisulphite gave polarographic peaks at peak potentials of -0.21, -0.40 and -0.62 V vs the $Ag^+/AgCl$ electrode, respectively. The sulphide wave could not be utilized for its estimation because it was partly driven-off by the nitrogen stream during the deaeration step. The residual sulphide peak did not interfere with either the sulphite or thiosulphate determination. Sulphide and methyl mercaptan were determined in an electrolyte of 0.2 M sodium hydroxide plus 0.3 M potassium chloride. The peak potentials of sulphide and mercaptan were -0.78 and -0.58 V vs the $Ag^+/AgCl$ electrode, respectively.

AQUEOUS CHEMISTRY OF THIOSALTS

The stability, degradation, and formation pathways of polythionates and thiosulphates have been widely investigated. The information found in the literature is presented in the following sections.

DECOMPOSITION OF POLYTHIONATES

Fundamental studies of the stabilities of polythionates in aqueous buffer solutions were reported by Kurtenacker et al. in 1935 (40). From the initial stable products observed, the major reactions proposed for pH > 7 were:

$$S_6O_6^{2-} \rightarrow S_5O_6^{2-} + S° \qquad \text{Eq 17}$$

$$6OH^- + 2S_5O_6^{2-} \rightarrow 5S_2O_3^{2-} + 3H_2O \qquad \text{Eq 18}$$

$$6OH^- + 4S_4O_6^{2-} \rightarrow 2S_3O_6^{2-} + 5S_2O_3^{2-} + 3H_2O \qquad \text{Eq 19}$$

$$6OH^- + 2S_3O_6^{2-} \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \qquad \text{Eq 20}$$

The relative rates of decomposition of $S_xO_6^{2-}$ at a given pH were x = 6 > 5 > 4 > 3. Trithionate is relatively stable under pH conditions where the higher polythionates decompose. Under these conditions, the complete decomposition of the higher polythionates is represented by:

$$6OH^- + 2S_6O_6^{2-} \rightarrow 5S_2O_3^{2-} + 2S° + 3H_2O \qquad \text{Eq 21}$$

$$6OH^- + 2S_5O_6^{2-} \rightarrow 5S_2O_3^{2-} + 3H_2O \qquad \text{Eq 22}$$

$$6OH^- + 4S_4O_6^{2-} \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad \text{Eq 23}$$

Under harsher conditions (pH ≥ 13, boiling) trithionate decomposes. The equations representing the complete decomposition of the polythionates are:

$$6OH^- + 2S_6O_6^{2-} \rightarrow 5S_2O_3^{2-} + 2S° + 3H_2O \qquad \text{Eq 24}$$

$$6OH^- + 2S_xO_6^{2-} \rightarrow (2x-5)S_2O_3^{2-} + (10-2x)SO_3^{2-} + 3H_2O \ (x = 3,4,5) \qquad \text{Eq 25}$$

Other products arise from secondary reactions. For example, in the presence of air, sulphite may be oxidized:

$$SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e \quad (E° = +0.93\ V) \qquad \text{Eq 26}$$

$$4e + 2H_2O + O_2 \rightarrow 4OH^- \quad (E° = +0.40\ V) \qquad \text{Eq 27}$$

$$SO_3^{2-} + 1/2O_2 \rightarrow SO_4^{2-} \quad (E° = +1.33\ V) \qquad \text{Eq 28}$$

Also, elemental sulphur may react with sulphite under alkaline conditions, especially at elevated temperatures (41).

$$SO_3^{2-} + \frac{1}{x}S_x \rightarrow S_2O_3^{2-} \qquad \text{Eq 29}$$

Upon changing the conditions from alkaline to neutral and mildly acidic, there is some evidence for alternative reaction paths to those indicated in the above equations. The results of Kurtenacker et al. suggest that pentathionate may also decompose according to (40):

$$S_5O_6^{2-} \rightarrow S^\circ + S_4O_6^{2-} \qquad \text{Eq 30}$$

Also, reactions whereby polythionates $S_{x+1}O_6^{2-}$ are produced from $S_xO_6^{2-}$ (x = 3 or 4) were detected as the solution pH was lowered.

These authors reported pseudo-first order decay rate constants of the individual polythionates as a function of pH (40). Some comparative data, based on their work are presented in Table 1.

Pollard et al. reported decomposition studies in the neutral to highly acidic range (42). Paper chromatography was employed to obtain qualitative measurements of the decomposition products when 20- to 50-mM solutions of $S_xO_6^{2-}$ in various hydrochloric acid media were permitted to stand at 20°C for 12 h. The acidity ranges, where no appreciable decomposition of solutions of individual polythionates was detected, are shown in Table 2.

Trithionate decomposed only slightly to form elemental sulphur as a product in solutions containing up to 8 M HCl. In 9 M HCl solution, tetrathionate was observed as a product, and in 10 M HCl solution a trace of hexathionate was detected.

After 12 h, tetrathionate decomposition to form elemental sulphur was observed only at acidities in excess of 10 M HCl. Pentathionate decomposed slightly to produce tetrathionate in 0 to 2 M HCl solutions, was stable in 3 to 6 M HCl, produced traces of both tetrathionate and hexathionate in 7 M HCl, and traces of sulphur only at acidities in excess of 7 M HCl.

Mizoguchi et al. reported on the decomposition of trithionate and tetrathionate in the presence of various amounts of sulphuric acid from 70 to 150°C, using sealed ampoules (43). Some data, interpreted from their results are presented in Table 3.

In excess of 70°C, trithionate was quite unstable, even at near neutral pH, decomposing according to:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad \text{Eq 31}$$

In the presence of sulphuric acid (or in unbuffered solutions) the appearance of elemental sulphur, tetrathionate, and sulphite was attributed to secondary reactions of the thiosulphate product that do not occur appreciably in near neutral solutions, even at elevated temperatures.

Tetrathionate was more stable than

Table 1 - Decomposition of polythionates at different pH values

pH	% remaining after t hours															
	t = 1 h				t = 10 h				t = 24 h				t = 48 h			
	S_6	S_5	S_4	S_3	S_6	S_5	S_4	S_3	S_6	S_5	S_4	S_3	S_6	S_5	S_4	S_3
11	0	40	56	96	0	0	0.3	70	0	0	0	42	0	0	0	17
~9 to ~5	96				70				42				17			
~1 to 0	98	100	100	96	79	100	99	70	58	99	98	42	not calc'd			
~ -0.7	99	10	96	0	87	0	70	0	71	0	42	0	50	0	17	0

After Kurtenacker et al. (40).

Conditions

Initial $S_xO_6^{2-}$ concentration = 80 mM
Temp. = 50°C

trithionate under near neutral conditions, and did not decompose appreciably until nearly 150°C. The initial reaction was said to be:

$$4S_4O_6^{2-} + 5H_2O \rightarrow 7S_2O_3^{2-} + 2SO_4^{2-} + 10H^+ \qquad \text{Eq 32}$$

Under more acidic conditions, decomposition of tetrathionate was apparently slower, and this was attributed to the regeneration of tetrathionate by secondary decomposition of thiosulphate that also produced sulphite and elemental sulphur. At these temperatures, trithionate was not observed as a stable intermediate.

Table 2 - Acidity ranges for no decomposition

Polythionate species	Stable range of acidity
$S_3O_6^{2-}$	no added acid to 1.5 M HCl
$S_4O_6^{2-}$	no added acid to 5 M HCl
$S_5O_6^{2-}$	3 to 6 M HCl

After Pollard et al. (42).

Conditions

Test duration = 12 h

Temp. = 20°C

Table 3 - Decomposition in sulphuric acid media

Species	Sulphuric acid concentration mM	pH		Products after 2 h (100 x moles product/moles $S_xO_6^{2-}$ initial)					
		Initial	Final	$S_4O_6^{2-}$	$S_3O_6^{2-}$	$S_2O_3^{2-}$	HSO_3^-	SO_4^{2-}	S°
$S_3O_6^{2-}$	0	7.0 (buffered)	4.8	-	14	96	-	86	-
	0	3.9 (unbuffered)	2.0	17	0	13	41	102	51
	10		1.9	9	0	8	46	113	67
	20		1.9	8	0	5	56	102	77
$S_4O_6^{2-}$	0	7.0 (buffered)	5.0	4	0	165	-	45	-
	0	4.5 (unbuffered)	2.2	59	0	21	21	52	41
	10		2.0	31	0	5	41	93	134
	20		2.0	18	0	0	20	113	185

After Mizoguchi et al. (43).

Conditions

1. $S_3O_6^{2-}$ initial concentration = 19.5 mM, Temp. = 110°C
2. $S_4O_6^{2-}$ initial concentration = 9.7 mM, Temp. = 150°C

THERMAL STABILITY OF POLYTHIONATES

Studies of the decomposition of solutions of polythionates have generally been conducted at elevated temperatures in order to obtain convenient rates (vide supra). Comparison of the studies done at various temperatures, however, makes it clear that the relative amounts of the decomposition products observed in addition to the absolute amounts of each product, change with temperature. This is probably due to the thermal instability of primary products such as trithionate and thiosulphate that makes it difficult to project results from studies at elevated temperatures to room temperature and below. Some comparative data on thermal effects are presented in Table 4.

EFFECTS OF THIOSULPHATE AND/OR SULPHITE ON THE DECOMPOSITION OF POLYTHIONATES

Both thiosulphate and sulphite react with polythionates under various conditions to provide alternative degradation pathways to the hydrolytic reactions already discussed under titrimetric methods. Since thiosulphate and sulphite are produced as products of the hydrolysis of polythionates, both pathways are related.

Thiosulphate catalyzes the decomposition of $S_xO_6^{2-}$, $x \geq 5$ under alkaline to mildly acidic conditions, to form lower polythionates and elemental sulphur. Under moderate to highly acidic conditions, thiosulphate reacts with penta-, hexa- and higher polythionates to produce polythionates $S_{x+1}O_6^{2-}$. The effect of thiosulphate on tetrathionate and trithionate decomposition is evidently slight. Some data related to these effects are shown in Table 5.

Sulphite ion accelerates the decomposition of $S_xO_6^{2-}$, $x \geq 4$, in alkaline to mildly acidic solutions. The products are trithionate, thiosulphate and protons. Trithionate is not degraded by sulphite under normal conditions. The stoichiometric equation for the degradation in the presence of excess sulphite when the reaction is spontaneous and quantitative is (44):

$$S_xO_6^{2-} + (x-3)HSO_3^{-} \rightarrow S_3O_6^{2-} + (x-3)S_2O_3^{2-} + (x-3)H^{+},\ x \geq 4 \qquad \text{Eq 33}$$

Table 4 - Effect of temperature on polythionate decomposition

					Products as 100 x moles/moles $S_xO_6^{2-}$ initial								
Thiosalt species	pH	Temp. °C	Conc. mM	Time h	S_6	S_5	S_4	S_3	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}	S°	Ref.
$S_5O_6^{2-}$	11.9	50	79	0.5	0	3	13	13	179	0	0	40	-
	-	20	25	1	0	13	24	4	143	0	0	34	40
	8.9	50	79	17	0	0	49	12	18	0	10	92	-
	-	20	26	5	0	100	0	0	0	0	-	-	-
$S_6O_6^{2-}$	8.9	50	66	1	0	53	44	4	5	0	0	155	-
	-	20	26	1.4	66	37	0	0	0	0	0	tr.	40
$S_4O_6^{2-}$	5	150	10	1	-	-	4	0	165	-	45	-	-
	2.2	150	9.7	2	-	-	59	0	21	21	52	41	43
	4.5	130	10	4	-	-	98	-	-	-	-	-	-
	5	20	30	12	-	-	100	-	-	-	-	-	42
$S_3O_6^{2-}$	2.1	110	19.5	2	-	-	17	0	13	41	102	51	-
	4.8	90	14	3	-	-	0	14	96	-	86	-	43
	2.1	70	13	3	-	-	2	53	22	-	-	-	-
	-	20	20	12	-	-	-	100	-	-	-	-	42

Under acidic conditions, the sulphite degradation reactions take place to a lesser extent, and has been attributed to effective removal of the sulphite ion by protonation; i.e., (45):

$$2H^+ + SO_3^{2-} \rightleftarrows H^+ + HSO_3^- \rightleftarrows (H_2SO_3) \rightarrow SO_2.H_2O \qquad \text{Eq 34}$$

Addition of formaldehyde causes similar effects under milder conditions of acidity because of the removal of sulphite as hydroxymethane sulphonate (45).

$$HSO_3^- + HCHO \rightarrow HOCH_2SO_3^- \qquad \text{Eq 35}$$

In acidic solution, however, complexation of sulphite does not enhance the stability of polythionates since reactions causing formation of higher polythionates are then favoured (42).

CHEMICAL MECHANISMS OF POLYTHIONATE DECOMPOSITION

Polythionates degrade either by hydrolysis, whereby water, protons or hydroxide ions are the attacking agents, or by alternative nucleophilic degradation whereby sulphite, thiosulphate or other nucleophilic species are the attacking agents, or by a combination of both. Dissolved oxygen appears to be involved in converting the initial products, thiosulphate and sulphite, to sulphate. Since the pathways of degradation are important in predicting the products which may be obtained under various conditions, some studies of the degradation mechanism are reviewed here.

Much of the behaviour of polythionates in the presence of sulphite and thiosulphate has been explained in terms of the equilibrium:

$$S_xO_6^{2-} + S_2O_3^{2-} \rightleftarrows S_{x+1}O_6^{2-} + SO_3^{2-} \qquad \text{Eq 36}$$

The equilibrium lies far to the left unless the reaction is driven by product removal (45). For

Table 5 - Effect of thiosulphate on polythionate decomposition

Thiosalt species	Conc. mM	pH or (M HCL)	Temp. °C	$S_2O_3^{2-}$ Conc. mM	Time h	Products, as 100 x moles/moles $S_xO_6^{2-}$ initial								Ref.
						S_6	S_5	S_4	S_3	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}	S°	
$S_6O_6^{2-}$	26.4	8.9	20	0	1.4	66	37	-	-	-	-	-	?	-
	-	-	-	33.6	1.4	0	44	50	10	2	-	-	166	-
	-	-	-	67.3	1.4	0	38	55	11	2	-	-	175	-
$S_5O_6^{2-}$	26	8.9	25	0	5.25	0	100	-	-	-	-	-	tr.	-
	-	-	-	1.96	5.07	0	59	37	4	1	-	-	33	40
	-	-	-	3.92	5.0	0	48	47	2	1	-	-	41	-
$S_6O_6^{2-}$	2.4	4.6	50	0	1.15	2.9	97	-	-	-	-	-	tr.	-
$S_5O_6^{2-}$	79.9	-	-	9.7	1.15	0	37	59	5	1	-	-	67	-
							(Amounts following are qualitative)							
$S_5O_6^{2-}$	~40	(0 to ~5)	20	0	12	-	x	tr.	-	-	-	-	-	-
	-	-	-	3.3	12	-	x	x	-	-	-	-	x	-
$S_5O_6^{2-}$	~20	(1.2 to 6.0)	20	0	12	tr.	x	tr.	-	-	-	-	-	-
	-	-	-	3.3	12	x	x	-	-	-	-	-	-	-
$S_4O_6^{2-}$	47	(0 to 7.9)	20	0	12	-	-	x	-	-	-	-	-	42
	-	(0.25 to 7.4)	-	3.3	12	-	-	x	-	-	-	-	-	-
$S_3O_6^{2-}$	~30	(0 to 1.5)	20	0	12	-	-	-	x	-	-	-	-	-
	-	-	-	3.3	12	-	-	-	x	-	-	-	-	-
$S_3O_6^{2-}$	~25	(1.5 to 8)	20	0	12	-	-	-	x	-	-	-	tr.	-
	-	(1.5 to 7)	-	3.3	12	-	-	-	x	-	-	-	x	-

example, the degradation by excess sulphite in alkaline solution (44), the acidic decomposition of bisulphite involving intermediate polythionates (46), the formation of higher polythionates in acidic solution in the presence of thiosulphate and/or in the presence of conditions for complexing sulphite (42), the disproportionation of tetrathionate under neutral to acidic conditions (47), and the formation of sulphur in the decomposition of higher polythionates (47), have been theorized to involve this equilibrium.

The above equilibrium as an actual mechanistic step in the degradation pathway has been criticized since it suggests attack of the terminal α sulphur atom of the polythionate (44). Experiments using radioactive labelled sulphite show, instead, that the β sulphur atom is attacked in the sulphite degradation of tetrathionate (44):

$$S_4O_6^{2-} + H\overset{*}{S}O_3^- \rightarrow {}^-O_3SS\overset{*}{S}O_3 + S_2O_3^{2-} + H^+ \qquad \text{Eq 37}$$

Schmidt and Siebert have reviewed an alternative theory, consistent with bonding theory for the polythionates, the labelling experiments, and the product stoichiometry when $S_xO_6^{2-}$ $x \geq 4$ is degraded in the presence of excess nucleophiles such as sulphite, sulphide, arsenite and cyanide ions (44). The β sulphur atom is said to be the most electrophilic and is attacked by the nucleophile, producing a sulphane monosulphonate fragment:

$$H^+ + Y^- + {}^-O_3SS\ S_xSO_3^- \rightarrow {}^-O_3SSY + HSS_{x-1}SO_3^- \qquad \text{Eq 38}$$

The sulphane monosulphonates are extremely reactive at the α (sulphydryl) site. In the presence of excess Y^-, they degrade rapidly via the lower sulphane monosulphonates to stable products:

$$Y^- + HSS_{x-1}SO_3^- \rightarrow YS^- + HS_{x-1}SO_3^- \qquad \text{Eq 39}$$

In the absence of excess Y^-, the sulphane monosulphonates react rapidly with other reagents; e.g., with oxidizing agents to form the corresponding polythionates, or by condensation to form polythionates, elemental sulphur and sulphide (42).

$$HSS_xSO_3^- \rightleftarrows {}^-SS_xSO_3H \qquad \text{Eq 40}$$

$$\begin{aligned} {}^-SS_xSO_3H + HSS_ySO_3^- &\rightarrow HO_3SS_xS_ySO_3^- \\ &+ HS^- + S° \qquad \text{Eq 41} \end{aligned}$$

The sulphide produced is then available as a degradation nucleophile.

This theory successfully predicts the observed facts in a number of cases. For example, with excess sulphite as Y^-, trithionate is produced as one product in the degradation of $S_xO_6^{2-}$ and the initial sulphane monosulphonate fragment becomes thiosulphate. With excess sulphide as Y^-, only thiosulphate is produced from the two initial sulphane monosulphonate fragments. Bonding concepts predict that the order of reactivity towards nucleophiles is $x = 6 > 5 > 4 > 3$. Trithionate, for example, requires an elevated temperature to be degraded by sulphite, sulphide or cyanide.

Sulphane monosulphonic acids are also implicated as intermediates in the sulphite degradation of elemental sulphur (48):

$$H_2O + S_x + SO_3^{2-} \rightarrow HS_xSO_3^- + OH^- \qquad \text{Eq 42}$$

$$\begin{aligned} HS_xSO_3^- + SO_3^{2-} &\rightarrow S_2O_3^{2-} + HS_{x-1}SO_3^{2-} \\ &\rightarrow S_2O_3^{2-}, \qquad \text{Eq 43} \end{aligned}$$

and in the reverse reaction involving the thiosulphate catalyzed degradation of $S_xO_6^{2-}$ ($x \geq 5$) to lower polythionates and elemental sulphur (47):

$$S_5O_6^{2-} + S_2O_3^{2-} \rightleftarrows S_4O_3^{2-} + SS_2O_3^- \qquad \text{Eq 44}$$

$$2\ ({}^-SS_2O_3) \rightarrow {}^-SS_3O_3^- + S_2O_3^{2-} \qquad \text{Eq 45}$$

$${}^-SS_7S_2O_3^- \rightarrow S_8 + S_2O_3^{2-} \qquad \text{Eq 46}$$

That thiosulphate and sulphite catalyze the degradation of polythionates makes it difficult to predict either the stabilities (i.e., decomposition rates) of mixtures of aqueous solutions of polythionates or the stoichiometries of overall reactions, e.g., prediction of potential acidity of mixtures of polythionates when decomposed, vide intra. Furthermore, pure salts of polythionates often contain sulphite and/or thiosulphate impurities; consequently, studies of the decomposition of aqueous solutions of these salts are actually studies of decompositions in the presence of certain amounts of catalysts (44).

The nature of the reaction pathways is also difficult to predict a priori because; e.g., water or hydroxide ions may function as degrading nucleophiles directly. This would appear to be the case in the decomposition of aqueous trithionate under approximately neutral to mildly alkaline conditions (49). When thiosulphate was present, an alternative reaction path was available, but this took place at considerably slower rates than the direct hydrolysis even when moderate amounts of thiosulphate were present.

The mechanisms for the decomposition of thiosulphate and polythionates under neutral to acidic conditions are relevant since these conditions pertain to effluents discharged to receiving waters.

Under neutral to mildly acidic conditions, the stoichiometric equations for hydrolysis of polythionates under alkaline conditions may be rewritten as:

$$3H_2O + 2S_6O_6^{2-} \rightarrow 5S_2O_3^{2-} + 2S^\circ + 6H^+ \qquad \text{Eq 47}$$

$$3H_2O + 2S_xO_6^{2-} \rightarrow (2x-5)S_2O_3^{2-} + (10-2x)HSO_3^{2-} + (2x-4)H^+ \qquad \text{Eq 48}$$

suggesting that acid, thiosulphate, elemental sulphur and sulphite are produced. Both sulphite and thiosulphate are subject to further degradation.

Pollard et al. have reviewed the general features of the decomposition of thiosulphate when alkaline solutions are neutralized with mineral acid, and have made the following conclusions (42):

(a) the actual products found are dependent on the conditions; e.g., acidity, original thiosulphate concentration, dilution factor, rate of mixing and temperature;

(b) in dilute acid, the major products are normally elemental sulphur and dissolved sulphur dioxide;

(c) at medium acidities, formation of sulphur oils (containing sulphanes) is also observed;

(d) polythionates may form to some extent at higher acidities.

Under mildly acidic conditions, the gross stoichiometry of the decomposition of thiosulphate has been said to proceed via sulphite (50,51):

$$H^+ + S_2O_3^{2-} \rightarrow S^\circ + HSO_3^- \text{ (slow)} \qquad \text{Eq 49}$$

$$HSO_3^- + 1/2O_2 \rightarrow SO_4^{2-} + H^+ \text{ (measurable)} \qquad \text{Eq 50}$$

$$S_2O_3^{2-} + 1/2O_2 \rightarrow S^\circ + SO_4^{2-} \text{ (slow)} \qquad \text{Eq 51}$$

This would suggest that thiosulphate decomposition is catalyzed by acid, but that acid is not produced or consumed in the reaction.

In contrast, a study by Levenson and Rumens suggests that decomposition of bisulphite proceeds according to the stoichiometry (52):

$$4HSO_3^- \rightarrow 2SO_4^{2-} + S_2O_3^{2-} + 2H^+ + H_2O \quad (60^\circ C,\ pH\ 4) \qquad \text{Eq 52}$$

If the initial reaction of thiosulphate is the production of bisulphite and elemental sulphur (as suggested by Kolthoff and Sandell immediately above), the net stoichiometry of the acid decomposition of thiosulphate by this pathway would be:

$$2H^+ + 3S_2O_3^{2-} \rightarrow 4S^\circ + 2SO_4^{2-} + H_2O \qquad \text{Eq 53}$$

This pathway could conceivably be followed in the presence of excess bisulphite and suggests that the decomposition of thiosulphate could occur with the consumption of acid.

Battaglia and Miller also studied the decomposition of bisulphite, and observed the intermediate formation of trithionate, stoichiometrically (46):

$$4HSO_3^{-} + S_2O_3^{2-} + 2H^+ \rightarrow 2S_3O_6^{2-} + 3H_2O$$
(70°C, pH 3.6-4.1) Eq 54

This corresponds to the reverse of the usual equation for the alkaline hydrolysis of trithionate given earlier under titrimetric methods. The acid hydrolysis of the trithionate produced was slow and was not observed until late in the reaction profile. To be consistent with the results of Levenson and Rumens, hydrolysis of trithionate must proceed according to the stoichiometry:

$$H_2O + S_3O_6^{2-} \rightarrow S_2O_3^{2-} + 2H^+ + SO_4^{2-} \quad \text{Eq 55}$$

Sulphur precipitation was not observed until bisulphite was completely consumed, presumably when thiosulphate decomposition occurred. Mizoguchi et al. studied the decomposition of trithionate and agree with the stoichiometry represented by the above equation (43).

The decomposition of thiosulphate in mild to moderately acidic media was studied from 70 to 150°C by using sealed ampoules (43). In the absence of added acid, thiosulphate decomposition was extremely slow even at 150°C. At pH 1 to 2, however, thiosulphate decomposed rapidly even at 70°C. Alternative reaction pathways were proposed depending on the acidity and temperature conditions:

(1) At low acidities, 70 to 130°C:

$$S_2O_3^{2-} + H^+ \rightarrow S° + HSO_3^{-} \quad \text{Eq 56}$$

and partly:

$$HSO_3^{-} + 1/2O_2 \rightarrow H^+ + SO_4^{2-} \quad \text{Eq 57}$$

(2) At low acidities, and to a considerable extent at higher acidities (pH 1 to 2), 70 to 150°C:

$$5S_2O_3^{2-} + 6H^+ \rightarrow 2S° + 2S_4O_6^{2-} + 3H_2O \quad \text{Eq 58}$$

The tetrathionate so formed does not decompose appreciably under these conditions unless the temperature exceeds 130°C when the reaction is:

$$4S_4O_6^{2-} + 5H_2O \rightarrow 7S_2O_3^{2-} + 2SO_4^{2-} + 10H^+ \quad \text{Eq 59}$$

In this case, the stoichiometry for the decomposition of thiosulphate via intermediate formation of tetrathionate is:

$$2S_2O_3^{2-} + 2H^+ \rightarrow 2SO_4^{2-} + H_2O \quad \text{Eq 60}$$

(3) The decomposition of sulphite/thiosulphate solutions (50 and 21 mM, respectively) was studied at 150°C in the presence of 0 to 40 mM sulphuric acid. In the presence of 0 to 20 mM acid, corresponding to a final pH of 8 to about 5, no decomposition was observed after 2 h. At higher acidities; e.g., final pH of about 4 to 2, sulphite decomposed to thiosulphate with the thiosulphate then decomposing in accordance with (2) above.

Thiosulphate may also be oxidized to form tetrathionate under milder conditions than those of (2) in the presence of catalysts; e.g., cupric ion (50):

$$2S_2O_3^{2-} + 2Cu^{2+} \rightarrow S_4O_6^{2-} + 2Cu^+ \text{ (fast)} \quad \text{Eq 61}$$

$$2Cu^+ + 1/2O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O \text{ (measurable)} \quad \text{Eq 62}$$

$$\overline{2S_2O_3^{2-} + 2H^+ + 1/2O_2 \rightarrow S_4O_6^{2-} + H_2O} \quad \text{Eq 63}$$

Tetrathionate may then decompose according to a variety of pathways outlined above, leading to the following stoichiometry for the total oxidation of thiosulphate via the tetrathionate pathway:

$$S_2O_3^{2-} + H_2O + 2O_2 \rightarrow 2SO_4^{2-} + 2H^+ \quad \text{Eq 64}$$

In summary, various chemical pathways exist for the total oxidation of polythionates and thiosulphate under mild to moderately acidic conditions corresponding to pH 7 to about 1. Since the product stoichiometries depend on the pathway, and the major pathways are determined by such factors as availability of reagents, presence of catalysts, acidity and temperature, a priori predictions are difficult. It is interesting to note that for those chemical pathways which result in elemental sulphur as a product, acid is either consumed or employed catalytically and is not produced. In contrast, for those pathways which involve intermediate formation of polythionates, followed by oxidation to sulphate, acid is produced. At normal temperatures in the absence of catalysts or strong oxidants, the oxidation of thiosulphate, trithionate, and tetrathionate to produce acid would be extremely slow. The rapid oxidation of thiosalts in river systems must, therefore, be due to the presence of biological and/or chemical catalysts.

MICROBIAL DEGRADATION OF THIOSALTS

Various thiobacteria are capable of rapidly oxidizing polythionates and/or thiosulphate to produce sulphuric acid under relatively mild conditions of pH and temperature. Some of the overall aerobic oxidation reactions accomplished by thiobacilli are (53):

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \qquad \text{Eq 65}$$

$$S_3O_6^{2-} + 2O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ \qquad \text{Eq 66}$$

$$S_4O_6^{2-} + \frac{7}{2}\,O_2 + 3H_2O \rightarrow 4SO_4^{2-} + 6H^+ \qquad \text{Eq 67}$$

$$2S^\circ + 3O_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ \qquad \text{Eq 68}$$

These reactions have the same stoichiometries as those of the various chemical oxidation pathways discussed above.

Thiosulphate may also be oxidized to tetrathionate either by side reactions or as part of the total microbial oxidation pathway. For example, with Thiobacillus neapolitanus (and in the presence of thiol binding reagents which inhibit the oxidation of polythionates), the stoichiometry is (53):

$$4S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 4OH^- + 2S_4O_6^{2-} \qquad \text{Eq 69}$$

Certain thiobacteria are also capable of degrading polythionates under anaerobic conditions. Thiobacillus ferrooxidans and T. neapolitanus, for example, produce 1 mole thiosulphate per mole of tetrathionate degraded; the reaction for T. neapolitanus is proposed as (53):

$$S_4O_6^{2-} + OH^- \rightarrow S_2O_3^{2-} + S^\circ + HSO_4 \qquad \text{Eq 70}$$

The degradation of trithionate by T. neapolitanus under aerobic or anaerobic conditions proceeds rapidly in contrast to the highly inert nature of trithionate attack by normal chemical reagents (53).

Various species of thiobacilli differ widely in their reactivity. For example, Kelley and Tuovinen have compared T. ferrooxidans, T. neapolitanus and T. A2 (53). T. A2 does not oxidize or produce polythionates in its metabolic pathways, but rapidly oxidizes thiosulphate. T. neapolitanus will oxidize both polythionates and thiosulphate (the latter at a faster rate), whereas T. ferrooxidans oxidizes polythionates at a faster rate than thiosulphate.

The thiobacilli also differ with respect to the optimum pH required for thiosalt degradation. T. ferrooxidans requires pH 1 to 4, whereas T. neapolitanus functions best near neutral pH, and T. A2 functions under slightly alkaline conditions (53). The action of thiobacteria is apparently drastically inhibited at pH greater than about 9, suggesting that degradation of thiosalts under alkaline conditions must proceed by the chemical mechanisms discussed previously and, therefore, at a much slower rate (51). Furthermore, the presence of thiol binding agents such as mercuric chloride can inhibit the bacterial degradation even under optimum pH conditions (53).

OXIDATION OF THIOSALTS BY CHEMICAL REAGENTS

A variety of chemical reagents are capable of rapidly oxidizing thiosulphate and/or polythionates to sulphate. Under neutral to acidic conditions, iodine (moderately strong oxidant) oxidizes only thiosulphate, and this to tetrathionate (54):

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \qquad \text{Eq 71}$$

In moderately alkaline solutions partial oxidation to sulphate occurs as well and is attributed to the presence of the hypoiodate ion (54):

$$I_2 + 2OH^- \rightarrow [IO^-] + I^- + H_2O \qquad \text{Eq 72}$$

$$S_2O_3^{2-} + 4[IO^-] + 2OH^- \rightarrow 2SO_4^{2-} + 4I^- + H_2O \qquad \text{Eq 73}$$

Potassium permanganate, potassium dichromate, and ceric sulphate are said to oxidize thiosulphate only partly to sulphate (54). Nevertheless, oxidation of thiosulphate by ceric sulphate has been employed in an analytical method with apparent success (28). The stoichiometry given is:

$$S_2O_3^{2-} + 8Ce^{4+} + 5H_2O \rightarrow 2SO_4^{2-} + 8Ce^{3+} + 10H^+ \qquad \text{Eq 74}$$

Stronger oxidants such as bromine, hypochlorite, chlorine and hydrogen peroxide can totally oxidize thiosulphate; e.g., (54):

$$S_2O_3^{2-} + 4Cl_2 + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8Cl^- \qquad \text{Eq 75}$$

$$S_2O_3^{2-} + 4H_2O_2 + 2OH^- \rightarrow 5H_2O + 2SO_4^{2-} \qquad \text{Eq 76}$$

Recently, a comparative study of the oxidation of thiosulphate by hydrogen peroxide and hypochlorite ion has been reported (55). With hydrogen peroxide, a system of competitive reactions was observed:

$$2S_2O_3^{2-} + H_2O_2 \rightarrow S_4O_6^{2-} + 2OH^- \qquad \text{Eq 77}$$

$$3S_2O_3^{2-} + 4H_2O_2 \rightarrow 2S_3O_6^{2-} + 2OH^- + 3H_2O \qquad \text{Eq 78}$$

$$S_2O_3^{2-} + 4H_2O_2 \rightarrow 2SO_4^{2-} + 2H^+ + 3H_2O \qquad \text{Eq 79}$$

$$S_4O_6^{2-} + 7H_2O_2 \rightarrow 4SO_4^{2-} + 6H^+ + 4H_2O \qquad \text{Eq 80}$$

$$S_3O_6^{2-} + 4H_2O_2 \rightarrow 3SO_4^{2-} + 4H^+ + 2H_2O \qquad \text{Eq 81}$$

At pH 4, reactions in Eq 79-81 were very slow, and only Eq 77 and 78 were observed. If Fe^{2+} was present, however, the direct oxidation reaction (Eq 79) was said to occur at pH $\geq$ 4; reactions in Eq 80 and 81 were also observed.

On the other hand, when hypochlorite was used as the oxidant, oxidation to sulphate was quantitative at all pH values observed:

$$S_2O_3^{2-} + 4ClO^- + H_2O \rightarrow 2SO_4^{2-} + 4Cl^- + 2H^+ \qquad \text{Eq 82}$$

FORMATION OF POLYTHIONATES

The circuits employed for the processing and concentration of sulphide ores often require alkaline conditions throughout (56,57). This would appear to include the various wet grinding stages of the processes (57). Although pathways for the formation of polythionates under acidic conditions are quite well worked out, those under alkaline conditions (where polythionate degradation is evidently favoured, vide supra) are perhaps less obvious. Based on the chemistry of thiosalts, the following modes of thiosalt production are possible in milling operations.

Grinding stages in sulphide ore processing appear to be significant contributors to thiosalt formation (58). Grinding of sulphide minerals can lead to sulphur dioxide production; e.g., in pyrite, marcasite, and pyrrhotite (59). In solution under alkaline conditions, sulphur dioxide exists as bisulphite (mildly alkaline conditions) or sulphite (moderate to strongly alkaline conditions). If elemental sulphur is present, reaction with sulphite can occur, particularly at elevated temperatures. Given favourable conditions; i.e., time, temperature and alkalinity, the reaction is complete to thiosulphate (41):

$$SO_3^{2-} + \frac{1}{x} S_x \rightarrow S_2O_3^{2-} \qquad \text{Eq 83}$$

This reaction, however, proceeds in stepwise fashion via sulphane monosulphonates (48). If insufficient excess sulphite is available, the sulphane monosulphonates can either oxidize or condense to form polythionates (vide supra). These would then proceed to degrade to lower polythionates, sulphur, sulphite and thiosulphate under alkaline conditions. Sulphide ion also reacts with sulphite to produce thiosulphate. These pathways of formation of thiosalts do not necessarily require molecular oxygen, and are, therefore, consistent with the observation that when flotation circuits are operated under a nitrogen atmosphere, thiosalt formation is not totally inhibited (56).

Sulphur dioxide in grinding circuits (i.e. sulphite in alkaline solution) would act as an oxygen scavenger and might be expected to inhibit oxidation reactions which occur as a result of the presence of molecular oxygen. Since sulphite also degrades higher polythionates and acts as a reagent for the production of thiosulphate in the presence of sulphide ores, it might be expected that the thiosulphate to polythionate ratio would increase under these conditions. The total thiosalt production on the other hand would not be reduced, and may in fact increase.

Molecular oxygen may contribute to thiosalt production by the oxidation of inorganic polysulphides and elemental sulphur; e.g., (41):

$$Na_2S_5 + \frac{3}{2} O_2 \rightarrow Na_2S_2O_3 + \frac{3}{x} S_x \qquad \text{Eq 84}$$

$$CaS_2 + \frac{3}{2} O_2 \rightarrow CaS_2O_3 \qquad \text{Eq 85}$$

Grinding in the presence of oxygen may therefore produce thiosulphate, and precursors of polythionates, elemental sulphur and sulphite.

PART TWO

CANMET THIOSALT PROGRAM STUDIES

CANMET THIOSALT PROGRAM CONCLUSIONS

During the CANMET thiosalt program, studies were carried out both by CANMET and outside contractors to define analytical methods, paths of thiosalt generation during milling, and thiosalt treatment techniques. Major findings are summarized below.

ANALYTICAL

Thiosalt-containing effluents were found to be somewhat unstable at ambient temperatures. Total thiosalt levels decreased by 7 to 15% within a 5-week period, though significantly higher changes occurred in individual species. Tests carried out by CANMET indicated that freezing offered the best means of sample preservation. Colorimetric analytical methods for thiosulphate, trithionate and tetrathionate in mill effluents were defined. Several other techniques were also investigated, including titrimetric methods using EDTA and excess barium. Since the available methods are limited to concentrations above 50 mg/L, techniques to determine micromole levels of thiosalts were evaluated; however, these were found to be subject to large uncertainties.

Infrared (IR) and ultraviolet (UV) thiosalt spectra were measured. Simultaneously, the crystal structures of trithionate and tetrathionate were studied. In all cases, complexities arose which militate against these techniques for the routine determination of thiosalts in milling effluents.

GENERATION OF THIOSALTS IN MILLING CIRCUITS

Both in-mill and laboratory studies were conducted to evaluate the factors related to the generation of thiosalts during milling. The amount of thiosalts produced was found to be related mainly to:

(1) pH of the operation and the alkalinity reagent;

(2) sulphide content of the ore;

(3) residence time during flotation;

(4) temperature.

Mass-balances were conducted at two mills to define the thiosalt production during various unit operations.

THIOSALT TREATMENT METHODS

A large number of thiosalt treatment techniques was evaluated technically and economically as part of the CANMET program as follows:

- Chemical oxidation (including H_2O_2, Cl_2, O_3).
- Membrane and electrochemical processes (reverse osmosis, electrodialysis and electro-oxidation).
- Air oxidation (alkaline oxidation, Cu-catalyzed air oxidation, SO_2-air oxidation).
- Biological oxidation (biological contactor, Noranda packed ponds).
- Other (reduction by metals, disposal to the sea).

Although most of these methods were evaluated in bench-scale tests or in preliminary studies, pilot-scale on-site tests were conducted to determine the feasibility of biological oxidation. Estimates of the operating and capital costs were provided for most of the methods considered; these costs should be considered with great caution, however, due to the very preliminary nature of the studies.

PREPARATION OF POLYTHIONATE REAGENTS

Polythionate compounds are generally not commercially available. Methods for the preparation of trithionates and tetrathionates for use in the thiosalt studies were described by Hitchen (60). A literature search indicated other methods for the preparation of pentathionates and hexathionates (61). These methods are presented in Appendix 1.

STABILITY AND PRESERVATION OF THIOSALT SAMPLES

The decomposition of thiosalts during storage was studied by Hitchen (62,63) both at ambient temperatures, and with frozen samples.

Initially, solutions of S_2O_3, S_3O_6, S_4O_6, and Na_2SO_4 were prepared and the pH adjusted to

10, 7, and 4 (after 4 weeks, a fourth sample of pH 3 was added). The solutions were then deaerated with nitrogen and the sample bottles stored in the dark. The samples were analyzed weekly. The results, presented in Table 6, indicate the following:

- Significant changes occurred in the pH of the solutions with an initial pH of 10 and 7.
- Changes in individual thiosalt levels occurred in all samples. Total thiosalts, however, decreased by only 7-15% during the 5-week period.
- During the storage period, turbidity gradually appeared. This was subsequently attributed to elemental sulphur formation.

Subsequently, additional tests were initiated, and the thiosalt solutions were frozen. Each week, samples were thawed and analyzed. The results, presented in Table 7, indicate the following:

Table 6 - Thiosalt stability at ambient temperature

	April 25 Start	May 2	May 9	May 13 Start	May 19	May 24	May 31
Solution No. 1							
pH	-	-	-	3.00	3.00	2.90	2.80
SO_3	-	-	-	-	0.52	0.69	0.76
S_2O_3	-	-	-	4.77	4.42	4.43	4.13
S_3O_6	-	-	-	1.95	1.32	0.74	0.64
S_4O_6	-	-	-	0.69	1.01	1.12	1.30
Total thiosalts	-	-	-	7.41	6.75	6.29	6.07
Solution No. 2							
pH	4.00	3.40	2.95	-	2.90	2.90	2.90
SO_3	-	-	<0.01	-	0.75	0.73	0.74
S_2O_3	4.83	4.83	5.05	-	4.89	4.89	4.71
S_3O_6	1.67	1.67	0.98	-	0.34	0.40	0.17
S_4O_6	0.75	0.72	0.78	-	1.12	1.12	1.27
Total thiosalts	7.25	7.22	6.81	-	6.35	6.91	6.15
Solution No. 3							
pH	7.00	3.45	3.00	-	2.90	2.90	2.90
SO_3	-	-	0.10	-	0.82	0.72	0.64
S_2O_3	4.71	4.83	5.17	-	5.00	5.00	4.83
S_3O_6	1.61	1.09	0.69	-	0.28	0.28	0.51
S_4O_6	0.78	0.98	0.92	-	1.07	1.18	1.27
Total thiosalts	7.10	6.90	6.78	-	6.35	6.46	6.61
Solution No. 4							
pH	10.25	3.50	3.00	-	2.90	2.90	2.90
SO_3	-	-	0.19	-	0.82	0.77	0.65
S_2O_3	4.83	4.94	5.23	-	5.11	5.11	4.83
S_3O_6	1.78	1.15	0.63	-	0.46	0.46	0.40
S_4O_6	0.75	0.92	0.89	-	1.04	1.10	1.12
Total thiosalts	7.36	7.01	6.75	-	6.61	6.67	6.35

All results except pH values are expressed in millimoles per litre.

Total thiosalt results are the summation of individual species.

- Freezing stabilized the thiosalt solutions. Total thiosalts decreased by 1-10% during the 5-week period.
- Changes in pH still occurred, but were not as great as in the previous tests. No attempt was made to determine whether the changes occurred in the frozen state or during thawing.

Based on the above tests, it was concluded that freezing would be the best technique for sample preservation although relatively small changes still occurred in the total thiosalt levels of the solutions.

ANALYTICAL METHODS

THIOSALTS

A number of CANMET workers investigated thiosalt analytical techniques during the program. Makhija and Hitchen (64) compared the Noranda titrimetric method (6) with a colorimetric tech-

Table 7 - Thiosalt stability after freezing

	June 9	June 10	June 15	June 16	June 24	June 29	July 7	July 13
Solution No. 1								
pH	-	3.0	-	3.6	3.85	3.9	3.95	4.3
SO_3	-	-	-	0.39	0.15	0.15	0.15	0.08
S_2O_3	-	4.89	-	3.28	3.16	3.16	3.22	3.22
S_3O_6	-	1.50	-	1.61	1.84	1.95	1.96	2.07
S_4O_6	-	0.71	-	1.47	1.43	1.26	1.06	1.06
Total thiosalts	-	7.10	-	6.37	6.43	6.37	6.24	6.35
Solution No. 2								
pH	-	4.0	-	4.7	4.7	4.7	4.85	4.85
SO_3	-	-	-	0.07	0.05	0.04	0.04	0.04
S_2O_3	-	4.89	-	4.25	4.48	4.60	4.60	4.42
S_3O_6	-	1.82	-	1.79	1.78	1.78	1.72	1.84
S_4O_6	-	0.61	-	1.01	0.99	0.74	0.69	0.80
Total thiosalts	-	7.32	-	7.05	7.25	7.12	7.01	7.05
Solution No. 3								
pH	7.0	-	6.05	-	5.3	5.2	5.3	5.2
SO_3	N.D.	-	N.D.	-	N.D.	N.D.	N.D.	N.D.
S_2O_3	4.66	-	4.37	-	4.77	4.83	4.83	4.77
S_3O_6	1.84	-	1.90	-	1.88	2.00	1.73	1.20
S_4O_6	0.78	-	0.78	-	0.84	0.57	0.60	0.56
Total thiosalts	7.28	-	7.05	-	7.49	7.40	7.16	6.53
Solution No. 4								
pH	10.0	-	9.05	-	8.2	8.2	8.2	6.0
SO_3	N.D.	-	N.D.	-	N.D.	N.D.	N.D.	N.D.
S_2O_3	4.89	-	4.60	-	5.06	4.88	4.83	4.83
S_3O_6	1.78	-	1.84	-	2.07	1.95	1.73	1.84
S_4O_6	0.69	-	0.66	-	0.63	0.52	0.63	0.60
Total thiosalts	7.36	-	7.10	-	7.76	7.35	7.19	7.27

All results except pH are expressed in millimoles per litre.

N.D. - not detectable (<0.01 mM/L)

Total thiosalt results are the summation of individual species.

nique (19) to test actual mill effluent samples. As indicated by the results in Table 8, the levels obtained by the titrimetric method (which determines the sum of polythionates, expressed as S_2O_3) compared favourably with those obtained by colorimetric methods (in which the individual species are determined). The Noranda method was found to be much simpler and faster. However, the authors recommended that the titration end-point in the presence of sulphite be changed to 8.2, with formaldehyde added to mask the sulphite.

Makhija and Hitchen proposed a titrimetric technique for thiosalts and sulphate based on back-titration of an excess of barium with EDTA (65). In principle, the method consists of removing metals by a cation-exchange resin, then determining (a) initial sulphate; i.e., the existing sulphate anions plus the sulphate obtained by oxidizing sulphite with iodine; (b) total sulphate obtained by oxidizing the polythionate anions (including the tetrathionate produced by oxidation of thiosulphate by iodine in (a) with acidic hydrogen peroxide; and (c) total sulphate obtained by oxidation of all thiosalts including dithionate with a mixture of hydrogen peroxide, potassium chlorate and concentrated nitric acid.

Rolia prepared a manual of procedures for the determination of thiosalts and sulphate in pulp solutions (66). A sequence of spectrophotometric procedures based on differential cyanolysis was adopted from Kelley et al. (18) and Mizoguchi and Okabe (19), and was used for the determination of thiosulphate, trithionate and tetrathionate in solution. Subsequently, it was found that the gravimetric method for sulphate originally presented in the manual was not suitable for solutions containing trithionate, and a new titrimetric method was devised (67).

Environment Canada evaluated high speed liquid chromatography (HSLC), paper chromatography, and the Noranda titrimetric procedure for the analysis of total thiosalts in synthetic solutions (68). They concluded that the titrimetric procedure was the most suitable. The paper chromatography method was found to have a detection limit of ~50 mg/L. The HSLC, besides requiring sophisticated instrumentation and high technical skills, was found limited to an analytical range over one decade and would require additional development work.

Although both the titrimetric and spectrophotometric methods outlined above gave acceptable results for thiosalt concentrations greater than 50 mg/L, results for levels below were less suitable (69). Hitchen and MacPherson (69) investigated spectrophotometric techniques suggested by Koh (22) for the determination of micromole concentrations of thiosulphate and tetrathionate by cyanolysis and solvent extraction. They concluded that the methods were subject to very large

Table 8 - Comparison of colorimetric and Noranda method analyses

Sample pH	Colorimetric $S_2O_3^{2-}$ mg/L*	Noranda titrimetric $S_2O_3^{2-}$ mg/L**	Difference mg/L
10.70	457.5	451.2	-6.2
10.31	374.5	369.5	-5.0
11.90	70.6	71.9	+1.3
10.8	57.2	58.0	+0.8
9.02	None	None	-

* The results shown are the summation of polythionates expressed as $S_2O_3^{2-}$.

**Average of two individual titrations.

uncertainties and required modification. No additional work was carried out, however, to improve these methods.

Leaver studied the effects of metals on the Noranda titrimetric method utilizing synthetic solutions of thiosulphate and tetrathionate (70). The determination of thiosulphate at 1000 mg/L was not affected by the presence of up to 500 mg/L Cd, 50 mg/L Pb or 50 mg/L Ag. Samples containing up to 100 mg/L Cu, 250 mg/L Zn or 200 mg/L Fe^{3+} could be analyzed for thiosulphate with errors of less than +10%, -6% and +7%, respectively. Ion exchange removal of these elements reduced the errors to about -4% for copper and zinc but for iron much greater negative errors were introduced due to the decomposition of the thiosulphate on the resin. The determination of tetrathionate at 5000 mg/L was not affected by the presence of up to 100 mg/L copper, ferric or zinc ions in the sample to be analyzed.

THIOSULPHATE

The iodometric titration is a well established wet chemical method for the determination of thiosulphate (7). Although Rolia analyzed thiosulphate spectrophotometrically as part of a sequence used to determine other thiosalt species, no other work has been carried out (66).

SULPHATE

Makhija and Hitchen developed a method to determine sulphate with an excess of barium chloride titrated with an EDTA solution (65).

PRESENTATION OF ANALYTICAL METHODS

A presentation of the Noranda and CANMET methods reviewed above is made in Appendix 2.

SPECTRAL AND CRYSTAL PROPERTIES

INFRARED SPECTRA AND MOLECULAR (IONIC) STRUCTURE OF THIOSALTS AND RELATED COMPOUNDS

Bartels and Farrell reviewed the literature regarding the infrared (IR) spectra of thiosalts (71). Although portions of all the spectra were found in the literature, they were for the most part referenced over some 50 years, and were obtained on a variety of instrumentation and under different sample conditions and instrument sensitivities. Many spectra in the literature were determined only in the 1100 to 900 cm^{-1} region and even in such a short range failed to exhibit sharp spectral characteristics such as peak splitting or weak shoulders. Subsequently, the IR spectra of K_2SO_4, Na_2SO_4, $Na_2S_2O_6.2H_2O$, $K_2S_3O_6$, $Na_2S_3O_6$, $K_2S_4O_6$ and $Na_2S_4O_6$ were determined in KBr media between 4000 and 200 cm^{-1}. These spectra are presented in Fig. 1 to 5.

The authors concluded that the analysis of the infrared spectra in conjunction with their structural characteristics indicated that the observed frequencies are a function of the cationic environment, the length of the S-S chains, the

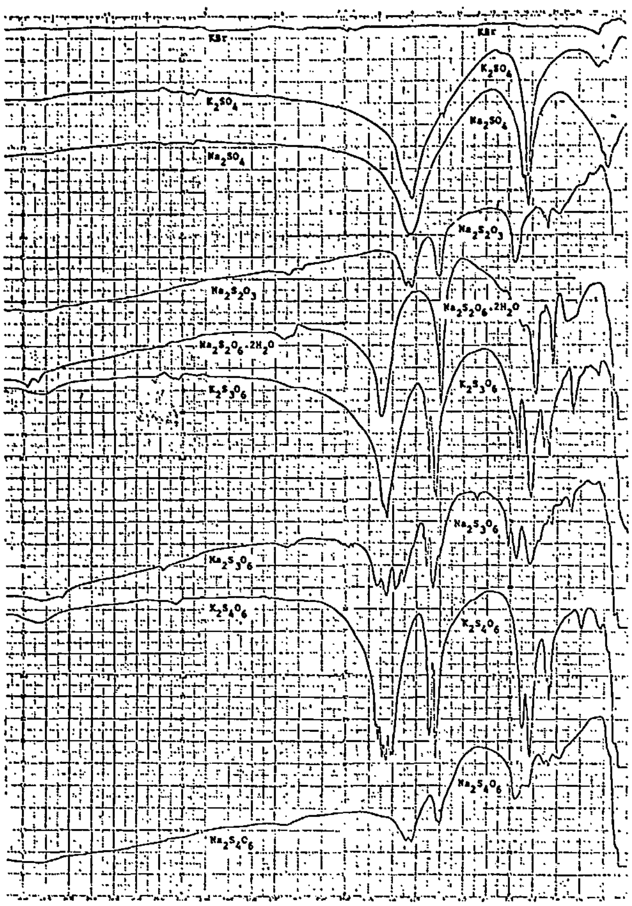


Fig. 1 - Composite infrared spectra of selected thiosalts in the spectral region 3200-200 cm^{-1}

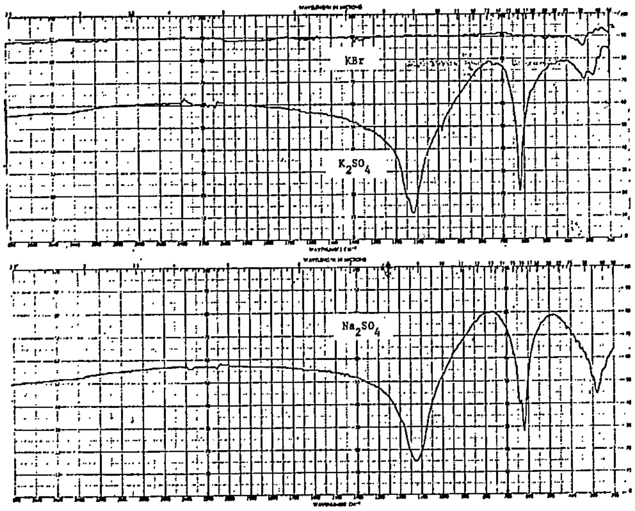


Fig. 2 - IR spectra of K_2SO_4 and Na_2SO_4 in the spectral region 4000-200 cm^{-1}

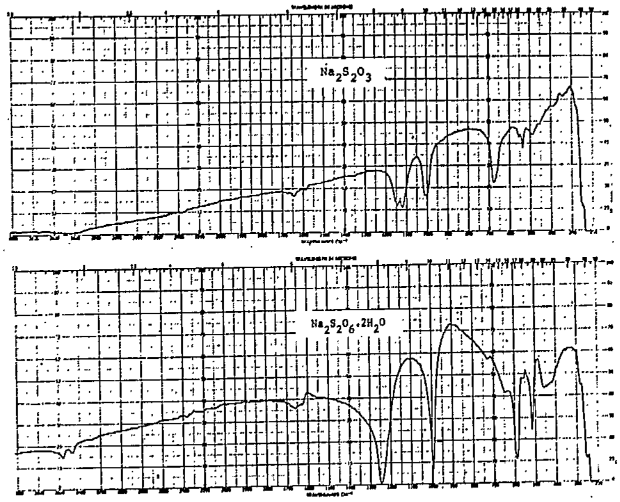


Fig. 3 - IR spectra of $Na_2S_2O_3$ and $Na_2S_2O_6.2H_2O$ in the spectral region 4000-200 cm^{-1}

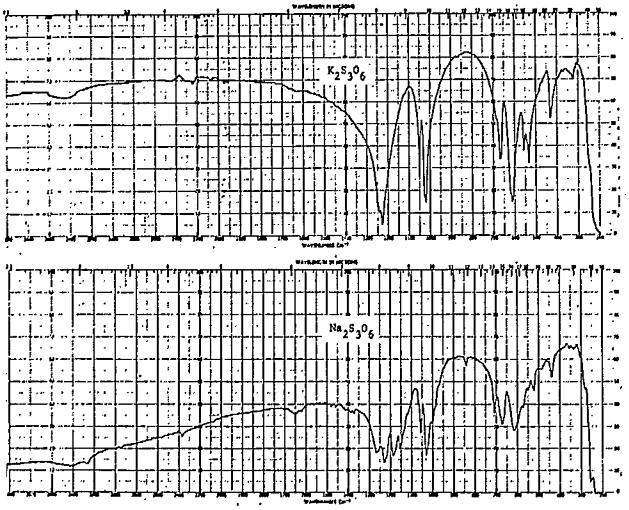


Fig. 4 - IR spectra of $K_2S_3O_6$ and $Na_2S_3O_6$ in the spectral region 4000-200 cm^{-1}

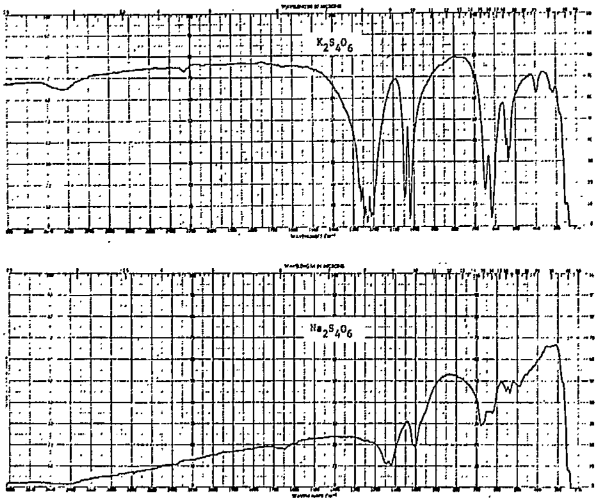


Fig. 5 - IR spectra of $K_2S_4O_6$ and $Na_2S_4O_5$ in the spectral region 4000-200 cm^{-1}

presence of S atoms bonded only to other S atoms, the presence of water of hydration and the media in which the spectra are taken. Corresponding relationships between successive polythionates should not be assumed since the above factors invoke varying degrees of influence on the IR spectrum of each sulphur oxyanion. Generally, the S-S bonds, the thionate group and the cation environment all play a part in determining the spectral characteristics of these compounds. Because significant overlap of the various thiosalt species exists, the IR method was not recommended for routine analytical purposes.

CRYSTAL STRUCTURE BY X-RAY DIFFRACTION

To provide precise molecular information for the interpretation of UV and IR spectral data, and to assist in the study of thiosalt oxidation, Stewart and Szymanski studied the crystal structure of potassium trithionate ($K_2S_3O_6$) and tetrathionate ($K_2S_4O_6$) (72,73).

The structure of $K_2S_3O_6$ was found to be orthorhombic. The two S-S bonds were found to be of unequal length, while one of the S-O bonds was found to be longer than the rest. The results of these studies are summarized graphically in Fig. 6 to 8.

The structure of $K_2S_4O_6$ was determined from two sets of X-ray diffractometer data. The two tetrathionate ions in the structure were comparable in geometry, though there was rotational displacement of SO_3 groups around the terminal S-S bonds. In both ions, the central bond is shorter than the other ones. Results of the study are summarized graphically in Fig. 9 to 11.

ULTRAVIOLET (UV) SPECTRAL CHARACTERISTICS

Thiosalts are known to absorb UV radiation. To characterize this property, Bartels

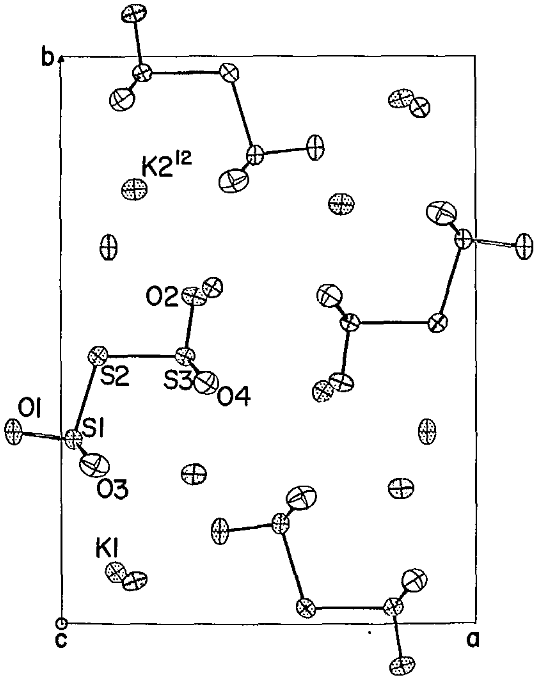


Fig. 6 - Structure of potassium trithionate projected on the ab plane. Atoms at z = 1/4 are stippled; those at z = 3/4 are shaded. The ellipsoids are drawn at 50% probability.

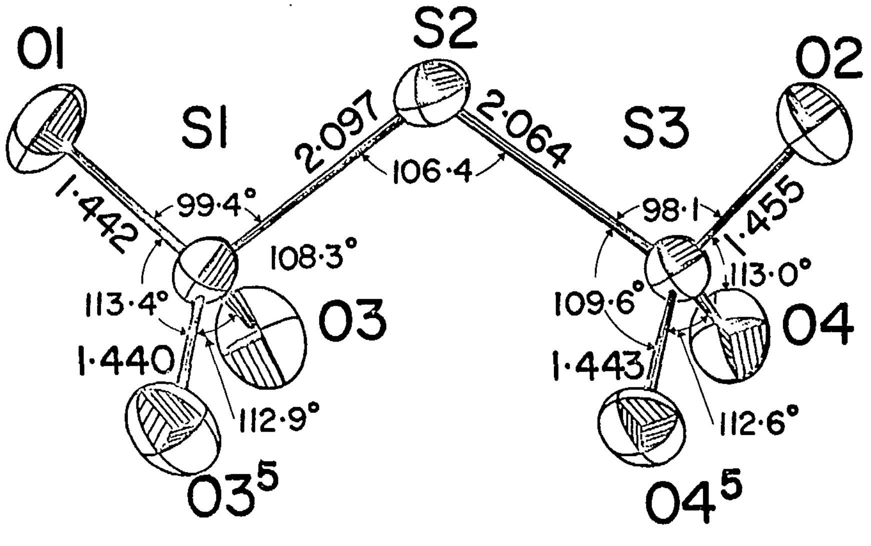
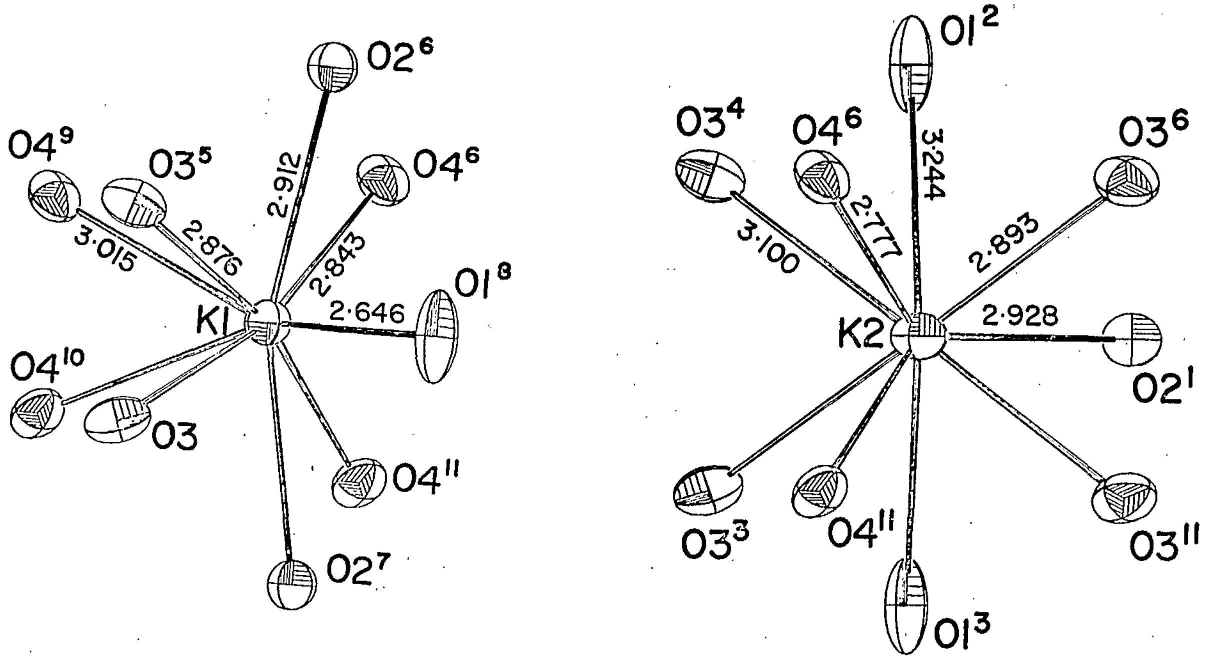


Fig. 7 - Geometry of the tritionate ion



(a)

(b)

Fig. 8 - Coordination polyhedra of potassium ions out to 3.5 Å: (a) K(1); (b) K(2)

measured the UV spectra of Na_2SO_4, K_2SO_4, $Na_2S_2O_6$, $Na_2S_2O_3$, $K_2S_3O_6$, $K_2S_4O_6$ and $Na_2S_4O_6$ (74). He found that sulphates and dithionate do not exhibit significant absorption in the UV region; thus was attributed to the lack of S atoms bound only to other sulphur atoms. Thiosulphate and higher polythionates were found to exhibit continuous absorption spectra from about 300 nm and to exhibit a characteristic absorption maxima at 214 nm in dilute solution (Fig. 12, 13).

In general, absorption characteristics for the sulphur oxyanions are due to the polythionate sulphur chain, and absorption intensity was found to increase with an increase in the number of sulphur atoms in this chain. Measurements made during the study indicated that the peak position and magnitude of the absorbance of the UV absorption bands of sulphur oxyanions in aqueous solution, hence the occurrence and magnitude of electronic transitions in these anions, are variously a function of the length of the $-S_n-$ chain, the character of the overall anion, the cation environment, and solution parameters such as concentration. Beer's law has been shown to hold for various restricted polythionate systems and linear empirical or absorption equations have been developed to relate absorbance and the concentration of various anion species in specific, well defined aqueous systems. However, because of the above complexities, the general use of UV spectroscopy for the quantitative determination of sulphur oxyanions of thiosalt effluents was not recommended.

GENERATION OF THIOSALTS IN MILLING CIRCUITS

To elucidate the mechanisms of thiosalt formation, CANMET conducted several in-mill surveys and laboratory studies. These are described below.

MILL SURVEYS OF THIOSALT GENERATION

Mill surveys were conducted by Rolia (75,76), and Rolia and Barbeau (77) at two north-

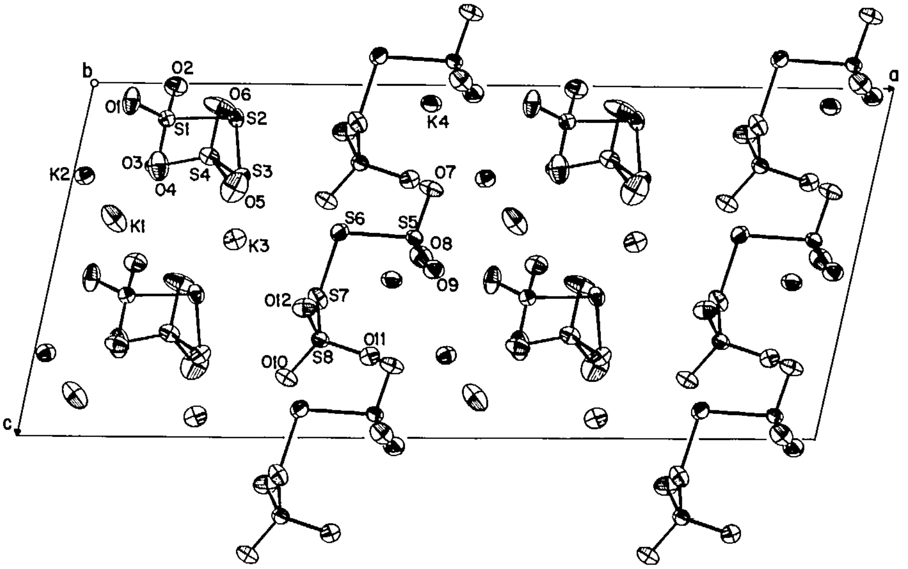
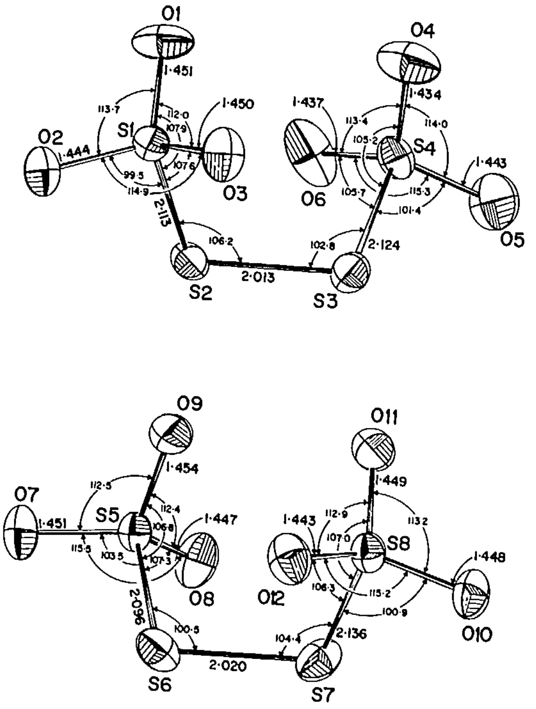


Fig. 9 - Structure of potassium tetrathionate projected on the ac plane



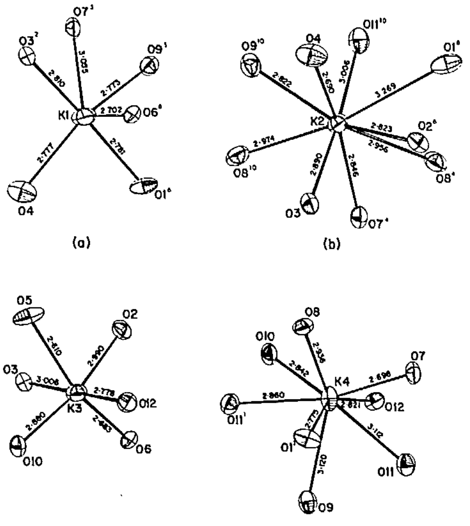


Fig. 10 - Geometries of the two independent tetrathionate ions

Fig. 11 - Coordination polyhedra of potassium ions out to 3.4 Å: (a) K(1); (b) K(2); (c) K(3); (d) K(4)

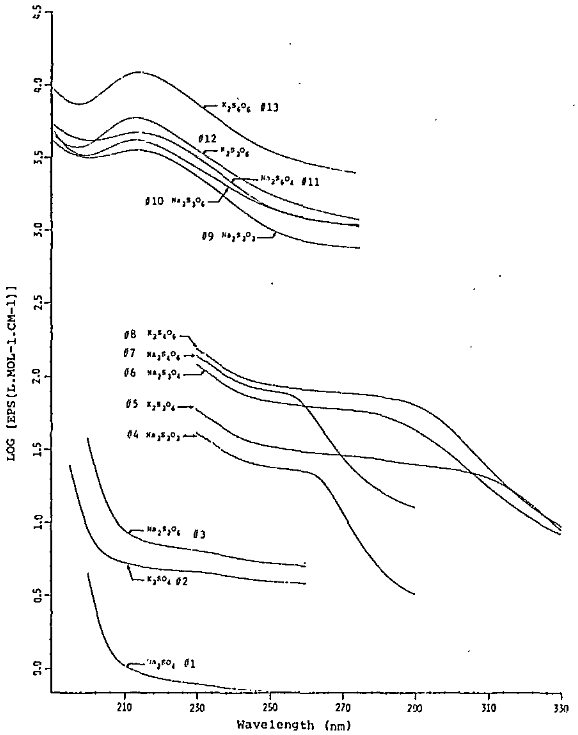
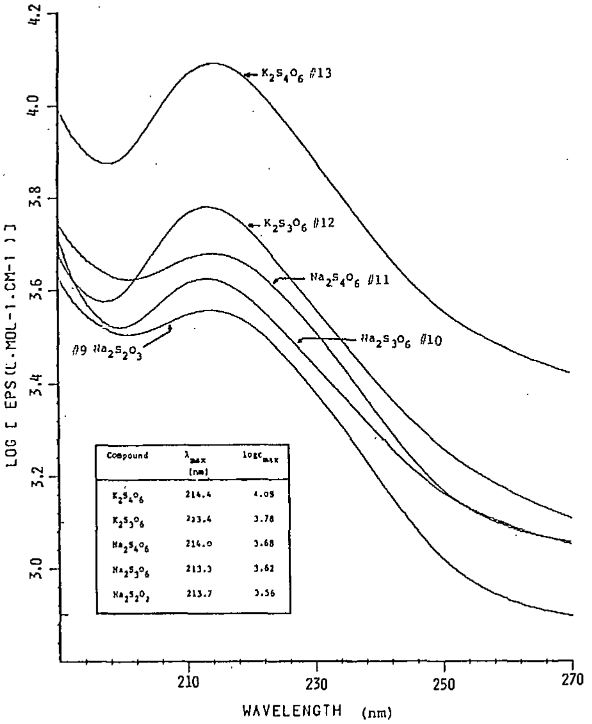


Fig. 12 - UV spectra of selected thiosalts in the region 330 to 190 nm



Compound	λ_{max} (nm)	$\log \epsilon_{max}$
$K_2S_4O_6$	214.4	4.05
$K_2S_3O_6$	213.4	3.78
$Na_2S_4O_6$	214.0	3.68
$Na_2S_3O_6$	213.3	3.62
$Na_2S_2O_3$	213.7	3.56

Fig. 13 - Details of the UV "peak" type spectra for selected thiosalts at 214 nm

eastern New Brunswick massive sulphide mines during 1977 and 1978.

Brunswick Mining and Smelting (BMS), operates a mine and mill processing 10,000 tons per day of Zn-Pb-Cu pyritic ore in three flotation lines. The basic processes include wet grinding, pulp aeration with SO_2 addition, flotation, and upgrading with heating. The contribution of these operations to the total thiosalts generated is presented in Table 9. As indicated, generation of thiosalts was found to originate mainly in flotation, aeration and grinding. The combined contribution of the addition of SO_2 and of heating the pulp to 85°C was determined to be about 12%.

Heath Steele Mines (HSM) processes 3500 tons per day of Zn-Pb-Cu pyritic ore. After grinding, aeration, and conditioning with promoters, bulk Cu-Pb concentrate is floated at the natural pH of the ore (pH 7.8-8.3). Sodium dichromate is used to depress lead during Cu-Pb separation, and for zinc flotation, lime is added to raise the Cu-Pb tails to pH 11.5.

The contributions of mill operations to the production of thiosalts is presented in Table 10. As indicated, 15.5% of the total thiosalts is generated during grinding, 12% during aeration, 34% in the Cu-Pb circuit, chiefly during Cu-Pb flotation, 17% in the primary zinc circuit, and 16% in the secondary zinc circuit. The combined overflows from zinc, copper, and lead concentrate thickeners contribute 5% of the total thiosalts.

Although BMS processes three times the tonnage of ore as HSM, it produces nine times the amount of thiosalts. A comparison of the mill process parameters is presented in Table 11. Rolia and Barbeau indicate that the difference in thiosalts generation can be partly explained by several factors (77):

(1) At BMS, grinding and aeration are carried out at pH 9.5, whereas at HSM, they take

Table 9 - Generation of thiosalts in the mill circuit at Brunswick Mining and Smelting*

Operation	Thiosalts generated g/min	% of Total
Adding internal reclaim water to lines 1 & 2	1363	5.6
Grinding (lines 1, 2, & 3)	3215	13.2
Aeration (lines 1 & 2)	3290	13.6
Flotation (lines 1, 2, & 3)	4316	17.8
Flotation (primary upgrading)	5193	21.4
Flotation (secondary upgrading)	4144	17.0
Adding SO_2 (primary upgrading)	454	1.9
Adding SO_2 (secondary upgrading)	1049	4.3
Heating 85°C (primary upgrading)	818	3.4
Heating 85°C (secondary upgrading)	445	1.8
Total	24287	100.0

*As determined during Sept. 19-30, 1977.

Table 10 - Generation of thiosalts in the mill circuit at Heath Steele Mines*

Operation	Thiosalts generated g/min	% of Total
Grinding	423	15.5
Aeration	322	11.8
Conditioning for Cu-Pb flot.	85	3.1
Bulk Cu-Pb flot.	693	25.3
Cu-Pb Scav and Cu-Pb Cl	162	5.9
Conditioning for Zn flot.	267	9.7
Primary Zn flot. and Cl	209	7.6
Second. Zn flot. and Cl	441	16.1
Zn thick O/F	80	2.9
Cu thick O/F	12	0.4
Pb thick O/F	46	1.7
Total	2740	100.0

*As determined during June 5-16, 1978.

Table 11 - Comparison of mill process parameters at Heath Steele Mines and at Bunswick Mining and Smelting

Size	Heath Steele			Brunswick Mining		
Ore milled, TPD	3500			10 000		
Sulphides in ore, %	75			80		
Grind	65% - 400M			68% - 400M		
Fresh water used, U.S. gal/min.	1832			2950		
Retention of ore in mill	1.5-2 h			3 h		
Metallurgy						
	Cu%	Pb%	Zn%	Cu%	Pb%	Zn%
Mill feed	1.0	1.5	4.5	0.3	3.0	7.0
Copper conc. grade	23	5	4	20.0	8.0	5
Lead conc. grade	2	30	4	0.3	36.0	6
Zinc conc. grade	<1	1.2	50	0.2	1.0	52
Bulk conc. grade	-	-	-	0.8	21.0	33
Recovery	60	50	74	40.0	60.0	80
Total thiosalts generated						
Thiosulphate ($S_2O_3^{2-}$), g/min	1800			12 000		
Trithionate ($S_3O_6^{2-}$), g/min	1100			10 000		
Tetrathionate ($S_4O_6^{2-}$), g/min	100			2 000		
Total thiosalts, g/min	3000			24 000		
Flotation lines						
				Line 3	Line 2	Line 1
Ore processed, TPM	2.43			2.43	2.25	2.25
Fresh water/ton, ore, U.S. gal	754			525	367	367
Thiosalts generated in:						
Grinding, g/min	423			1705	755	755
Aeration, g/min	322			-	1645	1654
Cu-Pb Rgh, g/min	778			776	1007	1007
Prim Zn Rgh, g/min	476			-	136	136
Prim Zn Upgr, g/min	135			2010	2010	2010
Sec Zn Upgr, g/min	441			1880	1880	1880
Cu-Pb separation, g/min	165			921	921	921
Total thiosalts, g/min	2740			7292	8354	8354

place at the natural pH of the ore. Only the zinc circuit is alkaline.

(2) Upgrading of concentrates at HMS is done by cleaning only, whereas SO_2 is used for Cu-Pb separation and to improve grade and recovery of Zn concentrate at BMS.

Rolia and Barbeau studied the contribution of sulphur dioxide to thiosalt generation in the flotation circuit at BMS (78). Their results indicated that bisulphite is formed initially upon addition of SO_2 to pulp slurries; the bisulphite then reacts with mineral particles, other thiosalts, and with air during flotation, resulting in more thiosalts.

LABORATORY STUDIES

To define the occurrence of thiosalts during beneficiation of sulphide ores, studies were conducted at CANMET from 1977 to 1980.

Rolia investigated the production of thiosalts during the grinding of pyritic ore from the BMS No. 12 mine (79). His findings were as follows:

(1) Thiosalts are produced during mixing of coarse ore (minus 10 mesh) with water, prior to any grinding. The amount generated increased directly with mixing time (Fig. 14).

(2) Thiosalts diminished by two-thirds during grinding with steel balls and billets at the natural pH of the ore (pH 8), but increased during grinding with pebbles. This is probably due to either the scavenging ability of abraded iron for oxygen or the reduction of thiosalts by iron.

(3) There is an increase in the production of thiosalts with pH over the interval of 9.4 to 10.7, as indicated in Fig. 15.

(4) Less thiosalts are produced per unit weight of ore during grinding at higher pulp densities than at lower pulp densities (Fig. 16).

(5) A direct logarithmic relationship was found

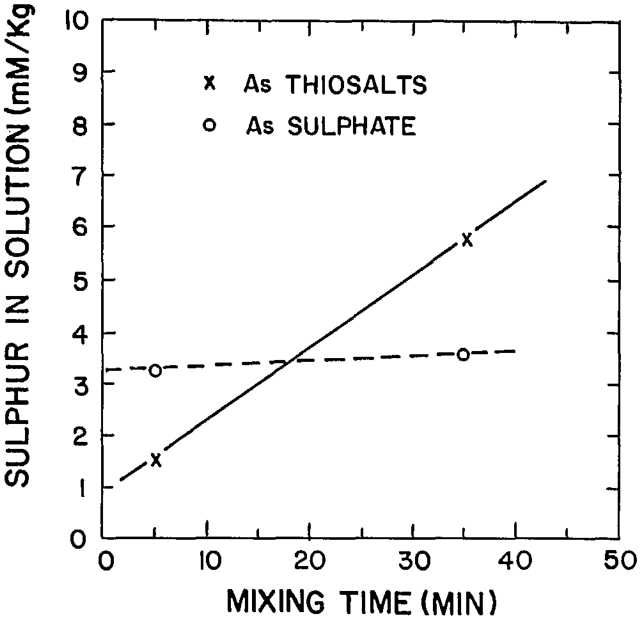


Fig. 14 - Effect of mixing time on the production of thiosalts from coarse ore in a closed circuit; 70 rpm, 30% pulp density, pH 11.2

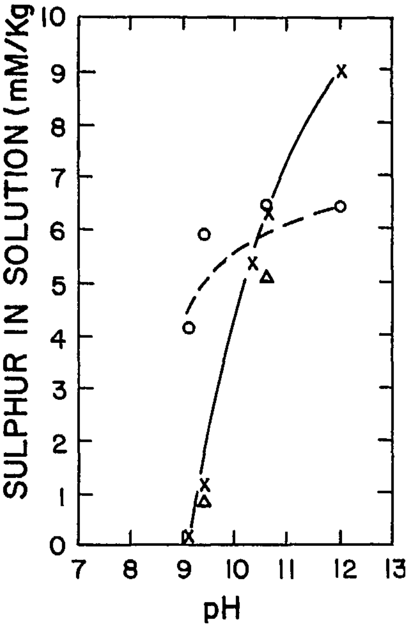


Fig. 15 - Effect of pH on thiosalt formation; closed circuit, 30 min, 60% pulp density, steel balls: X = thiosalts (Na_2CO_3-NaOH added); Δ = thiosalts (CaO added); o = sulphate

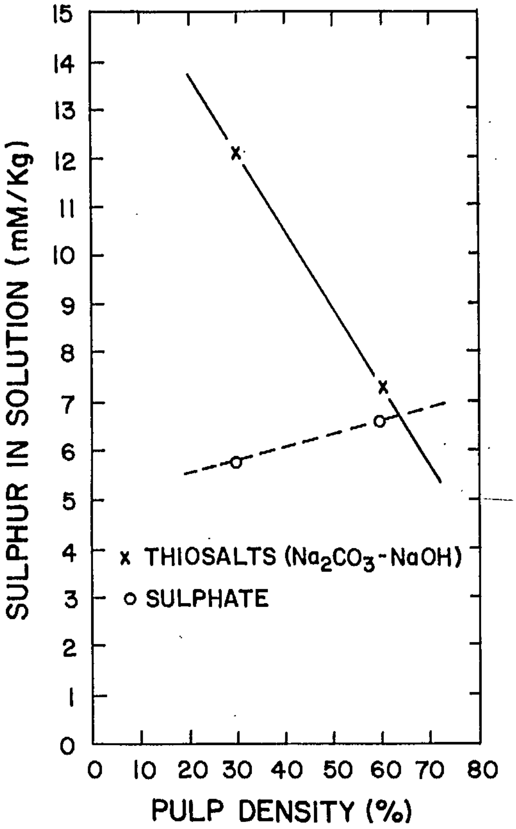


Fig. 16 - Effect of pulp density on thiosalt formation; closed circuit, 30 min, pH 10.7, steel balls

between the amount of thiosalts generated during grinding and the grinding time, as indicated in Fig. 17.

(6) Significant reduction of thiosalt generation (86%) occurred during grinding at pH 10.7 in a solution deaerated with nitrogen gas, indicating that production of thiosalts was repressed by exclusion of oxygen. Sulphite appeared as the principal sulphur species in the deaerated solution.

Investigations by the Noranda Research Centre indicated that some of the thiosalts in the ground pulp may originate from oxidized surfaces on the ore (80). Within the range of size distributions normally produced in grinding circuits, fineness of grind was found to have only a small effect on thiosalt generation during the grinding operation itself and subsequent flotation. The relative amounts of thiosalts originating from grinding and from flotation in a concentrator apparently depend largely on the pH in the two operations.

Other factors found to contribute to thiosalt formation were:

(1) Sulphide content of the ore; with five times the thiosalts generated in ores of 80-90% sulphides as with ores of 25-30% sulphides.

(2) Residence time during flotation; with the amount of thiosalts generated directly proportional to the residence time.

(3) Temperature; with thiosalt generation more than doubling from 25 to 40°C.

(4) Agitation rate in flotation; increased agitation promoted thiosalt formation.

Rolia and Barbeau studied the generation of thiosalts in a continuous process development mill at CANMET (Fig. 18) (81). The total amount of thiosalts generated was 959 g/t of ore; this compares with 1021 g/t of ore in the No. 3 flota-

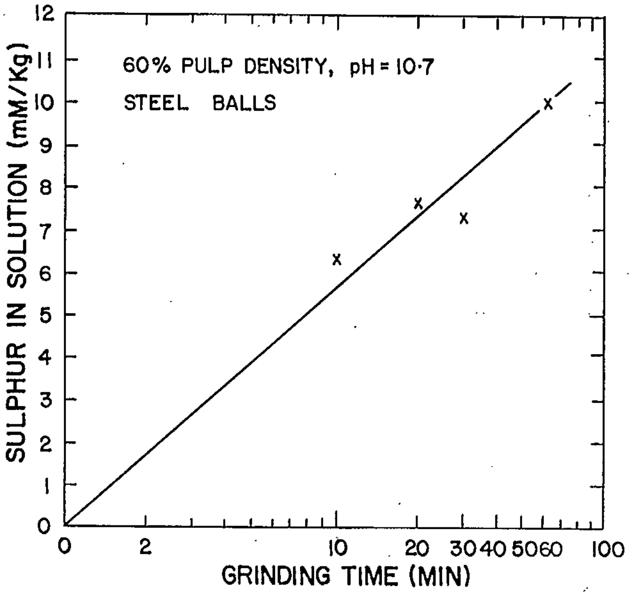


Fig. 17 - Effect of grinding time on thiosalt formation; closed circuit, 60% pulp density, pH 10.7, steel balls

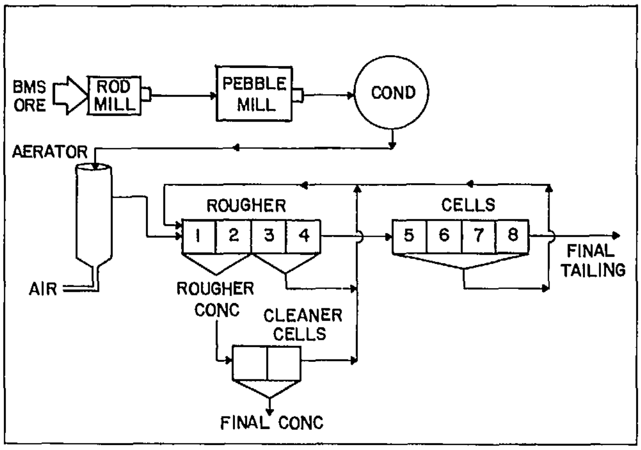


Fig. 18 - Continuous process development mill flowsheet at CANMET for the production of bulk concentrate

tion line at BMS before upgrading. A breakdown of thiosalt generation by operation was as follows:

Operation	% of Total
Grinding	17.6
Conditioning	37.0
Scavenging	45.5
Total	100.0

Steger investigated the effect of temperature, pH, particle size, and airflow on the formation and relative proportion of thiosalts in aqueous suspensions of samples of pyrrhotite, pyrite, chalcopyrite, galena, and sphalerite (82). An increase in the temperature or pH of a suspension resulted in an increase in sulphate and thiosalt formation. A decrease in the particle size of the mineral also resulted in increased sulphate and thiosalt formation. Changes in airflow had a marginal effect.

Rolia investigated generation of thiosalts during agitation of pulps on a variety of samples in a flotation cell (83). The results, presented in Fig. 19, indicated a clear correlation between the sulphur content and thiosalt production. No evident correlation was found between iron concentration and the amount of thiosalts generated.

THIOSALT TREATMENT METHODS

The CANMET thiosalt program evaluated a large number of thiosalt treatment alternatives. Most of these were limited duration bench-scale tests conducted inhouse. Two contracts were awarded - Noranda Research Centre evaluated pilot-scale biological removal of thiosalts using bacteria at Brunswick Mining and Smelting, Bathurst, N.B. and the University of Waterloo investigated catalyzed air oxidation of thiosalts using synthetic thiosalt solutions.

The following sections detail the studies which were conducted.

AIR OXIDATION

Solutions of thiosulphate and polythionates were aerated at pH 7 for 4 months under

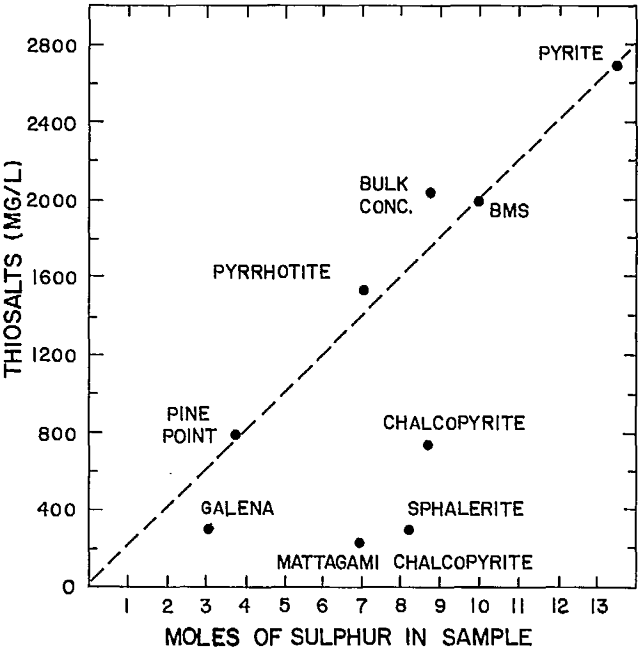


Fig. 19 - Influence of sulphide content of various materials on the amount of thiosalt production after 5-h aeration

sterile laboratory conditions at the Noranda Research Centre (80). During this time, minimal changes in the thiosalt concentration were observed (<10%). Thus, it was concluded that air oxidation alone was not suitable for the destruction of thiosalts.

CATALYZED AIR OXIDATION

Process Description

A process for the removal of thiosalts by copper catalyzed air oxidation was tested by Rempel and O'Driscoll of the University of Waterloo (84). In the process, the effluent passes through a two-stage continuous aerated reactor containing slurries of synthetic resins combined with copper. In the first stage, the thiosulphate and trithionate are oxidized employing quaternized polyvinyl pyridine-Cu (QPVP-Cu) catalyst. In the second stage polyvinyl pyridine-Cu (PVP-Cu) is used for tetrathionate oxidation. The pH in both stages is controlled at 3 to 4.

The two types of catalyst used in the oxidation stages (PVP-Cu and QPVP-Cu) both deactivate slowly with time. The cause of deactivation of the PVP-Cu catalyst and to some extent of the QPVP-Cu catalyst appears to be the continuous leakage (soluble loss) of copper from the polymer complex. Deactivation of the catalyst on prolonged use is also believed to result from a considerable amount of thiosalt adsorption (i.e., $S_2O_3^{2-}$ and $S_4O_6^{2-}$) as well as SO_4^{2-} adsorption on the polymer matrix. Hence, periodic catalyst regeneration is required that involves pretreatment of the spent catalyst consecutively with HCl and NaOH to remove adsorbed thiosalt species followed by recomplexing with divalent copper. A simplified flowsheet of the process is illustrated in Fig. 20.

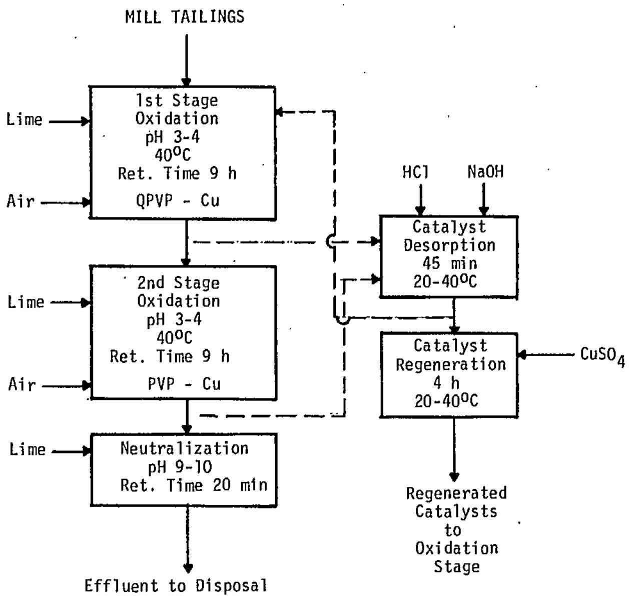


Fig. 20 - Simplified flowsheet for the copper-catalyzed air oxidation of thiosalts

Results of Tests

Tests of synthetic solutions containing 1680 mg/L S_2O_3 have been run at various temperatures and residence times using the catalyzed oxidation process. Based on these tests, optimum conditions appear to be pH 3 to 4, total residence time of 24 h (12 h per reactor), and temperatures from 35 to 40°C. To maintain an effluent quality of less than 100 mg/L thiosalts, desorption and regeneration of the PVP-Cu catalyst was required after 7 days of continuous operation. While desorption of the QPVP-Cu catalyst is also required after 7 days, regeneration is only necessary after 6 months. Typical results achieved during the tests are illustrated in Fig. 21.

Costs

Based on laboratory tests with synthetic solutions, Wong prepared preliminary capital and operating cost estimates for a plant capable of treating 1500 USGPM (5.67 m^3/min) mill tailings solution containing 5330 ppm $S_2O_3^{2-}$ (16 820 STPY or 15 255 MTPY) (85). The total fixed capital cost for this process in first quarter 1981 dollars is $17 495 000. The annual operating costs estimated for chemical reagents, catalysts and utilities only are $12 197 000 based on an assumed catalyst price of $2/lb with a life of one year. About 26% of the operating cost is for catalyst and 42% is for NaOH and HCl reagents. If the catalyst price is assumed to be $5/lb with

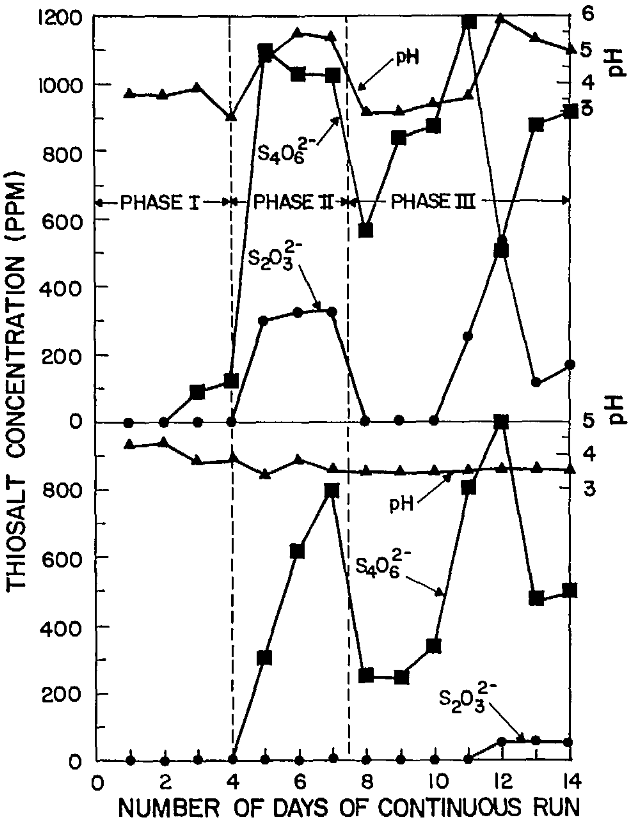


Fig. 21 - Continuous operating data for a two-stage copper-catalyzed reactor for thiosalt destruction: influent = 15 mM $S_2O_3^{2-}$ (1680 ppm); aeration rate = 1200 L/h; influent solution rate = 1.3 L/h (Day 1-4), 1.9 L/h (Day 5-7) and 1.5 L/h (Day 8-14). Reactor 1 (upper figure): QPVP-Cu (II) Catalyst (8.95% Cu (w/w), <75 μm); 2% (w/v) slurry; 12-L capacity; temp. 40°C. Reactor 2 (lower figure): Reilly-PVP-Cu (II) Catalyst (6.70% Cu (w/w) 50-500 μm); 2% (w/v) slurry; 12-L capcity; temp. 40°C (Day 1-5), 20°C (Day 6-7), 36°C (Day 8-14).

a life of one year, then the annual operating cost is $16 985 000 of which 47% is attributable to catalysts and 30% to NaOH and HCl reagents. On the basis of a catalyst life of 10 years, the estimated annual operating cost is from $9 324 000 to $9 803 000 for catalyst cost of $2 to $5/lb. However, the minimum possible operating cost is $8 253 000 if steam heating of the mill tailings solution is not required.

HYDROGEN PEROXIDE OXIDATION

Hydrogen peroxide is a strong oxidizing agent which is widely used industrially. Rolia investigated, in bench-scale tests, the oxidation of thiosalts utilizing hydrogen peroxide (86). He achieved complete oxidation of synthetic solutions (2.5 g/L thiosalts, as Na_2, S_2O_3 and $Na_2S_4O_6$) within 6 min using stoichiometric amounts of H_2O_2.

Reagent cost estimates (Dec. 1981), based on the treatment of 77 000 lb/d of thiosalts, amounted to $9.02 million per year. No capital cost estimates were provided.

CHLORINE OXIDATION

Rolia and Barbeau conducted laboratory tests to evaluate the kinetics and reagent requirements for the oxidation of synthetic solutions containing thiosulphate, tetrathionate, and trithionate using chlorine gas (87). They found that the oxidation rate depends directly on the rate of chlorine addition. The reaction required 2 moles chlorine for each mole of thiosalt sulphur. Reagent requirements for the destruction of 77 000 lb/d of thiosalts were estimated at $6 million per year (June 1979). No capital cost estimates were provided.

OZONE AND OTHER OXIDANTS

Environment Canada indicates that chemical oxidation of thiosalts may be achieved through the use of ozone, as well as chlorine sodium chlorate, sodium hypochlorite, and hydrogen peroxide (88). For ozonation, they propose the following reactions:

$$2\ S_2O_3^{2-} + 5\ O_3 + 2\ H_2O \rightarrow 4\ SO_4^{2-} + 3\ 1/2\ O_2 + 4\ H^+ \qquad \text{Eq 86}$$

or

$$5\ S_2O_3^{2-} + 2\ O_3 + 7\ O_2 + 5\ H_2O \rightarrow 10\ SO_4^{2-} + 10\ H^+ \qquad \text{Eq 87}$$

Their comparison of chemical treatment costs (Dec. 1975) is presented in Table 12.

SO_2-AIR OXIDATION

INCO has developed a process for the destruction of cyanide using SO_2-air oxidation. Preliminary tests carried out by INCO to evaluate thiosalt destruction using SO_2 and air were inconclusive due to a lack of analytical methods for thiosalt determination.

Rolia and Barbeau carried out tests to evaluate the effect of SO_2 and air on thiosalt solutions (87). They found minimal changes in thiosalt levels in tests of up to 48-h duration; in fact, in some tests, SO_2 combined with thiosulphate to produce more thiosalts. These tests were carried out without the addition of any catalysts (e.g., copper) which INCO utilizes for cyanide oxidation. In one of the tests, ferrous chloride was added, but it did not affect the results.

Oxidation of thiosalts by SO_2 and air and neutralizaton of acids thus produced probably occurs as follows:

(1) Formation of Caro's acid:

$$H_2O + SO_2 + O_2 \rightarrow H_2SO_5 \qquad \text{Eq 88}$$

(2) Oxidation of thiosulphate by Caro's acid:

$$S_2O_3^{2-} + H_2O + 4H_2SO_5 + 2H^+ \rightarrow 6H_2SO_4 \qquad \text{Eq 89}$$

(3) Neutralization of acid generated:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O \qquad \text{Eq 90}$$

Similar equations can be derived for the oxidation of other thiosalt species. Since SO_2 is converted to H_2SO_4, the neutralization requirements are greatly increased over other chemical oxidation methods.

Based on the above reactions, reagent costs (SO_2 and lime) for the destruction of 77 000

Table 12 - Comparison of chemical treatments for thiosalts (based on treating a 2 mgd stream of 1000 mg/L S_2O_3)

Chemical	Quantity required per lb S_2O_3	Estimated cost/lb $	Daily cost $	Estimated relative capital cost of facilities	Neutralization
Oxidants					
Ozone	1.06	0.16	3800	High	Yes
		0.125	2500	High	Yes
Chlorine	3.16	0.03	1900	Low	Yes
Calcium hypoclorite	3.22	0.40	8000	Low	Questionable
Buffers					
Sodium bicarbonate	1.5	0.0465	1400	Low	-
Soda ash	0.95	0.075	1425	Low	-
Neutralizing agents					
Limestone	0.89	0.0001	18	Low	-
Lime	0.50	0.001	100	Low	-

lb/d of thiosalts can be estimated at $6.6 million per year (June 1982), assuming on-site generation of SO_2 gas from sulphur.

ALKALINE OXIDATION

Polythionates are unstable in alkaline solution, decomposing to elemental sulphur, thiosulphate and sulphite. Rolia studied the reaction kinetics for the decomposition of tetrathionate, trithionate and thiosulphate in alkaline solutions (89). He found that tetrathionate degraded rapidly to thiosulphate and trithionate at pH >10 and at 35°C. At higher temperatures (e.g., at 100°C), trithionate was found to decompose to thiosulphate and sulphate. The rate of hydrolysis of trithionate was not affected to any great extent from pH 5.5 to 12.

Thiosulphate was oxidized to sulphate by dissolved oxygen in alkaline solutions. The reaction was characterized by an induction period whose duration increases with increasing pH and decreases with rising temperature and pressure.

The oxidation of thiosalts in strongly alkaline media was studied by Rolia using slaked lime [$Ca(OH)_2$], sodium carbonate (Na_2CO_3), and sodium hydroxide (NaOH). Oxidation was always incomplete when [$Ca(OH)_2$] was used (90).

Complete oxidation was achieved using Na_2CO_3 but the oxidation rate was 80% of that obtained using NaOH. Other process variables were concentration of alkaline reagent, temperature, oxygen pressure, and thiosalt concentration. For an effluent solution containing 2500 mg/L thiosalts, two sets of preferred conditions were identified:

	1	2
Temperature, °C	150	100
Partial pressure of oxygen, kPa	2070	2070
Retention time, h	0.022	0.2
NaOH conc., g/L	1.92	1.92

Craigen estimated operating costs (June 1981) for the alkaline oxidation, using lime, of a 2000 U.S. gal/min stream containing 2000 mg/L S_2O_3 from $1 million to $2.4 million depending on the cost of steam (91). No capital cost estimates were provided. More recently, Wong calculated the annual operating cost at $5.2 million and the capital cost at $8.9 million (106) (Jan. 1982). Wong's cost were based on NaOH since lime lead to incomplete oxidation.

ULTRAVIOLET (UV) INDUCED OXIDATION

Haque evaluated UV oxidation of thiosalt solutions using a laboratory-scale reactor (UV source - 500 W Hanowa mercury vapour lamp) with air or oxygen bubbled through the solution (92). His results are presented in Table 13, and indicate:

(1) In the presence of gaseous oxygen, UV brought down the concentrations of thiosalt species to less than 2 mg/L.

(2) Results with air are similar to those achieved with oxygen.

No cost estimates, either operating or capital were provided.

REVERSE OSMOSIS (RO)

Reverse osmosis involves the forcing of water under pressure through a specially designed membrane which has the capability of allowing passage of pure water while rejecting impurities.

Sastri conducted laboratory RO tests using a static cell with a cellulose acetate membrane and tested both synthetic thiosalts and actual mill solutions (93). In initial experiments, he investigated separation of individual salts, and found that in each, maximum separation was achieved at 300 psig. Subsequently, he conducted tests with twelve different actual mill solutions at 300 psig. As indicated by the results in Table 14, effluent concentrations of less than 200 mg/L total thiosalt were achieved in most cases.

Dutrizac quotes capital cost estimates for an RO installation of 4000 U.S. gal/min at $5.4 million Can. and calculates operating costs from $0.63 to $1.02/1000 U.S. gal (94) (Dec. 1978). These costs do not include pretreatment for calcium removal or disposal of concentrated effluent.

Table 13 - Results of UV experiments

Expt. No.	Initial pH	Reactions	Observations	$S_2O_3^{2-}$ mMole	$S_3O_6^{2-}$ mMole	$S_4O_6^{2-}$ mMole	Initial SO_4^{2-} mMole	Sulphur total g/L	Total S from SO_4^{2-} g/L
1	4-5	Irradiated in presence of bubbling oxygen for 2 h	Straw colored light ppt. settled at bottom of reaction vessel	<0.01 (5.5)*	<0.01 (4.7)*	<0.01 (0.2)*	(11.0)*	0.73	0.72
2	4-5	Thiosalt soln. & methanolic extract of chlorophyl (25 mL) irradiated for 3.5 h in bubbling oxygen	Straw colored light ppt. settled at bottom of reaction vessel	<0.01 (5.5)	<0.01 (4.7)	<0.01 (0.2)	(11.0)	0.83	0.69
3	4-5	Thiosalt soln. & 25 mL of methanolic extract of chlorophyl irradiated for 3.5 h in bubbling air	Light grey ppt. settled at bottom of reaction vessel	<0.01 (5.5)	<0.069 (4.7)	<0.01 (0.2)	(11.0)	0.81	0.69
4	4-5	Thiosalt soln. irradiated in bubbling air for 3.5 h	Light grey ppt. settled at bottom of reaction vessel	<0.01 (5.5)	<0.040 (4.7)	<0.01 (0.2)	(11.0)	0.85	0.85
5	4-5	Only air was bubbled through the thiosalt soln. (600 mL) for 18 h (dark reaction)	Light grey ppt. settled at bottom of reaction vessel	0.08 (3.3)*	0.020 (2.4)*	1.98 (0.3)*	(10.7)	0.88	0.67
6	4-5	Thiosalt soln. (600 mL) & methanolic extract of chlorophyl (25 mL) & oxygen gas bubbled for 3.5 h (dark reaction)	Light grey ppt. settled at bottom of reaction vessel	0.07 (3.3)	<0.01 (2.4)	2.03 (0.3)	(10.7)	0.85	0.67
7	7	Irradiated with 25 mL of methanolic extract of chlorophyl in bubbling oxygen for 3.5 h at pH 7.0	Whole reaction soln. turned milky and pH 5 to 6	0.22 (3.3)	0.01 (2.4)	0.01 (0.3)	(10.7)	0.85	0.67

* Initial concentrations

Table 14 - Results of reverse osmosis experiments

Sample No.		Species concentration - mg/L						
		SO_4^{2-}	Total thiosalts (as SO_4^{2-})	$S_2O_3^{2-}$	$S_4O_6^{2-}$	$S_3O_6^{2-}$	$S_2O_6^{2-}$	SO_3^{2-}
1	Feed	1085	3379	985	233	403	128	32
	Product	124	144	11	25	1	18	1
2	Feed	1344	3523	896	179	211	160	-
	Product	99	144	1	13	4	27	-
3	Feed	374	931	202	112	-	-	8
	Product	33	78	1	7	-	-	1
4	Feed	1450	2592	482	67	115	80	-
	Product	99	103	1	5	1	1	-
5	Feed	317	854	39	123	-	-	-
	Product	16	45	1	9	-	-	-
6	Feed	653	2362	426	314	192	160	88
	Product	54	54	1	9	1	1	1
7	Feed	1478	3715	616	1107	902	-	-
	Product	120	204	26	43	10	-	-
8	Feed	854	3005	750	1344	499	-	-
	Product	58	132	12	35	1	-	-
9	Feed	1344	4176	336	2137	1190	-	-
	Product	44	155	10	27	10	-	-
10	Feed	1642	4378	750	1250	1056	-	-
	Product	79	135	18	16	6	-	-
11	Feed	1325	3610	750	1004	749	-	-
	Product	81	156	27	9	6	-	-
12	Feed	1632	2918	370	1001	461	-	-
	Product	51	161	4	10	4	-	-

ELECTRODIALYSIS

Electrodialysis involves removing inorganic ions from water by impressing an electrical potential across the water, resulting in the migration of cations and anions to the cathode and anode, respectively. By alternately placing anionic and cationic permeable membranes, a series of concentrating and diluting compartments results with the solution between one pair of membranes becoming depleted in solute while the adjacent solutions become solute enriched. The amount of electric current required for the demineralization is proportional to the number of ions removed from the diluting compartments.

No experiments were conducted to evaluate electrodialysis for treatment of thiosalt solutions. Dutrizac indicates that industry spokesmen believe that membranes used for sulphate removal would also be effective for thiosalts, and quotes operating costs from \$0.50 to \$1.00/1000 U.S. gal (Dec. 1978) (94). This does not include costs for removal of calcium or disposal of concentrate. Capital costs of a recently-built 3 million U.S. gal/day plant to treat brackish water correspond to \$4 million Can. (Dec. 1978).

ELECTROOXIDATION

Bartels evaluated the treatment of thiosalts using electrooxidation (95). He outlined the main anodic reactions which are presented in Fig. 22. These can be divided into four general groups:

(1) Oxidation of thiosulphate in neutral-acid media.

(2) Oxidation of thiosulphate in alkaline media.

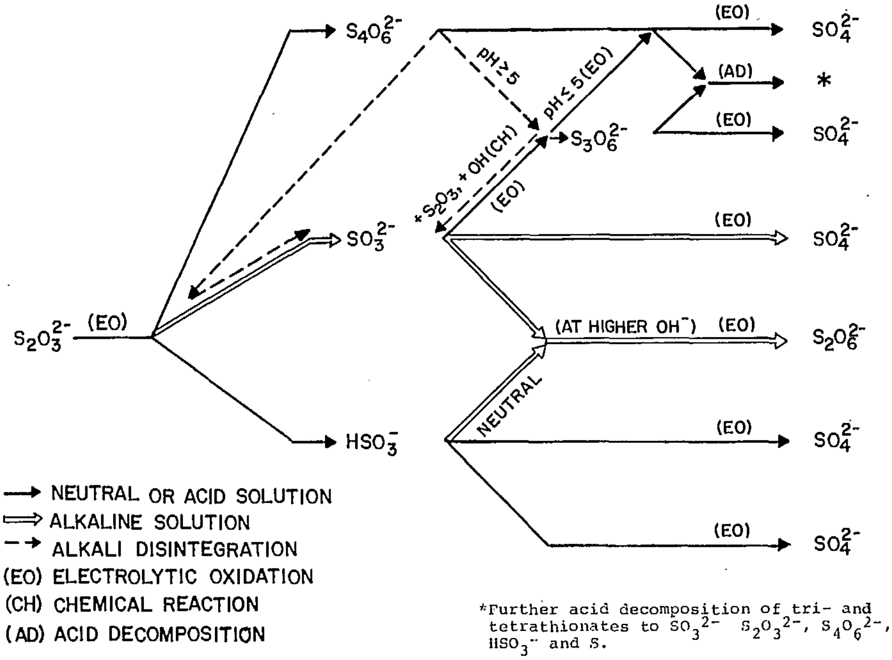
(3) Oxidation of polythionates in acid or alkaline media.

(4) Oxidation of sulphite and bisulphite in neutral, acid, or alkaline media.

Based on calculations for the direct oxidation of thiosalts on platinum, a thiosalt loading of 50 000 lb/d, and power costs of \$0.0350/kWh, Bartels estimated power costs at \$4.9 million per year. No capital cost estimates were provided. Among factors contributing to the high costs are:

(1) Complex multipath chemical and electrochemical reactions occurring during electrolytic oxidation.

(2) Buildup of dithionate which cannot be further oxidized anodically.



*Further acid decomposition of tri- and tetrathionates to SO_3^{2-} $S_2O_3^{2-}$, $S_4O_6^{2-}$, HSO_3^- and S.

Fig. 22 - Anodic reactions occurring during electrooxidation of thiosalts

(3) Significant drop in current efficiencies below 500 mg/L thiosalt concentrations.

As of the date of the report (Sept. 1979), improved design of electrochemical reactors for thiosalt oxidation has not been proven. The carbon fibre anodes tested have evolved oxygen rather than oxidize the anions.

REDUCTION BY METALS

Based on observations of the disappearance of thiosalts following wet grinding of ore using steel balls, Rolia investigated reactions between metals and synthetic thiosalt solutions (96). His preliminary results, presented in Table 15, indicate that thiosalts could be completely destroyed in 24 h in the presence of nickel or iron; the fastest destruction occurring with iron.

Subsequently, he investigated the iron-thiosalt reactions more closely, concentrating on the effects of excess iron, temperature, and thiosalt concentration. Based on his experiments, he derived the rate expression governing the reaction. Qualitative tests indicated the evolution of H_2S gas and the generation of colloids consisting of Fe_2O_4, FeO and FeS.

Table 15 - Reduction of thiosalts by metals (Temp. = 80°C)

Metal/S mMole/mMole	Time h	$S_2O_3^{2-}$ mM	$S_4O_6^{2-}$ mM	$S_3O_6^{2-}$ mM
Absence of metal.	0.1	4.7	5.6	4.0
	2	4.5	6.3	1.7
	4	4.3	6.4	0.9
	6	4.3	5.7	2.1
	24	4.3	5.8	1.6
Ni/S = 25.5/22.5	0.1	5.1	5.2	4.6
	2	6.3	2.6	3.8
	4	7.2	1.4	2.9
	24	Nil	Nil	Nil
Fe/S = 26.8/22.5	0.1	6.3	4.4	4.6
	2	12.3	0.1	3.9
	4	9.3	Nil	2.8
	21	Nil	Nil	Nil
Cu/S = 23.6/22.5	0.1	4.5	3.3	7.5
	1	3.7	4.5	6.0
	3	1.3	6.1	2.5
	5	Nil	6.6	0.8
Zn/S = 22.9/22.5	0.1	4.9	5.9	4.3
	2	5.5	6.4	1.9
	4	6.1	6.3	1.0
	21	9.6	4.7	Nil
	47	11.7	1.8	Nil

Estimated operating costs for removing thiosalts by metallic iron was $7.1 million per year (January 1982) based on an effluent flow of 3000 U.S. gal/min, and a loading of 33 000 lb/d thiosalts. This does not include expenditures for the disposal of H_2S or FeS. The capital cost was estimated at $38.4 million, mainly attributable to using a ball mill as necessary contactor between iron sponge and the effluents (106).

ACTIVATED CARBON TREATMENT

Activated carbon is finding increased use in the treatment of municipal and industrial effluents. Removal of waste products from water by activated carbon involves the accumulation or concentration of substances at a surface or interface by adsorption, a process in which matter is extracted from one phase (i.e., liquid) and concentrated at the surface of another (i.e., solid carbon).

Rolia evaluated the removal of thiosulphate, tetrathionate and trithionate in synthetic solutions by activated charcoal (87). Essentially, no removal was achieved, despite varying pH from 6 to 12, temperature from 20 to 65°C, and residence time from 30 to 230 min.

Noranda Research tests of a number of adsorbents - activated carbon, bone charcoal, bituminous coal, peat, alumina, diatomaceous earth, clay - indicated that only activated carbon was able to retain significant quantities of thiosalts (80). Of the six commercial brands of activated carbon examined, Calgon Filtrasorb 200 appeared to be the best, having a loading capacity of 10 lb/100 lb of carbon in batch tests. Results of a column test indicated that a 5-ft deep bed having a total volume of 53 000 ft^3 (1 600 000 lb of carbon) would be required to treat 3000 Imp. gal/min of effluent containing 800 mg/L thiosalts at pH 2. Alkaline regeneration of the carbon bed was uneconomic. Alternatives such as biological regeneration may be possible but were not investigated because of the apparent high capital and operating costs of a carbon adsorption system.

BIOLOGICAL OXIDATION

Treatment of base-metal mine effluents containing thiosalts was first studied by Schmidt and Conn, who reported complete removal of 1000 mg/L thiosulphate in a bench-scale biological reactor at room temperature and a residence time of 18 h (97). The predominant bacterial species was Thiobacillus thiooxidans.

Laboratory studies by B.C. Research evaluated bench-scale Rotating Biological Contactors (RBC) and activated sludge units utilizing a synthetic feed (98). The unit achieved an oxidation rate of 70 mg/L/h, and the RBC achieved 1600 mg/L/h at room temperature and 120 L/h at 8.5°C.

Environment Canada carried out tests utilizing both bench- and pilot-scale RBC units (99). A flow diagram of the pilot-scale unit is presented in Fig. 23. Oxidation rates achieved using synthetic effluent and bench-scale units at 2°C were from 450 to 700 mg/L/h. At 30°C, rates as high as 1450 mg/L/h were achieved. Pilot-scale tests, carried out on site utilizing mill effluent from a metal mining operation in New Brunswick, achieved oxidation rates as high as 760 mg/L/h. Based on the results of the pilot-scale tests, Environment Canada provided cost data for an RBC facility treating 2.3 million Imp. gal/d of effluent containing 1250 mg/L thiosalts. Capital cost was estimated at $1.66 million and operating cost at $428 000 per year (May 1980). These costs do not include pre-treatment facilities such as primary clarification, flow equalization, or post-treatment facilities like lime neutralization, clarification, and possible supplementary chemical oxidation treatment, and the operating costs associated with such facilities. Also, the mechanical complexity of the system and the corrosive nature of the treated effluent (pH 2) would require close supervision of the process during operation and result in high maintenance costs. During the pilot tests, extensive corrosion problems were encountered, thus dependable continuing operation was difficult to maintain.

Meuller studied the oxidation of thiosulphate from the flotation waste waters of a base metal mine at Meggen, Germany, in bench- and pilot-scale packed towers (100). Packing materials tested included Raschig rings, quartz pebbles,

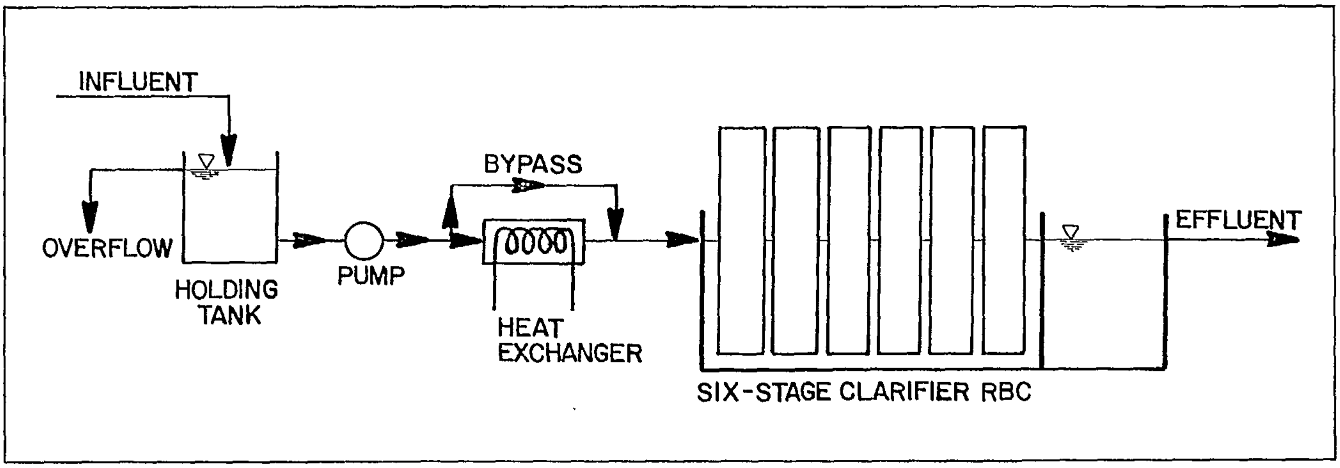


Fig. 23 - Flow diagram of the Environment Canada pilot-scale RBC

pilot-scale packed towers (100). Packing materials tested included Raschig rings, quartz pebbles, pyrite and native rock. The optimum thiosulphate oxidation rate was 470 mg/L/h in bench-scale tests and 200 mg/L/h in pilot-scale tests.

Noranda Research conducted bench-scale laboratory biological oxidation studies using a synthetic feed and on-site studies at Brunswick Mining and Smelting (BMS) using actual mill effluents (101). Two types of reactor were utilized: mixed aerated tanks (without packing) and extended surface packed reactors (using rock and foam packing). In addition, a rock packed column was evaluated.

Successful biological oxidation of thiosalt was achieved from 2.6 to 30°C, and the highest oxidation rates (about 1000 mg/L/h) were attained in the rock packed column and tank reactor. Lowering of the reaction temperature to 2.6°C resulted in an oxidation rate decrease of up to 50% over that achieved at room temperature. While the feed was generally pH 5 to 7, thiosalt oxidation resulted in the formation of sulphuric acid and subsequent pH depression. During optimal operation, the reactor effluent was pH 2.0 to 2.2.

It was noted that the packed reactors and columns were less sensitive to changes in feed composition and temperature than the mixed aerated tank. There was no evidence during the on-site tests of any toxic effect of components in the treated mill streams over a 5-month period. Colloidal sulphur, formed by acid decomposition of thiosulphate, was found to deposit on the packing material.

Dinardo carried out a literature review of thiosalt oxidation by thiobacilli species (102).

Silver and Dinardo studied the effects of temperature, initial pH, and concentration of ammonium, phosphate and heavy metals on the oxidation of thiosalts by an authentic strain of Thiobacillus thiooxidans (ATCC 8085) and by a mixed culture isolated from a base metal processing mill effluent pond (103). The optimum temperature was found to be 30°C and the optimum initial pH 3.75 for both cultures using thiosulphate and for the mixed culture using tetrathionate. T. thiooxidans ATCC 8085 did not oxidize tetrathionate. Highest rates of thiosalt destruction occurred at ammonium concentrations above 2 mg/L and in the presence of 1 mg/L of phosphate. Under optimal conditions, the pure culture oxidized thiosulphate at 55 mg/L/h; the mixed culture oxidized thiosulphate at 40 mg/L/h and tetrathionate at 50 mg/L/h.

Metal ions were found to cause inhibition in the kinetics of oxidation of thiosulphate by T. thiooxidans ATCC 8085, but only a slight additive effect was apparent in the presence of several of the metal ions. The mixed culture of thiosalt oxidizing bacteria was less sensitive to heavy metal inhibition; the order of inhibition of thiosulphate oxidation was Cd < Zn < Pb < Ag < Cu and tetrathionate oxidation Zn < Cd < Pb < Ag < Cu.

Noranda Research is presently carrying out pilot tests of biological thiosalt oxidation using an aerated pond, a rock-packed aerated pond, and packed aerated columns. A flowsheet and layout schematic of the facilities are presented in Fig. 24 and 25. The study is partly funded by the federal Department of Supply and Services. Preliminary results indicate considerable variation, likely caused by the bacteria-inhibiting effect of lead in the feed. The maximum oxidation rate

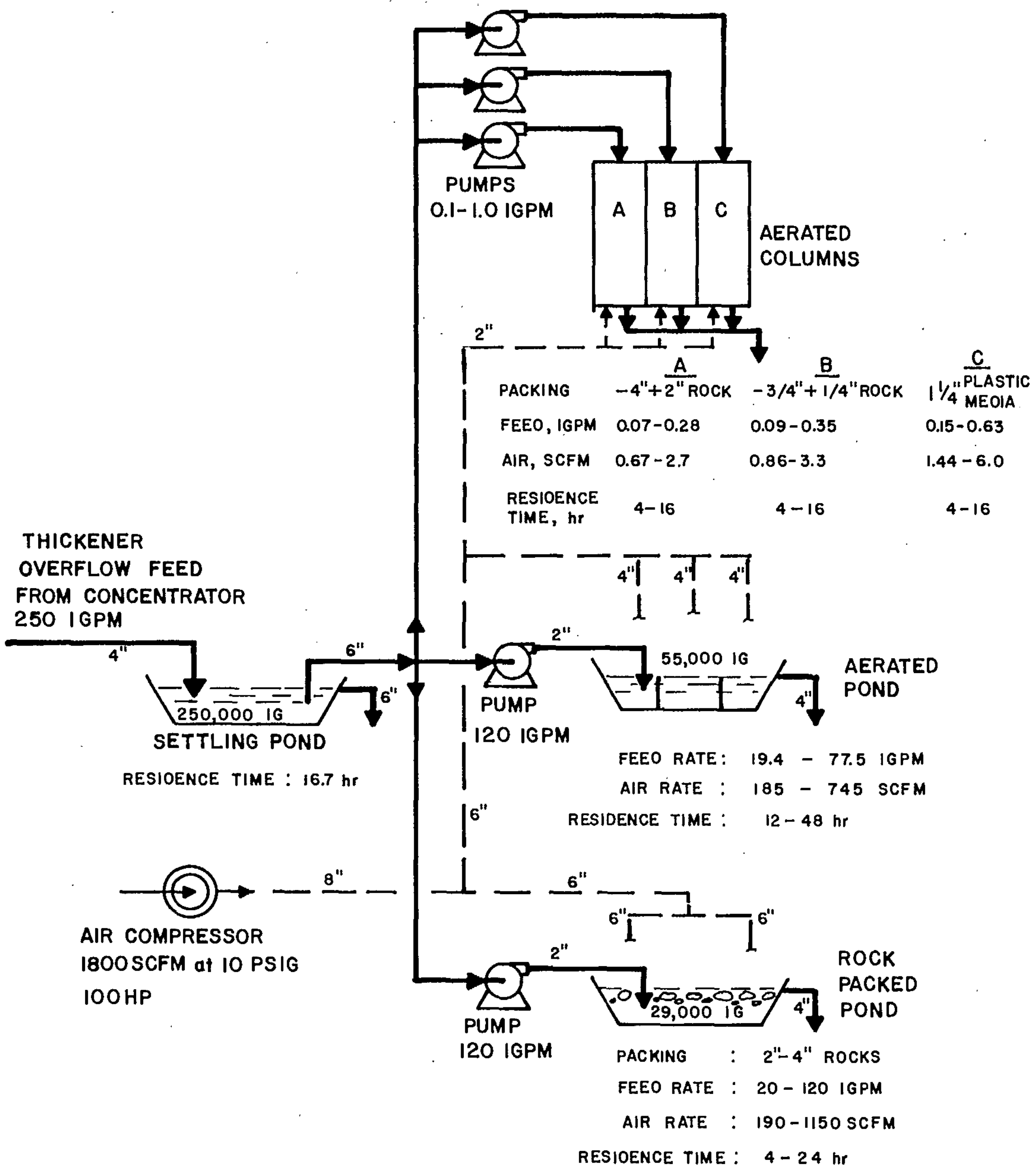


Fig. 24 - Flowsheet of the Noranada Research thiosalt pilot plant

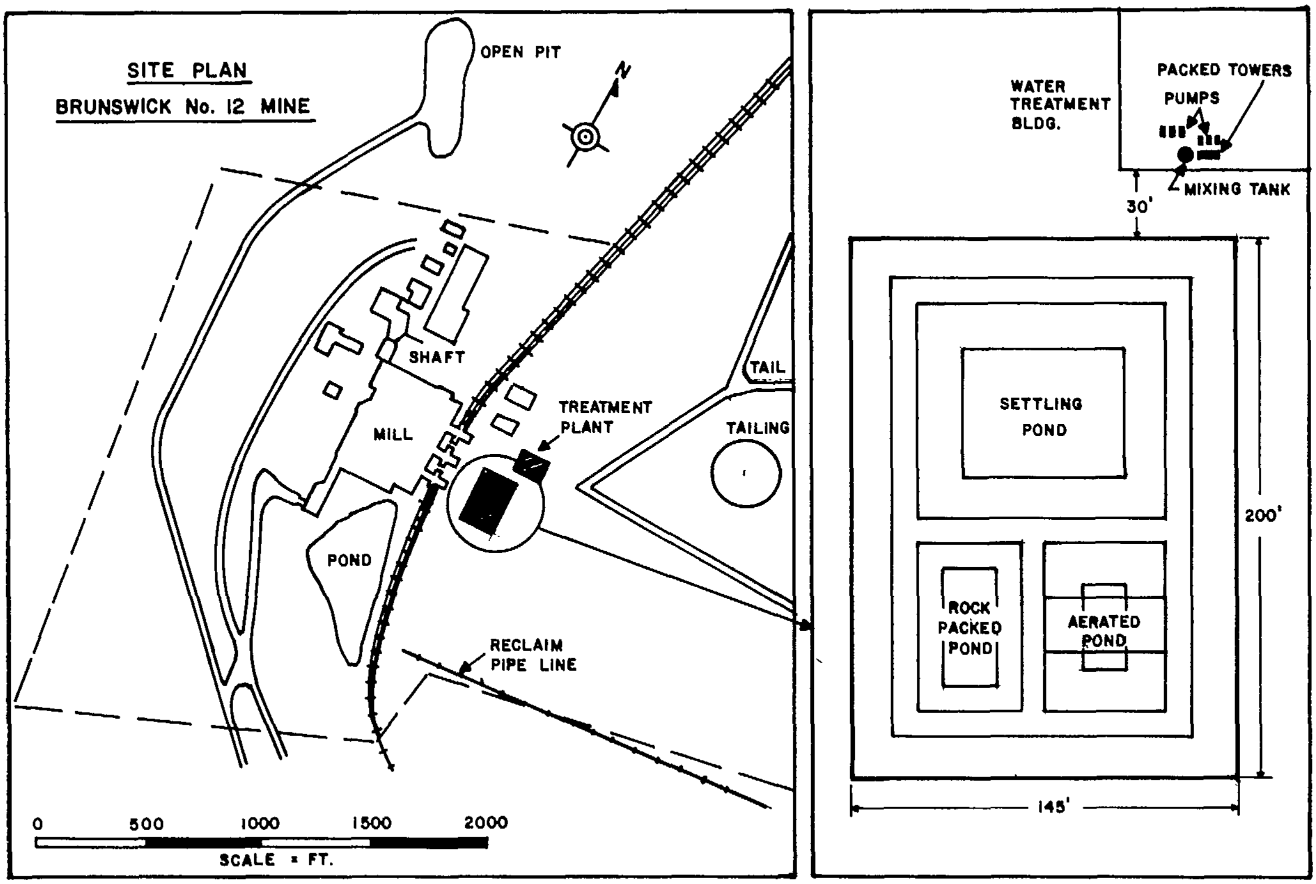


Fig. 25 - Schematic diagram of the Noranda Research thiosalt pilot-plant layout

achieved in the aerated columns was 160 mg/L/h and in the rock-packed aerated pond 70 mg/L/h. The process is also susceptible to fluctuations in the thiosalt concentration. Continuous operation was maintained during the winter months, with complete thiosalt removal being achieved at temperatures as low as 6°C.

Based on the results to date, it appears that a full scale system will require primary clarification, an auxiliary chemical oxidation system, lime neutralization, and secondary clarification facilities.

DISPOSAL TO THE SEA

Discharge of wastes to the sea is presently considered an acceptable disposal technique. In the U.S., the Environmental Protection Agency has designated more than 100 sites for ocean dumping of wastes (104). Generally, sea disposal methods involve careful control of discharge rates over sufficient discharge paths to ensure adequate dilution resulting in negligible changes in ambient seawater concentrations.

For mining operations located on or near a coastline and generating effluents containing significant levels of thiosalts, disposal of effluents to the sea may be a disposal alternative, if permitted by regulatory bodies. Francis carried out an assessment of a pipeline to carry effluents from a mine site near Bathurst, N.B., to Bathurst Harbour (105). A 75-cm O.D. pipeline fully powered with pumps and running a distance of 29 km including a 1.5 km long sea outfall would be required. A comparison of effluent thiosalt and metal concentrations with background seawater levels is presented in Table 16. Francis estimated that the effluent would have to be diluted by at least 15 times to prevent significant changes in the seawater pH. The dilution factor would result in negligeable changes in the sulphate and metal levels of the seawater. A comparison with a similar size sewage pipeline near Pompano Beach, Florida, indicated dilution factors of 70 to 250:1 near the discharge point, and 1000 to 10 000:1 at a distance of 1.5 km from the discharge depending on wind and current velocity.

His estimates indicated capital costs of $5.5 million and operating costs of $50 000 per year (Jan. 1977).

COMPARISON OF COSTS

A summary of the methods reviewed above that indicated technical promise for the treatment of thiosalts is presented in Table 17. Where available, original costs presented by the authors are quoted. It should be emphasized that these costs in most cases are very preliminary estimates based on bench-scale test results. Also, in most cases, pre- and post-treatment facilities would be required to fully complete the teatment system to provide water which could be discharged to the water course.

Table 16 - Thiosalt effluent and seawater quality

	Effluent	Seawater
pH	5.5	not reported
SO_4, mg/L	1500	2800
Fe, mg/L	1.0	0.003 - 0.01
Cu, mg/L	0.03	0.003
Zn, mg/L	0.15	0.005 - 0.01
Pb, mg/L	0.1	< 0.001
Total thiosalt mg/L	2000	-

Table 17 - Summary of thiosalt treatment methods and costs

Method	Ref	Original estimate			Comments
		Basis	Annual operating	Capital	
1. Catalyzed air oxidation	85	1500 U.S. gal/min 5330 mg/L S_2O_3 96 000 lb/d S_2O_3 1st Q, 1981	$8.25 million	$17.5 million	Does not include pre- and post-treatment, test only with synthetic solutions
2. Hydrogen peroxide	86	77 000 lb/d S_2O_3, 4th Q, 1981	$9.02 million	NA	Does not include pre- or post-treatment
3. Chlorine	87	77 000 lb/d S_2O_3, 2nd Q, 1979	$6.0 million	NA	Does not include pre- or post-treatment
4. Ozone	88	2 million imp. gal/d 1000 mg/L S_2O_3 17 000 lb/d S_2O_3 1975	$1.4 million	NA	Does not include pre- or post-treatment
5. SO_2-Air oxidation	-	77 000 lb/d S_2O_3, 2nd Q, 1982	$6.6 million	NA	Does not include costs for copper catalysts
6. Alkaline oxidation	91	2000 U.S. gal/min 2000 mg/L S_2O_3 48 000 lb/d S_2O_3 2nd Q, 1982	$5.2 million	$8.9 million	Includes all neutralization costs
7. Ultraviolet oxidation	92	-	NA	NA	-
8. Reverse osmosis	94	4000 U.S. gal/min 1500 mg/L S_2O_3 72 000 lb/d S_2O_3 4th Q, 1978	$1 to $1.6 million	$4.3 million	Does not include costs for calcium removal and disposal of concentrated solution
9. Electrodialysis	94	4000 U.S. gal/min 1500 mg/L S_2O_3 72 000 lb/d S_2O_3 4th Q, 1978	$0.7 to $1.5 million	$4.0 million	Does not include costs for calcium removal and disposal of concentrated solution
10. Electrooxidation	95	50 000 lb/d S_2O_3, Power = 3.5¢/kWh 2nd Q, 1979	$4.9 million		Does not include pre- or post treatment
11. Reduction by iron	96	3000 U.S. gal/min 33 000 lb S_2O_3/d 1st Q, 1982	$7.1 million	$38.4 million	Does no include costs for disposal of byproducts of H_2S and FeS
12. Activated carbon treatment	80	-	NA	NA	-
13. Biological oxidation - RBC	99	2.3 million gal/d 1250 mg/L S_2O_3 24 000 lb/d S_2O_3 2nd Q, 1980	$430 000	$1.67 million	Does not include pre- and post-treatment
- Noranda Packed ponds			NA	NA	
14. Disposal to the sea	105	75 cm OD pipeline, 29 km long 189 000 lb/d S_2O_3 1st Q, 1977	$50 000	$5.5 million	Does not include pre-treatment costs

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APPENDIX I

PREPARATION OF POLYTHIONATE REAGENTS

PREPARATION OF POTASSIUM TETRATHIONATE

Place 750 mL of distilled water in clean acid Winchester bottle, cool to 0°C in salt/ice bath mixture and saturate with SO_2. Dissolve 75 g (45 mL) of disulphur dichloride (S_2Cl_2) in 500-mL petroleum ether and cool the solution to 0°C in salt/ice bath mixture. Add the S_2Cl_2-petroleum ether in 100 mL portions to the cold SO_2 and cap the Winchester. Shake the mixture vigorously after each addition of the ether solution until the colour disappears and cool again to 0°C before adding the next portion. Loosen the screw cap slowly and carefully each time the ether solution is added to release the built-up pressure, otherwise the mixture may be expelled violently from the bottle. Transfer the mixture to a separatory funnel and drain the aqueous layer into beaker or flask. Discard the ether layer. Keep the aqueous layer under vacuum or bubble nitrogen through the solution until the odour of SO_2 disappears. Cool the solution to 0°C and neutralize to pH 6-7 with a solution of 150 g potassium hydroxide in 1 L 95% ethanol also cooled to 0°C (almost the whole litre of alkaline ethanol will be required). The potassium tetrathionate precipitates along with small amount of potassium chloride and elemental sulphur. Filter this mixture with suction on Buchner funnel and dry at room temperature. Yield = ~132 g crude $K_2S_4O_6$. Dissolve salt in a minimum of water preheated to 70°C while stirring vigorously. During this step, long warming and temperatures above 60°C should be avoided. Filter the solution rapidly through a No. 30 Whatman paper in a funnel kept warm by a heated jacket. Cool the filtrate to 0°C in ice bath to recrystallize the potassium tetrathionate. When thoroughly chilled, filter the product on Buchner funnel, wash with about 150-mL 95% ethanol and dry at room temperature. Add the ethanol wash liquid to the mother liquor to precipitate and recover additional pure tetrathionate.

Theoretical yield = 168 g $K_2S_4O_6$
Actual yeild, 1st crop = 67.3 g
2nd crop = 40.6 g
Total = 107.9 g

Analysis of the salt by ignition to K_2SO_4 at 700°C indicated it to be 99.93 ± 0.05% pure.

PREPARATION OF POTASSIUM TRITHIONATE

Bubble SO_2 gas into 800 mL 5 M potassium hydroxide solution (265 g 85% KOH/800 mL water) in a large beaker surrounded by ice until pH of 7 is obtained. Transfer solution to a 4-L bottle and cool to 0°C or less in salt/ice bath mixture. Prepare solution of 100 g (65 mL) of monosulphur dichloride (SCl_2) in 1.5-L petroleum ether and cool to 0°C or less in salt/ice bath mixture. Add the ether solution in 200-mL portions to the $KHSO_3$ solution, shaking each time until the colour disappears. Do not allow the temperature to rise above +10°C. Loosen the screw cap slowly and carefully each time the ether solution is added in order to release the built-up pressure, otherwise the mixture may be expelled violently. During this stage the $K_2S_3O_6$ precipitates together with a little elemental sulphur and potassium chloride. After all the solutions are mixed, cool to 0°C and filter the crystals on a Buchner funnel and discard the ether and aqueous filtrate. Wash the crystals quickly with a little acetone and dry at room temperature. Yield ~250 g crude $K_2S_3O_6$. Dissolve the crystals in a minimum of water (600-650 mL) at no more than 35°C and filter through No. 30 Whatman paper to remove the elemental sulphur and insoluble residue. Cool the filtrate to 0°C in ice bath to crystallize the $K_2S_3O_6$. Filter the crystals on a Buchner funnel. Transfer the filtrate to a large beaker and retain for the recovery of more $K_2S_3O_6$. Add sufficient acetone (200 mL) to the crystals in the Buchner funnel and stir thoroughly to wash. Apply suction to drain the acetone into flask and repeat the washing with acetone in the same way twice more. Transfer the crystals of pure $K_2S_3O_6$ to a dish and allow to dry at room temperature in air or under vacuum in a desiccator. Add acetone wash liquid to the aqueous filtrate previously retained and cool to 0°C to precipitate and recover additional crystals of $K_2S_3O_6$. Filter these crystals on a Buchner funnel and wash with acetone. Dry the crystals at room temperature in air or under vacuum in a desiccator.

Theoretical yield = 270 g $K_2S_3O_6$
Actual yield, 1st crop crystals = 123 g
2nd crop crystals = 36 g
Total = 159 g

Analysis of the first crop of crystals by ignition to K_2SO_4 at 700°C indicated it to be 99.72% pure. The second crop of crystals was estimated to be 94.5% $K_2S_3O_6$ with about 5.2% KCl and 0.3% water.

The yield of 108 g potassium tetrathionate was somewhat less than the 140 g obtained by Stamm et al., and was due to more water being added than was necessary to dissolve the crude crystals prior to purification. On the other hand, the current yield of 150 g potassium trithionate was almost twice that obtained by Stamm et al. This is perhaps due to misprints in the original reference.

PREPARATION OF POTASSIUM PENTATHIONATE

Dissolve 51-g SCl_2 in 200 mL carbon tetrachloride, charge the solution to a wide-necked flask of about 2-L capacity and cool the liquid to -15°C. Also prepare 250 g $Na_2S_2O_3.5H_2O$ solution in 400 mL water, using about 1% more water than would be calculated and cool to 0°C. In a third vessel mix 200 mL 36% hydrochloric acid and 200 mL water and cool to 0°C. Now, pour both the thiosulphate solution and the hydrochloric acid simultaneously and rapidly into the SCl_2-solution. Stopper the flask and shake at once vigorously. The solution will thereby undergo an instantaneous discoloration; at the latest, within 20 s. The aqueous layer will be almost clear; there must not be more than a very slight turbidity caused by separated-out sulphur. The temperature of the solution must not rise to more than 0°C during the conversion reaction. Add immediately to the mixture of reaction products 0.3 M iron(III) chloride solution, cooled to 0°C, in an amount sufficient to impart a light yellow coloration to the aqueous layer. This requires about 120 mL solution. During the addition of the iron(III) chloride, the solution takes on an intermediary dark coloration; this coloration, caused by the iron(III) sulphate complex, will however very rapidly disappear. Add the mixture of reaction products into a separatory funnel, separating aqueous solution and CCl_4. The aqueous solution which has a weak SO_2 odour, must be directly evaporated to about 170 mL at 12 mm Hg and at 35-40°C. Sodium chloride is separated out during the evaporation. Remove sodium chloride from the concentrate by filtering over a Buchner funnel, and cool thereafter to 0°C. Add to this solution, under constant vigorous stirring through a dropping funnel, a solution of potassium hydroxide in methanol (about 20 g KOH/100 mL methanol) which had been cooled to 0°C. Add the potassium solution drop by drop or in a thin jet, keeping in mind that the temperature of the solution must never exceed +10°C. Where the drops enter the solution, some iron(III) hydroxide will initially form, but this product will immediately dissolve. Whenever, at the dopping-in spot black-green hydroxide begins to separate out (at about pH = 3), stop adding potassium solution. Cool the liquid once more to 0°C and start adding potassium solution. Wash the yellowish product with a small amount of acetone until it looks white and dry it upon a clay plate. This yields 102-g salt containing 85% $K_2S_5O_6.1.5H_2O$. If an additional amount of alcoholic potassium solution (up to pH 5) is added to the mother liquor, 60 g product will again be settled out; it contains 30% $K_2S_5O_6.1.5H_2O$ and about 60% $K_2S_4O_6$.

The 85% product is contaminated by potassium chloride. To purify the primary product, heat 100 mL 0.5 N hydrochloric acid to 60°C and enter into this solution 50 g of crude 85% product; since the solution will thereby become materially cooler, reheat it rapidly to 50°C.

Now filter through a hot-water filter and bring the clear solution into a bowl placed on ice. Star-shaped crystals will separate out; filter them and wash with alcohol. The yield will consist of about 23 g 100% $K_2S_5O_6 \cdot 1.5H_2O$. By adding methanol to the mother liquor another crop of 13 g of ~80% potassium pentathionate can be produced.

PREPARATION OF POTASSIUM HEXATHIONATE

Dissolve 27 g S_2Cl_2 in 100 mL CCl_4, bring this solution into a wide necked flask of about 1-L capacity and cool the solution to -15°C. Prepare in 300-mL Erlenmeyer flask a solution of 100 g $Na_2S_2O_3 \cdot 1.5H_2O$ in 150-mL water. In another Erlenmeyer flask mix 80 mL 36% hydrochloric acid with 80-mL water. Now pour thiosulphate solution and hydrochloric acid simultaneously into the S_2Cl_2 solution. At once vigorously shake the reaction mixture until it looks colorless (it will do so after about 20 s). Immediately add cooled, about 0.6 M iron(III) chloride solution, until the aqueous layer is a pale yellow. This requires about 15-mL iron(III) chloride solution. Now bring the fluid - it must not be more than quite weakly opaque owing to the separated out sulphur - into a separatory funnel and recover the aqueous layer. The aqueous solution, which has a weak SO_2 odour, must be directly evaporated to 50 mL at 12 mm Hg and at 35°C. Filter the sodium chloride which separated out. The concentrate is cooled with ice water. Add to it drop by drop, under constant vigorous stirring, a solution of about 80 g KOH in 100-mL methanol cooled to 0°C. Filter off the sodium chloride which separated out. When the pH of the solution has risen to 1-2, owing to the addition of about 40-mL potassium solution (indicator paper), filter the crystal-paste product with a Buchner funnel. Wash the almost white crystals twice with 40-mL acetone each time. Dry upon a clay plate. The yield is 42 g crude product which contains 81% $K_2S_6O_6$ along with potassium chloride. By adding another portion of potassium solution to the mother liquor, up to pH 3-4, another portion of a crude product which contains 46% $K_2S_6O_6$ can be prepared.

To purify the product, dissolve 20 g 81% primary product in 30-mL 2 N hydrochloric acid. Heat the solution rapidly to 60°C and cool it immediately thereafter in ice water to 0°C, turning it around from time to time. Filter the separated-out crystals and wash with alcohol. The yield is 11 g 96% potassium hexathionate.

APPENDIX 2

ANALYTICAL PROCEDURES

NORANDA TITRIMETRIC METHOD

ANALYSIS OF THIOSULPHATE AND POLYTHIONATES

Principle

- Polythionate containing 3, 4 and 5 sulphur atoms react quantitatively with mercuric chloride to release acid in solution. The stoichiometric equation is:

$$2S_nO_6^{2-} + 3HgCl_2 + 4H_2O \rightarrow HgCl_2.2HgS + 8H^+ + 4Cl^- + 4SO_4^{2-} + (2n-6)S$$

A similar equation applies for thiosulphate:

$$2S_2O_3^{2-} + 3HgCl_2 + 2H_2O \rightarrow HCl_2.2HgS + 4H^+ + 4Cl_4^- + 2SO_4^{2-}$$

In both cases the acid generated may be titrated with standard caustic solution to determine the concentration of four sulphur anions:

$$S_2O_3^{2-},\ S_3O_6^{2-},\ S_4O_6^{2-},\ S_5O_6^{2-}$$

Apparatus

1. pH meter preferably with a combination electrode (Procedure 1 and 2).
2. Magnetic stirrer and stirring bar.
3. Two 25-mL burettes.
4. 100-mL beakers.
5. Hot plate.
6. Pipettes of various sizes.

Determination in the Absence of Sulphite

1.1 Pipette an aliquot of sample into 100-mL beaker. The aliquot size will be dependent upon the concentration range of the analysis:

- i) 0-50 mg/L as $S_2O_3^{2-}$ use 50-mL aliquot
- ii) 50-400 mg/L as $S_2O_3^{2-}$ use 25-mL aliquot
- iii) 400-2000 mg/L as $S_2O_3^{2-}$ use 5-mL aliquot
- iv) 2000-5000 mg/L as $S_2O_3^{2-}$ use 2-mL aliquot.

1.2 If necessary, dilute sample to about 30 mL.

1.3 With the beaker on a stirring mantle, insert the stirring bar and pH electrode. To ensure constant reproducible stirring, set the mantle variable control to a predetermined position.

1.4 Titrate to an initial end-point of 4.3 with 0.005 N acid. With very basic samples use 0.1 N acid to avoid excessive sample dilution.

1.5 Remove pH probe and stirring bar, rinsing each with distilled water into the sample.

1.6 Pipette 5-mL mercuric chloride solution into the sample. Dilute to a final volume of about 60 mL.

1.7 Allow the sample to stand at room temperature for about 5 min.

1.8 Heat solutions on hot plate bringing just to a boil. Remove from hot plate and allow to cool to room temperature.

1.9 With constant stirring, add potassium iodide solution slowly until the resulting orange precipitate which develops disappears again. Avoid adding large excesses of potassium iodide to the resulting pale yellow turbid solution.

1.10 Insert the pH electrode and maintain stirring similar to step 1.3.

1.11 Titrate with standard 0.005 N caustic to the pH 4.3 end-point. For best results, run the sample again in duplicate and average the titre values obtained.

1.12 Repeat steps 1.3 to 1.11 using 30-mL water, instead of a sample. Titrate the alkalinity which develops after potassium iodide addition with standard 0.005 N sulphuric acid to pH 4.3.

1.13 From the results of step 1.12, calculate the equivalent volume of standard 0.005 N caustic solution required to neutralize the acid added:

$$V = \frac{N_a T_a}{N}$$

where: V = equivalent amount of base in mL
N = normality of standard caustic solution (step 1.11)
N_a = normality of standard acid solution (step 1.12)
T_a = mL of standard acid added (step 1.12).

After having run this blank determination several times, a value for V will be established and need only be checked infrequently.

1.14 Calculate the concentration as thiosulphate:

$$\text{mg/L as } S_2O_3^{2-} = \frac{(T+V)N}{A} \times 56\ 000$$

where: T = mL of caustic solution added (step 1.11)
N = normality of caustic solution (step 1.11)
A = mL of sample pipetted (step 1.1)
V = equivalent amount of base in mL (step 1.13).

Determination in the Presence of Sulphite

If sulphite is present, high results will be obtained from procedure 1. The following modified procedure is recommended if sulphite concentration exceeds 10% of the polythionate concentration. An initial iodine addition oxidized sulphite to sulphate which does not interfere with the analysis.

2.1 Pipette an aliquot of sample into a 100-mL beaker. The aliquot size will be dependent upon the concentration range of the analysis:

i) 0-50 mg/L as $S_2O_3^{2-}$ use 50-mL aliquot
ii) 50-400 mg/L as $S_2O_3^{2-}$ use 25-mL aliquot
iii) 400-2000 mg/L as $S_2O_3^{2-}$ use 5-mL aliquot
iv) 2000-5000 mg/L as $S_2O_3^{2-}$ use 2-mL aliquot.

2.2 If necessary, dilute sample to about 30 mL.

2.3 With the beaker on a stirring mantle insert the stirring bar and pH electrode. To ensure constant reproducible stirring, set the mantle variable control to a predetermined position.

2.4 Titrate to an initial end-point of 4.3 with 0.02 N acid.

2.5 Titrate dropwise with 0.1 N iodine solution until a faint yellow colour develops.

2.6 Re-titrate to pH 4.3 with 0.02 N or 0.005 N caustic solution.

2.7 Remove the pH electrode and stirring bar. Rinse each with distilled water in the sample.

2.8 Pipette 20-mL mercuric chloride solution into the sample. Dilute to a final volume of about 60 mL.

2.9 Allow sample to stand at room temperature for about 5 min.

2.10 Heat solution on hot plate. Bring just to a boil. Remove from hot plate. Allow to cool to room temperature.

2.11 With constant stirring add potassium iodide solution slowly until the resulting orange precipitate which develops disappears again. Avoid adding large excesses of potassium iodide to the resulting pale yellow turbid solution.

2.12 Insert the pH electrode and maintain stirring similar to step 2.3.

2.13 Titrate with standard 0.005 N caustic to the pH 4.3 end-point. For best results, run samples in duplicate and average the titre values obtained.

2.14 Calculate the concentration as thiosulphate:

$$\text{mg/L as } S_2O_3^{2-} = \frac{T\ N}{A} \times 56\ 000$$

where: T = mL of caustic solution added (step 2.13)

N = normality of caustic solution (step 2.13)

A = mL of sample pipetted (step 2.1).

Determination for Mill Circuit Samples (Sulphite Absent)

3.1 Pipette aliquot of filtered sample into 250-mL Erlenmeyer flask. The aliquot size depends upon the concentration range of the analysis:

- i) 0-50 mg/L as $S_2O_3^{2-}$ use 50-mL sample
- ii) 50-400 mg/L as $S_2O_3^{2-}$ use 25-mL sample
- iii) 400-2000 mg/L as $S_2O_3^{2-}$ use 5-mL sample
- iv) 2000-5000 mg/L as $S_2O_3^{2-}$ use 2-mL sample.

3.2 Add 2-5 drops methyl orange indicator solution.

3.3 If the indicator in the solution is yellow, titrate to a red end-point with 0.02 N sulphuric acid. If it is red (see note below) titrate with 0.02 N caustic to yellow end-point.

NOTE: A red initial colour is an indication that high concentrations of sulphite may exist. Procedure 2 is recommended. The procedure below may be used if it is demonstrated that results comparable to procedure 2 are obtained.

3.4 Pipette 5-mL mercuric chloride solution into the sample.

3.5 Dilute sample to 60 mL.

3.6 Allow sample to stand at room temperature for about 5 min.

3.7 Heat solutions on hot plate. Bring just to a boil. Remove from hot plate. Allow to cool to room temperature.

3.8 With constant stirring add potassium iodide solution slowly until the resulting orange precipitate which develops disappears again. Avoid adding large excesses of potassium iodide to the resulting pale yellow turbid solution.

3.9 Titrate with standard 0.02 N caustic solution to end-point.

3.10 Calculate the concentration as the thiosulphate anion using the equation:

$$\text{mg/L as } S_2O_3^{2-} = \frac{T\,N}{A} \times 56\ 000$$

where: T = mL of caustic solution added (step 3.9)

N = normality of caustic solution (step 3.9)

A = mL of sample pipetted (aliquot size) (step 3.1).

Preparation of Reagents

1. Sodium hydroxide (caustic) solution

Caustic solution is prepared (0.005 N or 0.02 N) in CO_2-free water and standardized against potassium biphthalate. The 0.1 N caustic may be made up or purchased. It should be stored in tightly capped polyethylene containers for infrequent use. No standardization is necessary for the 0.1 N solution.

2. Sulphuric acid

Standard acid (0.005 N) is prepared by adding about 0.15 mL 98% acid to 1-L water. The solution used for titrating the blank in step 12 should be standardized by pipetting 10 mL into a beaker, diluting to about 30 mL and titrating to an 8.2 end-point with the standardized 0.005 N caustic solution. The 0.02 N acid is prepared with 0.6-mL 98% acid in 1-L and standardized. The 0.1 N is prepared by adding 2.6-mL 98% acid to 1-L water.

3. Mercuric chloride solution

A 2% solution is prepared by dissolving 20 g in 1-L water. Fresh solution should be prepared weekly.

4. Potassium iodide solution

A 20% solution is prepared by dissolving 200 g in 1-L water.

5. Iodine solution

A 0.1 N solution is prepared as outlined in the determination of thiosulphate by iodine titration.

6. Methyl orange

A methyl orange solution is prepared by dissolving 0.5-g sodium salt in 1-L water, adding 15-mL 0.1 N hydrochloric acid and filtering when cold if necessary.

7. Phenolphthalein

A phenolphthalein solution is prepared by dissolving 5 g in 500-mL methanol, adding 500-mL H_2O and filtering if necessary.

8. Standard caustic solutions

8.1 To obtain CO_2-free water, boil distilled water for about 15 min and cool rapidly with an inverted beaker over the mouth of the flask to prevent ingress of air.

8.2 Weigh about 40-g sodium hydroxide pellets and dissolve in 1-L CO_2-free water to obtain 1 N caustic solution (also may be purchased).

8.3 Pipette 5-mL 1 N caustic into 1-L volumetric flask and make up to volume with CO_2-free water to obtain 0.005 N caustic solution. Pipette 20-mL 0.02 N caustic solution.

8.4 To determine actual normality:

8.4.1 Add 2.042-g anhydrous potassium biphthalate to 1-L volumetric flask and make up to volume with CO_2-free water to obtain 0.01 N biphthalate solution.

8.4.2 Pipette 10-mL 0.01 biphthalate solution into 250-mL Erlenmeyer flask and dilute to about 50 mL with CO_2-free water.

8.4.3 Titrate with the 0.005 N or 0.02 N caustic solution to be standardized to an end-point pH = 8.2 (phenolphthalein end-point may be used instead of pH meter). Add 2-5 drops of phenolphthalein solution to the sample (see Preparation of Reagents, item 7).

8.4.4 Calculate the normality of the caustic solution:

$$\text{normality} = \frac{0.1000}{T}$$

where: T = No. of mL of caustic required. Caustic solution should be freshly prepared weekly and standardized.

Interferences

1. Sulphide ion

Mercuric chloride reacts with sulphide in solution to produce acidity and high results. The odour of rotten eggs upon excess acid addition indicates its presence. Drawing a vacuum on the sample while maintaining pH 4 will minimize this interference.

2. Sulphite ion

Mercuric chloride will oxidize sulphite to sulphate to produce acidity (high results). Formaldehyde addition will reduce sulphite interference. The presence of formaldehyde in these analytical solutions may generate toxic chlorinated ethers. To avoid this hazard procedure 2 is the recommended alternative.

3. Ferrous ion

High results were obtained with ferrous ion present. The addition of soda ash (5-mL 1 g/L Na_2CO_3 solution) to the sample prior to procedure 1 reduced errors to 5% at 20 mg/L $S_2O_3^{2-}$ and 1000 mg/L $FeSO_4$.

4. Buffer effects

Components which contribute to buffer effects near the titration's end-point will interfere. If a buffer effect is believed to occur, titrate to pH 8.2 end-point rather than 4.3. Buffers demonstrating an interference with pH 4.3 end-point are unlikely to be present in mill samples.

Determination of Sulphate in the Presence of Thiosalts

Reagents

- Disodium ethylenediamine tetraacetate, 0.01 M; 3.7224-g $Na_2EDTA \cdot 2H_2O$ dissolved in 1 L.
- Magnesium chloride 0.01 M.
- Barium chloride 0.02 M; 4.166-g $BaCl_2$ and a few drops of 1 M HCl in 1 L.
- Formaldehyde solution. To 50-mL water add 10-mL methanol and 40-mL formaldehyde solution (37%).
- Indicator solution. Dissolve 0.20-g Eriochrome

Black T and 0.02-g Methyl Red indicators in 100-mL methanol.

- Buffer solution, pH 10.0; 70-g ammonium chloride (NH_4Cl) and 570 mL of concentrated ammonium hydroxide (NH_4OH) in 1 L.
- Sodium carbonate 10% W/V.
- Hydrochloric acid ~1 M.
- Iodine 0.10 N.
- Sodium thiosulphate 0.004 N.

Procedure

1. To 10-mL sample and 10-mL water introduce a small piece of red litmus paper and make basic to litmus with 10% Na_2CO_3 solution. Add 5-mL formaldehyde solution and let stand 5 min to allow sulphite to react with formaldehyde. Add 1 M HCL until the litmus paper is red and add 0.10 N iodine solution until the medium is slightly yellow. Add enough 0.004 N thiosulphate solution to remove the yellow colour. Transfer the solution to a 50-mL volumetric flask containing 10.0-mL 0.02 M $BaCl_2$ solution, make to volume with water, shake well and allow the precipitate to settle for 30 min. Transfer 25-mL aliquot supernatant solution to 250-mL beaker, add 25-mL water, 3.0-mL standard $MgCl_2$ solution, 10-mL ammonia buffer solution (pH 10.0), 1-mL indicator solution and titrate rapidly with 0.01 M EDTA to a blue end-point thus ensuring a slight excess of EDTA. Add an additional 2.0-mL $MgCl_2$ solution and titrate with EDTA to the blue end-point.
2. Repeat the procedure without sulphate to obtain the EDTA titre (C.T.) due to 5.0-mL magnesium solution and 5.0-mL barium solution (C.T. = ~15.0-mL EDTA).

Calculations

For 10-mL sample aliquot, sulphate is 2 (C.T. - mL EDTA titre) millimoles.

IODINE TITRATION METHOD

ANALYSIS OF THIOSULPHATE

Principle

- The thiosulphate anion is oxidized to tetrathionate in weakly acid iodine solutions:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Sulphite is also oxidized to sulphate under similar conditions, but its interference may be eliminated by adding excess formaldehyde. This method is a well established wet chemical analysis and has been outlined previously by Brunswick Mining and Smelting in conjunction with the Canada Centre for Inland Waters.

Procedure

1. Pipette an aliquot of sample into 250-mL Erlenmeyer flask. The aliquot size should depend upon the thiosulphate concentrations:
   i) <100 mg/L use 50-mL aliquot
   ii) 100-1000 mg/L use 25-mL aliquot
   iii) 1000-2500 mg/L use 10-mL aliquot
   iv) 2500-5000 mg/L use 5-mL aliquot.
2. Add 2-mL formaldehyde solution for every 1000-mg sulphite anion present. Work in a fumehood to prevent exposure to volatile chlorinated ethers which might form in the presence of formaldehyde. Store wastes within the hood and dispose with care.
3. Dilute to about 50 mL with distilled water.
4. Adjust the pH to within the range of 4-5 with 10% H_2SO_4 or 10% NH_4OH. Litmus paper or a pH meter may be used.
5. Add 0.2-0.5 g of iodine indicator.
6. Titrate with 0.01 N standardized solution to the first permanent blue colour.
7. Calculate the concentration of thiosulphate:

$$\text{mg/L of } S_2O_3^{2-} = \frac{T\ N}{A} \times 112\ 000$$

where: T = mL of iodine solution added
N = normality of iodine solution
A = mL of sample used.

Preparation of Reagents

1. Sulphuric acid
   A 10% solution is prepared by adding 10 vol concentrated acid to 90 vol water.
2. Ammonium hydroxide
   A 10% solution is prepared as for the acid.
3. Formaldehyde solution
   A 40% solution in 10-15% methanol is available commercially.

4. Iodine indicator

British Drug House indicator (catalogue No. 20054); thyodene could probably be used.

5. Iodine solution

A 0.01 N solution is prepared daily by pipetting 25 mL 0.1 N iodine solution into a 250-mL volumetric flask, made up to volume with distilled water, and protected from the light by wrapping the flask with tin foil. The 0.1 N solutions are prepared and standardized according to the procedure outlined below.

6. Standard iodine solution

6.1 Dissolve 20-g potassium iodide (iodate-free) in 30-40-mL distilled water and add to 1-L volumetric flask.

6.2 Weigh 12.7 g iodine (analytical reagent grade) and add to the volumetric flask.

6.3 The flask is cooled and the solution swirled to dissolve the iodine.

6.4 Fill the volumetric flask to the mark with distilled water.

6.5 Weigh accurately about 5 g arsenious oxide (analytical reagent grade).

6.6 In 500-mL beaker, dissolve the arsenious oxide in about 50-mL concentrated sodium hydroxide prepared by adding about 5-g to 50-mL distilled water.

6.7 Dilute to about 350 mL and neutralize to a phenolphthalein end-point with 1 N hydrochloric acid.

6.8 Transfer to 1-L volumetric flask, add 5-g sodium bicarbonate and make up to volume.

6.9 Pipette 25-mL arsenious oxide solution into 250-mL Erlenmeyer flask.

6.10 Add about 50-mL distilled water and about 5-g sodium bicarbonate swirling to dissolve.

6.11 Add 0.2-0.5-g iodine indicator and titrate with the 0.1 N iodine solution to a blue end-point.

6.12 Calculate the solution normality:

$$\text{normality of } I_2 = \frac{25W}{49.46T}$$

where: W = weight of arsenious oxide added to 1 L
T = mL of I_2 solution required.

6.13 Store iodine solution in a glass-stoppered coloured bottle and prepare fresh 0.01 N solutions daily.

EXCESS IODINE METHOD

ANALYSIS OF THIOSULPHATE AND SULPHITE

Principle

- Both thiosulphate and sulphite are oxidized by acidic iodine solution. Thiosulphate may be determined by titration, but sulphite is best analyzed by adding it to an excess of iodine. The excess may be calculated by titrating with a known thiosulphate solution.

Procedure

1. Estimate the thiosulphate-sulphite concentration from a knowledge of the sample or by titrating with standard iodine without the addition of formaldehyde. This will allow the estimation of (i) the amount of excess iodine required and (ii) the aliquot size for the sample.
2. Calculate the required excess of iodine solution:

$$V_{est} = \left(\frac{AC_{est}}{112\ 000} + 0.1\right)\frac{1}{N}$$

where: V_{est} = mL of iodine required
A = mL of sample (aliquot size)
C_{est} = concentration of sulphite and thiosulphate estimated as thiosulphate
N = normality of iodine solution.

The result V_{est} in mL can be rounded upward by about 5 mL. The estimated concentration will determine the aliquot size of the sample:

i) <100 mg/L as $S_2O_3^{2-}$ use 50-mL aliquot
ii) 100-1000 mg/L as $S_2O_3^{2-}$ use 35-mL aliquot
iii) 1000-2500 mg/L as $S_2O_3^{2-}$ use 10-mL aliquot
iv) 2500-5000 mg/L as $S_2O_3^{2-}$ use 5-mL aliquot.

If the estimated excess iodine is too high, inconveniently large volumes of titre will be required. If the estimated excess is low then no blue colour will be obtained when the indicator is added. In both cases the excess will have to be re-evaluated and the titration repeated.

3. Add the estimated volume of iodine solution by pipette to 250-mL Erlenmeyer flask. If the excess required represents a large volume of 0.01 N use the 0.1 N solution.
4. Acidify the iodine solution with 0.5-mL concentrated sulphuric acid (98%).
5. Pipette the sample aliquot into iodine solution.
6. Add 0.2-0.5-g iodine indicator.
7. Titrate the excess remaining iodine with 0.01 N thiosulphate to a colourless end-point (T_2).
8. Repeat the analysis using distilled water rather than the sample (T_2) using exactly the same volume of iodine solution.
9. Calculate the concentration of the sample as thiosulphate:

$$\text{mg/L as } S_2O_3^{2-}\ (D_2) = (T_2 - T_1)\ \frac{N}{A} \times 112\ 000$$

where: T_2 = No. mL of thiosulphate solution required for a blank determination

T_1 = No. mL of thiosulphate solution required for a sample determination

A = aliquot size (mL of sample used).

10. To calculate the sulphite ion concentration, determine the thiosulphate concentration by the iodine titration method (D_1) and subtract from the result calculated in step 9 (D_2):

$$\text{mg/L } SO_3^{2-} = (D_2 - D_1)\ \frac{40}{112}$$

Preparation of Reagents

1. Sulphuric acid

   A 98% concentration.

2. Iodine solution

   A 0.01 N solution is prepared daily by pipetting 25-mL 0.1 N iodine solution into a 250-mL volumetric flask and making up to volume with distilled water. Protect from light by wrapping the flask in tin foil. The 0.1 N solutions are prepared and standardized according to the procedure outlined in "Analysis of thiosulphate" (Iodine Titration Method).

3. Iodine indicator

   British Drug House indicator (catalogue No. 20054) or thyodene.

4. Thiosulphate solution

   A 0.01 N solution is prepared by adding 1.2405-g $Na_2S_2O_3 \cdot 5H_2O$ to a 500-mL volumetric flask and making up to the mark.

Determination of Thiosalts by Back-Titration of Barium Chloride with EDTA

Apparatus

Ion-exchange columns: Prepare 1 cm diam column about 20 cm long using a suspension of Dowex 50WX8, 50 to 100 mesh resin in 1 M hydrochloric acid. Wash the column with distilled water and drain the solution to but not below the upper surface of the column.

Reagents

Potassium tri- and tetrathionate were prepared as described in Appendix 1. All other chemicals are of analytical grade.

Standard potassium tetrathionate solution 0.01 M

Dissolve 0.6049-g potassium tetrathionate in distilled water and dilute to 200 mL in a volumetric flask.

Standard sodium thiosulphate solution 0.01 M

Dissolve 2.50-g sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) in distilled water and dilute to 1 L. Standardize by iodometry.

Standard sodium sulphate solution 0.01 M

Dissolve 0.2840-g sodium sulphate in distilled water and dilute to 200 mL in a volumetric flask.

Standard sodium sulphite solution 0.01 M

Dissolve 0.2520-g sodium sulphite in distilled water and dilute to 200 mL in a volumetric flask.

Standard barium chloride solution 0.01 M

Dissolve 2.4431-g barium chloride ($BaCl.2H_2O$) in distilled water and dilute to 1 L. Standardize against the 0.01 M EDTA solution.

Standard EDTA solution 0.01 M

Dissolve 3.7224-g EDTA in distilled water and dilute to 1 L. Standardize against a standard lead solution prepared from high-purity lead metal.

o-cresolphthalein complexone indicator

Dissolve 0.3 g in 100-mL distilled water containing 0.5-mL concentrated ammonium hydroxide. This solution should be prepared freshly every week.

Initial sulphate*

- Pipette a suitable aliquot containing 4- to 7-mg total initial sulphate into 150-mL beaker and dilute to 25 mL with distilled water. Acidify the solution with a drop or two of 6 M hydrochloric acid and add dropwise 0.004 N iodine solution until a slight yellow colour persists. Boil the solution for several minutes to remove the excess iodine and then cool to room temperature. Pass the solution through the ion-exchange column to remove all metal ions. Wash the columns with distilled water three to four times (total volume ≃60 mL). Adjust the pH of the effluent to 3.5 and bring it to a boil, add a known amount of 0.01 M barium chloride solution in excess. Digest the precipitate for 3-4 h on a water-bath to render the precipitate coarsely granular and insoluble. Cool and neutralize the solution with dilute sodium hydroxide solution. Adjust the volume of solution to about 100 mL, add 3-4 drops of o-cresolphthalein complexone indicator and adjust the pH to 11.0 ± 0.1 with concentrated ammonium hydroxide. Titrate the excess barium immediately with 0.01 M EDTA solution until the blue colour changes to pale violet. One millilitre of 0.01 M barium solution precipitates about 1-mg sulphate. From the difference in volume of 0.01 M barium chloride originally added and the amount in excess as determined by EDTA, calculate the sulphate (plus sulphite) content of the sample.

Sulphate - after hydrogen peroxide oxidation**

- Pipette a suitable aliquot containing 4 to 70-mg combined sulphate into 150-mL beaker and dilute to 25 mL with distilled water. Acidify the solution with a few drops of 6 M hydrochloric acid, add 2-mL 30% hydrogen peroxide solution and heat at 80°C for 15 min, then boil vigorously for several more minutes until all signs of peroxide decomposition cease. Cool to room temperature and pass through the ion-exchange column to remove metal ions. Wash the column with distilled water as for "Initial sulphate". Adjust the pH of the effluent to 3.5 and follow the above procedure starting at the point of addition of 0.01 M barium chloride solution.

Sulphate - after potassium chlorate and nitric acid oxidation***

- To an aliquot identical to that used above add 2 mL 30% hydrogen peroxide solution. Heat the solution at 80°C for 15 min then add 0.10 to 0.25-g solid potassium chlorate and 2- to 5-mL concentrated nitric acid. Evaporate the solution to near dryness but do not bake. Cool, add 25-mL hot distilled water and sufficient concentrated ammonium hydroxide solution just to turn red litmus blue. Acidify with a drop or two of 6 M hydrochloric acid, boil the solution for several minutes, cool to room temperature and pass it through the ion-exchange

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* This is defined as the total sulphate resulting from the oxidation of sulphite by iodine and sulphate present in the original solution.

** The difference between the value obtained after hydrogen peroxide oxidation and initial sulphate is a measure of the thiosalts which are oxidized by hydrogen peroxide; i.e., $S_2O_3^{2-}$, $S_2O_3^{2-}$, $S_4O_6^{2-}$.

*** The difference between the value obtained after potassium chlorate and nitric acid oxidation and after hydrogen peroxide oxidation is a measure of the dithionate present.

column. Adjust the pH of the effluent to 3.5 and follow the "Initial sulphate" method for the completion of the determination of total sulphate starting at the point where the 0.01 M barium chloride is added.

Spectrophotometric Determination of Thiosulphate, Trithionate and Tetrathionate

- Sulphite does not interfere in this method, but iron and manganese, if present in the sample, must be removed. To accomplish this make a measured volume of sample alkaline with Na_2CO_3 (10% W/V), filter, wash and collect the filtrate in a suitable volumetric flask. Take a known volume of filtrate for the determination.
- The various sulphur species are determined by difference using three procedures: A, B and C. Difficulty is encountered in procedure B if the sample is too alkaline; i.e., pH > 11. In this case, upon addition of the thymolphthalein indicator, neutralize the sample aliquot with dilute sulphuric acid and then bring back the blue colour with dilute ammonia.
- Absorbance should be read at 460 nm within 30 min after colour development. If the solutions cannot be analyzed in this time period, they should be stored in the dark.

Solutions

- Potassium cyanide, 0.5 M: dissolve 17.2-g KCN in distilled water and dilute to 500 mL.
- Cupric chloride, 0.2 M: dissolve 17.6-g $CuCl_2.2H_2O$ in distilled water, add a drop of concentrated hydrochloric acid to prevent hydrolysis of cupric ions, dilute to 500 mL.
- Ferric nitrate-perchloric acid solution: dissolve 303-g $Fe(NO_3)_3.9H_2O$ in small volume of distilled water, add 186-mL concentrated perchloric acid (70 wt %), and dilute to 500 mL.
- Buffer solution, pH 4.5: dissolve 77-g ammonium acetate (CH_3COONH_4) in distilled water, add 60-mL of glacial acetic acid and dilute to 1 L.
- Ammonia water, 1 M: dilute 13.5-mL concentrated ammonium hydroxide solution to 100 mL, keep in a dropping bottle.
- Thymolphthalein, 0.1% W/V in ethanol: keep in a dropping bottle.
- Acetone, A.C.S. reagent.
- Ammonium thiocyanate, 0.1 M: prepare from purchased standard volumetric solution.
- Ammonium thiocyanate, 4 micromoles/mL: transfer 10 mL of standard solution (0.1 M) to 250-mL volumetric flask, and dilute to the mark.

Calibration Graph

- Transfer into 50-mL volumetric flasks, 1- to 5-mL aliquots of the standard ammonium thiocyanate solution. Follow Procedure A.
- Using a 1-cm · silica cell, a linear graph is obtained in the range 1-20 micromoles SCN^-/50 mL. For 20 micromoles SCN^-, the absorbance was 1.73.

Procedure A: Cupric Ion-Catalyzed Cyanolysis of Thiosulphate at pH 4.5

- Pipette an aliquot of the sample solution (1-10 mL) to 50-mL volumetric flask.
- To this, add 10-mL acetate buffer of pH 4.5, 1-mL potassium cyanide solution (0.5 M), and 1.5-mL cupric chloride solution (0.2 M), in this order with mixing.
- Finally, add 5-mL ferric nitrate-perchloric acid solution with continuous mixing and make up to 50-mL distilled water.
- Measure the absorbance of the solution against a reagent blank at 460 nm in a silica cell having 10-mm pathlength.
- The solution must be kept at 20°C or lower to prevent cyanolysis of higher polythionates. The thiocyanate equivalent can be obtained from the calibration curve prepared by using standard thiosulphate or thiocyanate solutions. Procedure A yields the thiosulphate concentration directly.

Procedure B: Cyanolysis of Tetrathionate in the Presence of Acetone, Followed by Cupric Ion-Catalyzed Cyanolysis of Thiosulphate

- Pipette a similar aliquot of the sample solution as taken in Procedure A to a 50-mL volumetric flask, and add water to give total volume of about 15 mL.
- Neutralize with 1 M ammonium water to thymol-

phthalein (3 drops), add 10-mL acetone and cool to 20°C.

- Add 2-mL potassium cyanide solution (0.5 M) and maintain at 20°C for 20 min.
- Add 1.5-mL cupric chloride solution (0.2 M), and apply the same ensuing manipulation as that in Procedure A. Procedure B yields the sum of the concentration of thiosulphate and twice that of tetrathionate.

Procedure C: Cyanolysis of Trithionate and Tetrathionate in a Boiling Water Bath, Followed by Cupric-Ion Catalyzed Cyanolysis of Thiosulphate

- Pipette a similar aliquot of the sample solution as taken in Procedure A to a 50-mL volumetric flask.
- Add three drops of thymolphthalein solution, 2-mL potassium cyanide solution (0.5 M) and 1 M ammonia water until a blue colour appears.
- Keep the flask in boiling water for 30 min, then cool to room temperature.
- Add 1.5-mL cupric chloride solution (0.2 M) and apply the same ensuing manipulation as that in Procedure A. Procedure C yields the sum of the concentration of thiosulphate, trithionate and twice the concentration of tetrathionate.

Unless otherwise stated, the quantities of each sulphur species are those in a 50-mL volume. The term "cyanolysis" denotes "cyanolysis in the absence of cupric ions", and is distinct from "cupric ion-catalyzed cyanolysis". The various sulphur-containing anions react with cyanide according to the following equations which occur during the three analytical procedures.

Procedure A: thiosulphate reacts in the presence of Cu^{2+}:

$$S_2O_3^{2-} + CN^- \xrightarrow{Cu^{2+}} SCN^- + SO_3^{2-} \qquad \text{Eq 2-1}$$

Procedure B: in the absence of Cu^{2+}, tetrathionate reacts:

$$S_4O_6^{2-} + CN^- + 2OH^- \rightarrow SCN^- + S_2O_3^{2-} + SO_4^{2-} + H_2O \qquad \text{Eq 2-2}$$

Subsequently, in the presence of Cu^{2+}, the thiosulphate generated by Eq 2 and that originally present react so that the overall equation is:

$$S_4O_6^{2-} + 2CN^- + 2OH^- \xrightarrow{Cu^{2+}} 2SCN^- + SO_3^{2-} + SO_4^{2-} + H_2O \qquad \text{Eq 2-3}$$

Procedure C: At the temperature of boiling water, in the absence of Cu^{2+}, both trithionate and tetrathionate react. Tetrathionate reacts according to Eq 2 and trithionate reacts:

$$S_3O_6^{2-} + CN^- + 2OH^- \rightarrow SCN^- + SO_3^{2-} + SO_4^{2-} + H_2O \qquad \text{Eq 2-4}$$

Subsequently, at room temperature, in the presence of Cu^{2+}, the thiosulphate generated by the tetrathionate and that originally present react as in Procedure A.

If S_A, S_B and S_C are the equivalents of thiocyanate formed by Procedures A, B, and C, respectively, then these thiocyanate equivalents are related to the thiosalt equivalents by the following:

$$S_A = (S_2O_3^{2-}) \qquad \text{Eq 2-5}$$

$$S_B = 2(S_4O_6^{2-}) + (S_2O_3^{2-}) \qquad \text{Eq 2-6}$$

$$S_C = (S_3O_6^{2-}) + 2(S_4O_6^{2-}) + (S_2O_3^{2-}) \qquad \text{Eq 2-7}$$

Then, the amounts of the various thiosalt species are given as follows:

$$(S_2O_3^{2-}) = S_A \qquad \text{Eq 2-8}$$

$$(S_3O_6^{2-}) = S_C - S_B \qquad \text{Eq 2-9}$$

$$(S_4O_6^{2-}) = 1/2(S_B - S_A) \qquad \text{Eq 2-10}$$

APPENDIX 3

APPENDIX 3A - LIST OF DIVISION REPORTS PRODUCED AS PART OF THE THIOSALT PROGRAM

Report No.	Title	Authors
MRP/MSL 76-128(FT) (1976)	Visit to Noranda Research Centre, Pointe Claire, Quebec	J.E. Dutrizac D.J. Francis E. Rolia H. Steger
MRP/MSL 76-208(LS) (1976)	A Review of Analytical Methods for the Determination of Polythionates, Thiosulphate, Sulphite and Sulphide in Mining Effluents	A. Hitchen C.W. Smith
MRP/MSL 76-223(LS) (1976)	Aqueous Solution Chemistry of Polythionates and Thiosulphate: A Review of Formation and Degradation Pathways	C.W. Smith A. Hitchen
MRP/MSL 76-273(FT) (1976)	Visit to Mine, Concentrator and Zinc Plant of Ecstall Mining Ltd., Timmins, Ontario, October 4-6, 1976	J.E. Dutrizac D.C. Harris
MRP/MSL 76-279(TR) (1976)	Preparation of Potassium Tetrathionate and Potassium Trithionate for Studies of the Thiosalt Problem in Mining Effluents	A. Hitchen
MRP/MSL 76-361(TR) (1976)	The Determination of Polythionates and Thiosulphate in Mining Effluents and Mill Circuit Samples	R. Makhija
MRP/MSL 77-21(TR) (1977)	Methods of Analysis for Sulphate, for Individual Thiosalts, and for Elemental Sulphur Produced During the Oxidation of Sulphide Ores	E. Rolia
MRP/MSL(CF) 77-25(TR) (Declassified) (1977)	Visit to Brunswick Mining and Smelting Corporation Limited, Bathurst, New Brunswick, June 22-24, 1977	E. Rolia
MRP/MSL 77-46(TR) (1977)	Analyses for Sulphate and Individual Thiosalts in Tailing-Pond Water and in Mill Solutions from Brunswick Mining and Smelting, Bathurst, New Brunswick	E. Rolia
MRP/MSL 77-126(TR) (1977)	The Disposal of Thiosalt Effluents from the Brunswick Mining and Smelting Corp. No. 12 Mine: A Preliminary Assessment of a Pipeline to the Sea	D.J. Francis

Report No.	Title	Authors
MRP/MSL 77-142(TR) (1977)	Interim Report on the Production of Thiosalts During the Grinding of a Pyritic Zn-Pb-Cu Sulphide Ore from Brunswick No. 12 Mine	E. Rolia
MRP/MSL 77-261(J) (1977)	Oxidation of Sulfide Minerals. V. Galena, Sphalerite and Chalcocite	H.F. Steger L.E. Desjardins
MRP/MSL 77-308(FT) (1977)	Field Trip to Brunswick Mining and Smelting Corporation Limited, Bathurst, New Brunswick, September 19-30, 1977	E. Rolia
MRP/MSL 77-401(TR) (1977)	Reverse Osmosis Treatment of Thiosalt Solutions	V.S. Sastri
MRP/MSL 78-44(FT) (1978)	A Field Trip to Heath Steele Mines Ltd., New Brunswick to Discuss the Application of Natural Zeolite for Treatment of Mine and Surface Drainage Water	A.J. Gilmore
MRP/MSL 78-46(TR) (1978)	Generation of Thiosalts in the Flotation Mill of Brunswick Mining and Smelting Corporation Limited, Bathurst, New Brunswick	E. Rolia
MRP/MSL 78-57(J) (1978)	A Titrimetric Determination of Sulphate, Thiosulphate and Polythionates in Mining Effluents	R. Makhija A. Hitchen
MRP/MSL 78-86(LS) (1978)	Off-Line Literature Search on Oxidation of Aqueous Thiosalt Mill Effluents	B. Nebesar
MRP/MSL 78-159(TR) (1978)	Thiosalt Generation in the Heath Steele Mines Concentrator: Comparison of Thiosalt Generation and of Effluent Treatment at Heath Steele Mines Limited to that at Brunswick Mining and Smelting Corporation Limited	E. Rolia F. Barbeau
MRP/MSL 78-173(TR) (1978)	The Contribution of Sulphur Dioxide to the Thiosalt Generation in the Flotation Mill of Brunswick Mining and Smelting Corporation Limited	E. Rolia F. Barbeau
MRP/MSL 78-190(LT) (1978)	An English Translation of the German Paper: Physical Characterization of Thiosalts $K_2S_3O_6$ to $K_2S_6O_6$; IR Spectra of the Thiosalts	K. Bartels

Report No.	Title	Authors
MRP/MSL 78-191(LT) (1978)	An English Translation of the German paper: Physical Characterization of Thiosalts $K_2S_3O_6$ to $K_2S_6O_6$: UV Extinction of Aqueous Thiosalt Solutions	K. Bartels
MRP/MSL 78-197(LS) (1978)	Literature Review of Thiosalt Oxidation by Thiobacilli Species	O. Dinardo
MRP/MSL 78-213(J) (1978)	The Effect of Temperature, pH, Particle Size and Air Flow on the Formation of Thiosalts in Sulphide Mineral Suspension	H.F. Steger
MRP/MSL 78-214(TR) (1978)	Chemical Abstract Index Compilation for Thiosalts and Related Compounds	K. Bartels
MRP/MSL 78-216(TR) (1978)	A Preliminary Evaluation of Reverse Osmosis and Electrodialysis for the Treatment of Thiosalt Effluents	J.E. Dutrizac
MRP/MSL 79-8(TR) (1979)	Effect of pH and Retention Time on the Degradation of Thiosalts	E. Rolia F. Barbeau
MRP/MSL 79-9(TR) (1979)	A Re-Determination of the Crystal Structure of Potassium Trithionate, $K_2S_3O_6$	J.M. Stewart J.T. Szymanski
MRP/MSL 79-10(TR) (1979)	The Crystal Structure of Potassium Tetrathionate, $K_2S_4O_6$	J.M. Stewart J.T. Szymanski
MRP/MSL 79-70(J) (1979)	An Analytical Procedure for Individual Thiosalts and for Sulphate in Flotation Mill Solutions	E. Rolia F. Barbeau
MRP/MSL 78-74(TR) (1979)	Thiosalt Generation During the Production of Bulk Concentrate from Brunswick Mining and Smelting Corporation Ore	E. Rolia F. Barbeau
MRP/MSL 79-85(TR) (1979)	Oxidation of Thiosalts by: SO_2 plus Air, Charcoal plus Air, and Chlorine	E. Rolia F. Barbeau
MRP/MSL 79-126(TR) (1979)	An Evaluation of the Destruction of Thiosalts by Electro-Oxidation	K. Bartels
MRP/MSL 80-23(TR) (1980)	A Study of the Comparative Rates of Thiosalt Generation from Cleaned Sulphide Mineral Concentrates and BMS Ores During Agitation in a Flotation Cell	E. Rolia

Report No.	Title	Authors
MRP/MSL 80-145(J) (1980)	Infrared Spectra and Molecular (Ionic) Structures of Thiosalts and Related Compounds	K. Bartels D.M. Farrell
MRP/MSL 80-160(OP&J) (1980)	Factors Affecting the Oxidation of Thiosalts by Thiobacilli	M. Silver O. Dinardo
MRP/MSL 81-8(TR) (1981)	UV Spectral Characteristics of Selected Thiosalts	K. Bartels
MRP/MSL 81-33(J) (1981)	The Kinetics of Decomposition of Tetrathionate, Trithionate and Thiosulphate in Alkaline Media	E. Rolia
MRP/MSL 81-75(TR) (1981)	The Kinetics of Decomposition of Thiosalts by Metallic Iron	E. Rolia
MRP/MSL 81-112(TR) (1981)	Preliminary Capital and Operating Cost Estimates for the Catalytic Oxidation of Thiosalts	W.S. Wong
MRP/MSL 81-132(TR) (1981)	The Oxidation of Thiosalts in Strongly Alkaline Media	E. Rolia
MRP/MSL 81-69(J) (1981) (M.Sc. Thesis)	The Kinetics of Decomposition of Tetrathionate, Trithionate and Thiosulphate in Alkaline Solution	E. Rolia
MRP/MSL 82-26(TR) (1982)	Preliminary Capital and Operating Cost Estimates for the Pressure Oxidation and Metallic Iron Reduction Processes for Thiosalt Removal	W.S. Wong

APPENDIX 3B - LIST OF MINERAL SCIENCES LABORATORIES (MSL) REPORTS PRODUCED AS PART OF THE THIOSALT PROGRAM

Report No.	Title	Authors
MSL-INT 78-33	Visit to the Laboratories of HSA Reactors Ltd., Etobicoke, Ontario, May 17, 1978	K. Bartels
MSL-INT 78-57	Field Trip to Heath Steele Mines Limited Newcastle, New Brunswick and to Brunswick Mining and Smelting Corporation Limited, Bathurst, New Brunswick, June 5-16, 1978	E. Rolia F. Barbeau
MSL-INT 79-109	Steering Committee Meeting on the Noranda Contract, Pointe Claire, Quebec, November 1, 1979	J.E. Dutrizac
MSL-INT 79-112	Visit with Professor G. Rempel, University of Waterloo, Waterloo, Ontario, December 4, 1979	J.E. Dutrizac
MSL-INT 80-50	Thiosalt Contract Project Review Meeting; Bathurst, New Brunswick, November 17, 18, 1980	J.E. Dutrizac
MSL-INT 81-8(TR)	The Effect of Some Elements on the Determination of Thiosulphate and Tetrathionate by the Mercuric Chloride-Acidimetric Titration Method	M.E. Leaver
MSL-INT 81-12(TR)	The Spectrophotometric Determination of Micro Amounts of Thiosulphate and Tetrathionate by Cyanolysis and Solvent Extraction	A. Hitchen D.R. MacPherson
MSL-INT 81-21	Thiosalt Seminar Program, Point Claire, Quebec, May 11, 1981	J.E. Durtrizac

APPENDIX 3C - SELECTED CANMET MEMOS PRODUCED AS PART OF THE THIOSALT PROGRAM

From	To	Date	Subject
W.A. Gow	L. Sirois	April 23, 1976	Thiosalt Formation
W.J.S. Craigen J.M. Skeaff	L. Sirois	May 13, 1976	Meeting on Thiosalt Problem
I.B. Klymowski	L. Sirois	May 20, 1976	Application of Reverse Osmosis to the Problem of Polythionates in Concentrated Effluents
J.E. Dutrizac	W.J. Craigen	June 17, 1976	Visit to Noranda Research Centre, Pointe Claire, Quebec
W.J.S. Craigen J.M. Skeaff	File P-1	September 24, 1976	Second Meeting on Thiosalt Problem
J.E. Dutrizac	All Participants in the Thiosalt Program	May 16, 1977	Thiosalt Analysis
E. Rolia	J.E. Dutrizac	June 2, 1977	The Effect of Temperature on the Storage of a Standard Solution of Potassium Trithionate
A. Hitchen	J.E. Dutrizac	June 3, 1977	Thiosalt Stability Tests
J.E. Dutrizac	A. Hitchen	July 18, 1977	Thiosalt Stability Tests; your memo of July 15, 1977
E. Rolia	J.E. Dutrizac	July 25, 1977	Analyses for Thiosalts in Brunswick Mining Solutions
J.E. Dutrizac	All participants in the Thiosalt Program	September 16, 1977	UV-induced Oxidation of Thiosalts
D.J. Francis	J.E. Dutrizac	October 20, 1977	Status Report - Thiosalt Disposal and Decomposition
R.G.L. McCready	M.C. Campbell	November 3, 1977	Thiosalts in Mine Effluents
J.E. Dutrizac	All participants in the Thiosalt Program	November 23, 1977	Minutes of Thiosalt Meeting held on November 17, 1977
J.E. Dutrizac	All participants in the Thiosalt Program	November 29, 1977	Meeting with Noranda Personnel to Discuss the Thiosalt Program

From	To	Date	Subject
J.E. Dutrizac	All participants in the Thiosalt Program	December 14, 1977	Thiosalt Removal
J.E. Dutrizac	A. Hitchen	December 29, 1977	Thiosalt Analysis
J.E. Dutrizac	H. Steger	February 2, 1978	Use of Natural Zeolites for Thiosalt Removal
J.E. Dutrizac	D.M. Farrell	July 6, 1978	Spectral Analysis of Thiosalts
J.E. Dutrizac	All participants in the Thiosalt Program	July 30, 1978	Minutes of Thiosalt Meeting Held on July 27, 1978
J.E. Dutrizac	W.J. Craigen	September 5, 1978	Summary of Thiosalt Meeting Held on August 15, 1978
W.J. Craigen	J.E. Dutrizac	October 24, 1978	Meeting of Steering Committee and Advisory Committee on Minerals Processing Projects under the GDA Canada-N.B. Agreement, Fredericton, October 29, 1978
J.E. Dutrizac	W.J. Craigen	November 15, 1978	Catalyzed Air Oxidation of Thiosalts
J.E. Dutrizac	All participants in the Thiosalt Program	January 19, 1979	Minutes of Thiosalt Meeting held on January 17, 1979
E. Rolia	J.E. Dutrizac	March 14, 1979	Analysis of Effluent Samples from Mattagami Lake Mines Ltd.
E. Rolia	J.E. Dutrizac	July 26, 1979	Correction of a Calculation Error in the Report "Oxidation of Thiosalts by: SO_2 plus air, charcoal plus air, and chlorine" (MRP/MSL 79-85(TR))
J.E. Dutrizac	W.J. Craigen	September 21, 1979	Minutes of the Thiosalt Meeting Held at CANMET, September 20, 1979
M. Silver	J.E. Dutrizac	September 24, 1979	Removal of Thiosalts
O. Dinardo	J.E. Dutrizac	November 1, 1979	Effect of Phosphate on Thiosalt Destruction
J.E. Dutrizac	W.J. Craigen	November 30, 1979	Thiosalt Program Project Progress Report

From	To	Date	Subject
J.E. Dutrizac	W.J. Craigen	March 31, 1980	Minutes of Thiosalt Meeting; March 28, 1980
J.E. Dutrizac	Participants of the Thiosalt Program	July 1, 1980	Preparation of Pentathionate
J.E. Dutrizac	G.M. Ritcey D.J. MacKinnon	February 3, 1981	Minutes of Progress Review Meeting January 29, 1981 - Treatment of Thiosalt Effluents - 4.3.0.6.03
W.J. Craigen	M.C. Campbell	June 4, 1981	Pressure Alkali Oxidation of Thiosalts Economic Considerations
E. Rolia	M.C. Campbell	December 11, 1981	Oxidation of Thiosalts by H_2O_2

APPENDIX 4

LIST OF EXTERNAL PERSONNEL INVOLVED IN THE THIOSALT PROGRAM

Participant	Organization
P. Spira	Noranda Research Centre 240 Hymus Blvd. Pointe Claire, Quebec H9R 1G5
J. Scott	Fisheries and Environment Canada Water Pollution Control Directorate Place Vincent Massey Ottawa, Ontario K1A 1C8
D. Webb	Kidd Creek Mines Limited B-2002 Timmins, Ontario P4N 7K1
J.R. Schnarr	Brunswick Mining and Smelting P.O. Box 3000 Bathurst, N.B. E2A 3Z8
G.L. Rempel	Department of Chemcial Engineering University of Waterloo Waterloo, Ontario N2L 3G1
O. Peter	Heath Steele Mines Ltd. P.O. Box 400 Newcastle, New Brunswick E1V 3M5
B. Jank	Wastewater Technology Centre Environment Canada P.O. Box 5050 Burlington, Ontario L7R 4A6
R.V. Typliski	Environmental Control Department Hudson Bay Mining and Smelting Co. Ltd. P.O. Box 1500 Flin Flon, Manitoba R8A 1N9
K.G. Wheeland	Noranda Research Centre 240 Hymus Blvd. Pointe Claire, Quebec H9R 1G5
E.A. Sorba	Technical Services Laboratory 1015-401 York Ave. Winnipeg, Manitoba R3C 0P8
K.D. Phinney	Montreal Engineering Company Ltd. 593 King Street Fredericton, New Brunswick
J.A.E. Bell	J. Roy Gordon Research Laboratory Inco Metals Company Sheridan Park Mississauga, Ontario L5K 1Z9
J.L. Shafer	Exxon Minerals Company P.O. Box 2180 Houston, Texas U.S.A. 77001
T.R. Johnston	Sherritt Gordon Mines Limited Lynn Lake, Manitoba R0B 0W0
E. Stuart Savage	Dravo Corporation Neville Island Pittsburgh, Pennsylvania U.S.A. 15225

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80-27E Generation and control of mine airborne dust; G. Knight;
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81-2E Acid extraction of alumina from Canadian non-bauxite sources at CANMET; Colin Hamer;
Cat. No. M38-13/81-2E, ISBN 0-660-10957-3; Price: $2.00 Canada, $2.40 other countries.

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Cat. No. M38-13/81-3E, ISBN 0-660-11007-5; Price: $3.75 Canada, $4.50 other countries.

81-4E Effect of Pore Size in MoO_3-CaO-Al_2O_3 Hydrocracking Catalysts; A.H. Hardin, M. Ternan and R.H. Packwood;
Cat. No. M38-13/81-4E, ISBN 0-660-11065-2; Price: $3.75 Canada, $4.50 other countries.

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81-10E CANMET Review 1980-81; Staff of Technology Information Division;
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