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OXIDATION OF THIOSALTS IN
BASE METAL MINING INDUSTRY EFFLUENTS USING
A ROTATING BIOLOGICAL CONTACTOR

OXIDATION OF THIOSALTS IN BASE METAL MINING
INDUSTRY EFFLUENTS USING A
ROTATING BIOLOGICAL CONTACTOR

by

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ABSTRACT

Partially oxidized sulphur compounds discharged from a tailings pond at a base metal mining industry at neutral or slightly alkaline pH have resulted in an acidic condition (pH 2.5-3.5) in the receiving stream. The problem has been attributed to the biological and/or chemical oxidation of thiosalts to sulphuric acid; biological oxidation is accomplished by sulphur-oxidizing bacteria in the receiving stream.

A literature review revealed that under aerobic conditions the autotrophic sulphur bacteria, Thiobacillus thiooxidans, can completely oxidize the thiosalts at pH's ranging from 1.5 to 5.5. Since this Thiobacillus species preferentially attaches itself to surfaces, the treatment process selected was the rotating biological contactor (RBC). This study was conducted to establish the feasibility of biological treatment and develop design criteria for process application.

Bench-scale laboratory experiments were conducted at temperatures ranging from 2 to 30°C using three-stage RBC units each having a total surface area of 6.2 m². The units were operated at flow rates ranging from 80-400 l/day treating synthetic wastes containing 1 and 6.6 g/l of sodium thiosulphate as S₂O₃. Experimental results indicated that reaction rates varied from first-order to zero-order depending on the applied loading and temperature. Oxidation rate temperature dependency followed the Arrhenius relationship. During an extended operational period at 23°C, the biological solids accumulation on the disc surfaces was negligible and the suspended solids in the effluent from the RBC units were consistently less than 10 mg/l.

Pilot-scale field studies were conducted at a base metal mining operation on process waste streams having thiosalts concentration ranging from 1.7 to 2.7 g/l as S₂O₃. A six-stage BIO-SURF unit having a surface area of 423 m² was operated at a temperature of 30 to 35°C at flow rates of 3.8 and 7.6 l/min. Rates of thiosalt oxidation were established for two different process streams and compared to bench-scale data.

The report includes an estimate of the capital and operating and maintenance costs for an RBC system treating 10,500 m³/day of process effluent containing 1,250 mg/l of thiosalts.

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1. INTRODUCTION

Partially oxidized sulphur compounds discharged at neutral or slightly alkaline pH from a tailings pond at Brunswick Mining and Smelting Company Ltd., a base metal mine at Bathurst, New Brunswick have caused an acidic condition (pH 2.5 - 3.5) in the receiving stream. The problem has been attributed to the biological and/or chemical oxidation of thiosulphate and thiosalts to sulphuric acid; biological oxidation is accomplished by sulphur-oxidizing bacteria prevailing in the receiving stream. The thiosalts were generated in the milling process during alkaline grinding and flotation of the sulphide ores and also from the use of aqueous sulphur dioxide in one of the upgrading circuits.

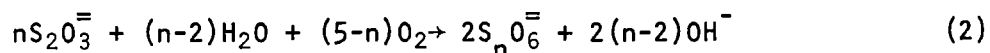
In recent years several processes for treatment of this wastewater have been investigated. Both biological and chemical methods have been employed successfully to treat the wastewater containing thiosulphates and polythionates. In both cases, the reduced sulphur compounds were oxidized to sulphate with the formation of sulphuric acid which, after neutralization, could be safely discharged into the receiving water.

The biological oxidation of thiosalts has been expressed by Graham (1962) in terms of three main chemical equations:

1. Complete oxidation of thiosulphate to sulphate:

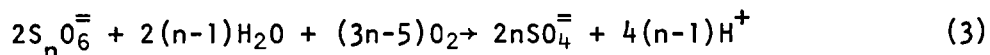


2. Partial oxidation of thiosulphate to polythionates:



where n may take the values of 2 to 6

3. Oxidation of polythionates to sulphate:



It can be seen that the complete oxidation of thiosulphate or polythionates is accompanied by an increase in acidity. Equation 1 indicates that the oxidation of 1 gram of thiosulphate results in the production of 1.72 grams of sulphate. This was used as a conversion factor in the study to calculate the theoretical sulphate production.

The objectives of this phase of the study were:

1. to investigate the feasibility of using the rotating biological contactor (RBC) to oxidize thiosalts;
2. to develop the kinetic relationship required to establish engineering design criteria for process application; and
3. to provide cost information for a full-scale treatment system.

A project was carried out by personnel of the Wastewater Technology Centre (WTC) to assess the chemical and biological processes which could provide thiosalts oxidation. This report deals with the phase of the project involving biological treatment of wastewater containing thiosulphate and polythionates. Initially, bench-scale studies were carried out at room temperature at the WTC to establish whether the RBC could be used to treat the wastewater containing thiosulphate. Results were so encouraging that the experimental program was extended to investigate thiosulphate oxidation at temperatures of 2, 15 and 30°C to establish the kinetic relationship for thiosulphate oxidation. On-site pilot-scale studies were carried out to verify the results obtained from the bench-scale operation.

2. LITERATURE REVIEW

2.1 Bacteriological Aspects

It has been known for many years that certain types of organisms are capable of oxidizing thiosulphates to sulphates. The reader is referred to the report by B.C. Research (1973) for a review of literature. Under aerobic conditions, the autotrophic sulphur bacteria of the genus Thiobacillus derive energy from the oxidation of reduced sulphur compounds. With the exception of T. novellus, members of this group are gram negative, non-spore forming mobile rods, typically measuring 0.5μ by 1 to 3μ . They are all polarly flagellated and chemo-autotrophic with the exception of T. novellus which is facultative autotrophic. The most typical substrates for thiobacilli are either thiosulphate or elemental sulphur with the former being the preferred medium.

Table 1 shows the species and some of the characteristics of the genus Thiobacillus. As can be seen, different species vary in their tolerance towards the acid condition. While T. thiooxidans and T. ferrooxidans are tolerant of extremely acid conditions, the other strains can grow only at neutral or alkaline pH.

Since sulphuric acid is the final product of the thiosalts oxidation, the acid tolerant species would be more desirable, and in fact, they are the predominant species in a biological system treating wastewater containing thiosalts.

Thiobacilli grow over a wide range of temperatures with the optimum being in the range of 28 to 35°C (Silverman and Lundgren, 1959; Torma et al 1970; Bryner and Jones, 1966). Species growing at temperatures as low as 2 and 3°C have also been identified (Tabita et al, 1969; Beck, 1969). In general, thiobacilli do not grow above 40°C, and at 45°C remarkable inhibition of oxidation has been reported (Torma et al, 1970; Bryner and Jones, 1966; Beck, 1969)

Studies with respect to the nutritional requirement of the thiobacilli for thiosulphate oxidation are limited. Santer et al (1960) demonstrated that inorganic phosphate is required for the complete oxidation of thiosulphate to sulphate by T. thioparus. Tuovinen et al (1971), in a

TABLE 1. CHARACTERISTICS OF THE THIOBACILLI (Schmidt and Conn, 1971)

Name	Substrates utilized other than Thiosulphate	pH characteristic	Remarks
<u>T. thiooxidans</u>	Sulphur Tetrathionate	Optimum pH 2 to 3 Range 1 to 6	Acidophilic; oxidizes thiosulphate rapidly to sulphate. Prefer to attach to a solid surface.
<u>T. ferrooxidans</u>	Ferrous ion, Sulphur, Trithionate, Tetra-thionate	Optimum pH near 3.5 Range 2 to 6	Acidophilic; unable to use sulphur rapidly. Optimum pH for oxidation of sulphur compounds is apparently pH 4-5. Prefer to attach to a solid surface.
<u>T. concretivorus</u>	Similar to <u>T. thiooxidans</u>	but differs principally	in that it can use both ammonia and nitrate.
<u>T. thioparus</u>	Sulphur, Trithionate, Tetrathionate, Dithionate	Optimum pH near neutrality	Oxidation of substrate causes the medium to become acid
<u>T. denitrificans</u>	Sulphur	Optimum pH near neutrality	Under anoxic conditions uses nitrate as a terminal respiratory electron acceptor.
	Cultivated aerobically this bacterium is indistinguishable from <u>T. thioparus</u> .		
<u>T. thiocyanoxidans</u>	Thiocyanate, Sulphur, Sulphide	Optimum pH near neutrality (pH 6.8 to 7.6)	Produces acid, oxidizes thiosulphate rapidly.
<u>T. novellus</u>	Various organics	Optimum pH near neutrality	Grows slowly, produces acid. Of all the above thiobacilli this is not an obligate autotroph but a facultative autotroph.

Note: All the thiobacilli oxidize thiosulphate to sulphate although the precise pathways have not yet been agreed upon.

literature review of the nutrient requirements of T. ferrooxidans, reported that ammonium ion and a phosphate source were essential for the growth of the micro-organisms, however, the minimum quantity required could not be established. In the treatment of synthetic wastewater containing thiosulphate, it was reported that the concentrations of ammonium and phosphate providing a $S_2O_3:N:P$ ratio of 1000:14:15 were adequate for the oxidation of thiosulphate in a RBC system (B.C. Research, 1973). In a 4-day operation, reduction of the nitrogen and phosphorus levels to a ratio of 1000:6:1.6 showed no adverse effect on the rate of oxidation.

Both T. thiooxidans and T. ferrooxidans have the ability to attach themselves to solid surfaces. Temple and Koehler (1954) found that during the oxidation of marcasite (FS_2), intensive growth of T. thiooxidans was observed on the mineral surface. Schaeffer et al (1963) reported that the same organism attached itself to a sulphur crystal and eroded the area immediately adjacent to the cell due to the acid formation. Dugan and Lundgren (1964) showed that T. ferrooxidans attached itself firmly to a sheet of aluminum. McGoran et al (1969) indicated that the same organism tended to attach to solid ferric compounds. This attachment characteristic of thiobacilli is of considerable practical importance in selecting a treatment process for wastewater containing thiosalts.

2.2 Biological Treatment of Wastewater Containing Thiosalts

Although a considerable number of articles concerning the thiobacilli have been found in the literature, little is known about the application of these organisms in a biological treatment system. The bench-scale bacterial filter used by Lockett (1913) probably was the first biological reactor used for the study of thiosulphate oxidation. The filter consisted of stoneware pipes 60 cm in length by 10 cm in diameter filled with 0.6 to 2.5 cm clinker. A sodium thiosulphate ($Na_2S_2O_3$) solution of 5 g/l and also solutions of tri-, tetra- and pentathionates up to 1 g/l were oxidized to sulphates with the production of free acid. Lockett concluded that the oxidation was mainly due to bacterial action and possibly was assisted by physical and chemical properties of the filter material.

In conjunction with the treatment of coking wastewaters, Graham (1962) carried out a study on the biological oxidation of thiosulphate using mixed cultures in a suspended growth reactor having a capacity of 3.6 liters. With a synthetic feed solution consisting of 3 to 10 g/l of thiosulphate, complete removal of thiosulphate was achieved at loadings of up to 5.6 kg $S_2O_3/m^3 \cdot day$ (347 lb $S_2O_3/1000 ft^3 \cdot day$). It should be noted that this is not necessarily complete oxidation of thiosulphate to sulphate as polythionates may have been generated during biological oxidation. At the loading of 9.1 kg $S_2O_3/m^3 \cdot day$ (566 lb $S_2O_3/1000 ft^3 \cdot day$), 95.6% treatment efficiency was attained. With diluted effluents from catalytic oil gas plants, 99.7 to 100% of thiosulphate was oxidized at loadings up to 7.0 kg $S_2O_3/m^3 \cdot day$ (436 lb $S_2O_3/1000 ft^3 \cdot day$). The reactor was operated within the pH range of 6-7.5 using sodium carbonate to neutralize the sulphuric acid formed. Identification of the organisms involved showed the presence of T. thiocyanoxidans and T. thioparus.

In the treatment of the tailings pond discharge from a base metal mining operation in New Brunswick, Schmidt and Conn (1971) reported that complete removal of 100 mg/l thiosulphate was achieved in a bench-scale suspended growth reactor operated at a detention time of 18 hours at room temperature. The predominant bacterial species for thiosulphate oxidation was reported to be T. thiooxidans. One of the problems encountered in the study was that the biomass produced would not settle at the pH conditions (pH = 2) prevailing in the treatment system.

A study by Aulenbach and Heukelekian (1955) indicated that activated sludge could be acclimatized to remove thiosulphate. In a 6-liter batch reactor, up to 750 mg/l of thiosulphate was removed with a 6-hour aeration period, of which up to 250 mg/l was oxidized completely to sulphate. However, sludge fed with thiosulphate had a higher sludge volume index than that of a control receiving no thiosulphate. Kreye et al (1974) reported that an activated sludge unit could be acclimatized to successfully oxidize thiosulphate up to a concentration of 3840 mg/l; however, the ability of the process to reduce BOD deteriorated and sludge with poor settling characteristics was encountered.

Laboratory studies by B.C. Research (1973) using a RBC, an activated sludge system and flasks incubated on a shaker indicated that the RBC was the most efficient system for thiosulphate oxidation. An oxidation rate of 35 g $S_2O_3/m^2 \cdot day$ (146 mg $S_2O_3/ft^2 \cdot hr$) and 64 g $S_2O_3/m^2 \cdot day$ (267 mg $S_2O_3/ft^2 \cdot hr$) was reported at 8.5°C and room temperature, respectively. Under similar operating conditions, the maximum thiosulphate oxidation rate achieved in the suspended growth system was only 1/47 of that obtained in the RBC unit. In the activated sludge system, bacterial growth occurred over the wall of the reactor and no floc formation was observed. Attempts made to create artificial flocs were unsuccessful.

From the foregoing it is evident that thiobacilli are very resistant to severe environmental conditions. The ability to completely oxidize the reduced sulphur compounds to the most stable form of sulphate, together with the extremely acid tolerant characteristics, make the thiobacilli ideal for the treatment of wastewater containing thiosalts. The attachment characteristic of the micro-organisms indicates that the use of a fixed film reactor would be more advantageous than a suspended growth reactor.

3 EXPERIMENTAL PROGRAM

3.1 Experimental Schedule

The study to investigate the biological oxidation of thiosulphate was divided into two phases. The first phase was a laboratory scale study conducted under different loading conditions using synthetic wastewater. The second phase of the study was a pilot-scale operation performed at Brunswick Mining and Smelting Company Ltd., Bathurst, New Brunswick. Table 2 is an outline of the experimental schedule for both the bench-scale and the pilot-scale studies.

The experimental program began with the operation of a two-stage RBC at room temperature (23°C). The reactor was operated for approximately three months to determine sludge production and to investigate the stability of the system over an extended period of time. To evaluate the performance of the RBC at other temperatures, two three-stage RBC units were set up in a temperature controlled room and operated at flow rates ranging from 80 to 400 l/day treating synthetic wastewater containing 0.95 to 6.61 g/l of thiosulphate.

To verify the results obtained from the bench-scale study, on site pilot-scale studies were conducted at Brunswick Mining and Smelting Company Ltd. in Bathurst, New Brunswick. A six-stage RBC unit was operated at flow rates of 3.8 and 7.6 l/min using two different process waste streams.

3.2 Reactors for Experiments

During the extended operation period at 23°C, a 25-liter RBC unit was used. It consisted of two compartments of 15 discs each, spaced at 1.9 cm. The 38 cm diameter discs were mounted on a horizontal shaft and placed in a semi-circular tank. Except for the supporting shaft which was made of stainless steel, fibreglass was used for the construction of the unit. The surfaces of the discs had been roughened to ensure attachment of bacterial growth. The 30 discs provided a total effective surface area of 6.7 m² (73 ft²). The discs were driven at 3 rpm by a 1/3 hp motor combined with a gear reducer and pulley system. A peristaltic pump was used to deliver the feed solution to the reactor.

Two additional identical RBC units which were used in a temperature controlled room, were designed and fabricated by B.C. Research. Each

TABLE 2. EXPERIMENTAL SCHEDULE

A. Laboratory-Scale Study

Days of Operation	No. of Stages	Operating Temp. (°C)	Concentration of S ₂ O ₃ (g/l)	Flow Rate (l/day)
104	2	23	0.95	300
27	3	2	1.03	200
28	3	2	2.05	100
14	3	2	1.00	300
44	3	2	1.03	100
14	3	2	0.99	150
17	6	30	6.61	80
12	6	30	3.05	160
12	6	30	1.56	320
4	6	15	1.61	100
8	6	15	3.19	160
14	6	15	1.68	200
5	6	15	1.44	400

B. Pilot-Scale Study

Days of Operation	No. of Stages	Inf. Temp. (°C)	Waste Stream	Flow Rate (l/day)
30	6	37-47	Circuit 12	5,400
60	6	25-50	Circuit 12	10,800
55	6	31-61	Circuit 6	5,400
28	6	22-61	Circuit 6	10,800

unit having a total liquid capacity of 6.6 liters, was divided into three equal compartments. The shaft supported 75 closely spaced discs with 25 discs in each compartment. The discs, made from 3 mm roughened plexiglass, were 20 cm in diameter providing a total effective surface area of 4.7 m^2 in each unit. A schematic diagram of the unit is shown in Figure 1.

Dye studies using the equal tanks series model showed that the two three-stage bench-scale reactors operated in series was equivalent to a system of ten equal sized CSTR's (constant stirred tank reactors) in series. This indicated that the hydraulic pattern in the reactor approached that of plug flow.

The pilot-scale RBC unit which had 2 m diameter polystyrene discs, was manufactured by Autotrol Corporation. There were 12 discs per stage in the six-stage unit giving a total effective surface area of 423 m^2 (4550 ft^2). The liquid holding capacity of the unit was 990 liters. A 2240-liter (80 ft^3) clarifier with a surface area of 3.3 m^2 (35 ft^2) was incorporated into the RBC unit to facilitate removal of settleable solids from the effluent. A flow diagram of the pilot-scale system is shown in Figure 2.

An on-site dye study was carried out in the pilot-scale reactor. Unfortunately, data collected were not adequate to characterize the hydraulic pattern of this reactor.

Table 3 presents some of the important features of the RBC units used for the bench-scale and pilot-scale operations. As indicated, the surface area per stage of the pilot-scale reactor was approximately 44 times greater than that of the bench-scale reactor. To compare the performance of the two treatment systems, the flow rate applied to the pilot-scale reactor was increased accordingly as shown in Table 2, so that the comparison could be made under similar loading conditions.

3.3 Composition and Characteristics of Feed Solution

The feed solution used in the bench-scale operation was prepared by dissolving sodium thiosulphate, ammonium sulphate and potassium dihydrogen phosphate in tap water at a $\text{S}_2\text{O}_3:\text{N}:\text{P}$ of 1000:14:15. The amount of

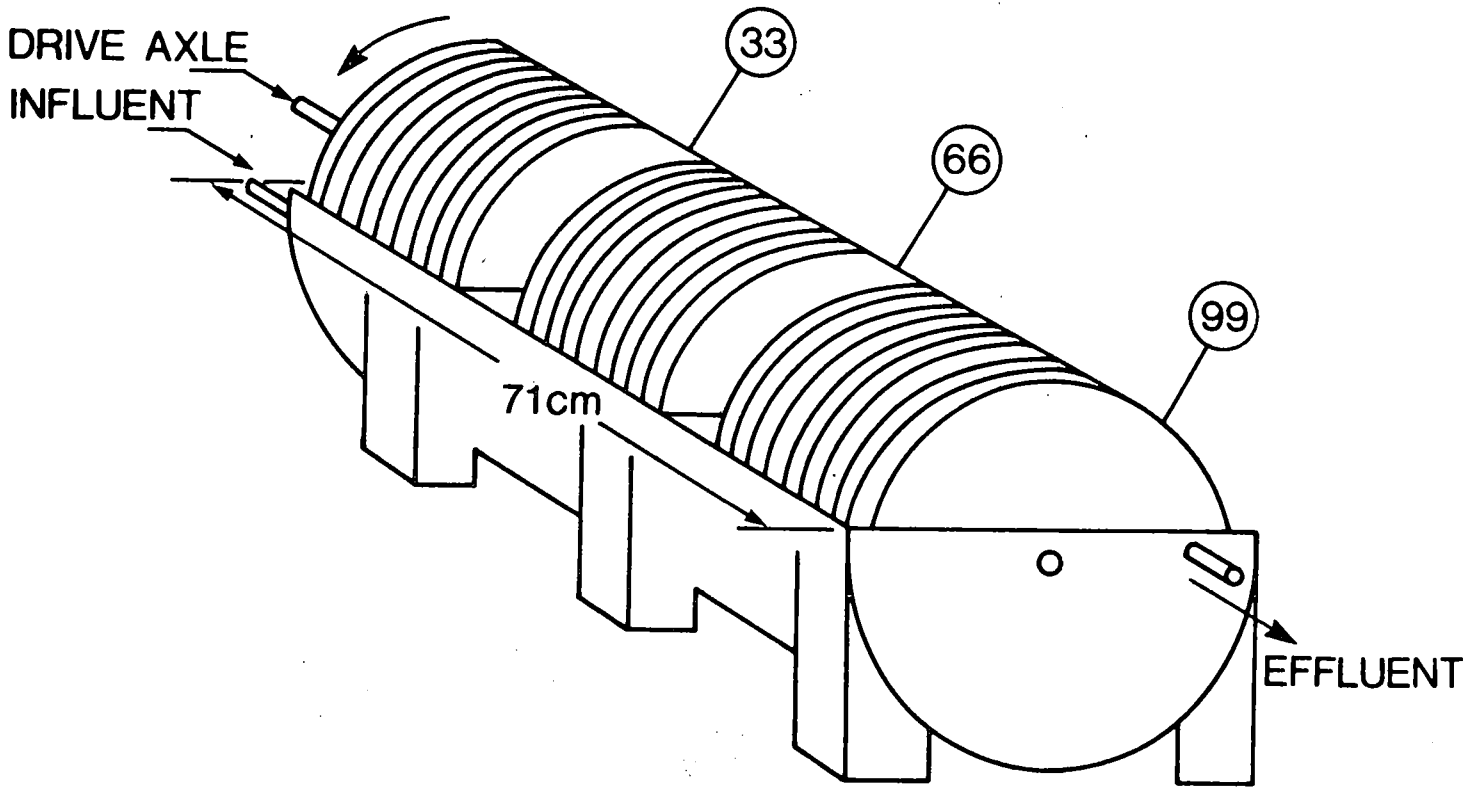


FIGURE 1. SCHEMATIC DIAGRAM OF THE BENCH-SCALE RBC

TABLE 3. CONFIGURATION AND DIMENSIONS OF RBC'S

	Bench-Scale Reactors		Pilot Scale Reactor
Number of Stages	2	3	6
Diameter (cm)	38	20	200
Per Stage			
- Number of Discs	15	25	12
- Surface Area (m ²)	3.4	1.6	71
- Volume * (liter)	12.5	2.2	330

* Measured with discs in the reactors

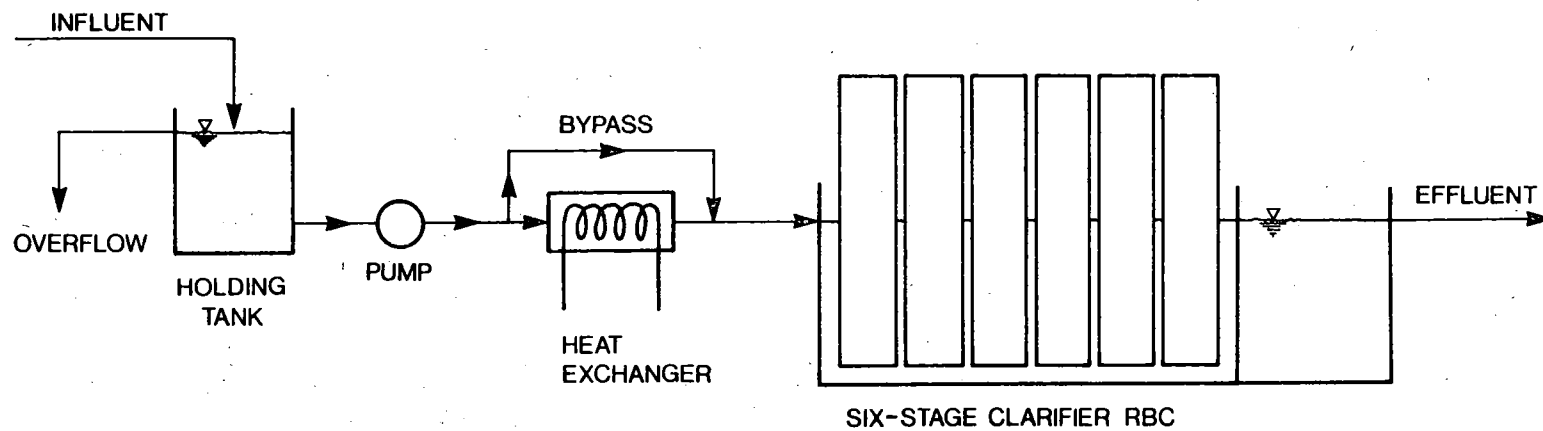


FIGURE 2. FLOW DIAGRAM OF THE PILOT-SCALE RBC

nutrient added was adequate to support the growth of thiosulphate oxidizing bacteria (B.C. Research, 1973). While the concentration of thiosulphate varied according to the applied loading desired, the ratio of thiosulphate to ammonium to phosphate remained the same for all the bench-scale operations. No attempt was made in the study to investigate the nutrient requirements for thiobacilli in the oxidation of thiosulphates.

The wastewater used in the pilot-scale operation is identified throughout the report as circuits No. 6 and 12 of the milling operation. The circuit No. 6 effluent was actually the No. 5 thickener overflow (the upgrading thickener), while circuit No. 12 effluent was No. 3 pond overflow. The characteristics of these waste streams are presented in Table 4. It can be seen that the wastewater from circuit No. 6 was higher in sulphur compounds than circuit No. 12.

3.4 Experimental Procedures

3.4.1 Bench-Scale Operation

On initial start-up, the RBC unit was operated as a batch reactor to develop cultures for thiosulphate oxidation. The reactor was inoculated with a mixed culture from the tailings pond of the mining operation or, if available, from the effluent of the pilot-scale RBC unit operated in the field. All bench-scale reactors were operated at 3 rpm and monitored by following the changes in pH, thiosulphate and sulphate concentrations. After approximately a two-week acclimation period, the reactor was put into continuous operation. Upon establishment of steady-state conditions, grab samples were taken daily from each stage for pH, thiosulphate and sulphate analyses. When the reactor was operated at 30°C, regular determination of total thiosalts was also included in the experimental program.

3.4.2 Pilot Plant Operation

On start-up the pilot-scale RBC unit was also operated as a batch reactor until viable cultures developed on the discs surface. When this occurred, the unit was placed in continuous operation. Normally, a three-week period was required for acclimation after the reactor was put in continuous operation and a 24-day conditioning period was necessary following a shift in operating conditions. Initially, when the wastewater from circuit No. 12 was treated, no temperature control was practiced on the

TABLE 4. WASTEWATER CHARACTERISTICS

Circuit No. 6

Parameter	10%*	Median	90%*
pH	3.2	4.3	5.3
Temperature (°C)	24	42	60
Thiosulphate (mg/l)	180	440	1100
Sulphate (mg/l)	560	900	1430
Total Thiosalts as S ₂ O ₃ (mg/l)	1100	2050	3900

Circuit No. 12

pH	4.0	4.8	5.5
Temperature (°C)	35	40	46
Thiosulphate (mg/l)	50	175	610
Sulphate (mg/l)	360	520	1050
Total Thiosalts as S ₂ O ₃ (mg/l)	1400	1775	2200

* Percent of observations less than stated value

incoming waste. The reactor received an influent exhibiting temperature changes ranging from 22 to 61°C. Later, when the waste stream from circuit No. 6 was used, the feed was pumped through a heat exchanger to reduce the temperature to approximately 40°C before entering the reactor. Because the nutrient concentration in the wastewater was not adequate, ammonium sulphate $[(\text{NH}_4)_2\text{SO}_4]$ and potassium dihydrogen phosphate (KH_2PO_4) were added to provide a $\text{S}_2\text{O}_3:\text{N}:\text{P}$ ratio of 1000:14:15 (B.C. Research, 1973). The RBC unit was rotated at 6 rpm throughout the study. After steady-state conditions were established, grab samples were collected from each stage on a daily basis for thiosulphate sulphate and total thiosalts determination. pH and temperature were measured as part of the monitoring program.

3.5 Analytical Procedures

Analytical procedures which were used in this study for thiosulphate, sulphate and total thiosalt are presented in Appendix A, B & C, respectively. All other analytical procedures were carried out using the procedure specified in Standard Methods (1971).

4 RESULTS AND DISCUSSIONS

4.1 Bench-Scale Operation

To investigate whether it was feasible to use a fixed film reactor to treat wastewater containing thiosulphate, the bench-scale studies began with the operation of a two-stage RBC at room temperature. The reactor was operated for 105 days under one loading condition.

Further studies were carried out in two identical three-stage RBC units operated in parallel in a temperature controlled room. Temperatures investigated were 2, 30 and 15°C. At 2°C, four hydraulic loadings and two thiosulphate concentrations were evaluated. At 30 and 15°C, the two reactors were combined and operated in series as a 6-stage RBC unit. Three different combinations of flow rates and thiosulphate concentrations were investigated at 30°C and four combinations were evaluated at 15°C. The operating conditions and experimental results are presented and discussed in the following sections.

4.1.1 Two-Stage Bench-Scale Operation

The RBC unit was operated to collect preliminary information on thiosulphate oxidation, to investigate the sludge production and to evaluate the reliability of the system during long term operation. A synthetic solution having a thiosulphate concentration of 950 mg/l was fed to the reactor at 300 l/day with a corresponding retention time of 2.2 hours. The pH of the feed solution was adjusted to greater than 9 which was originally considered to be the pH of the mill wastewater.

The experimental results obtained during the steady-state operation have been averaged and are presented in Figure 3. For comparison, the expected theoretical and actual sulphate production are also shown. The theoretical sulphate was calculated by multiplying the reduction of the thiosulphate concentration in each stage by 1.72; the factor converting thiosulphate to sulphate (Equation 1). As can be seen, 87% of the applied thiosulphate was oxidized; of which 80% was completely oxidized to sulphate with the rest being in the form of polythionates. The difference between the theoretical and actual sulphate production implied the presence of polythionates and was reported in the figures as the predicted polythionate concentration (as S_2O_3). The formation of sulphuric acid resulted in a significant

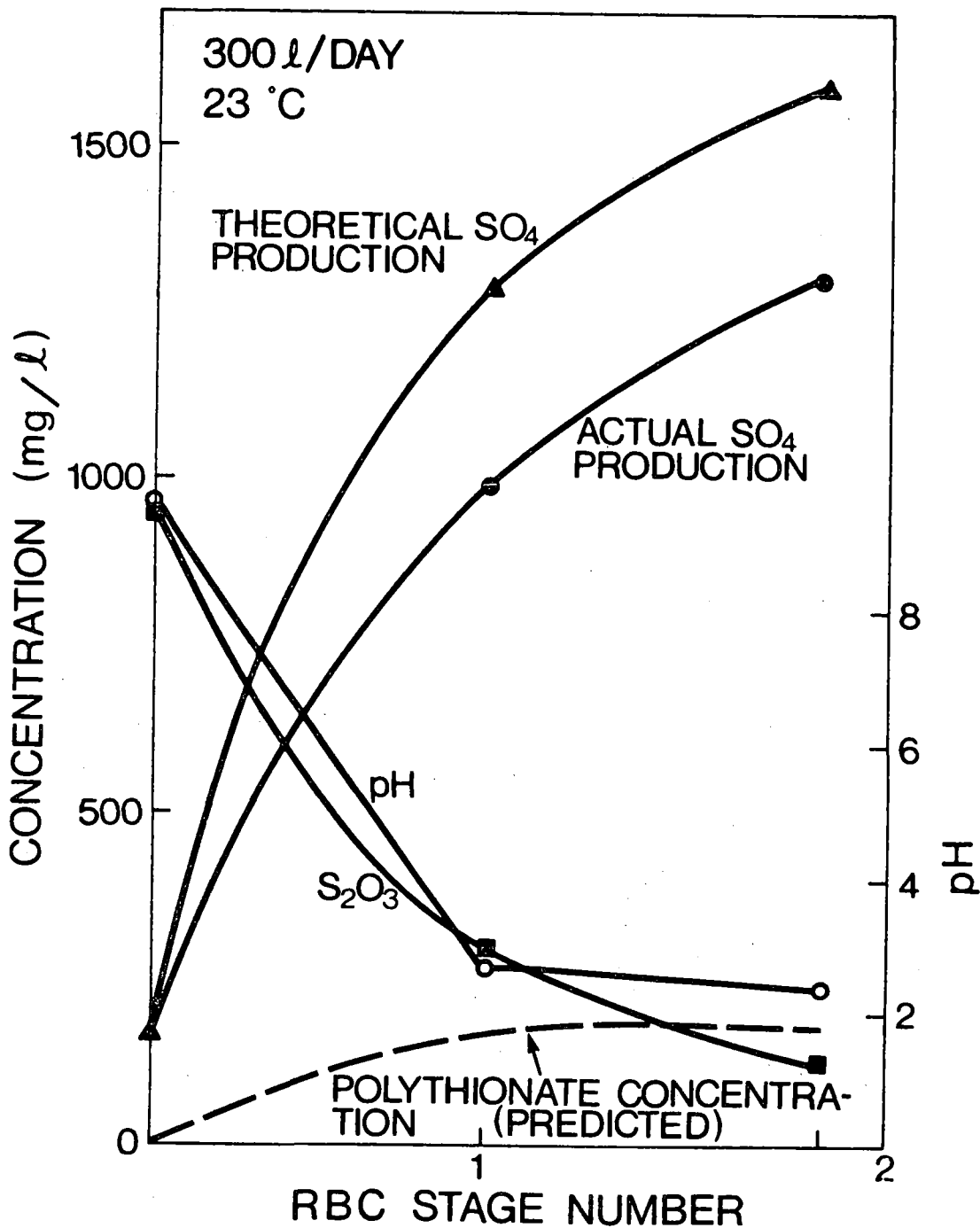


FIGURE 3. EXPERIMENTAL RESULTS OF TWO-STAGE BENCH-SCALE RBC

decrease of pH from greater than 9 to 2.4.

During the 105 days operation, although growth of the biomass on the reactor surface was observed, the accumulation of sludge in the reactor was negligible, and therefore, there was no requirement for sludge wasting. On several occasions, an appreciable amount of white colloidal sulphur formed in the reactor due to the thiosulphate disproportionation reaction which occurs at low pH, however, this did not present a significant problem because the effluent suspended solids concentration was consistently less than 10 mg/l throughout the study.

4.1.2 Bench-Scale Operation at 2°C

As the wastewater temperature in the winter months could be as low as 2°C, an experimental program was set up to investigate the thiosulphate oxidation at this temperature. Two three-stage RBC units were operated in parallel under different loading conditions in order to establish the kinetics of thiosulphate oxidation. Four hydraulic loadings, 100, 150, 200 and 300 l/day, and two thiosulphate concentrations, approximately 1 and 2 g/l, were investigated in this part of the operation.

Experimental results of each loading condition are graphically presented in Figures 4, 5, 6, 7 and 8, indicating the change in pH and concentrations of thiosulphate and sulphate in each stage. The theoretical sulphate production and the predicted polythionate concentration are also included. As shown in the figures, the lower applied loading resulted in a more complete oxidation of thiosulphate and a greater decrease in the pH.

As indicated in equations 2 and 3, incomplete oxidation of thiosulphate results in the formation of polythionates, which will eventually be oxidized to sulphates, a stable final product of thiosulphate oxidation. In the study, only the thiosulphate which is completely oxidized to sulphate, is considered to be "removed". Therefore, the performance of the treatment system is evaluated on the basis of sulphate production instead of thiosulphate reduction. The sulphate produced is divided by 1.72 to yield thiosulphate concentration. This thiosulphate concentration, representing the equivalent total thiosalts which have been oxidized to sulphates, is then used in combination with the total thiosalts applied to the treatment system to calculate the percent thiosalts removed.

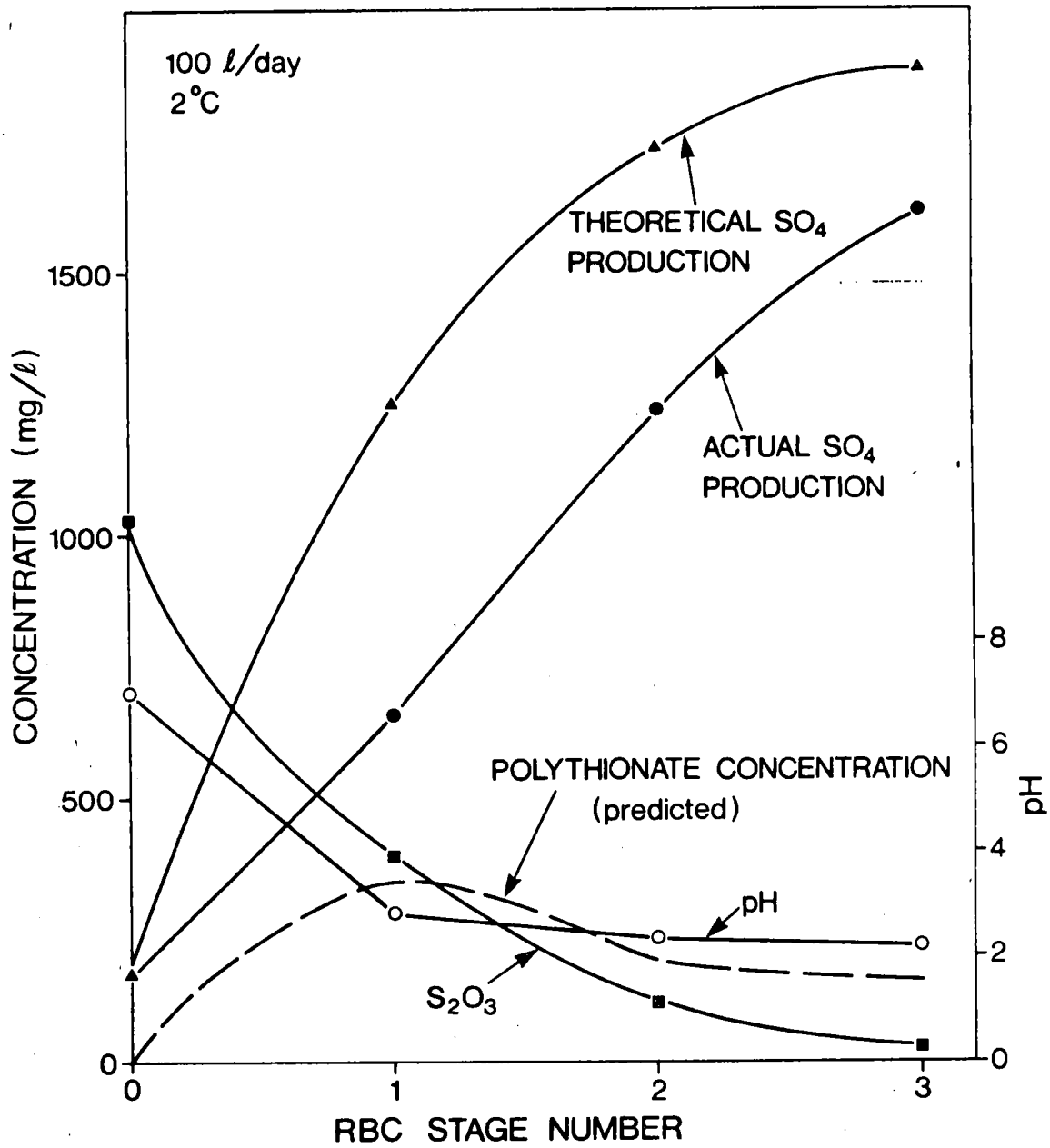


FIGURE 4. EXPERIMENTAL RESULTS OF THE THREE-STAGE BENCH-SCALE RBC AT 100 L/DAY AND 1 G/L AS S₂O₃

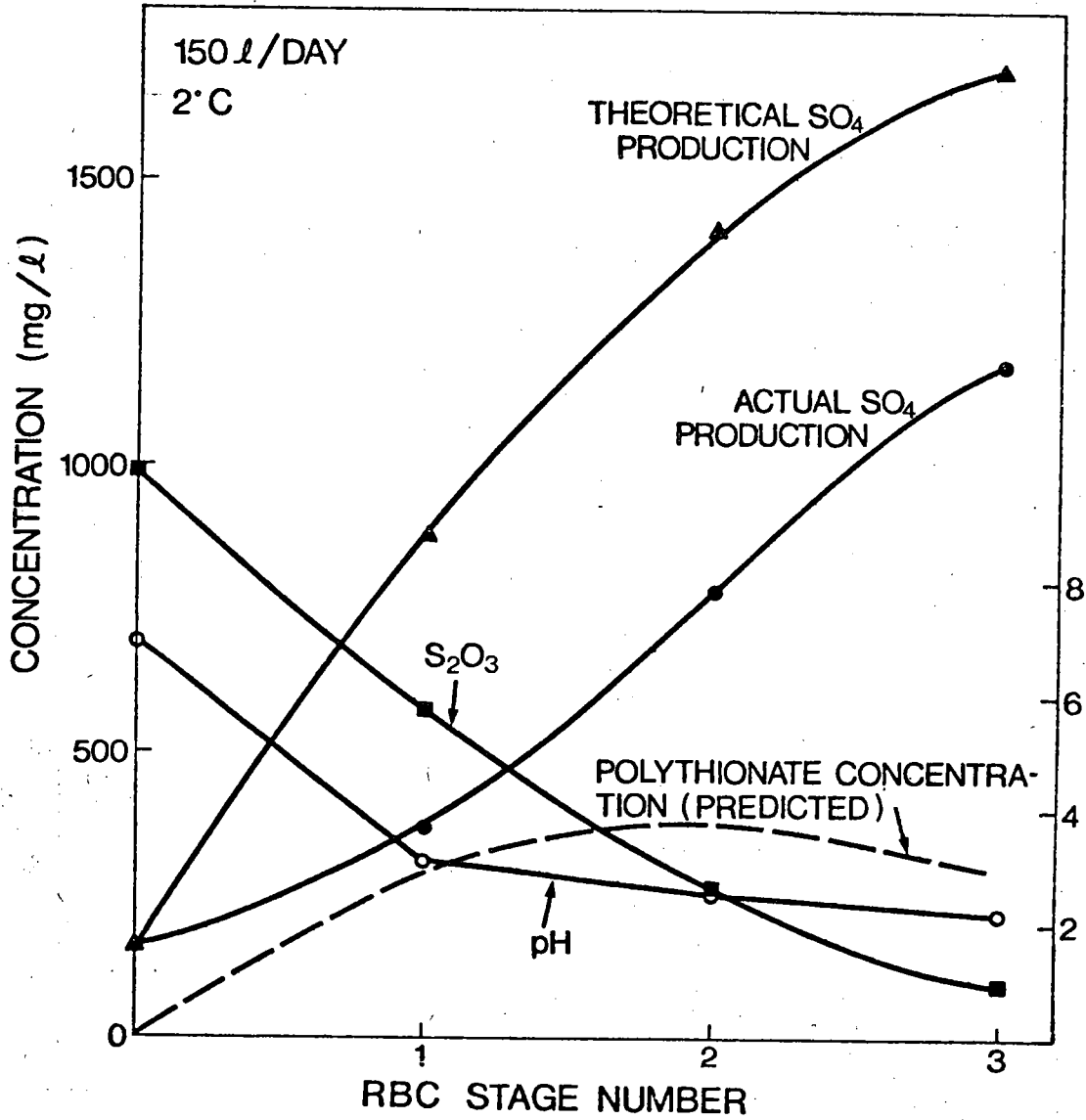


FIGURE 5. EXPERIMENTAL RESULTS OF THE THREE-STAGE BENCH-SCALE RBC AT 150 L/DAY

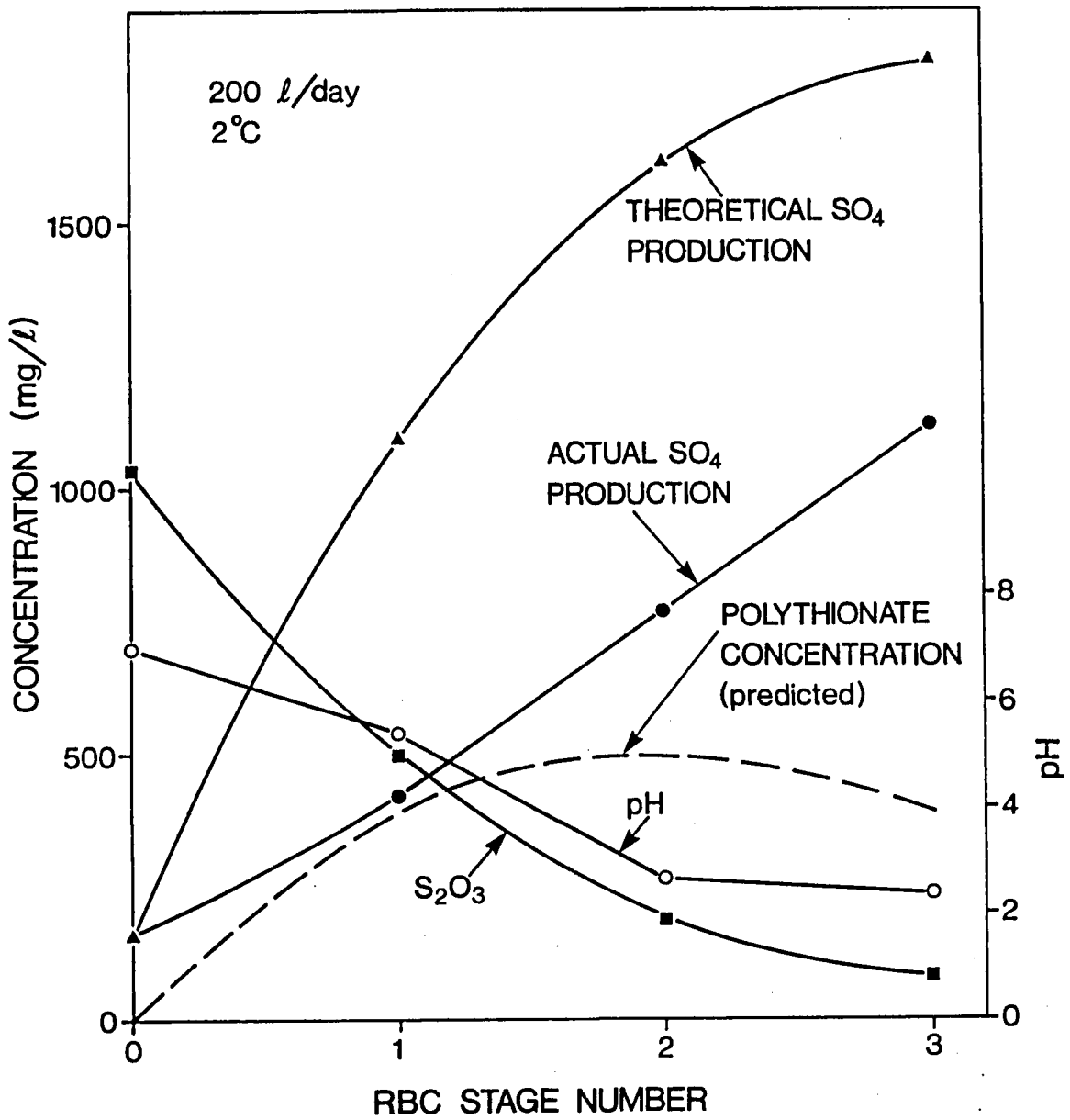


FIGURE 6. EXPERIMENTAL RESULTS OF THE THREE-STAGE BENCH-SCALE RBC AT 200 L/DAY

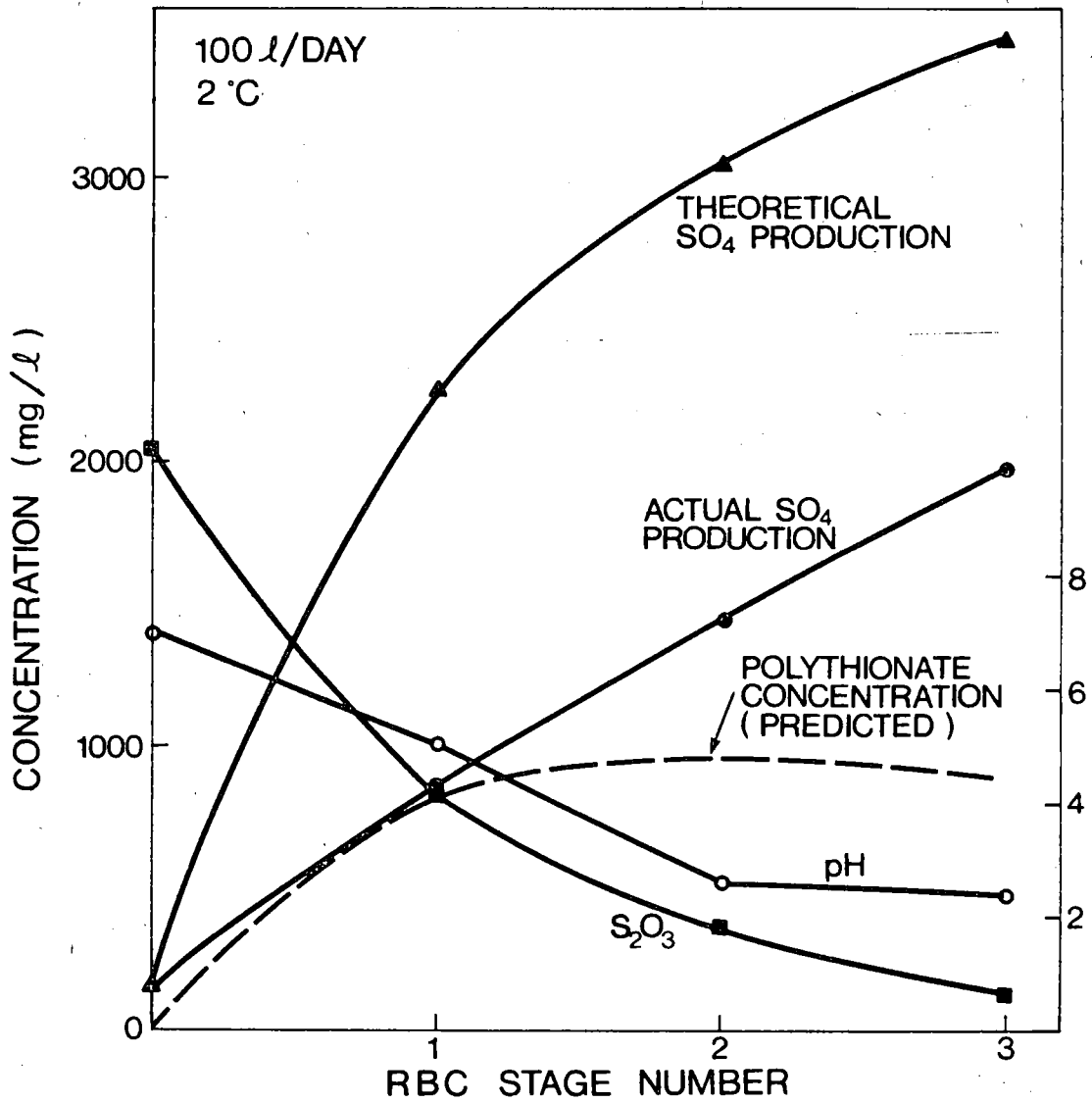


FIGURE 7. EXPERIMENTAL RESULTS OF THREE-STAGE BENCH-SCALE RBC AT 100 L/DAY AND 2 G/L AS S₂O₃

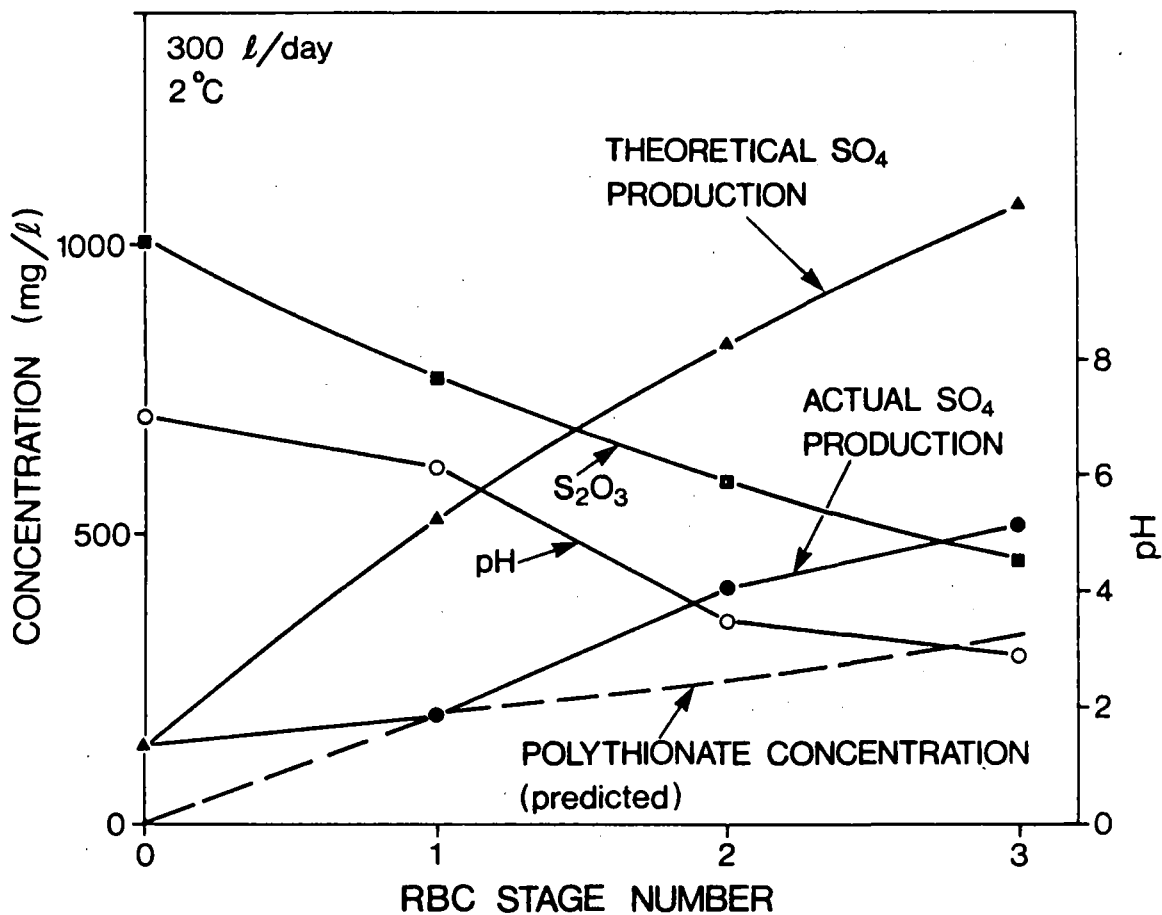


FIGURE 8. EXPERIMENTAL RESULTS OF THE THREE-STAGE BENCH-SCALE RBC AT 300 L/DAY

Using this approach, the overall treatment efficiency of the RBC operating under different loading conditions at 2°C was calculated. The results are presented in Table 5.

As indicated in Table 5, the treatment efficiency decreased with the increase in applied loading. There was no significant difference in treatment efficiency between the operating conditions of 200 ℓ/day at 1.03 g S₂O₃/ℓ and 100 ℓ/day at 2.05 g S₂O₃/ℓ, suggesting that flow rate (or detention time) and thiosulphate concentrations were correlated. Within the range of flow rates and concentrations investigated, as long as the applied loading remained the same, the change in either parameter should not have any significant effect on the performance of the treatment system.

As indicated in Section 3.2, the hydraulic pattern of the reactor was close to plug flow. To evaluate the kinetics of thiosulphate oxidation, each stage of the RBC was treated as a single reactor and the total thiosalts applied to each stage was plotted against the removal rate as shown in Figure 9. As can be seen, at lower thiosulphate loadings, the oxidation rate was concentration dependent, while at higher loadings, zero-order reaction applied. This suggested that the kinetics of the thiosulphate oxidation could be approximated by the Michaelis-Menton theory. At loadings higher than 60 g S₂O₃/m²·day, the oxidation rate remained essentially constant and independent of the applied loading.

The operation of RBC's at 2°C indicated that thiosulphate oxidation was also feasible at a low temperature. No operational problems were encountered during the 4-month operating period.

4.1.3 Bench-Scale Operation at 30°C

To investigate the thiosulphate oxidation at elevated temperatures and to compare the performance with that at 2°C, further studies were carried out at 30°C. The two 3-stage RBC units were combined and operated in series as a 6-stage reactor. Three flow rates, namely, 80, 160 and 320 ℓ/day with the corresponding thiosulphate concentration of 6.61, 3.05 and 1.56 g/ℓ were investigated in this part of the operation.

The average pH and concentrations of thiosulphate and sulphate, together with the predicted polythionate concentration and theoretical sulphate production in the individual stages are presented in Figures 10, 11, and 12. When the reactor was operated at 160 ℓ/day, in addition to

TABLE 5. COMPARISON OF THE OVERALL TREATMENT EFFICIENCY UNDER DIFFERENT LOADING CONDITIONS AT 2°C

Feed Rate (ℓ/day)	Thiosulphate Conc. (g/ℓ)	Total Thiosalts Applied (g S ₂ O ₃ /day)	Total Thiosalts Removed (g S ₂ O ₃ /day)	(%)
100	1.03	103	85	86
150	0.99	149	89	59
200	1.03	206	112	54
100	2.05	205	106	52
300	1.00	300	66	22

TABLE 6. COMPARISON OF THE OVERALL TREATMENT EFFICIENCY UNDER DIFFERENT LOADING CONDITIONS AT 30°C

Flow Rate (ℓ/day)	Thiosulphate Conc. (g/ℓ)	Total Thiosalts Applied (g S ₂ O ₃ /day)	Total Thiosalts Removed (g S ₂ O ₃ /day)	(%)
80	6.61	529	445	84
160	3.05	488	460	94
320	1.56	499	424	85

TABLE 7. PILOT-SCALE RESULTS SUMMARY

Flow Rate (ℓ/min)	Total Thiosalts (mg/ℓ)					
	Circuit 12			Circuit 6		
	Inf.	Eff.	% Red.	Inf.	Eff.	% Red.
3.8	1630	36	98	2190	150	98
7.6	1780	120	93	2800	1160	59

* Mean values

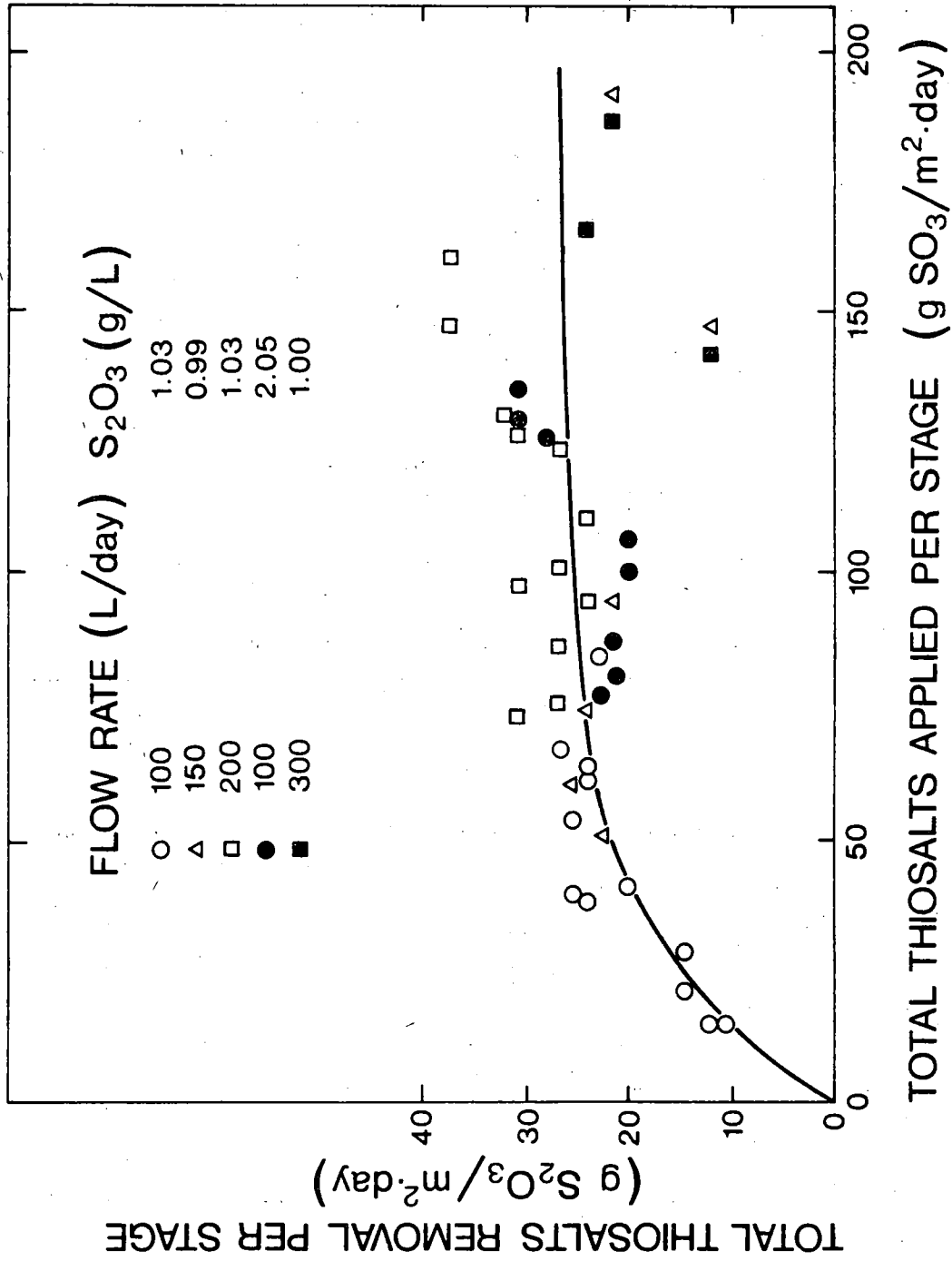


FIGURE 9. THIOSULPHATE OXIDATION RATE FOR THREE-STAGE BENCH-SCALE RBC AT 2°C

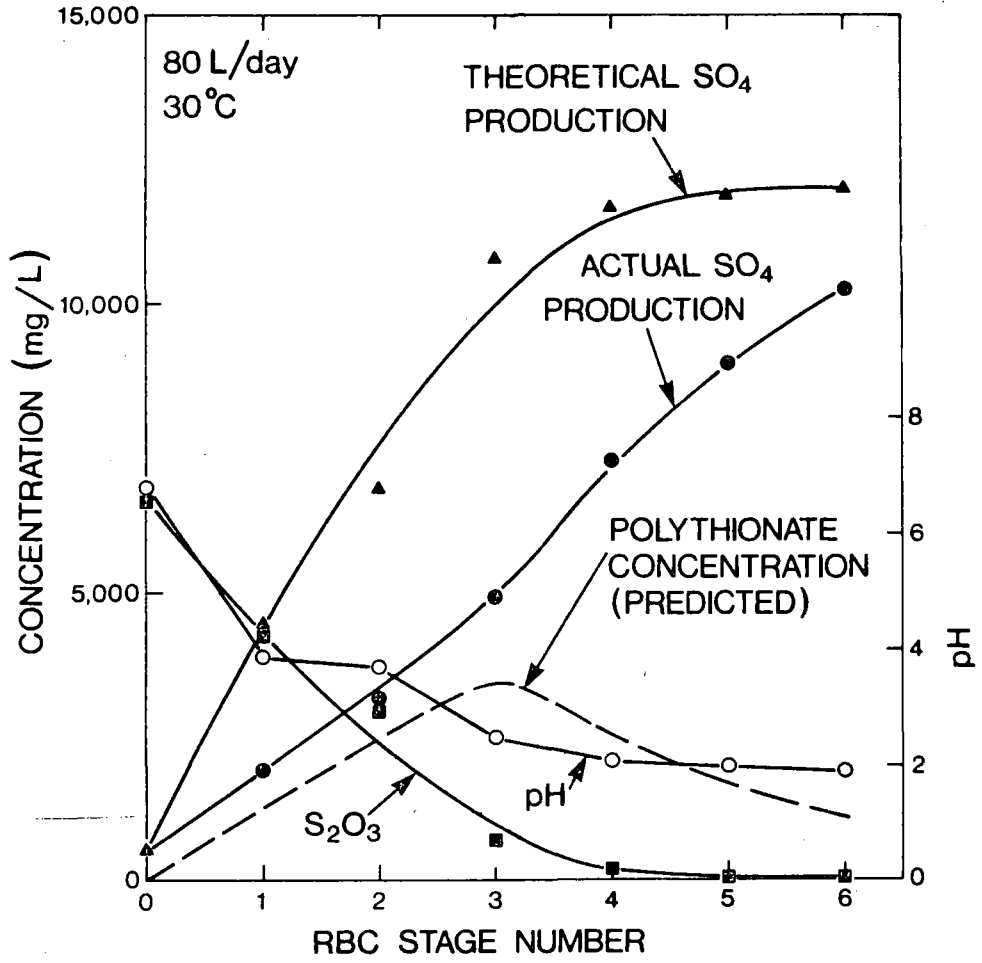


FIGURE 10. EXPERIMENTAL RESULTS OF SIX-STAGE BENCH-SCALE RBC AT 80 L/DAY

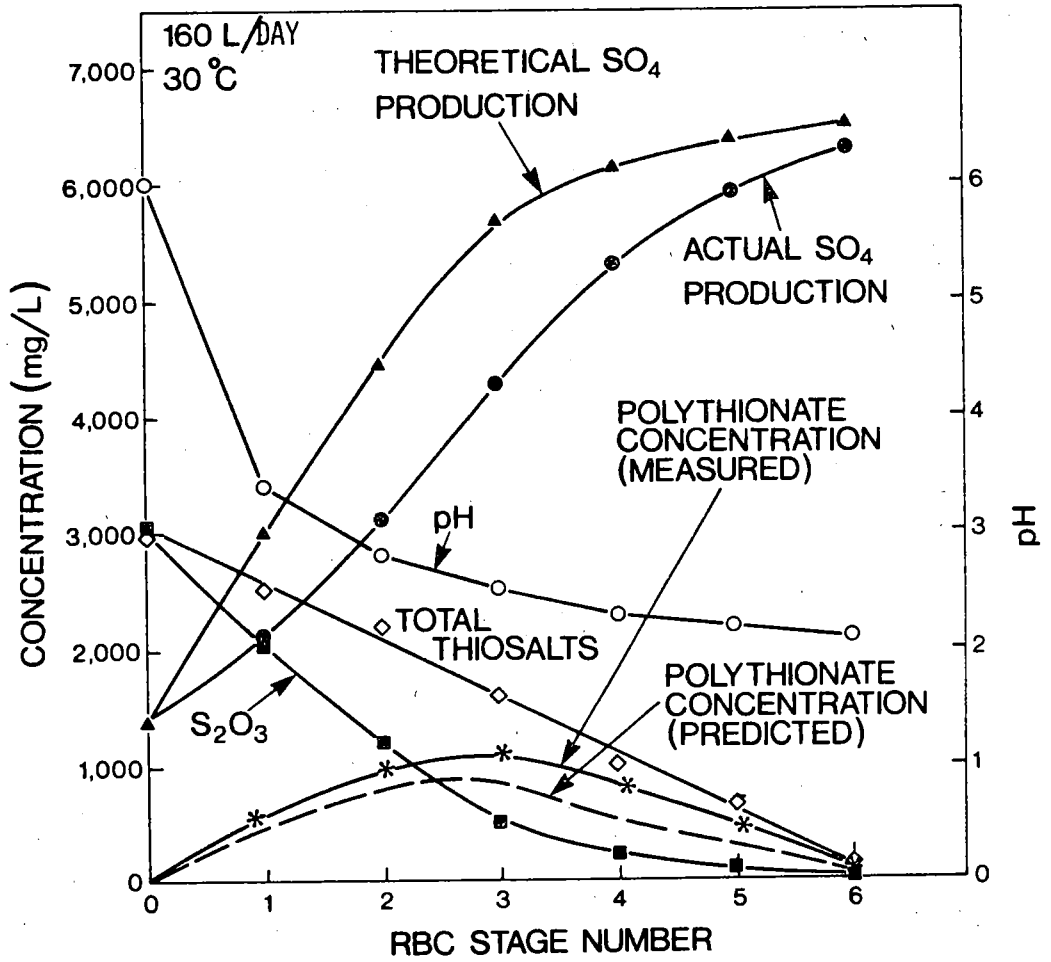


FIGURE 11. EXPERIMENTAL RESULTS OF SIX-STAGE BENCH-SCALE RBC AT 160 L/DAY

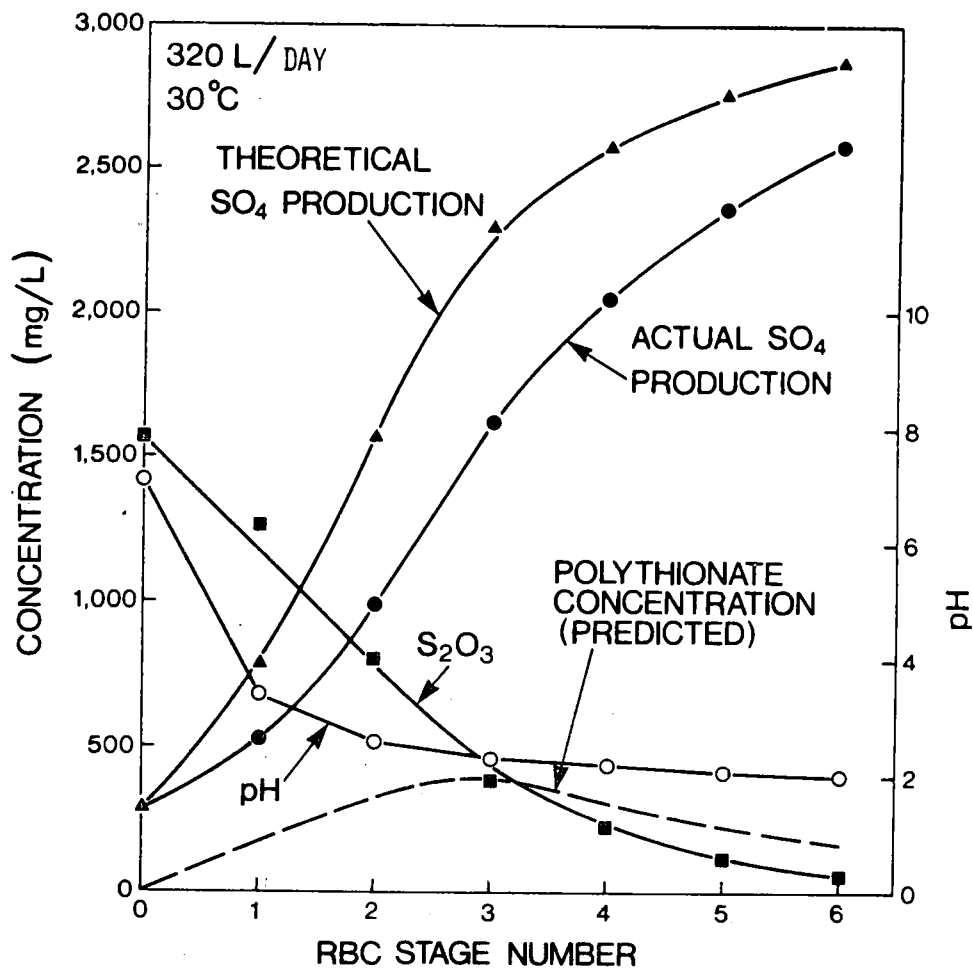


FIGURE 12. EXPERIMENTAL RESULTS OF THE SIX-STAGE BENCH-SCALE RBC AT 320 L/DAY

the thiosulphate and sulphate concentrations, total thiosalts were also determined regularly and the results are presented in Figure 11. The difference between the total thiosalts and thiosulphate concentrations is a measure of the polythionate concentration. The results presented in Figure 11 are almost identical to the predicted polythionate concentration. This indicated that a well balanced system existed with respect to sulphur compounds.

B.C. Research (1973) reported that only 85 to 95% of the oxidized thiosulphate was accounted for as the sulphuric acid and no explanation was given for the incomplete sulphur balance. Results from the present study indicated that the sulphate unaccounted for may be explained by the presence of polythionates in the effluent, which could not be detected by the analytical techniques used by B.C. Research.

A comparison of the treatment efficiency under different loading conditions is presented in Table 6. Comparing the results with those shown in Table 5, it can be seen that significant improvement in thiosulphate oxidation was achieved at the elevated operating temperature.

The relationship between total thiosalts applied and removal for each stage is graphically shown in Figure 13. Again, the reaction rates varied from first-order to zero-order depending on the applied loading. Therefore, the Michaelis-Menton theory may also be used to describe the kinetics of thiosalts oxidation at 30°C.

As indicated in Figure 13, reduced oxidation rates of thiosalts were observed at an applied loading greater than 270 g S₂O₃/m²·day. Because the rate of thiosalts oxidation was calculated based on sulphate production, the decrease in oxidation rates could be explained by the fact that under higher loading conditions, more polythionates, and thus less sulphates were generated due to incomplete oxidation of thiosulphate. A similar phenomenon is also observed in the bench-scale operation at 15°C as indicated in the following section.

4.1.4 Bench-Scale Operation at 15°C

After the completion of the experiments at 2 and 30°C, a program was set up to investigate the thiosalts oxidation at an intermediate temperature of 15°C. Four hydraulic rates with the thiosulphate concentration

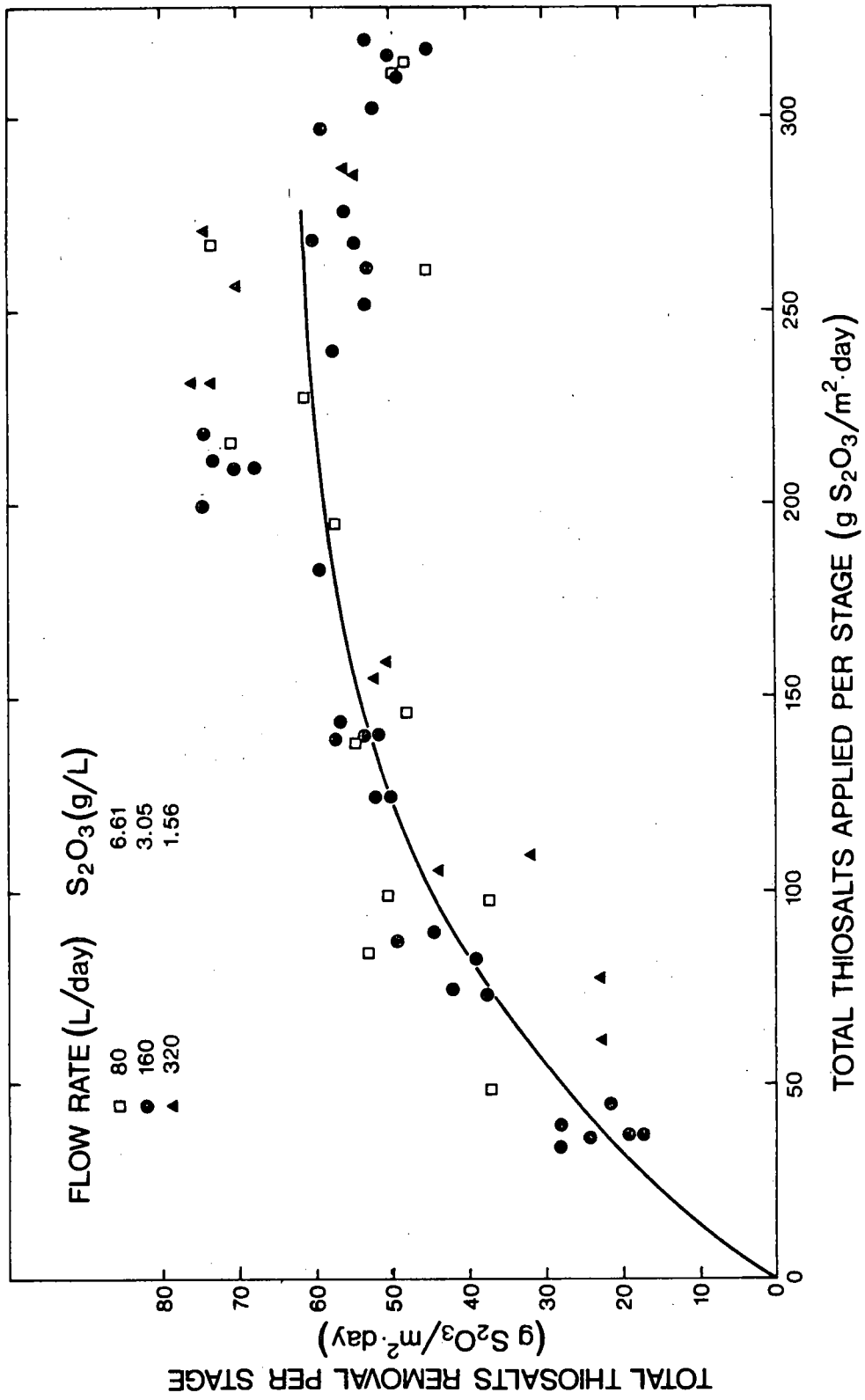


FIGURE 13. THIOSULPHATE OXIDATION RATE FOR THE SIX-STAGE BENCH-SCALE RBC AT 30°C

ranging from 1.44 to 3.19 g/l as S_2O_3 were studied. Results are presented in Figure 14. As in the case of 30°C, higher applied loadings resulted in a decreased oxidation rate of total thiosalts. Therefore, the maximum applied loading should be limited to 250 g $S_2O_3/m^2 \cdot day$ in order to avoid overloading conditions to the reactor operating at 15°C. Since the change in pH, concentration of thiosulphate and sulphate in each stage followed the same pattern as shown in Figures 4 to 8 for 2°C and 10 to 12 for 30°C, to avoid replication, a graphical presentation of these results were not made for 15°C.

4.1.5 Establishment of Kinetics of Thiosulphate Oxidation at Other Temperatures

Bench-scale studies at 2, 15 and 30°C indicated that the oxidation of thiosulphate to sulphate could be successfully achieved in a RBC unit and that the kinetics followed the Michaelis-Menton relationship. To establish the equation for the kinetics of the thiosulphate oxidation, the reciprocal of the applied loading was plotted against the reciprocal of the removal rate. By using the method of least squares, the equations obtained for the three temperatures investigated were established and are shown below:

For 2°C:

$$K_s = \frac{S}{0.774 + 0.0327 S} \quad (4)$$

For 15°C:

$$K_s = \frac{S}{1.063 + 0.0209 S} \quad (5)$$

And for 30° C:

$$K_s = \frac{S}{1.178 + 0.0119 S} \quad (6)$$

where:

K_s = removal rate of total thiosalts per stage in
g $S_2O_3/m^2 \cdot day$, and

S = total thiosalts applied per stage in
g $S_2O_3/m^2 \cdot day$.

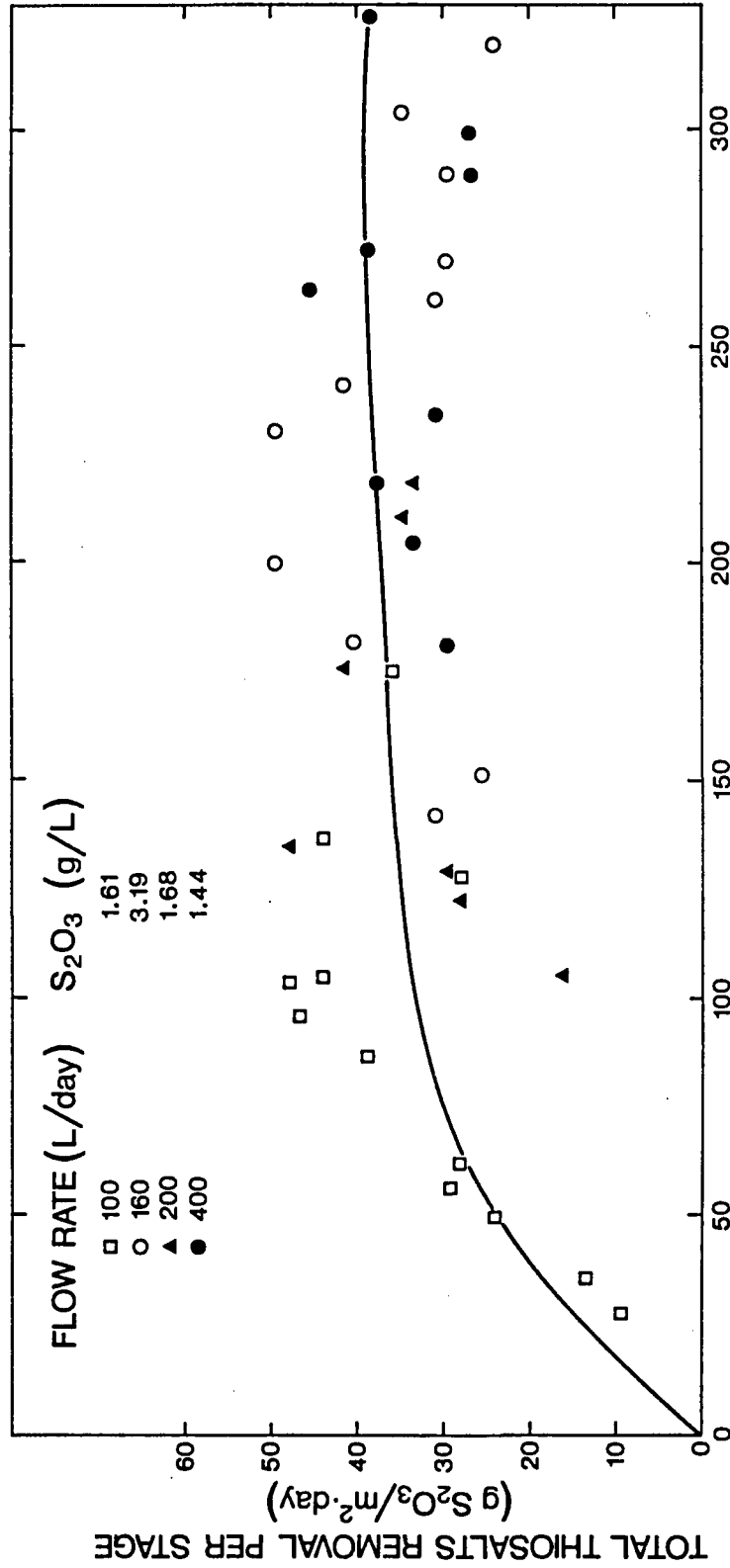


FIGURE 14. TOTAL THIOSALTS APPLIED PER STAGE ($g S_2O_3/m^2 \cdot day$)
RBC AT 15°C

The first constant in the denominator of the equation represented the slope of the curve at the zero point and the second constant the reciprocal of the maximum reaction rate. The maximum rate of total thiosalts oxidation at 2, 15 and 30°C was calculated to be 30.6, 47.9 and 84.0 g S₂O₃/m²·day, respectively.

The effect of temperature on the oxidation rate of thiosalts is demonstrated in Figure 15. A plot of the maximum rates at the three temperatures investigated versus the reciprocal of the absolute temperature yielded a linear relationship as shown in the figure. This indicates that the temperature dependency of thiosalts oxidation followed the Arrhenius equation. Based on the results obtained at 2, 15 and 30°C and by means of interpolation, it was possible to determine the constants representing the slope and the maximum oxidation rate of thiosalts at other temperatures. For example, the constants for the equations established at 10, 20 and 25°C are shown below:

For 10°C:

$$K_s = \frac{S}{0.926 + 0.0238 S} \quad (7)$$

For 20°C:

$$K_s = \frac{S}{1.099 + 0.0167 S} \quad (8)$$

And for 25°C:

$$K_s = \frac{S}{1.136 + 0.0143 S} \quad (9)$$

Curves corresponding to these equations and representing the kinetics of thiosalts oxidation are presented in Figure 16.

Based on the equations 7, 8 and 9, the maximum oxidation rates of total thiosalts at 10, 20 and 25°C were calculated to be 42.0, 59.9 and 69.9 g S₂O₃/m²·day, respectively.

The oxidation rate of thiosalts at any applied loading may be obtained from the curves or calculated from the equations.

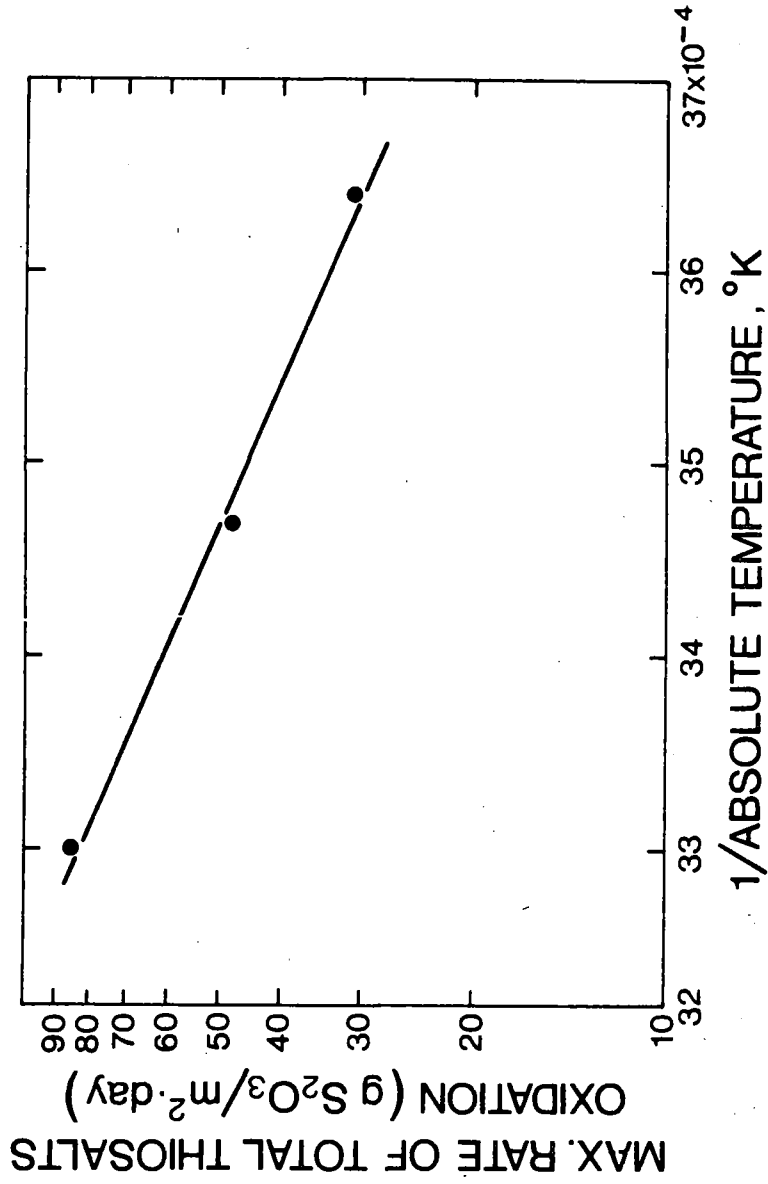


FIGURE 15. TEMPERATURE DEPENDENCY OF THIOSALTS OXIDATION

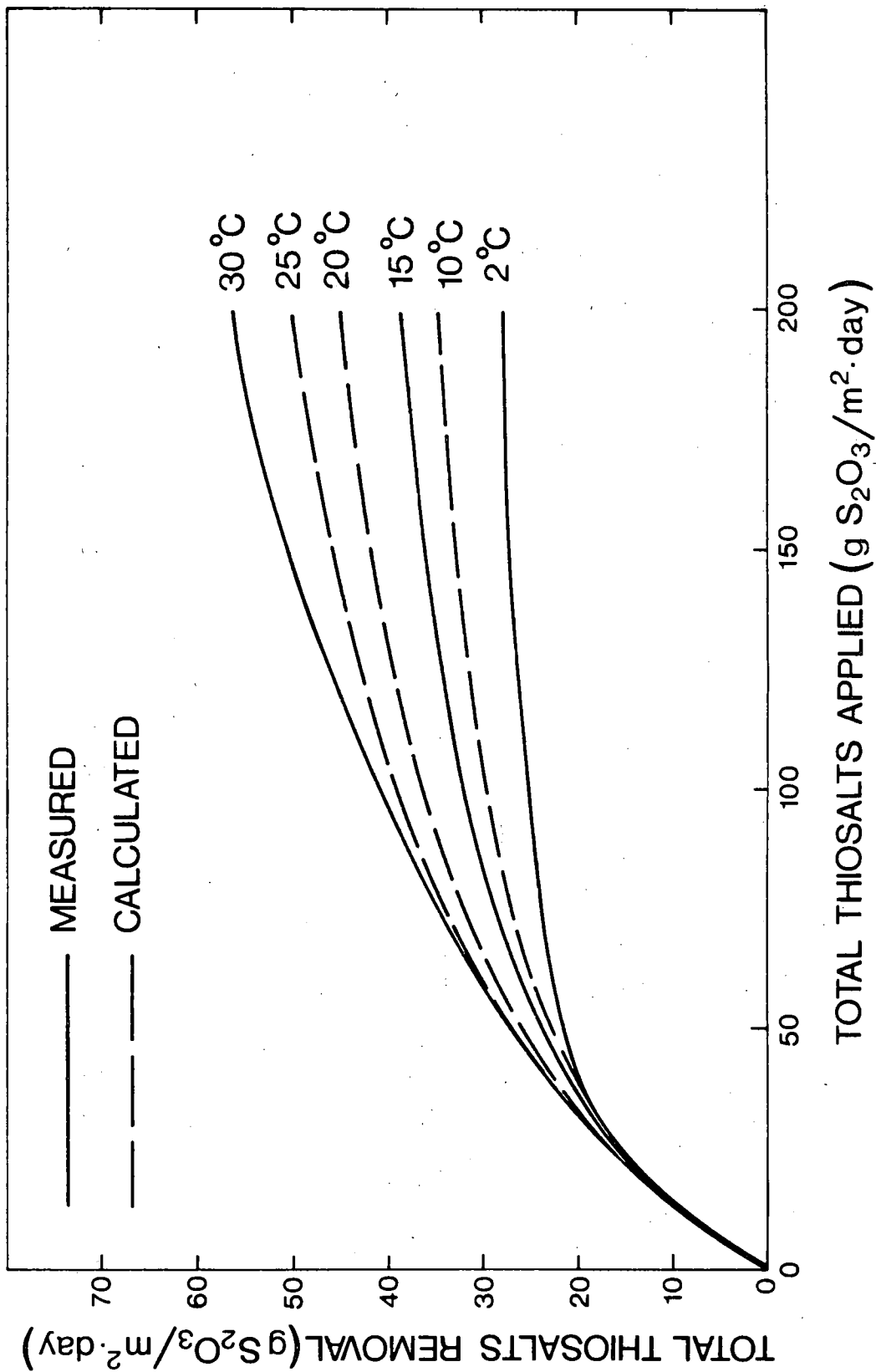


FIGURE 16. MEASURED AND CALCULATED THIOSALTS OXIDATION RATE

4.2 Pilot-Scale Operation

4.2.1 Thiosalts Oxidation

The pilot-scale studies involved operation of a 2 m diameter RBC unit at Brunswick Mining and Smelting Company Ltd. in Bathurst, New Brunswick. Two flow rates; 3.8 and 7.6 l/min (0.8 and 1.6 l/gpm) and two waste streams were investigated during the 6-month operating period.

Due to the great variability in thiosalts concentration and temperature of the wastewater and also the occasional pump failure, a continuous steady-state operating condition was difficult to attain in the treatment system. Although samples were collected and analyzed on a daily basis, only the data representing the steady-state operation were selected and presented in the report for interpretation.

The selected data were divided into three groups according to the operating temperature encountered in each stage, namely; 17-20, 21-24 and 25-28°C. The total thiosalts applied versus removal in each stage is plotted in Figure 17 and 18 for circuit No. 12 and 6, respectively. For comparison, the thiosalts removal relationships estimated from the bench-scale results for the average of the three temperature ranges are also presented. As can be seen, the pilot-scale results for the two lower temperature ranges were comparable with those calculated from the bench-scale studies. However, considerable difference existed between the pilot-scale and bench-scale results for the highest temperature range. Points deviating substantially from the curve were mostly results of thiosalts oxidation in the first stage. Although no experiments were carried out to investigate the exceptionally high oxidation rate that occurred in this stage, it was considered that this may be partially attributed to chemical oxidation.

Probability plots of the influent and final effluent thiosalts concentration for the two flow rates are shown in Figures 19 and 20 for circuit No. 12. For circuit No. 6, the data are plotted in Figures 21 and 22. Mean values for each relationship are summarized in Table 7.

As indicated, an increase in flow rate from 3.8 to 7.6 l/min resulted in a decrease in treatment efficiency with a substantial increase in effluent thiosalts concentrations for both wastewaters. For circuit No.

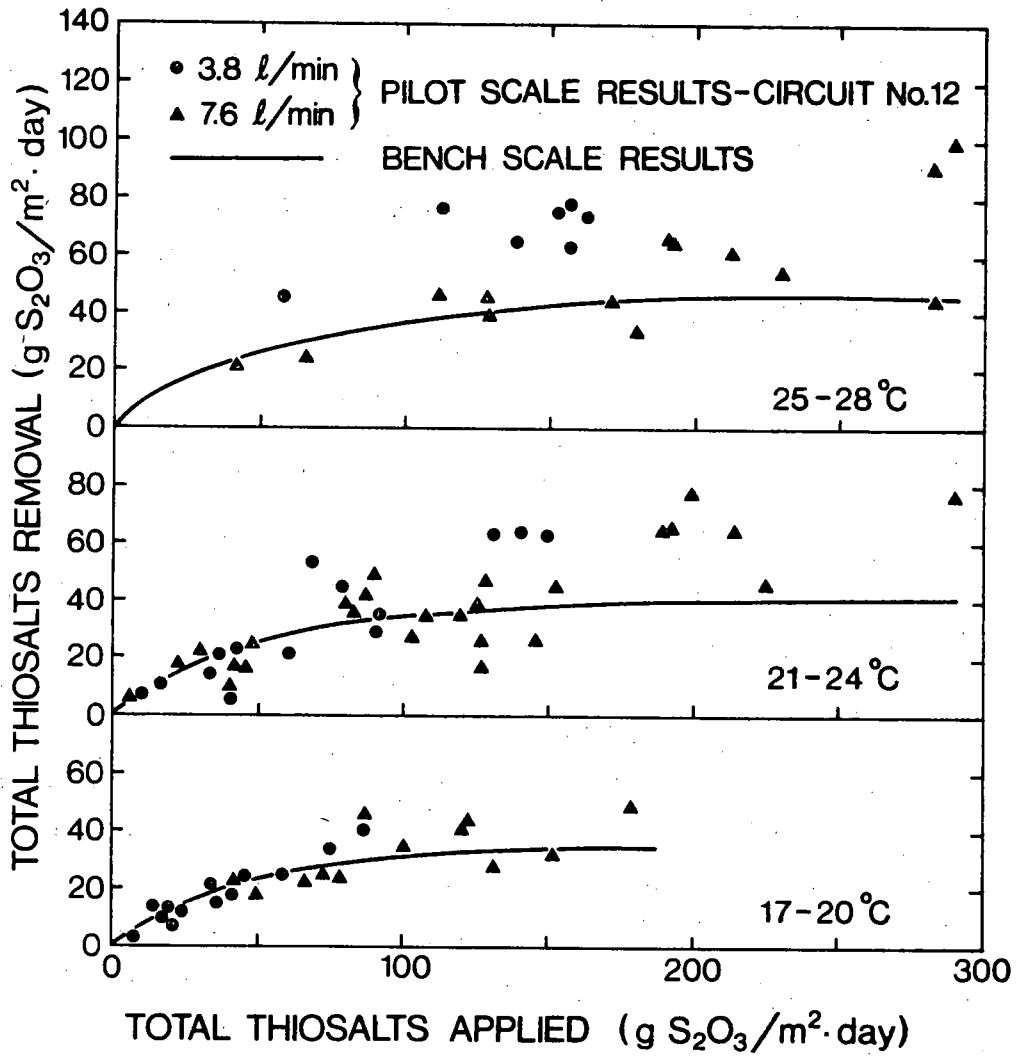


FIGURE 17. COMPARISON OF PILOT-SCALE AND BENCH-SCALE RESULTS FOR CIRCUIT NO. 12.

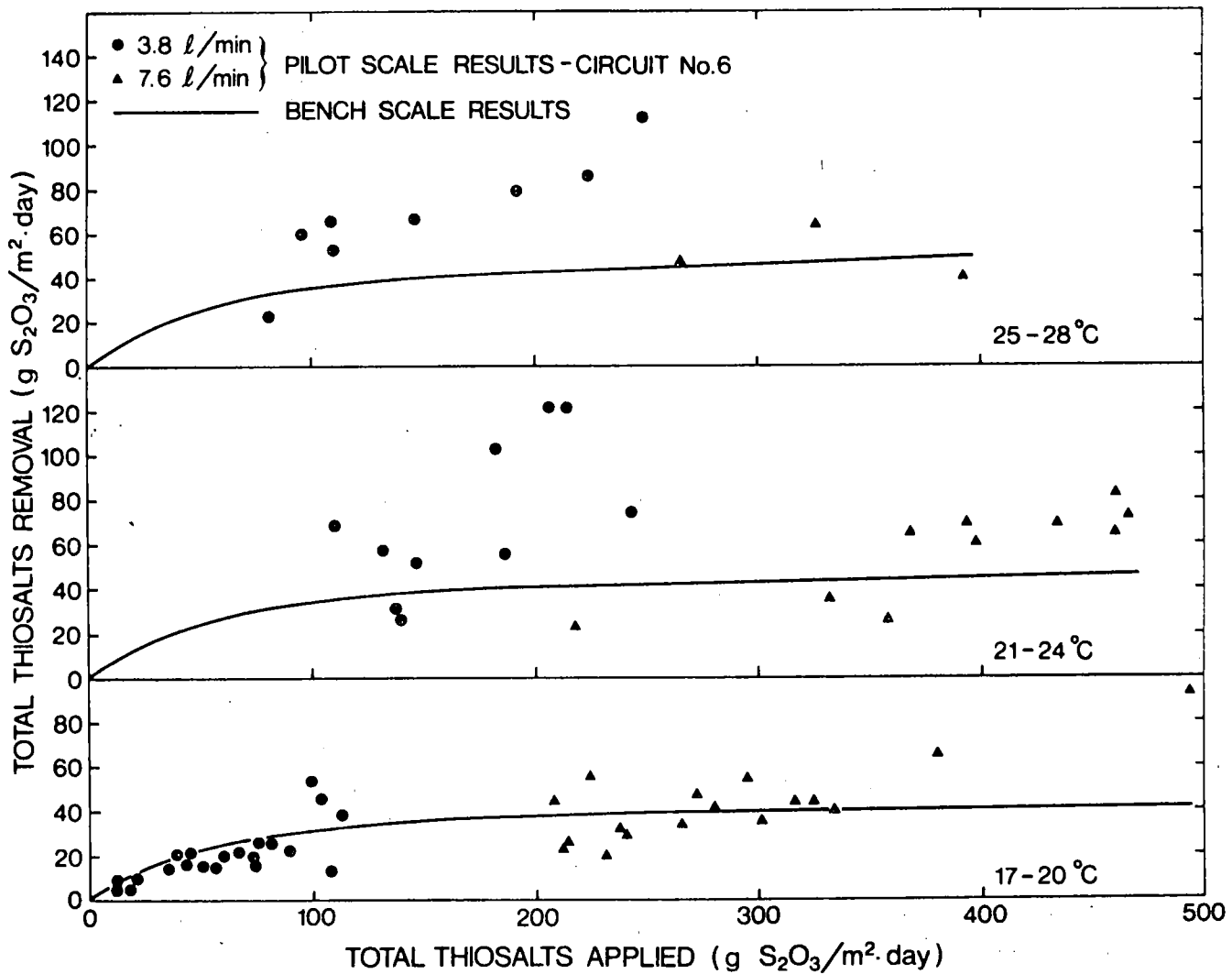


FIGURE 18. COMPARISON OF PILOT-SCALE AND BENCH-SCALE RESULTS FOR CIRCUIT NO. 6

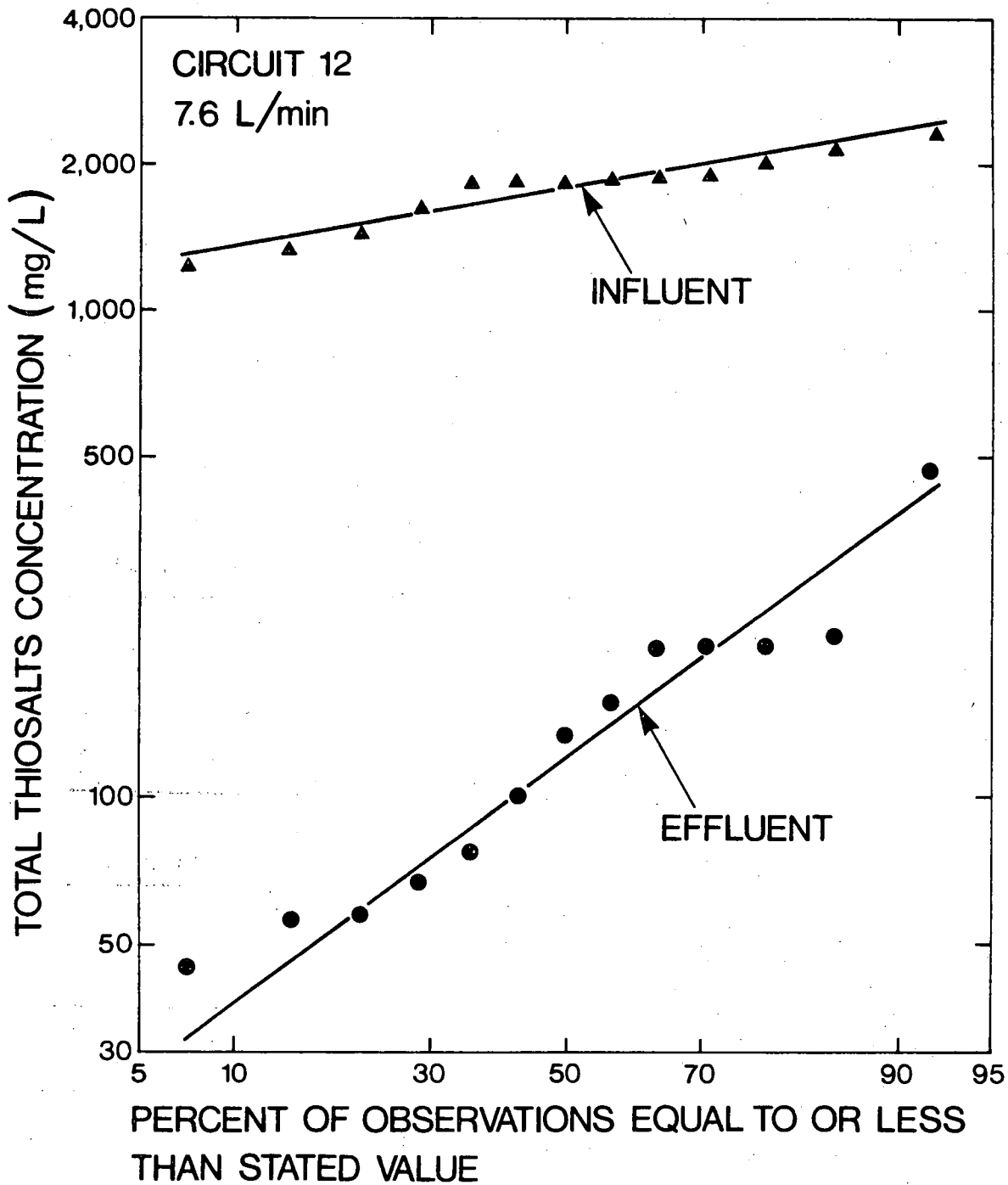


FIGURE 19. INFLUENT AND EFFLUENT THIOSALTS CONCENTRATIONS FROM THE PILOT-SCALE OPERATION AT 7.6 L/MIN FOR CIRCUIT 12

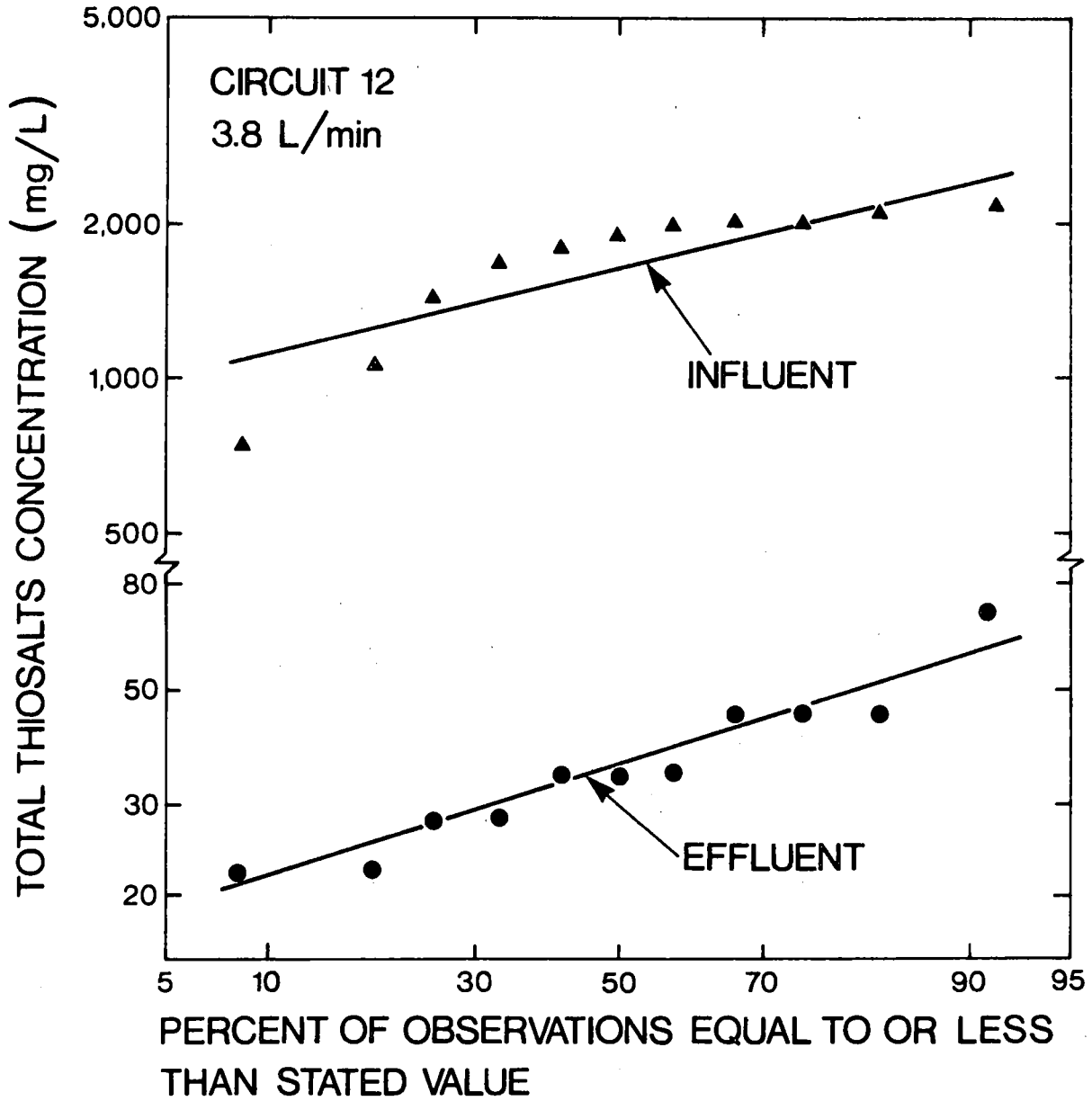


FIGURE 20. INFLUENT AND EFFLUENT THIOSALTS CONCENTRATIONS FROM THE PILOT-SCALE OPERATION AT 7.6 L/MIN FOR CIRCUIT 12

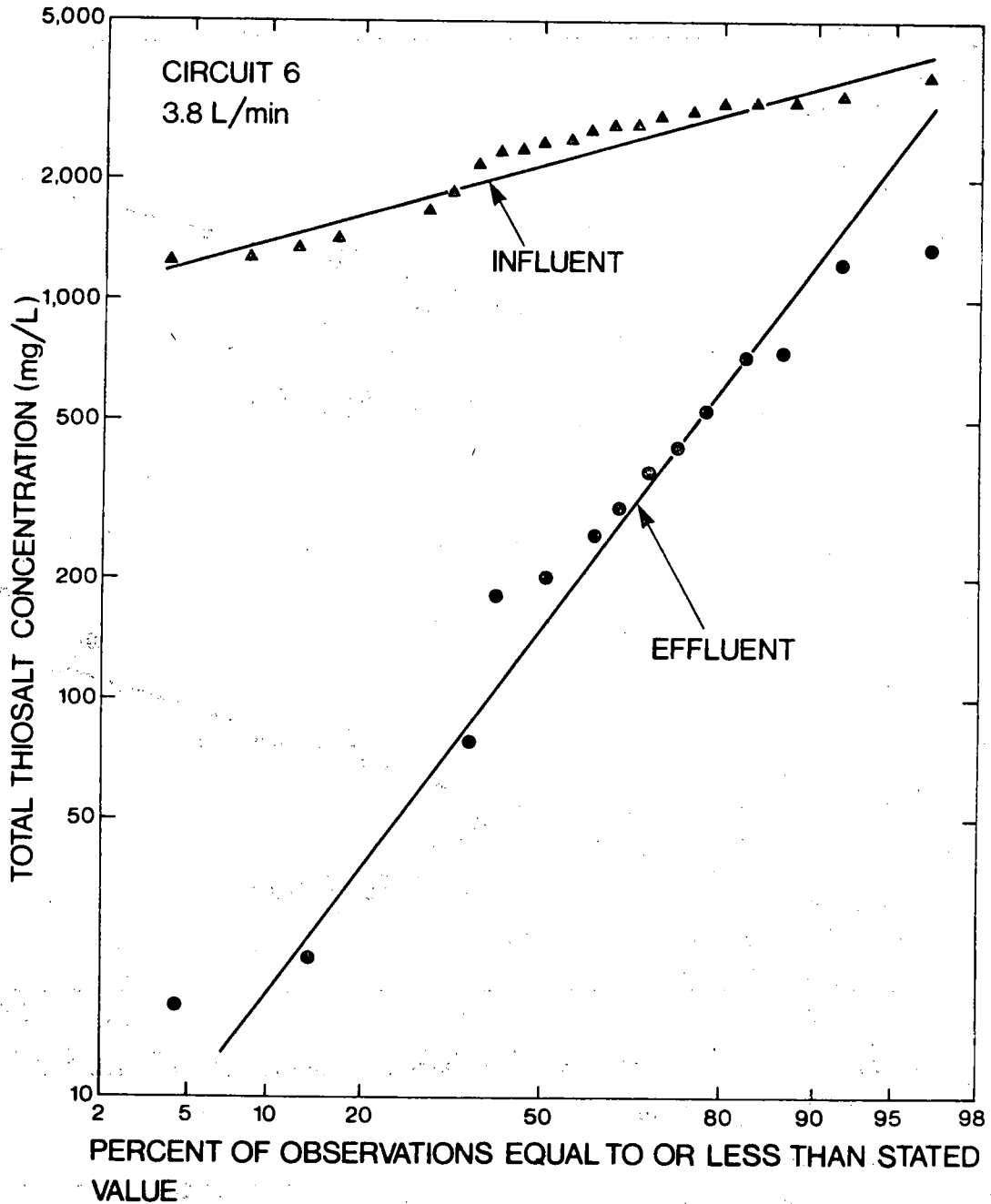


FIGURE 21. INFLUENT AND EFFLUENT THIOSALTS CONCENTRATIONS FROM THE PILOT-SCALE OPERATION AT 3.8 L/MIN FOR CIRCUIT 6

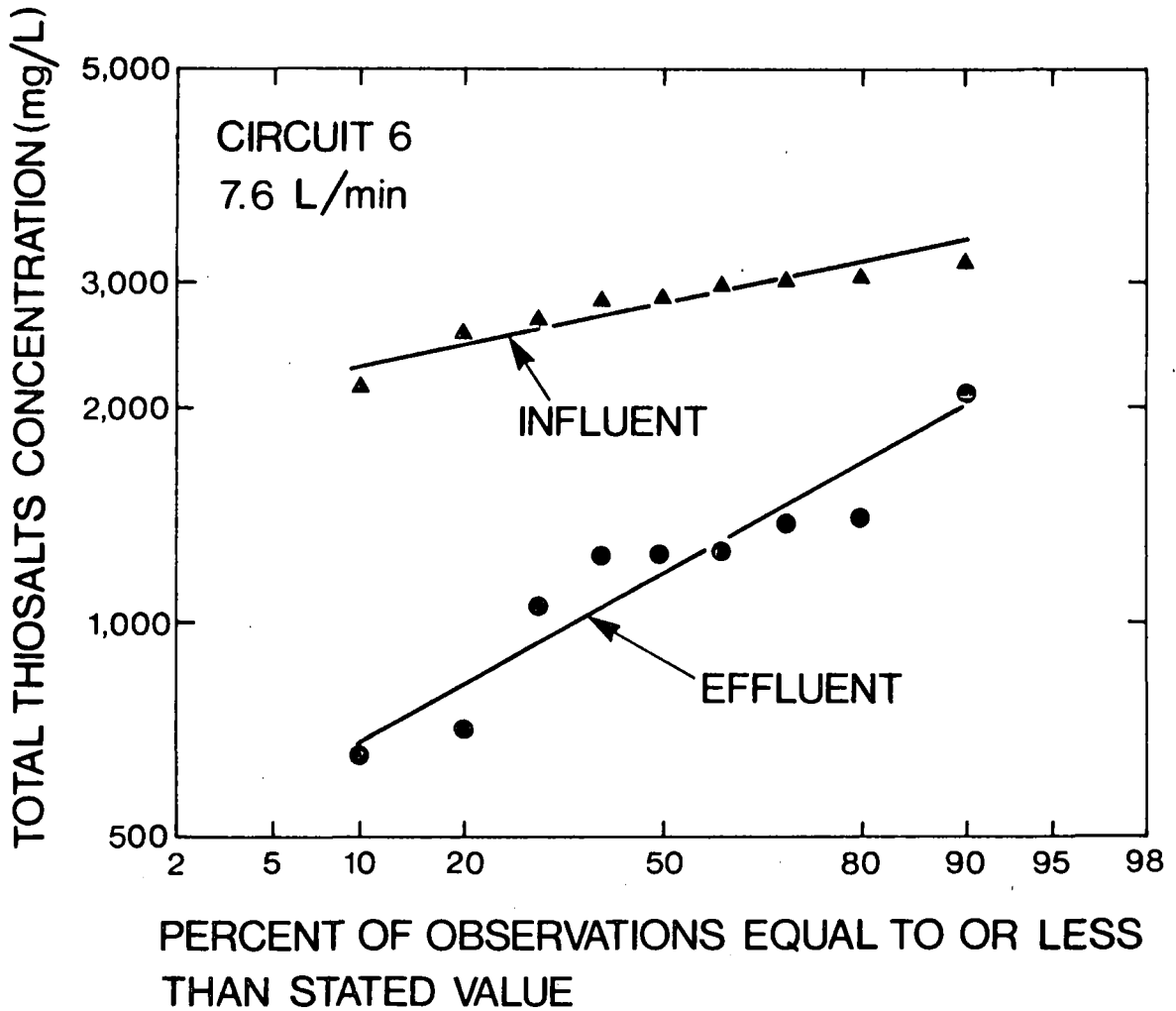


FIGURE 22. INFLUENT AND EFFLUENT THIOSALTS CONCENTRATIONS FROM THE PILOT-SCALE OPERATION AT 7.6 L/MIN FOR CIRCUIT 6

6 there was also a remarkable increase in thiosalts concentration after the flow rate was doubled. Apparently, under this operating condition, the reactor was overloaded as indicated by the poor effluent. Because the results of the pilot-scale and the bench-scale operations were comparable, it was feasible to use bench-scale data to predict the performance of a RBC treating mill process effluents containing thiosalts. For design purposes, the bench-scale kinetic relationships were used for sizing the full-scale reactors.

4.2.2 Heat Transfer Characteristics of the RBC

As the RBC is an efficient heat transfer device, the heat transfer characteristics of the pilot-scale RBC were investigated. This was required because the temperature dependency of the thiosalts oxidation necessitated an evaluation of the temperature in each stage so that the oxidation rate in the individual stages could be determined accordingly. This is of particular importance when considerable difference existed between the wastewater and ambient temperature, such as the case encountered in the pilot-scale operation.

To describe the heat transfer for the RBC used in the field study, the following model applied by Wilson (1975) was used:

$$V \cdot C_p \cdot (T_1 - T_2) = k \cdot A \cdot t \cdot (T_{av} - T_{air}) \quad (10)$$

- Where V = Liquid volume of reactor (ℓ)
 C_p = Specific heat of wastewater ($\text{kcal}/\ell \cdot ^\circ\text{C}$)
 T_1 = Influent wastewater temperature ($^\circ\text{C}$)
 T_2 = Effluent wastewater temperature ($^\circ\text{C}$)
 T_{av} = $(T_1 + T_2)/2$ ($^\circ\text{C}$)
 T_{air} = Ambient air temperature ($^\circ\text{C}$)
 k = Heat transfer coefficient ($\text{kcal}/\text{m}^2 \cdot \text{h} \cdot ^\circ\text{C}$)
 A = Total disc surface area (m^2)
 t = Hydraulic detention time of wastewater (h)

Based on results of the pilot-scale operation, the relationship between the temperature driving force and the change in wastewater temperature was developed as shown in Figure 23 for the two flow rates investigated. To enable calculations on the temperature change to be made for other flow rates, the relationships for 1.9, 5.7 and 15.2 ℓ/min are also presented. RBC's with similar surface-volume ratio, i.e. $2.15 \text{ m}^2/\ell$ could be expected to behave in a similar fashion.

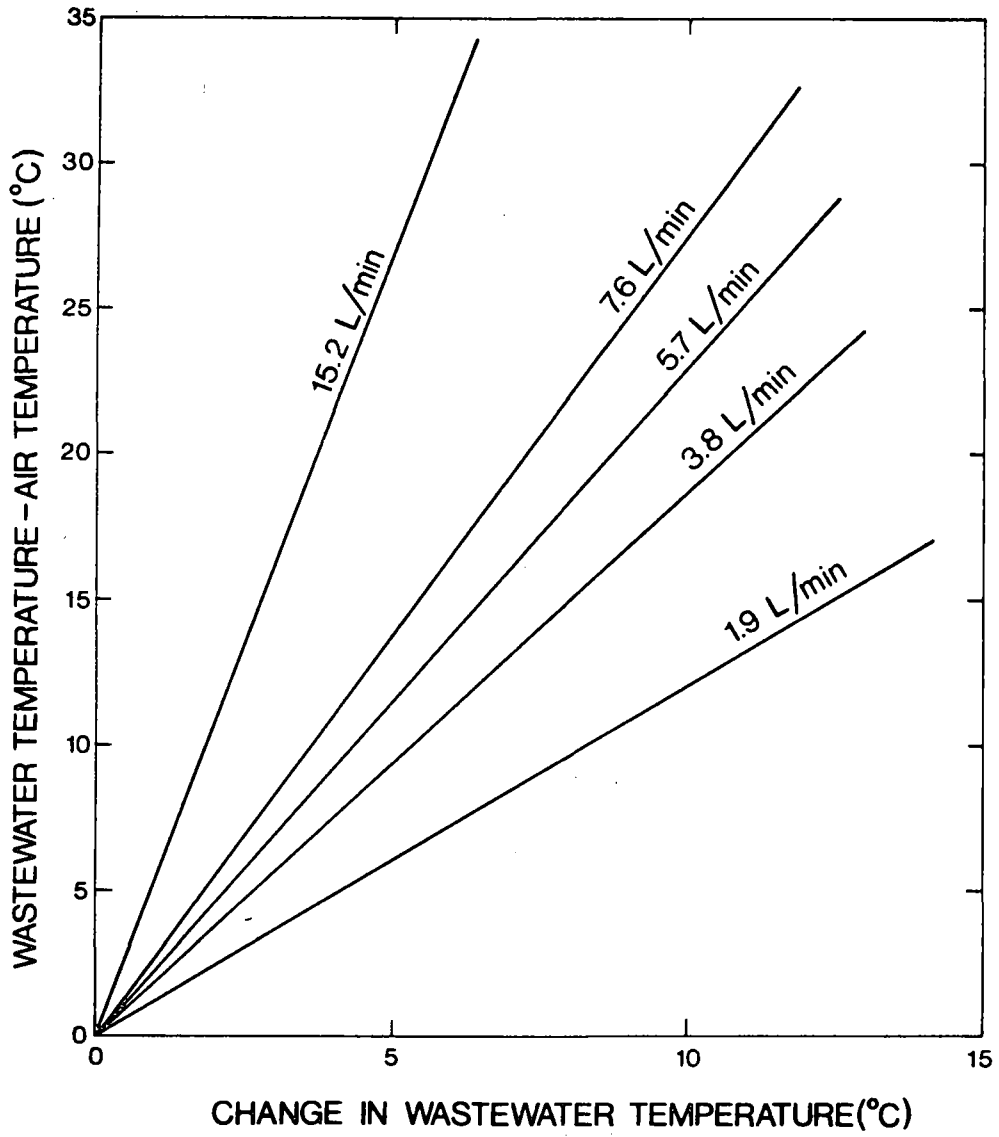


FIGURE 23. HEAT TRANSFER FOR THE PILOT-SCALE RBC

Assuming an air and wastewater temperature of 20 and 40°C, respectively; an estimate of the temperature profile through the pilot-scale RBC is plotted in Figure 24. The temperature change in each stage as shown in the figure compare favourably with the measured values under similar operating conditions. As expected, a greater drop in temperature occurred in the reactor operated at the lower flow rate.

4.2.3 pH Profile Through the RBC

The untreated wastewater from circuits No. 6 and No. 12 had a pH ranging from 3.2 to 5.7 and from 3.6 to 5.9, respectively. After treatment, the pH dropped successively through the RBC unit due to the formation of sulphuric acid. The change in pH in the individual stages during the pilot-scale operation is presented in Figures 25 and 26. As indicated, there was a similarity in the pH profile for all the operating conditions investigated. Although the production of sulphuric acid in each stage was approximately the same, the decrease of the pH in the first-stage was much greater than that in the subsequent stages. Because pH is expressed as the negative logarithm of the hydrogen-ion concentration, to bring about a unit drop in the pH value, a highly acidic solution will require a significantly greater amount of hydrogen ions than a slightly acidic solutions such as the untreated mill wastewater. Similar phenomena were also observed in the bench-scale reactor as shown in Figures 10, 11 and 12.

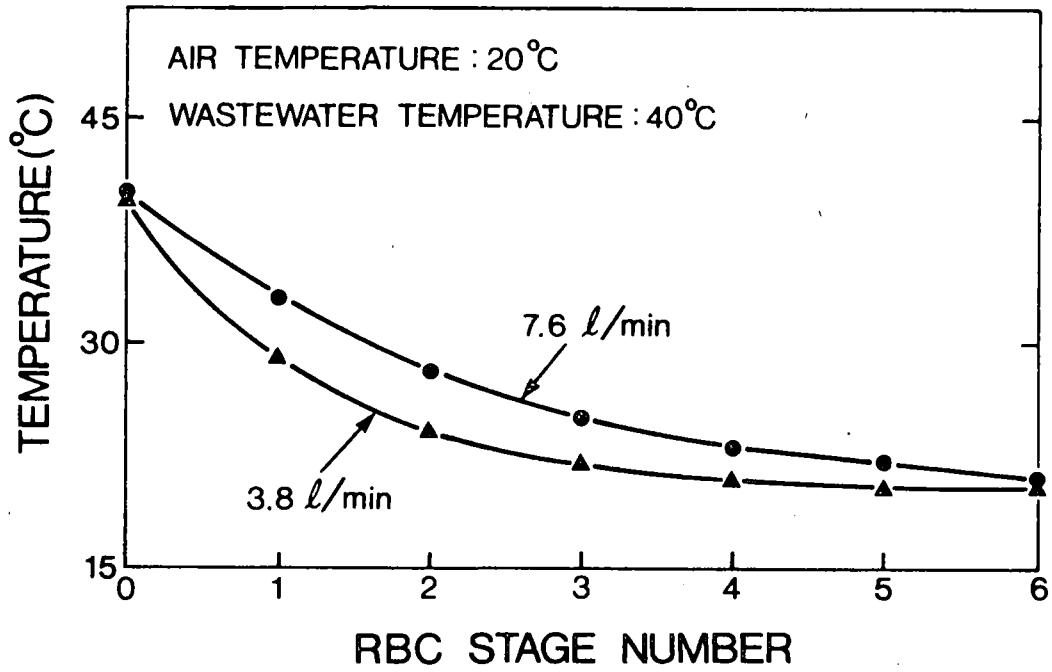


FIGURE 24. TEMPERATURE PROFILE THROUGH THE PILOT-SCALE RBC

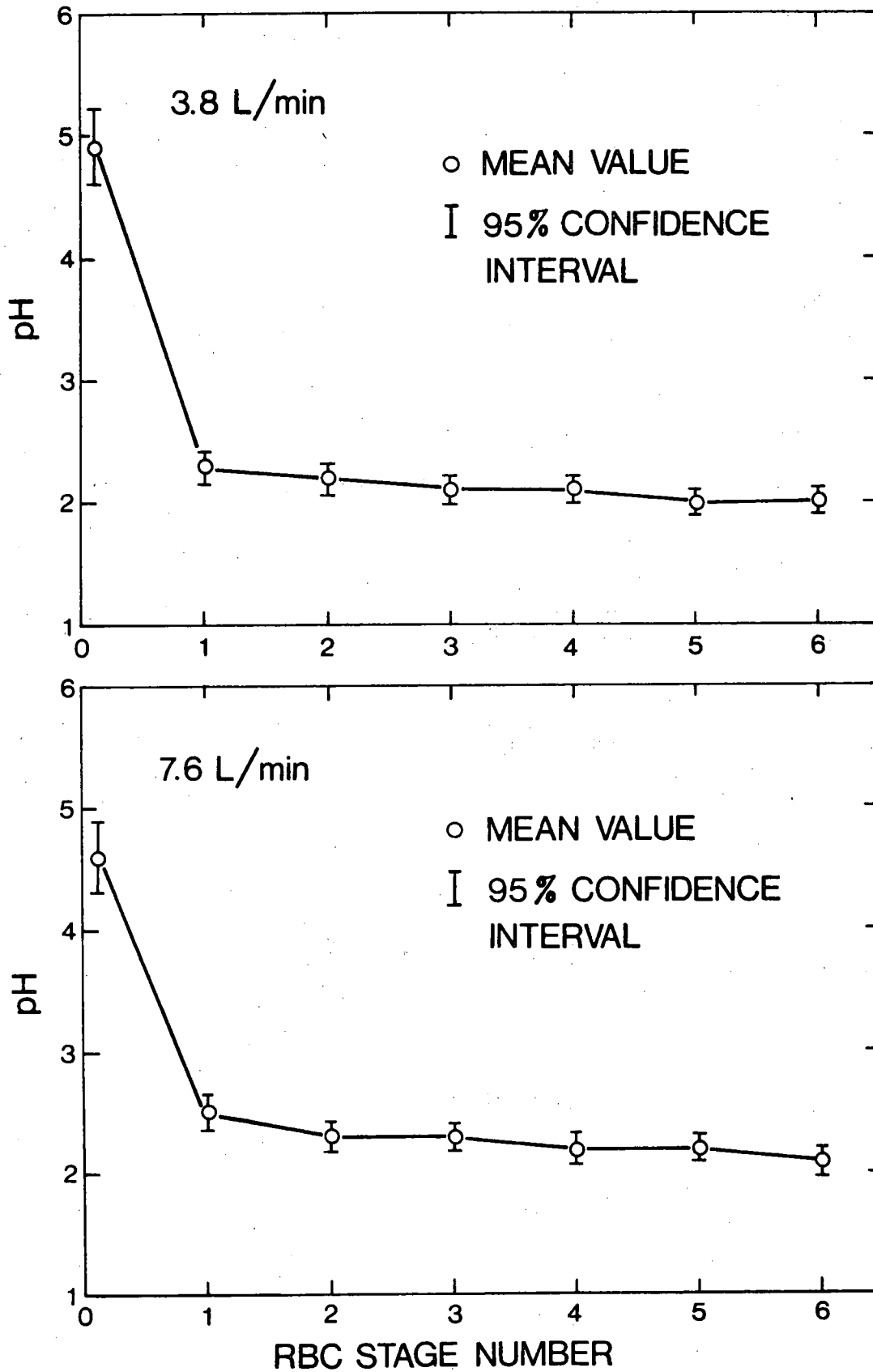
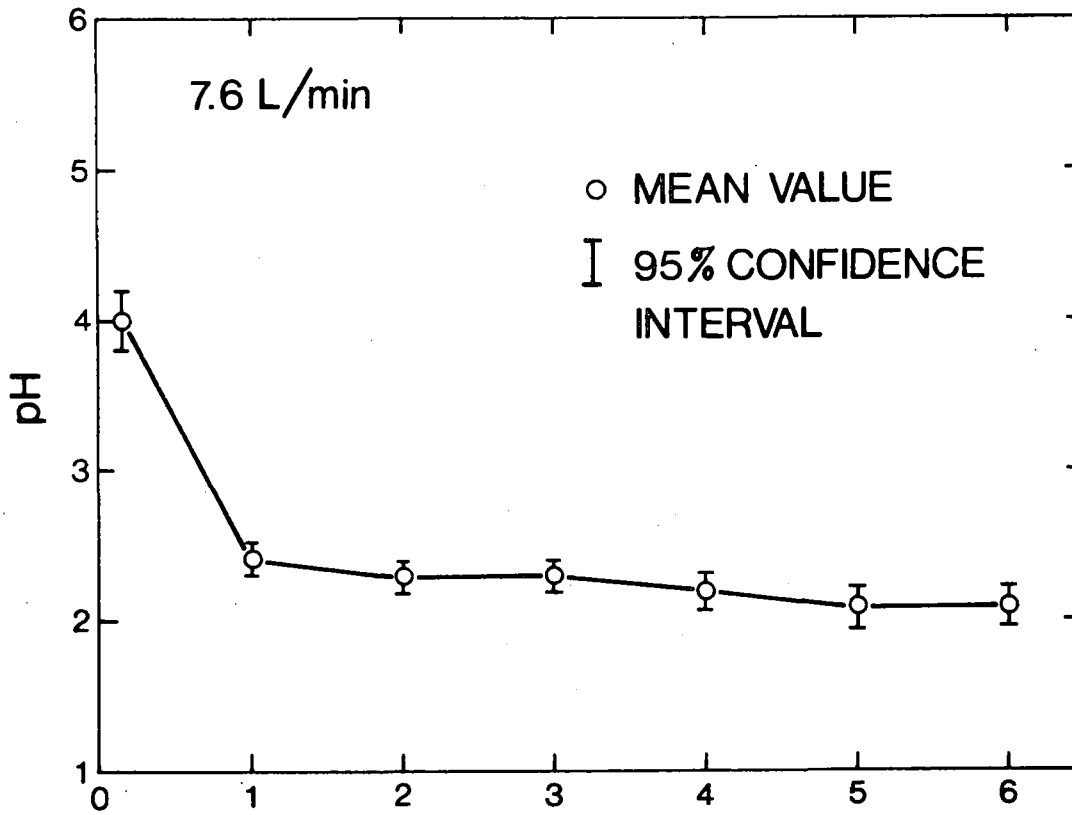
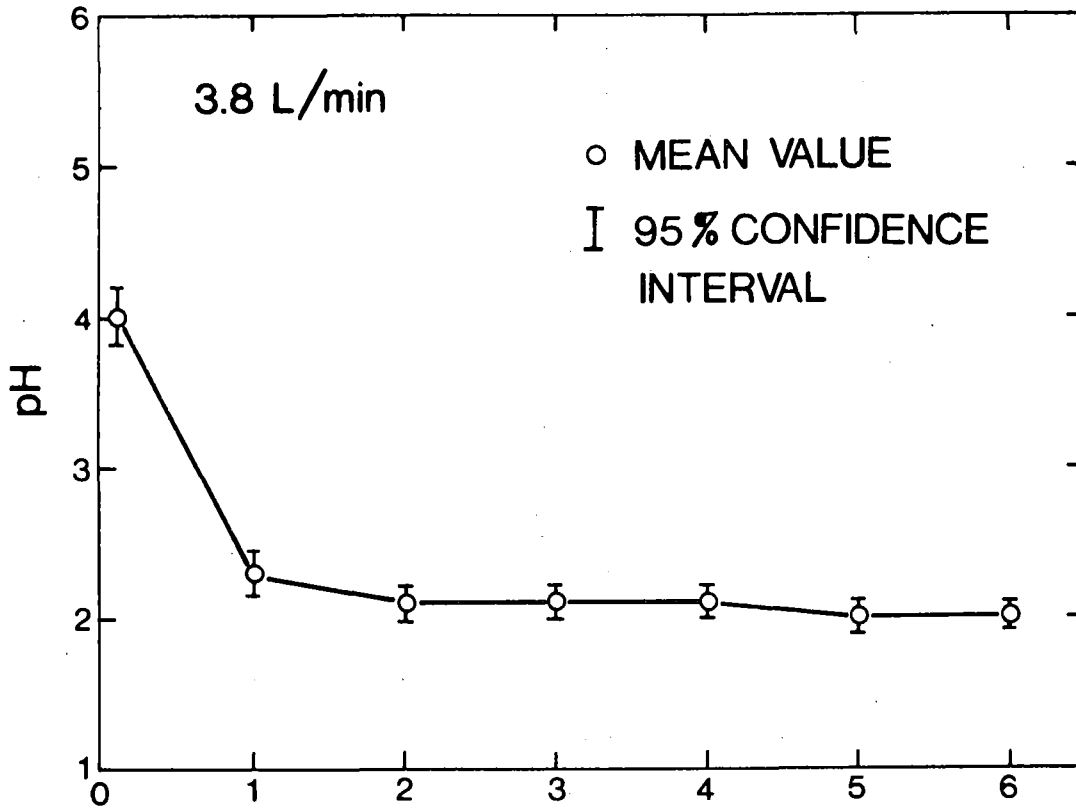


FIGURE 25. pH PROFILE FOR CIRCUIT NO. 12



RBC STAGE NUMBER

FIGURE 26. pH PROFILE FOR CIRCUIT NO. 6

5. DESIGN CALCULATION AND COST ESTIMATION FOR THE FULL-SCALE RBC

Based on the kinetic relationships obtained from the bench-scale and the pilot-scale studies, it is possible to design a full-scale RBC plant to treat the process effluent from the base metal mining operation in Bathurst, New Brunswick. The design will be based on the assumption that process water will be reused by recirculating from the tailings pond effluent. The treatment facility will be designed to treat the process water blowdown, a concentrated wastewater stream having a reduced volume and increased liquid temperature. The latter is most critical as it is essential to keep the liquid temperature high to optimize the biological reaction rates, and thus, reduce the surface area requirement of the fixed film reactor.

The following is a design calculation estimating the capacity as well as the cost of the RBC system. Alternatives in the design to meet different effluent quality levels were also examined. The assumptions used in the calculation are as follows:

Quantity of Wastewater:	10,500 m ³ /day (1600 lpm)
Total thiosalts concentration:	1,250 mg/l as S ₂ O ₃
Wastewater temperature:	43°C
Ambient temperature:	25°C

These assumptions were based on the average values which would be encountered during the summer operation of the mill. For winter operation, a slightly higher thiosalts concentration (1520 mg/l) was expected, however, the flow rate is only half of that encountered in the summer months. A comparison of the reactor capacity required under the summer and winter conditions indicated that the surface area required for the summer operation was greater and therefore the design calculation was based on summer conditions only.

5.1 Design Method

The procedures used to design a RBC unit to meet a desired effluent quality are as follows:

1. Based on the air and wastewater temperature, establish a temperature profile of the wastewater throughout the reactor using the approach identified in Section 4.2.
2. Select a hydraulic loading and calculate the applied loading to the first stage by multiplying the hydraulic loading by the thiosalts concentration. It should be noted that overloading conditions may result in incomplete oxidation of thiosalts as indicated in Sections 4.1.3 and 4.1.4. To include a safety factor in the design, an applied loading of greater than 250 g S₂O₃/m²·day is not recommended.

Therefore, for a wastewater having a thiosalts concentration of 1,250 mg/l, the hydraulic loading should not exceed 200 l/m²·day.

3. Using the applied loading and temperature, determine the rate of thiosalts oxidation or the thiosalts removal by the method of interpolation using the family of curves shown in Figure 16.
4. Obtain the applied loading to the second and subsequent stages by subtracting the amount of thiosalts removed from the applied loading in the previous stage. The concentration of thiosalts in each effluent stage may then be calculated by dividing the exit loading by the hydraulic loading.
5. Repeat the above procedure until the desired effluent quality is achieved. If the desired effluent quality is not achieved select a new hydraulic loading and repeat the design procedure.

This approach was used to establish a relationship between effluent quality and hydraulic loading for a wastewater having a total thiosalts concentration of 1250 mg/l and air and liquid temperatures of 25 and 43°C, respectively. The relationship established using this procedure is presented in Figure 27. The relationship was used to calculate the surface area of a RBC required to treat 10,500 m³/day of wastewater to meet a number of different effluent qualities. The results are summarized in Table 8.

As indicated in the table, the effect of staging on the required surface area is quite significant. For example, to produce an effluent containing 50 mg/l of total thiosalts, the surface area required in a three-stage RBC is approximately 2.1 times greater than a five-stage unit. This shows that the use of staging will result in a substantial capital cost saving.

5.2 Cost Estimation

The Autotrol Corporation, Milwaukee, Wisconsin, produces a standard RBC unit consisting of 3.7 m (12 ft) diameter discs mounted on a 7.6 m (25 ft) shaft. The unit provides a total surface area of 13,900 m² (150,000 ft²). As the RBC must be operated at a pH of 2.0-2.5, a corrosion resistant material is required. The F.O.B. Bathurst, New Brunswick capital cost for

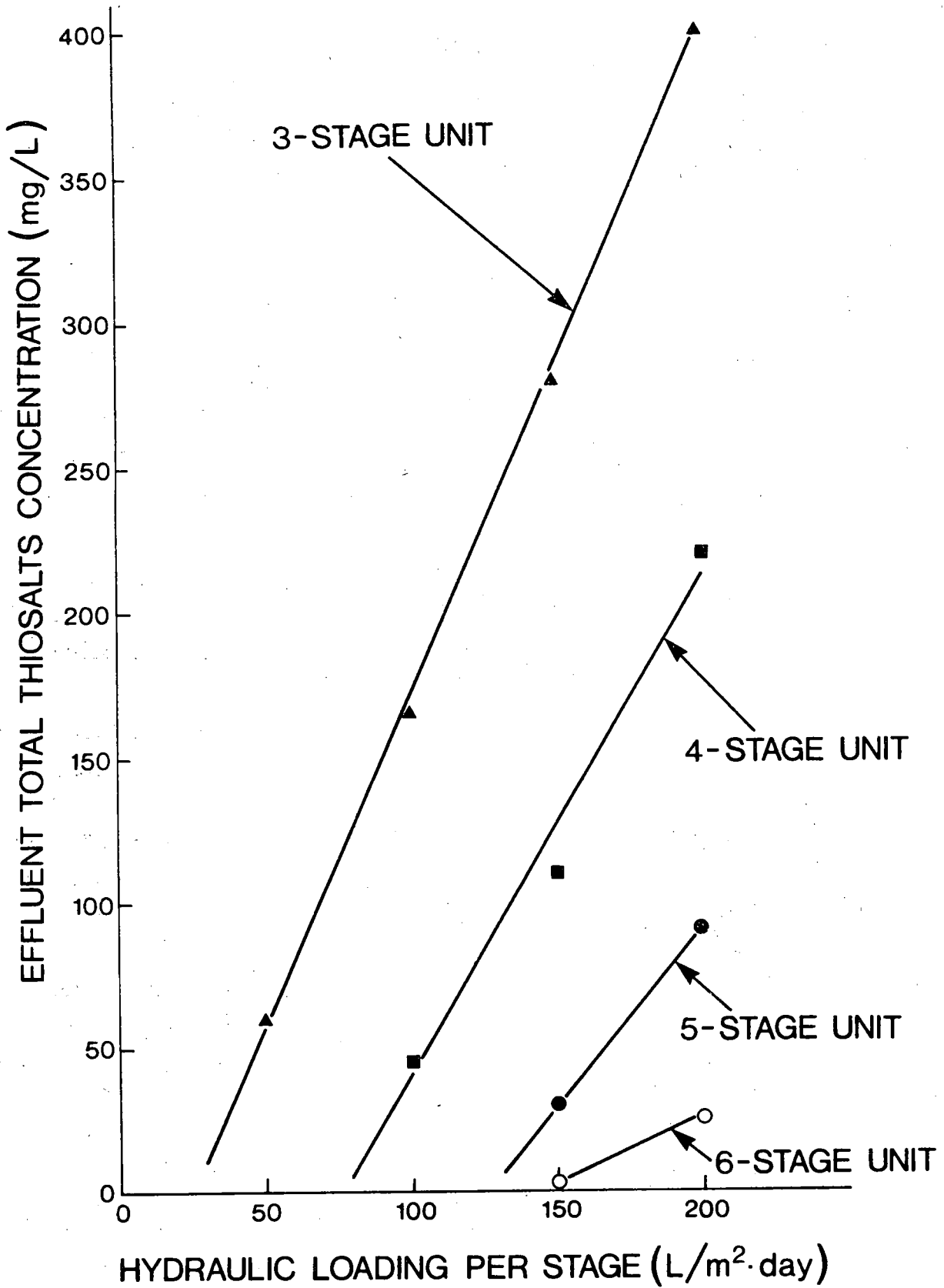


FIGURE 27. RELATIONSHIP BETWEEN HYDRAULIC LOADING AND EFFLUENT QUALITY.

the corrosion resistant unit would be \$52,500 plus \$6,000 for the insulated plastic cover as quoted by the supplier in May of 1980. The cover is required for the winter operation to prevent excessive heat loss from the RBC. Provisions should be made to facilitate a rapid dissipation of heat from the wastewater to the air during summer operation.

TABLE 8. SURFACE AREA REQUIREMENTS

Desired Thiosalts Concentration in the Effluent (mg/l)	Number of Stages	Total Surface Area Required (m ²)
50	3	656,000
	4	396,000
	5	316,000
100	3	450,000
	4	313,000
200	3	281,000

If it is desirable to treat the wastewater to produce an effluent containing 100 mg/l of total thiosalts, 24 RBC units consisting of four stages would be required to handle 10,500 m³/day (2.3 MGD) of wastewater containing 1,250 mg/l of total thiosalts. The total cost of 24 units would be \$1,404,000. The installation cost including site preparation, concrete tankage, acid resistant lining, piping, wiring, labour, etc., was estimated to be \$11,000 per unit or \$264,000 for 24 units. Therefore, the total cost to install the 24 units would be \$1,664,000.

A breakdown of annual operating and maintenance (O & M) costs for the RBC system is presented in Table 9. It was assumed that a wastewater treatment plant operator, a mechanic and a laboratory technician would be required for the operation of the RBC system. The power requirements for each RBC shaft were estimated to be 4.5 kw with the power cost (May, 1980) being 2.7 cents per kwh. The cost of chemicals was based on the utilization of (NH₄)₂SO₄ and H₃PO₄ at a S₂O₃:N:P ratio of 1000:14:15. Because of the extremely corrosive nature of the RBC effluent, the annual maintenance costs were estimated to be 5% of the capital cost of the RBC system. Based on this cost estimate, the unit O & M costs for the RBC system was calculated to be 11.2 cents/m³ (51¢/1000 gal).

TABLE 9. ANNUAL O & M COSTS* FOR THE RBC SYSTEM

Labour	\$ 60,000.
Power	\$ 25,000.
Nutrients	\$260,000.
Maintenance (5% of Capital Cost)	\$ 83,000.
Total -----	<u>\$428,000.</u>

* Estimated costs are based on May 1980 prices

As there was no attempt made to optimize the nutrient requirements, the estimated nutrient cost may be much higher than the cost at optimal nutrient addition rates. The estimated maintenance cost may also be high. To minimize the maintenance costs and assess the feasibility of operating a system in the corrosive environment, it would be desirable to operate one 3.7 m diameter, 7.6 m shaft, as a demonstration unit for at least two years prior to the design of the full scale system.

In addition to the RBC system, pre-treatment and post-treatment facilities will be required. Pre-treatment facilities would include flow equalization and/or primary clarification; the requirement and actual design of these facilities will be based on the composition and variability of the concentrated wastewater stream. Post-treatment of the oxidized effluent will involve neutralization followed by clarification. This should be a mechanical high density sludge system. The chemical costs for neutralization were not included in the O & M costs presented in Table 9.

6 CONCLUSIONS

Based on results of the study, the following conclusions can be made:

1. Successful treatment of wastewaters containing thiosalts was achieved in a rotating biological contactor operating at temperatures ranging from 2 to 30°C.
2. The accumulation of the biomass in the reactor was negligible and sludge wasting was not required. Although an appreciable amount of colloidal sulphur particles was occasionally observed in the reactor, no operational problems were encountered, and the effluent suspended solids was consistently less than 10 mg/ℓ.
3. The results of the bench-scale and the pilot-scale operations were comparable. It was feasible to use the data of a bench-scale reactor treating synthetic wastewater to predict the performance of a rotating biological contactor treating process effluents.
4. The Michaelis-Menton Theory could be used to describe the kinetics of the thiosalts oxidation. The temperature dependency of the oxidation rates followed the Arrhenius relationship in the temperature range investigated.
5. For the treatment of 10,500 m³/day of process effluent containing 1,250 mg/ℓ of thiosalts at a reactor liquid temperature of 25°C, the total cost of the equipment and installation was estimated to be approximately \$1,664,000. The annual operating and maintenance costs for the RBC system was estimated to be \$428,000. These costs do not include pre-treatment and neutralization of the RBC effluent.

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APPENDIX A
DETERMINATION OF THIOSULPHATE

1.0 Scope and Application

The lower limit of this method is 10 ppm S_2O_3 .

2.0 Principle of Method

Thiosulphate ion is titrated under acidic conditions with a standard Iodine solution, using Thyodene as the indicator.

3.0 Interferences

Sulphite interferes, but formaldehyde added to sample will mask the sulphite ion.

4.0 Sampling Procedure

Tightly cap sampling containers immediately after collecting sample. This prevents air oxidation of thiosalts but does not prevent the oxidation from one form to another.

5.0 Apparatus

5.1 pH meter

5.2 Magnetic stirrer and stirring bars

5.3 Burette

5.4 Beakers - 100 ml

6.0 Reagents

6.1 Hydrochloric Acid: 10% v/v

Mix 10 volumes of conc. HCl with 90 volumes of distilled water.

6.2 Ammonium Hydroxide: 10% v/v

Mix 10 volumes of conc. NH_4OH with 90 volumes of distilled water.

6.3 Formaldehyde Solution: 40% v/v solution in 15% v/v Methanol

Mix 40 ml of formaldehyde with 60 ml of 15% v/v methanol. (Prepared by mixing 15 ml of methanol with 85 ml distilled water).

6.4 Thyodene

6.5 Iodine Solution: Stock Solution (approx. 0.1N)

Dissolve 20 g of iodate - free potassium iodide in 30-40 ml of water in a glass stoppered one-litre flask. On a rough balance,

12.7 g of A.R. or resublimed iodine is weighed and then transferred using a small dry funnel into the potassium iodide solution. The solution is shaken under cold water until all the iodine has dissolved. Finally the solution is allowed to come to room temperature and filled to the mark with distilled water. Standardize with A.R. arsenious oxide.

Standardization Procedure:

CAUTION: Arsenious oxide is poisonous.

1. Weigh out accurately 2.5 g of A.R. arsenious oxide.
2. Dissolve it in a 400 ml beaker containing 20 ml of 10% w/v NaOH [Prepared by dissolving 10 g of NaOH in 100 ml of water.]
3. Dilute to 200 ml and neutralize with 1 N HCL using phenolphthalein.
4. Transfer the contents quantitatively to a 500 ml volumetric flask, add 2 g sodium bicarbonate, and dilute to mark.
5. Transfer accurately 25.0 ml of arsenious oxide solution into a 250 ml flask.
6. Add 25-50 ml of water, 5 g of sodium bicarbonate and a dash of Thyodene.
7. Swirl solution until bicarbonate dissolves.
8. Titrate slowly with the prepared iodine solution to the first blue colour.

Equivalent Weight of arsenious oxide = 49.46

$$\text{Normality of } I_2 = \frac{\text{Weight of Arsenious Oxide} \times 2 \times 25}{49.46 \times \text{Volume of Iodine Titrated}}$$

6.6 Standard Iodine Solution: [Approx. 0.01 N]

Prepare daily the required amount of working iodine solution by a ten fold dilution of the stock solution.

7.0 Procedure

- 7.1 Pipet 10 ml aliquot of sample (or amount of sample containing at least 100 mg $S_2O_3^{=}$ and preferably 1000 mg $S_2O_3^{=}$) into a flask.
- 7.2 Add 2 ml formaldehyde solution
- 7.3 Dilute to about 50 ml with distilled water
- 7.4 Adjust pH to about 4.5 (± 0.2) with 10% HCL or 10% NH_4OH .
- 7.5 Add thyodene.
- 7.6 Titrate with 0.01 N Iodine to first permanent blue colour.

8.0 Calculations

$$\text{mg S}_2\text{O}_3^{=} / \text{l} = \frac{\text{T} \times \text{N} \times 112,000}{\text{A}}$$

Where T = Titre of iodine solution

N = Normality of iodine solution

A = Aliquot of sample (ml)

APPENDIX B

DETERMINATION OF SULPHATE

1.0 Scope and Application

This method is applicable to mine waste water samples in the range 100 to 5000 ppm. Measure samples of higher concentrations than this by appropriate dilution of aliquots. Samples of lower concentration than this can be measured by using a $BaCl_2$ titrant of lower molarity.

2.0 Principle of Method

Sulphate ion is titrated in an alcoholic medium with a standard barium chloride solution using Thorin as the indicator. The titration is performed under controlled acid conditions.

3.0 Interferences

Cations cause error due to co-precipitation; this interference can be overcome by treating sample with ion exchange resin. Sulphite interferes but the addition of formaldehyde to complex sulphite removes this interference. Thiosulphate will interfere also; a slight excess of iodine solution added to the sample will convert thiosulphate to tetrathionate.

4.0 Sampling Procedure

Sample container should be tightly capped as soon as sample is collected. This prevents air oxidation of thiosalts but does not prevent the oxidation from one form to another.

5.0 Apparatus

- 5.1 pH Meter
- 5.2 Magnetic Stirrer and Stirring Bars
- 5.3 Burette (25 ml calibrated in .10 ml)
- 5.4 Beakers - 250 ml

6.0 Reagents

- 6.1 Methanol A.R. grade
- 6.2 Ammonium Hydroxide: 5% v/v solution
Mix 5 volumes conc. ammonium hydroxide, NH_4OH , with 95 volumes of distilled water.

6.3 Hydrochloric Acid: 5% v/v solution

Mix 5 volumes conc. hydrochloric acid, HCL, with 95 volumes of distilled water.

6.4 Thorin: 0.2% w/v

Dissolve 0.2 g Thorin [2(2-hydroxy-3,6-disulfo-1-naphthylazo) benzene arsonic acid] in 100 ml of distilled water.

6.5 Barium Chloride Stock Solution: 0.10M

Dissolve 24.4 g barium chloride, $BaCl_2 \cdot 2H_2O$, in one litre of distilled water. Standardize with 0.10M sulfuric acid, H_2SO_4 .

Standardization Procedure:

Pipet 10 ml of the 0.10M sulfuric acid into a 250 ml beaker. Dilute to 50 ml with distilled water; add 50 ml methanol and adjust the pH to 3.0-3.5. Add 5 drops of Thorin indicator. Titrate with the barium chloride stock solution to the first permanent pink colour. Do three such titrations and obtain an average value.

$$\text{Molarity of } BaCl_2 \text{ Solution} = \frac{V \times M}{T}$$

V = Volume of .10M H_2SO_4 used = 10 ml

M = Molarity of H_2SO_4 = .10M

T = Titre (average of 3 Titre values)

6.6 Standard Barium Chloride Solution: .05M

Prepare daily the required amount of .05M. $BaCl_2$ solution by appropriate dilution of the .10M $BaCl_2$ stock solution.

6.7 Ion Exchange Resin: Strong acid, cation type

6.8 Formaldehyde Solution: 40% v/v solution in 15% v/v methanol

Mix 40 ml of formaldehyde with 60 ml of 15% v/v methanol. [Prepared by mixing 15 ml methanol with 85 ml distilled water].

6.9 Iodine Solution: 1N

Dissolve 20 g of iodate - free potassium iodide in 30-40 ml of water in a glass stoppered 100 ml flask. On a rough balance, 12.7 g of A.R. or resublimed iodine is weighed and transferred using a small dry funnel into the potassium iodide solution. The solution is

shaken under cold water until all the iodine has dissolved. The solution is then allowed to come to room temperature and filled to the mark with distilled water.

6.10 Stock Sulphate Solution: 2000 mg $\text{SO}_4^{=}$ /l

In a one litre volumetric flask dissolve 6.690 g sodium sulphate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in distilled water. Make up to mark with distilled water.

6.11 Standard Sulphate Solutions

Prepare standard solutions by diluting suitable aliquots of stock sulphate solution with distilled water. The standard solutions should be within the same range as samples being analyzed.

7.0 Procedure

7.1 Add 10 ml formaldehyde solution to 50 ml sample and standard solutions.

7.2 Add 1.0 N iodine solution dropwise until a pale yellow color is obtained.

[N.B. An excess of iodine solution will make it more difficult to obtain a good end point with titration].

7.3 Add several grams of ion exchange resin to sample and stir for about five minutes. Allow to settle.

7.4 Pipet out an aliquot containing at least 5,000 $\mu\text{g SO}_4^{=}$.

7.5 Dilute to 40 ml with distilled water.

7.6 Add 40 ml methanol.

7.7 Adjust pH to 3.0-3.5 with ammonium hydroxide (5% v/v) or hydrochloric acid (5% v/v).

7.8 Add 5 drops Thorin indicator.

7.9 Titrate with the 0.05 M BaCl_2 solution to the first permanent pink colour.

8.0 Calculations

$$\text{mg. SO}_4^{=} / \text{l} = \frac{T \times M \times 96,000}{A} \times \frac{60}{50}$$

T = Titre BaCl_2 solution

M = Molarity of BaCl_2 solution

A = Aliquot used for analysis (ml)

APPENDIX C

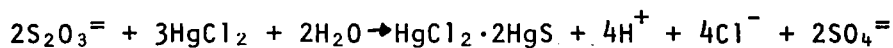
DETERMINATION OF TOTAL THIOSALTS

1.0 Principle

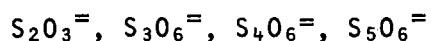
Polythionates containing 3, 4 and 5 sulphur atoms react with mercuric chloride to quantitatively release acid in solution. The stoichiometric equation is:



A similar equation applies for thiosulphate:



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



2.0 Apparatus

1. A pH meter preferably with a combination electrode
2. A magnetic stirrer and stirring bar
3. Two 25 ml burettes
4. 250 ml beakers
5. A hot plate
6. Pipettes of various sizes

3.0 Procedure

1. Pipette an aliquot of sample into a 100 ml beaker. The aliquot size will be dependent upon the concentration range of the analysis:
 - a) 0-50 mg/l as $S_2O_3^{=}$ use 50 ml aliquot
 - b) 50-400 mg/l as $S_2O_3^{=}$ use 25 ml aliquot
 - c) 400-2000 mg/l as $S_2O_3^{=}$ use 5 ml aliquot
 - d) 2000-5000 mg/l as $S_2O_3^{=}$ use 2 ml aliquot
2. Dilute sample to about 30 ml, if necessary, to allow adequate immersion of the pH electrode.
3. Insert the stirring bar and pH electrode into the solution with the beaker on the stirring mantle. To insure constant stirring for both initial and final end-points, set the variable control on the magnetic stirrer at the same position for all titrations.

4. If it is known that neither the sulphite anion nor weak acids whose salts will buffer the solution around $\text{pH} = 4$ are present in insignificant amounts, titrate the solution with sulphuric acid to $\text{pH} = 4.3$ as an initial end-point. Use 0.005N acid except in cases where large amounts of soda ash or lime are known to be present and a large aliquot of sample is required. In this situation use 0.1N acid to avoid excessive dilution especially in cases where the total thiosalts concentration is likely to be less than 50 mg/l as $\text{S}_2\text{O}_3^{2-}$.
5. If the sulphite anion is present at concentrations >40 mg/l and only small quantities of alkaline buffer components, such as soda ash, are present, add 3 ml formaldehyde solution to remove interference from sulphite and titrate to an end-point of $\text{pH} = 8.2$ with 0.005N caustic solution. Again 0.1N caustic solution should be used if it is necessary to avoid excessive dilution.
6. Remove the pH electrode and stirring bar, rinsing with distilled water into the sample.
7. Pipette 5 ml of mercuric chloride solution and dilute sample to a final volume of 60 ± 10 ml.
8. Allow sample to stand at room temperature for about 5 minutes.
9. Heat solutions on a hot plate bringing rapidly to a boil. Remove from heat and allow solutions to cool to room temperature.
10. Place on stirring mantle. With constant stirring add the potassium iodide solution slowly until the resulting orange precipitate that develops disappears again. This eliminates excess mercuric chloride and prevents its hydrolysis from generating acidity. Avoid adding large excesses of potassium iodide to the resulting pale yellow turbid solution.
11. Titrate with standard 0.005N caustic solution to the initial end-point ($\text{pH} = 4.3$ or 8.2). For best results run samples in duplicate and average the titre values obtained.
12. Repeat using about 30 ml of water rather than sample. Titrate the alkalinity which develops following potassium iodide addition with standard 0.005N sulphuric acid to the end-point ($\text{pH} = 4.3$ or 8.2).

13. Calculate the equivalent standard 0.005N caustic solution that the standard acid added in step 12 would neutralize:

$$V = \frac{N_A T_A}{N}$$

where V = the equivalent amount of base in ml

N = normality of standard caustic solution used

N_A = normality of standard acid solution (step 12)

T_A = ml of standard acid added in step 12.

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

14. Calculate the concentration of total thiosalts as thiosulphate

$$\text{mg/l as } S_2O_3 = \frac{(T+V)N}{A} \times 56,000$$

where T = ml of caustic solution added

N = normality of caustic solution

A = ml of sample pipetted

V = equivalent amount of base in ml

4.0 Preparation of Reagents

1. Sodium hydroxide (caustic) solution; 0.005N prepared in CO₂-free water and standardized against potassium biphthalate as outlined in detail below. The 0.1N caustic may be made up or purchased. It should be stored in tightly capped polyethylene containers for infrequent use. No standardization is necessary in the case of the 0.1N solution.
2. Sulphuric acid; 0.05N standard acid is prepared by adding about 0.15 ml of 98% acid to one litre of 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 0.005N caustic solution. The 0.1N acid is prepared by adding 2.6 ml of 98% acid to one litre of water. It need not be standardized.
3. Mercuric chloride solution; 2% solution prepared by dissolving 20 g in one litre of water. Fresh solution should be prepared weekly.
4. Potassium iodide solution; 20% solution prepared by dissolving 200 g in one litre of water.

5. Formaldehyde solution; 40% solution in 15% methanol (available from Fisher Scientific).

5.0 Preparation of Standard Caustic Solutions

1. To obtain CO₂-free water, boil distilled water for about 15 minutes and cool rapidly with an inverted beaker over the mouth of the flask to prevent ingress of air.
2. Weigh out about 1.0 g of sodium hydroxide pellets and dissolve in one litre of CO₂-free water to obtain a 1N caustic solution (Also may be purchased from Fisher Scientific).
3. Pipette 5 ml of 1N caustic into a one litre volumetric flask and make up to volume with CO₂-free water to obtain about 0.005N caustic solution.
4. To determine the actual normality:
 - a) Add 1.021 g of anhydrous potassium biphthalate to a one litre volumetric flask and make up to volume with CO₂-free water to obtain a 0.005N solution of biphthalate.
 - b) Pipette 10 ml of 0.005N biphthalate solution into a 250 ml erlenmeyer flask and dilute to about 50 ml with CO₂-free water.
 - c) Titrate with the 0.005N caustic solution to be standardized to an end-point of pH = 8.2
 - d) Calculate the normality of the caustic solution

$$\text{normality} = \frac{0.05000}{T}$$

where T = no. of ml of caustic required

Caustic solution should be freshly prepared weekly and standardized.

6.0 Interferences

1. Sulphide ions; mercuric chloride will react with sulphides in solution to produce acidity. They may be detected by acidifying the solution and noting the odour of rotten eggs. Drawing a vacuum on the sample at pH = 4 will eliminate this species from solution.
2. Sulphite ion; mercuric chloride will oxidize sulphite to sulphate to produce acidity. Formaldehyde addition will eliminate most of the sulphite from solution. At pH = 8.2 laboratory tests have indicated that 1000 mg/l of sulphite may be effectively reduced to a level where the analysis detects sulphite as 50 mg/l thiosulphate. At pH = 4.3 this error is much larger. The analysis indicates 250 mg/l as thiosulphate

when 1000 mg/l sulphite is suppressed with formaldehyde. As a result, to effectively reduce interference from sulphite a pH = 8.2 end-point has been recommended.

3. Ferrous ion; high results have been obtained in the presence of ferrous ion but laboratory investigation indicates that any interference may be completely eliminated with soda ash addition and titration to the pH = 4.3 end-point. The low solubility of ferrous carbonate reduces the concentration of ferrous ion in solution.
4. Components which contribute to buffer effects will interfere, such as soda ash at pH = 8.2 or acetic acid at pH = 4.3. Avoiding an end-point pH in the buffer range will eliminate the problem.