OXIDATION OF SODIUM THIOSULFATE
IN
WEAK KRAFT BLACK LIQUOR

by

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ABSTRACT

The oxidation of sodium thiosulfate in weak kraft black liquor (obtained from a hardwood pulping mill) was investigated in an oxygen-sparged semibatch reactor which operated between 90°C and 100°C and at one atmosphere total pressure. It was found that sodium trithionate ($Na_2S_3O_6$) is a dominant product of the oxidation of thiosulfate in weak kraft black liquors. For the first time closure of the mass balance on inorganic sulfur was demonstrated after black liquor oxidation, based on trithionate as an intermediate. Trithionate ($S_3O_6^{2-}$) accounts for 25% - 35% of the total inorganic sulfur product after quantitative conversion of thiosulfate. The remainder (65% - 75%) is in sulfate form. An original analytical method for the chemical determination of trithionate in black liquor was developed.

A nickel aluminum alloy (50% nickel, 50% aluminum) was identified as having a catalytic effect on the oxidation of thiosulfate. The rates of thiosulfate oxidation and trithionate production increased with catalyst concentration (1 - 10 grams per liter) and liquor turbulence (800 - 4000 rpm), but decreased with the concentration of sodium hydroxide (12 - 40 grams per liter).

The thermal value of the black liquor decreases by about 10% for the noncatalytic oxidation and 18% for catalytic oxidation with the nickel aluminum alloy. A fraction of the liquor organics is partially oxidized to form CO_2, some of which is reabsorbed to form sodium carbonate in the alkaline black liquor. Oxidation reactions reduce the liquor pH from 13 to about 9.7.

RÉSUMÉ

L'oxydation de thiosulfate de sodium dans la liqueur noire kraft faible (obtenue d'un moulin de pâte à papier de bois dur) fut examinée dans un réacteur à semilot aspergé d'oxygène qui fonctionnait entre 90°C et 100°C, à pression totale de une atmosphère. On découvrit que le trithionate de sodium ($Na_2S_3O_6$) est un produit dominant de l'oxydation de thiosulfate dans les liqueurs noires kraft faibles. Pour la première fois la fermeture de la balance de masse sur le soufre inorganique, après l'oxydation de la liqueur noire basée sur le trithionate comme intermédiaire, fut démontrée. Le trithionate ($S_3O_6^{2-}$) compte pour 25% - 35% du produit total de soufre inorganique après conversion quantitative de thiosulfate. Le reste (65% - 75%) est en forme de sulfate. On développa une méthode analytique initiale pour la détermination chimique de trithionate dans la liqueur noire.

Un alliage de nickel et d'aluminium (50% nickel, 50% aluminium) fut identifié comme ayant une action catalytique sur l'oxydation thiosulfate. Les taux d'oxydation de thiosulfate et de production de trithionate augmentèrent avec la concentration de catalyseur (1 - 10 grammes par litre) et la turbulence de la liqueur (800 - 4000 rpm) mais diminuèrement avec la concentration d'hydrate de sodium (12 - 40 grammes par litre).

La valeur thermique de la liqueur noire diminue d'environ 10% pour l'oxydation non catalytique et de 18% si on emploie l'alliage de nickel et d'aluminium comme catalyseur. Une fraction des organiques de la liqueur est en partie oxydée au CO_2, un certain nombre est réabsorbé pour former du carbonate de sodium dans la liqueur noire alcaline. Les réactions d'oxydation réduisent le pH de la liqueur de 13 à 9.7.

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NOMENCLATURE

a, b, c, d : stoichiometric coefficients

f, x, y, z : stoichiometric coefficients

$A(t)$: thiosulfate concentration at any time (gpl)

$B(t)$: sulfate concentration at any time (gpl)

$B(T)$: sulfate concentration at time T (gpl)

$B(T_o)$: sulfate concentration at time zero (gpl)

dB/dt, D' : rate of sulfate formation (gpl/min.)

k_1 : thiosulfate zero order rate constant (gpl/min.)

k_2 : thiosulfate second order rate constant $(\text{gpl}\cdot\text{min.})^{-1}$

k_3 : sulfate kinetic rate constant in numerator

k_4 : sulfate kinetic rate constant in denominator

k_5 : kinetic rate constant

n, m, p : kinetic powers

m_i : number of data points in i^th set of replicates

$\hat{s}_i^2$: variance of the i^th replicate set

l : number replicate sets

$\hat{s}_p^2$: pooled variance estimate

s_p : standard deviation

(SO_4^{2-}) total equivalent : inorganic sulfur as sulfate (gpl)

$(SO_4^{2-})_{exp.}$: expected inorganic sulfur as sulfate (gpl)

ABBREVIATIONS

ave. : average per cent deviation with inorganic sulfur balance (%)

atm. : atmospheres

AB, AC, AD, AE : experimental replicates

BLOX : black liquor oxidation

DCE : direct contact evaporator

FBR : fluid bed reactor

gpl : grams per liter

IC : ion chromatograph

lpm : liters per minute

NA : data not available

NiAl : nickel aluminum alloy catalyst

ppm : parts per million

rpm : impeller revolutions per minute

SODABLOX : oxidation with incremental NaOH added

THR : total heat recovery

TOC : total organic carbon

TRS : total reduced sulfur

% diff. : per cent difference with total inorganic sulfur balance

1. LITERATURE REVIEW AND BACKGROUND

1.1 Introduction to the Kraft Recovery Process

The kraft pulping process is the dominant chemical pulping technology at the present time. Chemical pulping accounts for two-thirds of the annual world wood pulp production, and the kraft process represented 88% of the world chemical pulp production in 1983. The widespread use of this process is attributable to the facts that:

i) the wood fibres are degraded much less in kraft pulping than any other process;

ii) the technology can handle any type of wood;

iii) it is possible to recover and utilize the by-product materials from this process.

This last point, which refers to the chemical/energy recovery cycle, is particularly important given today's stringent environmental regulations for industrial waste discharges. Although the problem of stream pollutants has been minimized with efficient chemical/energy recovery, the production of large quantities of sulfur gases from the cycle remains a source of concern.

The process of kraft pulping consists of cooking wood chips in an alkaline solution called "white liquor". This is typically made up of sodium hydroxide (NaOH), sodium sulfide (Na_2S), and sodium carbonate (Na_2CO_3). These substances total 12.5 weight per cent of the liquor. The active cooking chemicals are sodium hydroxide and sodium hydrosulfide. Sodium hydrosulfide is formed in the white liquor through equation (1).

$$Na_2S + H_2O \longrightarrow NaOH + NaSH \qquad (1)$$

These white liquor chemicals promote the cleavage of bonds in the basic lignin structure within the woodchip, and renders the lignin extractable and soluble in the liquor. The woodchips are typically dissolved in the white liquor for one to three hours at a process temperature of 160°C. The cooking liquor promotes the hydrolysis of lignin to alcohols and acids. Mercaptans are also formed as a by-product.

The spent cooking solution from the digester, which contains about 50% of the raw wood substance, is commonly referred to as 'weak black liquor'. The total quantity of all of the various dissolved substances ranges from between 14% and 18% by weight. The exact percentage is a function of wood species, type, and amount of chemicals used in digestion, and quantity of wash water used.

Black liquor is a complex colloidal solution consisting of residual white liquor chemical components, lignin, and other decomposition products from the wood. These are dissolved in the liquor during pulping. Approximately 60% of the liquor organics are present as lignin. The remainder is mainly in the form of a wide variety of carbohydrate derived acid forms. The black liquor also contains the cooking chemicals NaOH and NaHS. Sodium hydrosulfide (NaHS) is partially transformed into organic forms including thiolignin and mercaptans in the complex digestion reactions. These organic sulfurous forms may account for up to 30% of the total sulfur in the black liquor.

The weak black liquor from the digesters is pumped to an oxidation unit via a blow tank. There the liquor is contacted with air (Fig. I, Appendix 1). Sodium hydrosulfide is oxidized to sodium thiosulfate; mercaptans and organic sulfides are oxidized to dimethyl disulfide. The purpose of oxidation is to reduce the sulfur gas emission in the subsequent evaporation stage. Weak black liquor (14%-17% solids) from the oxidation unit is concentrated to strong liquor in a series of multiple effect evaporators. The strong liquor (45% - 50% solids) is further concentrated to about 65% to 70% solids in the Direct Contact Evaporator (DCE). It is subsequently sprayed into a specially designed boiler known as a recovery furnace. In this reactor the organics are burned to recover their energy value. The inorganics (sodium carbonate and sodium sulfide), form a liquid smelt in the char bed. Sulfur oxyanions including thiosulfate and sulfate, are reduced in the char bed. The bed is continuously formed from pyrolysed liquor organics in the lower furnace area.

The smelt is continuously withdrawn from the boiler. It flows from there into the dissolving tanks from which the "green liquor" is formed. The green liquor from the dissolver is treated with burned lime to convert sodium carbonate to sodium hydroxide (equation 3),

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (2)$$

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH \qquad (3)$$

and thus regenerate the white liquor constituents. The precipitated $CaCO_3$ is removed by filtration and is sent to a lime kiln to be calcined to CaO (equation 4).

$$CaCO_3 + heat \longrightarrow CaO + CO_2 \qquad (4)$$

1.2 Black Liquor Oxidation Theory & Practice

Since the early pioneering work of Bergstrom and Trobeck (1939), black liquor oxidation (BLOX) has become an integral part of the kraft chemical/energy recovery cycle. BLOX is currently used to oxidize sodium sulfide to sodium thiosulfate. This practice prevents volatilization of the sulfur as H_2S (equations 5, 6) in the Direct Contact Evaporator.

$$Na_2S + CO_2 + H_2O \longrightarrow Na_2CO_3 + H_2S \qquad (5)$$

$$Na_2S + SO_2 + H_2O \longrightarrow Na_2SO_3 + H_2S \qquad (6)$$

The hot flue gases from the recovery furnace contain sulfur dioxide (SO_2) and carbon dioxide (CO_2). These are used to concentrate the liquor to 65% solids. Oxidation increases the valency of inorganic sulfur from -2 (S^{2-}) to +2 ($S_2O_3{}^{2-}$) thereby preventing these reactions. If inorganic sulfur is present as thiosulfate, rather than sulfide, TRS emissions can be reduced from 800 ppm to less than 15 ppm in the DCE according to Clark (1976).

In the pulp and paper literature, the oxidation of sodium sulfide usually infers oxidation to sodium thiosulfate. However, oxidation of sodium thiosulfate to sodium sulfate under the conventional BLOX conditions, has never been discussed in the literature. That is the subject of the present research endeavour.

The terms "stabilization" or "fixation" are often used interchangeably with black liquor oxidation because the black liquor is not combusted, as the term "oxidation" can imply. Rather, oxidation in this sense refers to a low temperature aqueous phase reaction which transforms sulfide into a variety of less volatile sulfur oxyanion forms. Most of this is in the form of thiosulfate. The organic constituents of black liquor are also affected by the oxidation reactions. However, they are never completely oxidized in commercial BLOX even under the most strenuous of process conditions. Typical process conditions utilized in industrial BLOX include temperatures ranging from 80°C to 100°C, and a total air pressure of one atmosphere.

A frequently encountered term in the literature is "oxidation efficiency". This refers to the per cent conversion of sulfide in the liquor. It is defined by equation (7).

$$\text{\% efficiency} = \frac{\text{mass } Na_2S \text{ feed} - \text{mass } Na_2S \text{ out}}{\text{mass } Na_2S \text{ feed}} \qquad (7)$$

Cooper (1973) notes that oxidation efficiency is a function of both chemical and physical parameters. Chemical parameters include oxygen ratio, liquor temperature, liquor pH, and wood species. Wood species is particularly important because the quinone structures in the liquor which are derived from the wood, have been found to be effective catalysts for the sulfide oxidation. Physical parameters known to affect oxidation efficiencies are liquor Reynolds number and liquor solids content. In general, the BLOX efficiency is proportional to increases in the pH, oxygen ratio (actual O_2 supplied for BLOX divided by stoichiometric O_2), oxygen partial pressure, and liquor Reynolds number.

The pH of black liquor is a critical parameter in BLOX. It is a function of the chemicals added to the digesters, sulfidity content of cooking liquor, and the nature of wood extractives. The pH of weak black liquor is typically in the range of 11 to 13. Conventional oxidation lowers the liquor pH from between 0.1 and 0.3 because of acids generated from organic and inorganic oxidation reactions.

Tsuchiya and Johanson (1972) studied the effects of liquor pH and oxidation efficiency on TRS emissions from the recovery cycle. They found that TRS emissions throughout the entire recovery cycle decrease with increases of oxidation efficiency and liquor pH (Figs. II & III, Appendix 1). Morgan et al. (1970) explain the role of oxidation by noting that the concentration of sulfide is reduced to essentially zero. This causes the equilibrium vapor pressure of the hydrogen sulfide above the liquor to also approach zero as indicated by equation (8).

$$H_2S(g) = H_2S(l) = HS^- = S^{2-} \tag{8}$$

Liquor alkalinity or pH is a major factor in determining the ultimate TRS emission from the cycle. This is understood by considering the full reaction stoichiometry of equation (8) which is given by Ueno (1976) in equation (9).

$$H_2S + 2OH^- = HS^- + H_2O + OH^- = S^{2-} + 2H_2O \tag{9}$$

Clearly, a decrease of liquor pH causes the equilibrium of equation (9) to shift to the left. This causes an increase in the amount of hydrogen sulfide liberated from aqueous solution.

BLOX is an exothermic reaction that results in a decrease of the heating value of the liquor. Liquor heating value, or thermal value, refers to the amount of heat energy which is dissipated when the liquor organics are combusted. BLOX decreases the heating value of the black liquor through the partial oxidation of the lignaceous organic compounds. Thermal value is also lost in the oxidation of inorganic sulfur constituents. Grace (1977) states that this is 5.39 kJ/(g Na_2S) when the sulfide is oxidized to thiosulfate, and 12.9 kJ/(g Na_2S) if the sulfide is further oxidized to sulfate.

1.3 Advantages & Disadvantages of BLOX

Some of the advantages that black liquor oxidation offers a pulp and paper mill were summarized by Collins (1950) and are listed below.

i) Increased liquor sulfidity after BLOX because more sulfur is retained in the recovery cycle. Tomlinson and Ferguson (1956), noted a 15% to 20% increase after installing BLOX at Domtar Fine Papers in Cornwall;

ii) Reduction in the amount of lime required in the causticizer because of the higher sulfidity of the liquor;

iii) Partial elimination of odor from the evaporators, DCE, and recovery furnace including a 90% reduction of TRS in evaporators;

iv) Permits a decrease of saltcake makeup if the maximum attainable sulfidity obtained with BLOX is not desired;

v) Reduced corrosion in the evaporators and scrubbers.

Some of the disadvantages of BLOX have been summarized by Sarkanen et al. (1970). They include:

i) Elemental sulfur or polysulfide ions may be formed due to incomplete oxidation defeating the original purpose of BLOX;
ii) Loss of liquor heating value and loss of process heat from heating of oxidation air;
iii) Foaming and soap production problems associated with BLOX of resinous wood species.

Another underlying drawback of oxidation which Sarkanen et al. failed to mention, is the problem of "burkeite scaling". Burkeite is a double salt composed of sodium carbonate and sodium sulfate. Depending on the wood species being pulped and white liquor chemical charge, burkeite precipitates from the black liquor at 40% to 50% solids content.

1.4 The Impact of BLOX on the Chemical Recovery Cycle

Thoen et al. (1968) have found that BLOX does not reduce sulfur gas emissions in the recovery boiler. Landry (1963) has stated that thiosulfate, under the conditions found in the boiler, decomposes to sulfur dioxide and not hydrogen sulfide. This is shown in equation (10).

$$2Na_2S_2O_3 + C^o \longrightarrow 2Na_2S + 2SO_2 + CO_2 \quad (10)$$

This results in a smaller volatile emission of H_2S but a proportionally larger liberation of SO_2.

Collins (1962) and Menzies (1968) stated that the sequential oxidation of thiosulfate to sulfate is necessary to bring about a high percentage retention of sulfur in the dried liquor when it is smelted. More recently, Strohbeen and Grace (1982) investigated the effect of oxidation of sulfur compounds on sulfur emission. This was done in a pyrolysis study with black liquor model compounds sodium gluconate and vanillic acid (Fig. IV, Appendix 1). The pertinent results were that:

i) between 85% to 100% sulfur volatilized as Na_2S;
ii) between 20% to 45% sulfur volatilized as $Na_2S_2O_3$;
iii) between 0% to 10% sulfur volatilized as Na_2SO_3;
iv) between 0% to 4% sulfur volatilized as Na_2SO_4.

These results indicate that the volatilization of inorganic sulfur decreases with an increase of sulfur valence. Hence, a minimal sulfur loss is associated with the highest sulfur valency state - sulfate. The stability of inorganic sulfur as sulfate in the recovery boiler can be attributed to equation (11). In this reaction the inorganic sulfur is not volatilized.

$$Na_2SO_4 + 2C^o \longrightarrow Na_2S + 2CO_2 \tag{11}$$

Hence, if all the inorganic sulfur could be quantitatively oxidized to the sulfate form, sulfur gas emissions could be reduced in the recovery boiler.

1.5 Kinetics of Sulfide Oxidation in Black Liquor

Murray (1971) has shown that there are two processes which influence the rate of oxidation of black liquor. These are:

i) rate at which O_2 is absorbed into solution;
ii) rate at which sulfide and oxygen react chemically in solution.

Shaw and Christie (1984) have stated that when the concentration of sulfide is high (above 2 gpl), the kinetics of oxidation are pseudo-zero order. Below 2 gpl S^{2-}, the kinetics are pseudo-first order in the sulfide concentration. The term "pseudo order" indicates that the concentration of oxygen does not enter into the kinetic rate equation. Murray and Morgan (1971) found that the oxidation rate of sulfide in kraft black liquors is adequately represented by equation (12).

$$-\frac{d(S^{2-})}{dt} = \frac{K_m k_s\, P(O_2)(S^{2-})}{k_s(S^{2-}) + K_m H} \qquad (12)$$

where:
S^{2-} is sulfide concentration
K_m is mass transfer constant
k_s is kinetic rate constant
$P(O_2)$ is oxygen partial pressure
H is Henry's Law constant of O_2 in black liquor.

When the concentration of sulfide is high (above 2 gpl), equation (12) can be simplified as equation (13).

$$\frac{-d(S^{2-})}{dt} = K_m P(O_2) \qquad (13)$$

For low sulfide concentrations $K_m H >> k_s(S^{2-})$, so that equation (14) is applicable.

$$\frac{-d(S^{2-})}{dt} = \frac{k_s\ P(O_2)(S^{2-})}{H} \qquad (14)$$

Murray and Prakash (1980) have found that the rates of sulfide oxidation in black liquor are much higher than those found in pure salt solutions of sodium sulfide. They concluded that the best catalyst for the oxidation of aqueous sulfides is black liquor.

Lindberg and Nordstrom (1959) found that it is the phenolic compounds in the black liquor which catalyze the oxidation of sulfides. They observed that phenols such as catechol and pyrogallol, catalyze the uptake of oxygen by alkaline solutions to yield thiosulfate.

Cooper (1974) mentioned that the catalytic effect exhibited by black liquor is a very strong function of wood species employed, and that this catalysis is greater for hardwoods than for softwoods. This is due to the increased aromatic ring structures of hardwoods. The catalytic effect increases with temperature and pH. Hermans (1984) explained the pH behavior by noting that the quinone structures, which are partly the cause of the catalysis, are stabilized at lower pH thus reducing their effectiveness.

Murray (1959) reported that temperatures below 71°C result in the partial formation of elemental sulfur. The formation of free sulfur in the liquor as the predominant oxidation product of sulfide is undesirable because it subsequently degenerates back to the sulfide form (equation 15). This is known as the reversion reaction and is given by equation (15).

$$S_8 + 12NaOH \longrightarrow 4Na_2S + 2Na_2S_2O_3 + 6H_2O \qquad (15)$$

Reversion can be prevented if the process temperature of the liquor is maintained above 90°C. In a survey of ten mills across North America, Christie (1972) noted that increases of the sulfide concentration from reversion reactions totalled between 2% and 4% after weak liquor oxidation.

Morgan et al. (1970) postulated a reaction pathway for the reaction pathway of the inorganic sulfur oxidation in black liquor.

$$16S^{2-} + 7O_2 + 14H_2O \longrightarrow 2S_8^{2-} + 28OH^- \qquad (16)$$
$$2S_8^{2-} + 2H_2O + O_2 \longrightarrow 2S_8 + 4OH^- \qquad (17)$$
$$2S_8^{2-} + 9O_2 + 12OH^- \longrightarrow 8S_2O_3^{2-} + 6H_2O \qquad (18)$$
$$2S_2O_3^{2-} + 5O_2 \longrightarrow 4SO_4^{2-} \qquad (19)$$

According to this reaction scheme the sulfide is initially oxidized to polysulfide (S_8^{2-}) through equation (16). Polysulfide oxidation reactions can proceed through equations (17) or (18) to produce free sulfur or thiosulfate respectively. Reversion occurs as a result of polysulfide reacting through equation (17). Thiosulfate can be further oxidized to sulfate through equation (19).

1.6 Industrial Practice

Black liquor oxidation technology can be roughly classified into three different eras. The first of these (1940-1965), was one in which the oxidation of weak liquors was practised with a variety of plate and packed-type towers (Fig. V, Appendix 1). The first generation oxidation technology featured high air flow rates and short contact times. Implementation of oxidation equipment in the recovery cycle was primarily aimed at easing the growing public outcry over the foul smells surrounding kraft pulp and paper mills.

The distinguishing feature of the second era (1965-1975) was the concept of strong black liquor oxidation. Strong black liquor (45%- 55% solids) was oxidized to reduce the foaming problems of weak liquors. Weak liquor oxidation was not practical, particularly in the south, due to the need of large reactor vessels to handle the large quantities of foam.

Foams are caused by fatty acid salts or surfactants present in the liquor. When air is bubbled through, it becomes entrapped in the liquor and results in a frothy foam formation. The higher surface tension and viscosities of strong liquors prevents such excessive foam formation. However, the liquor organics are more severely oxidized and degraded in this process.

The dominant technology of the second era was the air-sparged back-mixed tank reactors (Fig. V). This design featured the oxidation of sodium sulfide by sparging air from near the bottom of the vessel through a high head of liquor (2.5 - 4 meters). Reactor heights were usually designed 2 to 3 times the depth of the liquor head to compensate for the expansion of the liquor at the high superficial gas velocity. Usually 2-stage designs were employed, with an average liquor residence time of 2-3 hours.

A number of innovative oxidation schemes came of age in the third era (1975- present). The most prominent of these is the the combined weak and strong BLOX strategy. In this process weak liquor oxidation is used to prevent TRS emissions in the multiple effect evaporator. Strong oxidation is practised to oxidize any remaining sulfide present from incomplete weak liquor oxidation and reversion reactions. In this process a 100% oxidation efficiency of sulfide is achieved before the liquor is fed to the Direct Contact Evaporator.

The dominant technologies of the present-day era are the air-sparged tank reactors and plug-flow pipeline reactors. Some of the plug-flow reactors (PFRs) now employ the Total Heat Recovery Concept (THR). In THR, a PFR is found ahead of the first effect of the multiple effect evaporator. Zecchini (1986) has found that this location maximizes the heat recovery from the exothermic BLOX reactions. THR can recover nearly 100% of the heat of oxidation.

2. OBJECTIVES, ~~SCOPE,~~ AND RATIONALE FOR CURRENT RESEARCH

2.1 Objectives

1. To carry out a preliminary screening to determine a suitable catalyst for the oxidation of the inorganic sulfur fraction of kraft black liquor with molecular oxygen gas (90°C - 100°C, 1 atm. O_2);

2. To study the effects of liquor, residence time[a], rpm, and catalyst concentration on the rate of thiosulfate oxidation, and sulfate yield;

3. To investigate the effect of incremental caustic soda addition (NaOH) on the thiosulfate oxidation rate, sulfate yield, and post-oxidation liquor pH;

4. To measure the extent of organic oxidation by correlating with the thermal value and with the total organic carbon;

5. To determine kinetic rate models for thiosulfate and sulfate in weak kraft black liquors for noncatalytic oxidation (94° +/- 2°C, 1 atm. O_2);

6. To evaluate the feasibility of conversion of thiosulfate in kraft black liquors with the current industrial practice.

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[a] Within the context of this thesis the term "residence time" is used to denote the reaction time of the bulk black liquor, and in specific references, to the reaction time of chemical constituents in the black liquor.

2.2 Scope:

At the present time there is no fundamental study on the oxidation of sodium thiosulfate in kraft liquors; all published studies to date have dealt exclusively with the oxidation of sodium sulfide. It is widely assumed in the pulp and paper literature that the only product of the oxidation of thiosulfate is sulfate.

Thiosulfate oxidation, as it pertains to kraft black liquors, is an important aspect of the overall inorganic sulfur reaction pathway. A sizable fraction of the sulfide is further oxidized to sulfate through the thiosulfate intermediate in conventional oxidation process strategies, particularly in weak liquor oxidation. Consequently, the intent of the present research endeavour is to investigate the oxidation of sodium thiosulfate in weak kraft black liquors (15% - 17% solids). Furthermore, it is necessary to examine the feasibility of quantitative thiosulfate conversion with the current industrial practice.

The experimental process conditions employed were chosen to simulate the current industrial practice as closely as possible. All experiments were conducted in an agitated bottom-sparged semibatch reactor at temperatures between 90°C and 100°C, and a total O_2 pressure of one atmosphere. This approach was taken so that a qualitative assessment of the commercial viability of thiosulfate oxidation could be established.

The experimental program consisted of seven major parts. These were:

i) Construction and commissioning of the apparatus required for the experimental program;
ii) Screening experiments to identify ~~a~~ suitable catalyst for the oxidation of sodium thiosulfate in weak kraft black liquors;
iii) Experiments to elucidate the roles of residence time, rpm, O_2 flowrate, catalyst concentration, and characteristics of the liquor on the yield of sulfate and the rate of oxidation of thiosulfate;
iv) Development of a method for the chemical detection of trithionate in oxidized kraft black liquors;
v) Use of the method described in iv to close the overall inorganic sulfur mass balance for both noncatalytic and catalytic oxidation;
vi) Investigation of the effects of NaOH addition and residence time on the pH of the liquor and the rate of oxidation of thiosulfate;
vii) Experiments to quantify the extent of organic oxidation after thiosulfate conversion.

Both noncatalytic and catalytic oxidation of thiosulfate have been addressed in the present study. The subjects of catalyst deactivation, regeneration, and recoverability were considered to be beyond the scope of the present work, however.

2.3 Rationale For Current Research

Weak black liquor oxidation in the kraft pulp and paper industry is presently practised to control sulfur gas emissions. This is done by stabilizing sodium sulfide in the less volatile form of sodium thiosulfate. This practice prevents sulfur emission from the multiple effect and direct contact evaporators. Sulfur losses in the follow-up pyrolysis and gasification operations in the recovery boiler are not significantly affected, however. A process strategy which could increase the present sulfur recovery from the recovery boiler, and hence reduce makeup saltcake requirements, could be a valuable asset to the industry.

Fallavollita (1984) has stated in a related project report that a possible drawback to the Fluid Bed Recovery Concept for the gasification of kraft black liquor lies in the degree of volatile sulfur compounds produced during pyrolysis. Strohbeen and Grace (1981) studied the pyrolysis of black liquor model compounds at temperatures similar to the recovery boiler operation. They showed that if all the inorganic sulfur is present as sulfate, then less than 4% of the total sulfur is volatilized. Hence, gases associated with pyrolysis and gasification in the fluid bed could be minimized if most of the inorganic sulfide could be oxidized to the sulfate form. This basic principle is the motivation behind the present work.

The oxidation of inorganic sulfur is studied in weak black liquor (15% - 17% solids) throughout the course of this study. The rationale for this is based on Cooper's finding (1973) that the sulfate yield is maximized in weak black liquors above 80°C. Production of sodium sulfate in thick liquors (45% - 50%) is not practical because of competing organic oxidation side reactions. Hermans (1984) demonstrated that "high intensity oxidation" of strong liquors results in poor rheological properties. The liquors become so viscous that they do not flow without alkali addition.

The most common objection to the production of sulfate from oxidizing weak liquors is with the problem of evaporator scaling (from the sodium salts of carbonate and sulfate). In a comprehensive study by the Institute of Paper Chemistry (1977), it was demonstrated that both sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) precipitate on the evaporator heat transfer surfaces when their bulk solubilities are exceeded at approximately 45% liquor solids. The double salt "burkeite", has a molar makeup which is typically $2Na_2SO_4 \cdot Na_2CO_3$. It has been found to have a greater scaling tendency than either of the salts in the absence of the other. This soluble scale formation decreases the evaporator heat transfer capacity. Moreover, it forms a rough surface on which additional suspended liquor solids are readily deposited.

Almond Jr. and Hedrick (1985) have recently developed a new technology which makes the sodium salts of sulfate and carbonate crystallize in the bulk black liquor, rather than on the heat transfer surfaces. They have shown that a properly designed falling film type evaporator system can produce a liquor solids concentration above 80% without appreciable sodium salt fouling. This technology has been implemented in two commercial installations with favorable results. It has clearly diminished the importance of the sodium salt precipitation problem on heat transfer surfaces.

MacMillan Bloedel Research (1977) has found that there is no linkage between high efficiency BLOX and scaling and/or plugging tendencies in the Direct Contact Evaporator (DCE). They observed that of the mills employing high efficiency oxidation of black liquor, about half reported an increase in the rate of plugging in their DCE, but half did not experience any such effect. Moreover, some degree of precipitation of black liquor solids in direct contact evaporators was reported both by mills practising BLOX, and by mills not practising BLOX.

The loss of black liquor thermal value with oxidation is not quite as critical any more since the successful implementation of the Total Heat Recovery Concept (THR). THR can harness nearly 100% of the heat liberated in oxidation. When this heating resource is used for the drying of the weak liquor, a substantial saving in the evaporator steam requirements is realized.

Grace (1982) has noted that a loss of liquor thermal value upstream from the recovery boiler can sometimes be a beneficial characteristic of black liquor oxidation. When a boiler is "overloaded" for instance the mill is prevented from practising incremental pulp production. This is because the black liquor throughput exceeds the design capacity which causes an increased heat release from the exothermic pyrolysis reactions. Under these conditions the temperature in the upper oxidizing zone increases from the combustion reactions of liquor organics. This results in a loss of sodium through volatilization. If the thermal value of the liquor is decreased by intense black liquor oxidation upstream of the recovery boiler, the heat release at the boiler is lower per unit mass of black liquor solids supplied. This means that the liquor throughput can be increased proportionally without incurring additional sodium losses. The incremental boiler throughput capacity permits an increase in the overall production rate.

In summary, strong oxidation of weak black liquor yielding sulfate as the only end product of inorganic sulfur oxidation is justifiable on three accounts. These are:

i) increased chemical recovery of sulfur and decreased TRS emission at the recovery boiler;
ii) potential application to the fluidized bed reactor concept;
iii) increased boiler throughput capability, resulting in incremental pulping capacity for a mill.

3. EXPERIMENTAL METHOD

3.1 Design of Reactor System

One of the goals of this research program was to build an experimental setup dynamically similar with the current industrial practice. The results generated from this study could then be expected to provide some insight into the nature of the oxidation reactions which take place in a commercial oxidation plant. With this objective in mind, oxidation experiments were carried out in a bottom-sparged agitated semi-batch reactor using molecular oxygen gas as the oxidant (Fig.1). The sparging design is the most widespread form of oxidation technology currently employed by the industry.

Pure oxygen, rather than air, was used as the oxidizing medium to reduce the diffusional limitations associated with the oxygen mass transfer. In addition, the use of O_2 minimizes the stable foam formation which is produced when inert nitrogen gas is bubbled through weak black liquor.

In all experiments the process temperature of the liquor was maintained between 90°C and 100°C and the total pressure at one atmosphere. Condensed water was not refluxed back to the reactor. These conditions were adopted primarily to match the current industrial trends. The temperature range that could be used was quite limited because of the strong tendency of sulfide reversion below 90°C. A sizable fraction of the sulfide oxidation product below 90°C is elemental sulfur and not thiosulfate. Temperatures above 100°C are not suitable because the liquor approaches its atmospheric boiling point. This results in a high rate of evaporation from the liquor during an experiment.

3.2 Equipment

A process flowsheet of the experimental apparatus is given in Fig.1. The reactor system configuration consists of the reaction vessel for black liquor oxidation, and ancillary flow and electrical equipment. The system was designed to handle a continuous flow of gas. It had the capability of measuring the %O_2 in the reactor off-gas continuously by an O_2 analyzer. The relative oxidation extent of inorganic sulfur species was measured via the Paprican BLOX sensor. The oxygen analyzer (Taylor Servomex model OA 272), used the paramagnetic principle of detection for the continuous measurement of oxygen in the reactor off-gas. High precision readings of the %O_2 were obtained by connecting electrical leads from the analyzer to a digital-readout multimeter.

The reactor used for all experiments was an Autoclave Engineers Inc., one U.S. gallon bolted-closure vessel, equipped with a variable-speed motor-driven impeller. A tachometer was used to prepare a calibration chart for the agitator rpm. This was consulted for setting agitation levels in all ensuing oxidation experiments. The temperature of the liquor was measured by a TYPE-K thermocouple inserted into a thermowell, which extended into the body of the reactor.

The vessel was electrically heated by a series of three heaters evenly placed along the body of the reactor heating jacket. The jacket temperature was measured by a second k-type thermocouple and was recorded by a multi-channel temperature indicator. Valves for the sparging, vent, and sampling lines were on the body of the reactor.

The autoclave's internals featured a cooling coil, gas sparging line, gas vent line, sample withdrawing tube, motor-driven impeller, and a thermocouple well. The sparger was located below the impeller to provide good dispersion of oxygen into the liquor. A second foam-breaking impeller (Fig. 2) was secured near the top of the shaft. The British Disintegrator type design of this impeller caused a rapid foam breakdown by taking advantage of the high centrifugal force developed at the 2500 rpm agitation rate.

The cooling coil was removed so that the Paprican BLOX sensor could be put in its place. The BLOX sensor, developed by Mortimer and Fleming (1985), consisted of two, one-quarter inch diameter roulon insulated electrodes. The millivolt output, which was known to be inversely proportional to the inorganic sulfur oxidation extent, was recorded continuously by a high input impedance multimeter.

Oxygen or nitrogen was supplied to the vessel from pressurized cylinders through a pressure regulator, a series of flowmeters, and check valves at the desired flowrate (1 - 2 lpm). Check valves were connected on line, before the oxygen and nitrogen flowmeters. This was done to ensure that no mixing of gases was possible. A third check valve was connected immediately ahead of the sparger valve inlet. This prevented the flow of liquor - due to liquor foaming - through the sparging line and into the flow equipment.

After contacting the liquor, the [illegible]saturated gas was discharged through a gas vent at the top of the reactor. The gas then passed through a steam trap and was subsequently sent to a water-cooled condenser. Following condensation the resulting cool dry gas was directed to a flowmeter for instantaneous flow measurement. It was then sent to a wet test meter which was used to keep a running record of the accumulated gas flow. The outflowing gas from the wet test meter was split into two streams; 150 cc./min. was bled to the oxygen analyzer and the remainder was purged to the fume hood. To prevent damage to the oxygen analyzer cell from excessive flowrates, flowmeters were installed before and after the analyzer. A peristaltic pump was required to push the gas through the silica-gel packed impinger. The analyzer was calibrated with pure O_2 and N_2 gases before an experiment.

3.3 Experimental Procedure

The autoclave was charged with two liters of weak kraft black liquor (15% - 17% solids) obtained from the Domtar hardwood pulping mill in Cornwall. For catalytic oxidation experiments an appropriate amount of the chemical was added to the liquor before the reactor was sealed. The three electrical heaters situated on the body of the reactor were then switched on and the impeller agitation rate was set. The temperature of the liquor was allowed to rise to between $90^{o}C$ - $100^{o}C$. To prevent oxidation of the liquor prior to the start of an experiment, the reactor was purged with nitrogen gas until the oxygen analyzer digital readout displayed 0.0%. At that point the nitrogen flow valve was shut. This practice ensured that no oxygen was trapped in either the gas space above the liquor, or in the copper tubing leading up to the reactor.

When a steady-state temperature was attained the experiment was initiated by opening the valve on the oxygen cylinder. At the same time a stopwatch was turned on which kept a running record of residence time. The temperature of the liquor was maintained constant by switching the heaters on and off as the need arose during an experiment.

Between 15 and 20 samples were taken periodically during an experiment which was typically run for about two hours. During the first 15 minutes where the rate of inorganic sulfur oxidation is fast, a relatively large number of samples were taken. The residence time, BLOX sensor millivolt output, liquor temperature, accumulated gas flow, and %O_2 in the off-gas were recorded at the sample withdrawl times. The oxygen inlet flow was closely monitored throughout the experiment and was adjusted when necessary.

Following the completion of an experiment the amount of condensed water in the steam trap was noted. The oxidized liquor product was drained and the reactor was cleaned and prepared for the next trial.

Samples taken during an experiment were collected and the chemical analyses that are listed below were performed:

i) All samples were analysed for inorganic sulfur species by ion chromatography within 24 hours of the experiment;

ii) All samples were analysed for weight % solids content;

iii) Some samples were analysed for total sulfur and thermal value;

iv) Some samples were analysed for trithionate by potentiometric titration;

v) Analyses for carbonate, sodium, calcium, sodium hydroxide, and total organic carbon were done for some experiments.

3.4 Ion Chromatography Analysis

3.4.1 Commissioning of the High Pressure Ion Chromatograph

All analyses for the aqueous phase inorganic sulfur species (S^{2-}, $SO_3{}^{2-}$, $SO_4{}^{2-}$, $S_2O_3{}^{2-}$) except trithionate ($S_3O_6{}^{2-}$), were performed using a Dionex Model 2000i High Pressure Ion Chromatograph, in accordance with Tappi Standard T699 pm-83. In some cases the concentrations of carbonate ($CO_3{}^{2-}$) and oxalate ($C_2O_4{}^{2-}$) were also measured by the ion chromatography (IC) technique. At the time this project was initiated the IC was not calibrated for the ions of interest.

Consequently, a commissioning study was initiated to investigate the following:

i) concentration ranges over which each of the inorganic sulfur species (SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$) was linear;

ii) linear ranges for these species for a variety of IC output sensitivity ranges (3, 10, 30 microsiemens);

iii) precision of the method for each of the measured constituents;

iv) reproducibility of the concentration data after 4 and 24 hours (since 24 hours was the estimated time lag between experiment and analysis);

v) evaluation if a multi-component standard containing sulfite, thiosulfate, and sulfate could be prepared without affecting changes on the equilibrium concentrations of each of the individual species;

vi) determination of the most appropriate dilution factor, IC output sensitivity range, and integrator commands for black liquor chemical analysis.

The pertinent results from this study (Tables I, II, and III, Appendix 2), were used in the estimation of error for black liquor chemical analyses by the IC method.

Table I shows that the precision for the sulfate and thiosulfate concentration data is better than 3% up to 24 hours after the preparation of the standard aqueous solutions. Sulfite, however, is the most unstable of the measured constituents. It is partially oxidized within four hours after preparation. Fortunately, the concentration of sulfite in kraft liquors is small (<0.2 gpl). Any error from this source does not significantly affect the mass balance on inorganic sulfur. These results indicate that no significant error is introduced with the data collection if the chemical analyses are performed within 24 hours after the completion of an experiment.

There was no evidence of interaction effects between individual components in solution. The equilibrium ionic concentrations of sulfite, thiosulfate, and sulfate were not affected by the presence of the other two. This result demonstrated that standard solutions containing all three inorganic species could be prepared and calibrated simultaneously with a single sample injection.

3.4.2 Black Liquor Chemical Analysis By IC

It was found that the most appropriate range for the chemical analysis of oxidized kraft black liquors is at 10 microsiemens for sulfite and sulfate, and 3 or 10 microsiemens for thiosulfate (Table II, Appendix 2). Depending upon the concentration of the sample, the oxidized liquor samples could be classified into three general categories for progressively stronger oxidation (Table III, Appendix 2). Typical concentration ranges of the three measured species are listed in each category. The corresponding dilution factor and IC output ranges recommended for best detection and quantification are shown. In the last category where the oxidation is virtually complete, the concentration of thiosulfate is below 0.5 gpl and almost out of the range of accurate chemical detection. Only the concentration of sulfate is measured in this case, but at high dilution so that any interference from trace thiosulfate concentrations between successive sample injections is eliminated.

The black liquor samples were brought to the required concentration range by a series of two dilutions in 100 ml volumetric flasks. In the first flask 1 ml black liquor was pipetted using a standard volumetric pipette and diluted with distilled deionized water. After mixing vigorously, a predetermined amount of the diluted liquor (depending on dilution factor as given in Table III) was pipetted into a second flask and further diluted. A well rinsed syringe was used to inject five to ten ml of the sample in the second flask for chemical analysis. The average retention time per sample was about 15 minutes. Any samples that were observed to be affected by temporary baseline drifts, or out of the range of reasonable experimental error at the time of the analysis were repeated.

3.4.3 Preparation of Standards

All standards were carefully prepared by weighing reagent crystals with a Mettler model AE 166 Analytical Balance. The reagent salts were diluted with distilled water to appropriate volumes with Pyrex laboratory volumetric flasks. Stock standard solutions containing 100 ppm of the ionic constituents were reprepared every two days. Purity of the crystals was taken into account in the calculation of the weights required for the standard solutions. Standard calibration solutions were prepared by pipetting appropriate amounts of the 100 ppm stock solutions into volumetric flasks. They were diluted to obtain the desired concentration range which is specified in Table II, Appendix 2. Three calibration solutions, containing 1, 2, and 5 ppm of sulfite, sulfate, and thiosulfate, were used to calibrate the IC on a daily basis. When a large number of samples were being processed, all the calibrations were repeated after a few hours of continuous use.

3.5 Determination of Trithionate in Kraft Black Liquors

3.5.1 Introduction

A method has been developed to detect and quantitatively estimate the concentration of trithionate ($S_3O_6^{2-}$) in oxidized kraft black liquor. The method is based on the Noranda mercuric chloride potentiometric titration method. Originally developed by Jay (1953), it was modified in this work for the determination of trithionate in oxidized kraft black liquors. There is no other method presently available for the chemical detection of trithionate in kraft black liquors.

3.5.2 Theory

Polythionates containing 3,4, and 5 sulfur atoms react quantitatively with mercuric chloride ($HgCl_2$), to release acid in solution. The stoichiometric equation is:

$$2S_nO_6^{2-} + 3HgCl_2 + 4H_2O \longrightarrow HgCl_2 \cdot 2HgS + 8H^+ + 4Cl^- + 4SO_4^{2-} + (2n-6)\,S \qquad (20)$$

Hence for trithionate,

$$2S_3O_6^{2-} + 3HgCl_2 + 4H_2O \longrightarrow HgCl_2 \cdot 2HgS + 8H^+ + 4Cl^- + 4SO_4^{2-} \qquad (21)$$

Similar equations can be deduced for tetrathionate and pentathionate. Mercuric chloride also reacts with thiosulfate.

$$2S_2O_3^{2-} + 3HgCl_2 + 2H_2O \rightarrow HgCl_2 \cdot 2HgS + 4H^+ + 4Cl^- + 2SO_4^{2-} \quad \ldots\ldots (22)$$

In both cases the acid generated may be titrated with standardized NaOH solution to determine the concentration of the four sulfur anionic species: $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$. Wasserlauf and Dutrizac (1982) have stated that the only polythionate that is stable in hot alkaline solutions, such as the case for the present black liquor oxidation study, is trithionate. It follows that any acid produced from the mercuric chloride addition to the liquor after quantitative conversion of thiosulfate, must be generated from the trithionate reaction.

The method described below is not applicable when sulfide is present. This is because sulfide also reacts with mercuric chloride to liberate acid in solution. If sulfide is present its interference must be eliminated by acidifying to pH 4.0. Vacuum must then be applied for approximately 30 minutes to remove the sulfide as hydrogen sulfide gas (H_2S).

3.5.3 Apparatus

The apparatus required for the chemical detection of trithionate is listed below.

- pH meter preferably with a combination electrode
- magnetic stirrer and stirring bar
- 2, 25ml burettes
- sufficient 150 ml beakers for all samples to be tested
- hot plate
- pipettes of various sizes

3.5.4 Method of Analysis

1. Before attempting any trithionate analyses all sulfur species that can be detected by ion chromatography (Tappi Standard T699 pm-83) must be measured ie. S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, SO_4^{2-}.
2. Pipette a 2 ml aliquot of oxidized liquor into a 150 ml beaker and dilute to about 40 ml with distilled water. From step 1, if the concentration of sulfite is present in a proportion greater than 10% of the anticipated trithionate concentration, then add 2 ml formaldehyde per gram of sulfite in solution. In kraft liquors the concentration of sulfite is usually less than 0.2 gpl so the formaldehyde addition can be omitted.
3. With the beaker on a stirring mantel insert the stirring rod and glass electrode and dropwise reduce the pH to 4.30 with 1N H_2SO_4. In case of acid overshoot use 0.1N NaOH to return the pH to 4.30, and similarly use 0.1N H_2SO_4 when the pH is only marginally above 4.30.

4. Remove the pH probe and stirring bar rinsing each with distilled water into the sample but being careful not to over dilute the sample.
5. Pipette 5 ml of 2 weight % $HgCl_2$ solution into the sample and stir vigorously with a glass rod to ensure mixing. Allow the sample to sit for approximately 5 - 10 minutes covered with a watch glass. Repeat steps 1 through 5 for all the samples to be tested while the samples are in the 'sitting period'.
6. Heat the sample solution(s) over a hot plate bringing just to a boil and being careful not to overheat. If the hot plate is large enough all the samples should be heated at the same time. This is to ensure reproducible heating conditions between the set of samples. Cool the solution with cold running water or in an ice bath to room temperature.
7. Pipette 5 ml of a solution of KI (20 weight %), stir to mix, then insert pH electrode and maintain stirring.
8. Titrate with standardized 0.01N NaOH to the pH 4.30 endpoint. Typically pH values before titration are between 4.0 to 4.1 for strongly oxidized liquors. Near the endpoint add NaOH dropwise. Let the sample stir for a few seconds to ensure that solution homogeneity is attained. If the pH decreases titrate again with a few drops to the endpoint. For best results run the sample again and average the titre values obtained.
9. <u>KI Correction</u>

   The KI is used to complex excess $HgCl_2$ but causes a slight alkalinity of the sample. To account for this excess alkalinity in the calculations, repeat steps 3 to 8 using 40 ml distilled water instead of the sample. Titrate the alkalinity developed with standardized 0.005N H_2SO_4 to pH 4.30.

10. Convert the titre value obtained in step 9 above to the equivalent 0.01N NaOH volume and add this volume to the titre value of the sample.

11. Thiosulfate Correction

    If thiosulfate is known to be present from ion chromatography analysis, then calculate the volume of acid that is produced from its reaction based on its measured concentration value from stoichiometry given in equation 22. Convert this acid volume to the equivalent 0.01N caustic soda required to neutralize, and subtract from caustic volume obtained in step 10 above. This difference represents the equivalent acid liberated from the trithionate reaction only.

12. The volume NaOH obtained from step 11 or 10 is the amount required to neutralize the acid from the trithionate reaction. Convert this volume to liters and call it V_B.

13. Calculate the concentration of trithionate. A sample calculation is presented in Appendix 4.

3.6 Total Sulfur

Total sulfur, which includes both inorganic and organic sources, was measured by the Chemical Analysis Department at the Pulp and Paper Research Institute of Canada (Paprican). The procedure that was used for the chemical detection of total sulfur uses the principle of wet combustion, and can be found in CPPA Standard Method J.15P (v). The experimental procedure involves a wet washing of the sample with nitric and perchloric acids, followed by a gravimetric determination of the total sulfur as barium sulfate. Nitric acid is used to oxidize and eliminate the organic material from the liquor. The use of perchloric acid is required to oxidize all the sulfur to sulfate form. After adding a 10 w/w % aqueous $BaCl_2$ solution to a slightly acidic sample solution, filtering, and igniting the precipitate formed at 800°C, the sulfur can be determined gravimetrically as barium sulfate ($BaSO_4$).

3.7 Total Sodium and Calcium

Sodium and calcium were measured by the Paprican Chemical Analysis Department by Atomic Absorption Spectrophotometry (CPPA Standard Methods J.15P (iv & xiv) respectively).

3.8 Sodium Hydroxide

Sodium hydroxide was measured by Paprican Chemical Testing by the standard potentiometric titration method given in CPPA Standard J.15P xii.

3.9 Thermal Value

The thermal value of black liquor was determined by Paprican Chemical Testing Department using the standard method of bomb calorimetry (CPPA Standard Method J.15P xv). Thermal value is defined as "the quantity of heat liberated by a unit mass of black liquor solids when combined with oxygen in an enclosure of constant volume."

3.10 Total Solids

Black liquor solids content was estimated by Tappi Standard Method T 625 ts-64. One modification that was made for this research was that the black liquor samples were dried for 48 hours, instead of the 24 hours suggested in the standard method. It was found that a steady-state solids concentration could only be obtained by allowing the samples to dry for this extended period of time.

3.11 Total Organic Carbon

Total organic carbon (TOC) was measured by the Paprican Chemical Testing Department using a "Technicon Auto-Analyzer". A brief description of the method is included below.

step 1: An aliquot of black liquor is acidified with 1N H_2SO_4, to which is added potassium persulfate. The sample is then treated under uv radiation. Organic carbon is combusted to CO_2 in this manner and is dialyzed through a silicone rubber membrane into a weakly buffered phenolpthalein indicator solution. The decrease in color of the indicator solution, due to formation of carbonic acid, is proportional to the TOC plus the carbonate carbon in the original black liquor sample. The color decrease is detected with a spectrophotometer at 550 nm.

step 2: Step 1 measures both the inorganic carbonate carbon (CO_3^{2-}) and the organic carbon. The total inorganic carbon can be calculated by repeating step 1, but without adding the potassium persulfate and by eliminating the uv digestion process.

step 3: The TOC concentration can be calculated by subtracting the inorganic carbon obtained from step 2 from the total black liquor carbon obtained in step 1.

ie. TOC (gpl) = $\text{carbon}_{(\text{step 1})} - \text{carbon}_{(\text{step 2})}$

Precision of the method is reportedly +/- 3%.

3.12 Experimental Uncertainty Estimates

The measured black liquor species in this work included the ions of sulfite, sulfate, trithionate, oxalate, and carbonate. The concentration of sodium hydroxide was also measured. In addition, the thermal value, total sulfur content, calcium, sodium, total organic carbon (TOC), pH and total solids of black liquor samples were measured. The methods to measure each of these have been described or listed in the previous sections. Table IV, Appendix 3 presents the relative % error and standard deviation data in gpl for each of the ion constituents measured. Errors and standard deviations associated with all of the other chemical analyses performed on the liquors are shown in Table V, Appendix 3. All error estimates shown are calculated on the basis of at least three replicate measurements. They represent the average expected error in all cases.

Standard deviations for the total sodium and the frequently measured ions (SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, $S_3O_6^{2-}$) were calculated on the basis of 'pooled sample variances'. A pooled sample variance is a weighted average of sample variances of replicate data from different experiments. It is defined by equation (23).

$$\hat{s}_p^2 = \sum_{i=1}^{l} (m_i - 1)\, \hat{s}_i^2 \Big/ \sum_{i=1}^{l} (m_i - 1) \qquad (23)$$

A sample calculation for the sulfate data is given in Table VI, Appendix 3. Standard deviations listed for all the other nonpooled measured constituents are calculated on the basis of one set of three to six replicate data.

A pooled estimate takes into account the experimental measuring technique, the degree of reproducibility of the chemical analysis method employed, and the subtle variations between day to day experimental conditions. It is a reflection of the total experimental uncertainty associated with black liquor sampling, analysing, storage time, and method. A standard deviation from only one set of data on the other hand, does not include an estimate of the variations between successive experiments of the parameters specified above.

4. RESULTS AND DISCUSSION

4.1 Design of Experiments

Three different batches of hardwood kraft black liquor (taken at approximately one month intervals) were obtained from the Domtar pulp mill in Cornwall, Ontario for the oxidation experiments. All three liquors had similar chemical properties (Table 1), but had different physical properties. For the sake of clarity and brevity, the three liquors used for this thesis will be denoted as Liquors A, B, and C. It was decided early in the experimental program to use actual kraft black liquor from an operating mill rather than simulated liquors.

The experimental feature that was common to all three liquors was the measurement of the rate of oxidation of sodium thiosulfate to sodium sulfate between 90°C and 100°C and at one atmosphere total pressure. The rate of oxidation of thiosulfate was studied by performing experiments with and without catalysis. To determine where oxygen mass transfer limitations were eliminated, a sequence of experiments with variable agitation levels and O_2 flowrates were performed with Liquors A and B.

The catalyst that is referred to above was obtained by performing a series of screening experiments with different chemicals. These chemicals included sodium hydroxide (NaOH), cupric chloride ($CuCl_2$), activated charcoal, hydroquinone, reduced iron, manganese, cobaltous chloride ($CoCl_2$), manganese dioxide (MnO_2), and a nickel aluminum alloy (NiAl). The chemicals were added to the unoxidized liquor in a concentration of 10 gpl, and their effects on the rate of thiosulfate oxidation were studied.

If an acceleration of the rate was found, another experiment with a lower concentration was performed.

Although the oxidation of thiosulfate to sulfate was the key focus of interest of this research, various other aspects of black liquor oxidation were also studied. For example, the concentration of oxalate ($C_2O_4^{2-}$) was quantified in all experiments with Liquor A. The thermal value and total sulfur were measured in experiments with Liquor B. The total organic carbon (TOC), and the ions of hydroxide, carbonate, and trithionate were measured for the experiments with Liquor C. It was not practical to measure all the properties for the three liquors. Rather, it was assumed that if a characteristic (such as thermal value decline) could be demonstrated for one liquor, then it could be assumed to be valid for the other two.

The concentration of oxalate was measured in experiments with Liquor A to investigate whether oxidation contributes to an increase in its concentration. Franklin (1982) noted that the presence of oxalate in kraft liquors "implicates the potential buildup of harmful scale deposits." Hence, measurement of the concentration of oxalate might give an indication of the scaling tendencies of strongly oxidized liquors.

The concentration of total sulfur was measured before and after experiments with Liquor B. This was to determine if a significant amount of sulfur species was volatilized during an oxidation experiment. Measurement of both total sulfur and trithionate (measured for Liquor C), were essential to close the overall mass balance on inorganic sulfur.

The thermal value for Liquor B samples was measured after various extents of oxidation. This study was initiated to evaluate the impact of quantitative thiosulfate oxidation on the extent of organic oxidation. A further indicator of the extent of organic oxidation is the decline of total organic carbon (TOC). TOC, carbonate, and sodium hydroxide were measured in experiments with Liquor C to estimate what percentage of the organics is oxidized to CO_2. It was also important to determine what proportion of the CO_2 is reabsorbed by the alkaline liquor to form sodium carbonate.

Concentration/time data for all the measured constituents were corrected for the evaporation of water which occurred during the course of an experiment. All presented data is expressed on the basis of grams constituent per liter of black liquor charged to the reactor before oxidation (gpl). The concentrations of all chemical additions (catalyst, screening chemicals, and NaOH) are also expressed on the basis of grams chemical per liter of black liquor charged charged to the reactor.

The rate of evaporation was quantified independently for each experiment. This was done by noting the amount of liquid condensate in the steam trap (Fig. 1) at the sample withdrawl times during an experiment. The rate of evaporation was found to be 2.4 +/- 0.1 ml/min. at the temperature range used for most of the experiments in this research (94°C +/- 2°C), and was constant at this value during an experiment. All concentration data presented in this thesis were corrected (based on this evaporation rate) to grams of constituent per liter of unoxidized black liquor charged to the reactor. During a typical experiment the solids concentration of the liquor increased between 3 - 4% (from about 16% to 19%) for an experiment that was run for

120 minutes. /The uncertainty with the measurement of the evaporation rate is included in the estimation of experimental errors for concentration data of all measured constituents given in Appendix 3.

When required replicate experiments were performed. Good reproducibility of the experimental data was obtained in all cases.

4.2 Noncatalytic Oxidation

4.2.1 Effect of Impeller rpm, O_2 Flowrate, and Liquor on Oxidation Rate

Noncatalytic oxidation experiments for Liquor A were used to determine the effect of impeller rpm, and oxygen flowrate on the thiosulfate oxidation rate. In addition it was necessary to quantify residence times required for the conversion of thiosulfate. This information was used to set conditions for other experiments with Liquors B and C.

Figure 3 shows concentration/time data for sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), oxalate ($C_2O_4^{2-}$), and thiosulfate ($S_2O_3^{2-}$). The experimental conditions were set at an oxygen flowrate of 2.4 liters per minute (lpm), a temperature of 100°C, and an impeller agitation rate of 1500 rpm. Estimates of the experimental errors associated with those chemical constituents are given in Table V, Appendix 3. The thiosulfate concentration is initially 2.71 grams per liter (gpl). It increases to 5.20 gpl at 4.5 minutes, and declines thereafter (Table 2). The concentration of sulfate rises gradually to a value of 7.62 gpl at 72 minutes.

The initial increase of the thiosulfate concentration is from oxidation of sulfide (S^{2-}), hydrosulfide (HS^-), polysulfide (S_x^{2-}), and elemental sulfur (S^o). These constituents are all initially present in the unoxidized liquor. The sulfide concentration was measured at 0.5 gpl in the unoxidized liquor. Polysulfides were also traced. A chemical analysis of the yellow residue (Table 1) floating freely on the surface of the liquor prior to oxidation, showed that this substance was 91.8% by weight elemental sulfur. From these observations it was thought that most of the unoxidized inorganic sulfur initially present in the liquor was in the form of elemental sulfur rather than sulfides.

When subjected to an oxidizing atmosphere, elemental sulfur is converted to thiosulfate. Pryor (1962) has stated that the oxidation of elemental sulfur to thiosulfate follows the disproportionation reaction shown in equation (24), at temperatures near 100°C.

$$S_8 + 8NaOH \rightarrow 2Na_2S_2O_3 + 4NaHS + 2H_2O \qquad (24)$$

The chemical determination of the concentration of elemental sulfur in unoxidized black liquor is very difficult. As a result only the thiosulfate, sulfite, and sulfate constituents were measured in all ensuing experiments. Accurate knowledge of the species elemental sulfur (S^o), polysulfide (S_x^{2-}), and sulfide (S^{2-}) is not critical to the present study. This research focuses on the sequential oxidation of thiosulfate to sulfate.

The concentration of oxalate is initially 1.06 gpl in the unoxidized liquor (Table 2). It increases to a maximum of 1.59 gpl at 35.5 minutes and decomposes to 1.20 gpl at 43 minutes. It then increases to 1.41 gpl at 72.0 minutes. The concentration of sulfite is relatively stable at 0.3 +/- 0.1 gpl. Table 7 shows a set of data under similar process conditions.

Figure 4 illustrates the effect of O_2 flowrate and impeller rpm on the rate of thiosulfate oxidation. At a flowrate of 1.2 lpm O_2 and 800 rpm (Table 4), the oxidation rate is O_2 diffusion controlled. The thiosulfate concentration remains above 3.9 gpl even after 189 minutes of oxidation. At 1500 rpm (Table 5), the oxidation rate has increased to the point where the concentration of thiosulfate is reduced to 0.35 gpl in just 73 minutes. At 2500 rpm (Table 6), no further acceleration of the rate of thiosulfate oxidation is observed. This result indicates that oxygen diffusional limitations are eliminated at 1500 rpm if the O_2 flowrate is not the rate determining step. If the O_2 flowrate is not in sufficient excess to satisfy the total liquor oxygen demand, the oxidation rate would still be in the diffusion regime.

To investigate if the O_2 flowrate is in sufficient excess at 1.2 lpm O_2, another experiment at 1500 rpm and 2.4 lpm O_2 was performed. Since no increase of the rate of thiosulfate oxidation is observed even at the higher flowrate (Fig. 4), it can be concluded that the reaction is kinetic controlled at 1500 rpm and 1.2 lpm O_2.

Figure 5 shows the effect of O_2 flowrate and rpm for the sulfate and oxalate concentration/time data. No increase of sulfate rate is observed above 1500 rpm and 1.2 lpm O_2. This is consistent with results found for the thiosulfate oxidation. Oxidation reactions apparently promote the formation of oxalate (Tables 2, 6). This may indicate scaling tendencies of the strongly oxidized liquors.

Tables 8, 9, and 10 present the thiosulfate and sulfate concentration data for Liquor B at 1.2 lpm O_2 and 800 rpm. The concentration of thiosulfate before oxidation is approximately 4.6 gpl. This is higher than the values noted in Tables 2 - 7. The higher initial $S_2O_3^{2-}$ concentration is presumably the result of free sulfur oxidation to thiosulfate before the experiment. When the experiment is initiated the concentration of thiosulfate reaches a maximum after approximately five minutes (Fig. 6) and falls slowly to 1.7 gpl after 100 minutes of oxidation. Figures 6 and 7 show that good reproducibility is obtained between the replicates for the thiosulfate and the sulfate concentration/time data respectively.

The effect of agitation of the liquor on the rates of thiosulfate oxidation and sulfate production is compared in Figs. 8 and 9 respectively for Liquor B. At 800 rpm the rate of oxidation is clearly O_2 diffusion limited, analogous to the result for Liquor A. In this case the concentration of thiosulfate is approximately 4.1 gpl after 40 minutes of oxidation (Tables 9, 10). In comparison the thiosulfate concentration is reduced to 0.29 gpl with an agitation rate of 1500 rpm, also at 40 minutes (Table 11). Under these conditions the concentration of sulfate attains a steady-state value of approximately 8.7 gpl after conversion of thiosulfate. At 2000 rpm (Table 12) no significant change is noted in the thiosulfate concentration profile, but the steady-state sulfate concentration increases to 8.90 gpl after 45 minutes. At 2500 rpm (Table 13) the concentration of thiosulfate can be reduced to 0.47 gpl in 30.2 minutes, and the sulfate concentration levels off at about 9.7 gpl after 100 minutes of oxidation.

If the agitation is maintained at 2500 rpm and a baffle is added, a further increase of the rate of thiosulfate oxidation is noted. The concentration of thiosulfate can be reduced to 0.34 gpl in 25.9 minutes under these conditions (Table 14). Replicate data (Tables 15, 16, 17) confirm this acceleration of oxidation rate. The steady-state concentration of sulfate remains the same at approximately 9.7 gpl. Its production rate increases, however, (Fig. 9) because of the higher rate of thiosulfate oxidation.

At 3200 rpm with a baffle (Table 18), the rate of oxidation of thiosulfate is not further accelerated. The concentration of sulfate levels off at 10.3 gpl at 120 minutes. At 4000 rpm (Table 19) the sulfate concentration gradually rises to 10.3 gpl after 240 minutes of oxidation.

In summary, results from the oxidation of Liquor B demonstrate that the rate of thiosulfate oxidation is oxygen diffusion limited without a baffle and operating below 2500 rpm. This result differs with data presented for results from Liquor A. There it was shown that diffusional resistance is eliminated at 1500 rpm without a baffle. When diffusional limitations are removed, it takes just over 70 minutes to reduce the thiosulfate concentration to below 0.5 gpl in experiments with Liquor A (Table 2); this is about 25 minutes for Liquor B (Table 19), and 35 minutes for Liquor C (Table 20). Clearly, thiosulfate kinetics are very strongly influenced by the black liquor characteristics, and these characteristics do change at a mill. All three liquor samples were taken from the same location at the same mill over a three month period. During this period of time, the wood furnish to the mill did not change (mixed hardwoods).

One explanation for the difference of oxidation rate could be the difference of foaming properties on agitation for the three liquors. Qualitatively, it was observed that Liquor B showed the highest degree of foaming; Liquor A was the least foamy at any given rpm. Another factor that could affect the rate of oxidation is the composition of the organic fraction. The liquors do not have exactly the same organic content (Table 1) or species distribution. Hence, the relative catalytic effect between liquors could be different.

4.2.2 Experimental Evidence for an Inorganic Sulfur Intermediate Oxidation Product

To close a mass balance on inorganic sulfur it is necessary to know if a significant portion of the sulfur is volatilized from the aqueous phase during the experiment. Table 21 examines the total sulfur concentration after various extents of oxidation with Liquor B. Thiosulfate concentration data are also presented to indicate the extent of inorganic sulfur oxidation at the residence times shown.

Before oxidation (at time zero), the concentration of total sulfur (which includes sulfur from both organic and inorganic sources), is 5.3 +/- 0.2 gpl. It does not decrease with residence time, which indicates that no appreciable sulfur is volatilized during oxidation. Hence a mass balance on inorganic sulfur should be closed based on the aqueous phase constituents, thiosulfate and sulfate.

The mass balance on inorganic sulfur will be considered closed if the amount of sulfate present after oxidation is equal to the sum of the initial sulfate before BLOX, plus the amount of sulfate that is produced from quantitative thiosulfate decomposition from its maximum value, $(S_2O_3{}^{2-})_{max.}$. From equation (25) it can easily be shown that 1.71 grams $SO_4{}^{2-}$ should be produced for every gram of $S_2O_3{}^{2-}$ reacted.

$$Na_2S_2O_3 + 2NaOH + 2O_2 \longrightarrow 2Na_2SO_4 + H_2O \qquad (25)$$

Therefore the expected inorganic sulfur concentration, expressed as sulfate, at any time, $(SO_4^{2-})_{exp.}$, is given by:

$$(SO_4^{2-})_{exp.} = (SO_4^{2-})_{initial} + 1.71(S_2O_3^{2-})_{max.} \qquad (27)$$

Due to the rapid oxidation of sulfide, hydrosulfide, and elemental sulfur, it was difficult to obtain samples whose thiosulfate concentration was at the peak of the concentration/time profile. A reliable estimate of this peak could only be obtained at 800 rpm where the rate of oxidation of thiosulfate is O_2 diffusion controlled. By noting that the average maximum concentration of thiosulfate is 5.2 gpl (Tables 8, 9, 10), the amount of sulfate that should be produced from the oxidation can be calculated.

The initial sulfate concentration is 4.60 gpl (Table 8). From equation (27), the total inorganic sulfur as sulfate at any time should be equal to 13.5 gpl.

$$(SO_4^{2-})_{exp.} = 4.60 + 1.71(5.21) = 13.5 \text{ gpl}$$

At 95.2 minutes, the concentrations of sulfate and thiosulfate are 6.35 gpl and 2.01 gpl respectively (Table 8). The concentration of total inorganic sulfur expressed as sulfate equivalent from these two sources is equal to 9.79 gpl (equation 27).

$$(SO_4^{2-})_{exp.} = 6.35 + (1.71)(2.01) = 9.79 \text{ gpl}$$

The difference with the expected value is therefore -27.5%.

$$\% \text{ diff.} = \left(\frac{9.79 - 13.5}{13.5}\right)(100) = -27.5\%$$

This calculation reveals that the mass balance on inorganic sulfur is not closed after BLOX, based on the constituents thiosulfate and sulfate only. Similar discrepancies with the mass balance on inorganic sulfur are presented in Tables 8 - 18. It is apparent that the per cent sulfur unaccounted increases steadily after thiosulfate has reached its peak concentration. After conversion of thiosulfate, the per cent sulfur unaccounted as sulfate is 25% - 35%. This sulfur imbalance is consistent and is clearly too large to be attributed only to experimental errors. Moreover, the sulfate concentration data are always low, never high, by approximately the same amount.

The per cent sulfur unaccounted decreases with rpm. The steady-state sulfate concentration increases from 8.7 gpl at 1500 rpm (Table 11) to 9.7 gpl at 2500 rpm (Table 14). The concentration of sulfate reaches 10.3 gpl at 3200 rpm (Table 18), despite no coinciding increase of the rate of thiosulfate oxidation, over that observed at 2500 rpm. Table 19 indicates that the sulfate concentration increases several hours after thiosulfate has been quantitatively oxidized from aqueous solution. Since the liquor is oxidized there is no possibility that the missing sulfur source is any one of sulfide, polysulfide, hydrosulfide, elemental sulfur, or sulfite. In fact it was stated earlier that the concentrations of sulfide, polysulfide, and sulfite are very small, even in the unoxidized black liquors.

An interesting observation which led to the next major part of the work is now discussed. Five black liquor samples from different experiments were set aside in storage for six weeks. The residual thiosulfate concentrations in all stored samples were below the detectable limit of the ion chromatograph. When the samples were reanalysed six weeks later, the concentration of sulfate had increased by an average of 15%. It was evident from this result that there was another product of the thiosulfate oxidation which could slowly oxidize to sulfate given sufficient time.

Fones and Sapp (1960) showed that quantitative oxidation of thiosulfate to sulfate is possible at higher temperature (> 100°C) and pressure (> 10 atmospheres) than that used in this research. Based on that finding a BLOX experiment was performed in this research with Liquor B under similar process conditions (130°C and 210 psig or 1450 kPa). For this experiment a mass balance on inorganic sulfur was closed to within 6% which is within the acceptable error limitations. Hence, it was possible to reproduce the literature values with these methods, therefore lending credence to the significance of the previous +/- 25% discrepancies.

Experimental evidence suggesting the formation of a stable intermediate product of the oxidation of thiosulfate is summarized below.

i) lack of closure of the inorganic sulfur mass balance despite experimental evidence showing that there was no significant volatilization of sulfur from aqueous solution;
ii) increases of the sulfate concentration (+/- 15%) after sample storage, even though essentially no thiosulfate was originally present in solution;
iii) closure of the inorganic sulfur mass balance with high pressure, high temperature oxidation which provides strong evidence to support the experimental methodology;

iv) increases of the sulfate production rate above 2500 rpm even though there was no corresponding increase of the rate of thiosulfate oxidation.

Results from other related black liquor oxidation studies support these observations. Parthsarathy and Basu (1981) showed that when sulfide was oxidized to thiosulfate a mass balance on inorganic sulfur based on thiosulfate and sulfate alone was consistently 10% to 15% low. In another related study on black liquor oxidation Galeano and Amsden (1973) showed deviations with the inorganic sulfur balance of up to 15%. If the thiosulfate had been quantitatively oxidized in either case these deviations would have been even higher. Closure of the mass balance on total inorganic sulfur after BLOX has never been demonstrated in any conventional type black liquor oxidation study to date (80°C - 100°C, 1 atm. total pressure).

An extensive study (unrelated to black liquor) was carried out by Canmet, Ottawa, on the subject of oxidation of thiosalts ($S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$) in mildly alkaline mining and metallurgical tailings. Wasserlauf and Dutrizac (1982) noted there that both sulfate and polythionates ($S_nO_6^{2-}$, $n = 3,4,5,6$) are products of the oxidation of thiosulfate. Rolia (1981) showed that the only polythionate that is stable in hot alkaline solutions is trithionate ($S_3O_6^{2-}$); tetrathionate ($S_4O_6^{2-}$) decomposes to trithionate at pH > 10. All higher order polythionates are stable only under acidic conditions.

Based on this literature there was strong evidence to suggest that the inorganic sulfur unaccounted after BLOX was in the form of trithionate. This is the first time that a linkage has been made between polythionates in black liquor and mining effluents. Emphasis is placed here on this point to put forth the thesis that trithionate is the unaccounted intermediate in the oxidation of thiosulfate in kraft black liquor. An analytical method for the chemical detection of trithionate was then sought to support this hypothesis.

4.2.3 Measurement of Trithionate Concentration in Black Liquor

An analytical method was developed here for the chemical determination of the concentration of trithionate in kraft black liquors. There is no other published method presently available. Because of the dark color of black liquor, and the presence of many interfering sulfur species, analysis of polythionates in black liquors is extremely difficult. The standard spectrophotometric method which is described by Kelly et al. (1969) was tried. It failed, however, because of interference from the color of the liquor. Ion chromatography methods are as yet only in the developmental stages and are not well established for such analysis. Consequently, the only method that seemed suitable for the detection of trithionate in oxidized kraft black liquors was the mercuric chloride titrimetric method, described in Section 3.5 of this thesis.

4.2.4 Closure of the Inorganic Sulfur Balance

Figure 10 shows concentration/time data for trithionate and closure of the inorganic sulfur mass balance for an experiment at 4000 rpm. The total inorganic sulfur was calculated from the three sources: $S_2O_3^{2-}$, SO_4^{2-}, and $S_3O_6^{2-}$. It was expressed on a common basis of "sulfate total equivalent". The concentration of sulfite (SO_3^{2-}) was not included in this calculation because it was shown from Tables 2 - 7 that its concentration is only 0.2 +/- 0.1 gpl. This small contribution does not significantly affect the sulfur balance calculation. The % difference between expected sulfate total equivalent and that calculated on the basis of the three major ions is shown in the right-most column of Table 19. Since the average deviation is only -3.2%, the mass balance on inorganic sulfur can be considered closed.

Table 20 shows results for a noncatalytic oxidation experiment with Liquor C. The initial concentration of sulfate in Liquor C is 4.0 gpl. This is lower than the 4.6 gpl obtained for both Liquors A and B. As a result, the expected sulfate total equivalent concentration is also lower. From equation (27), the total inorganic sulfur expressed as sulfate at any time is,

$$\begin{aligned}(SO_4^{2-})_{exp.} &= 4.00 + (1.71)(5.21)\\ &= 12.9 \text{ gpl.}\end{aligned}$$

The average deviations with the total inorganic sulfur mass balance calculations are -6.2%, (Table 20), -2.6% (Table 22), -1.3% (Table 23), and -1.6% (Table 24) from replicate experiments. Fig. 11 demonstrates that the trithionate concentration/time data are reproducible. Calculations based on tetrathionate ($S_4O_6^{2-}$) as the reactive intermediate are consistently high (Appendix 4). This is evidence that the missing source of inorganic sulfur is trithionate - not a combination of trithionate and tetrathionate.

During the first ten minutes of oxidation, the concentration of trithionate was not measured for many samples because of chemical interference from many unoxidized inorganic sulfur constituents (S^{2-}, S^{o}, S_x^{2-}). These samples are denoted by 'NA' (data not available) in the tables. In a few samples, the interference from sulfide was eliminated by acidifying the sample to pH 4.0, and applying vacuum for 30 minutes to remove the sulfide as H_2S.

Fig. 11 shows that the concentration of trithionate is initially zero in the unoxidized black liquor. It increases when oxidation is initiated and reaches a maximum value of approximately 3.5 gpl at 30 minutes. This coincides with the time where the concentration of thiosulfate is reduced to below 0.5 gpl (Table 24). The concentration of trithionate is reduced only marginally thereafter, possibly because of the hydrolysis reaction given by Rolia (1981) in equation (26).

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad (26)$$

Trithionate hydrolysis might explain why the concentration of sulfate increases long after thiosulfate is removed from solution for Liquor B (Fig. 10), Liquor C (Fig. 11), and for the experiment in which six oxidized samples were stored for six weeks.

Table 25 compares the experimentally measured yields of sulfate and trithionate after elimination of thiosulfate. The effects of black liquor and rpm on these yields is investigated; the effect of chemical addition is discussed in Section 4.4. ~~Without chemical~~ addition the yields of sulfate are 64% for Liquor A and 62% for Liquor C (of the total inorganic sulfur). The remainder is in the form of trithionate. Results from Liquor B show that the yield of sulfate increases with agitation of the liquor, and is approximately 70% of the total inorganic sulfur when the oxidation rate becomes kinetic controlled at 2500 rpm. All sulfate and trithionate data presented in Table 25 are calculated from experimental measurement, and not by arithmetic difference. The mass balance on total inorganic sulfur is closed to within 4% in all cases.

In an unrelated study (not on black liquor), Yokosuka et al. (1975) observed that the reaction products of the alkaline thiosulfate oxidation (pH = 10) in pure aqueous solution with hydrogen peroxide, were 72% sulfate and 28% trithionate. This result agrees with the yields obtained for the oxidation with Liquor B at 4000 rpm (Table 25).

4.2.5 Thiosulfate Oxidation Kinetics

Kinetics of the noncatalytic inorganic sulfur oxidation in black liquor were studied at the temperature ($94^{o}C$ +/- $2^{o}C$) and pressure (1 atm. O_2) employed in this research. Rate expressions were determined at 2500 rpm and an oxygen flowrate of 1.2 lpm O_2 where it was demonstrated that the O_2 diffusional limitations were eliminated. The effect of black liquor on the relative rate of oxidation was studied as an independent variable.

It should be emphasized that all kinetic rate models presented in this thesis were found by empirical curve fitting. Due to the sheer complexity of the chemical composition of black liquor, it was not possible to obtain kinetic models from fundamental principles. In Section 4.2.7 of this thesis it is shown that caustic soda (NaOH) is one of the active liquor constituents involved in the thiosulfate oxidation kinetics.

From Figures 12 - 14 inclusively it is evident that the oxidation rate of thiosulfate is governed by two general phenomena. When the concentration of thiosulfate is between 0.5 gpl and 5.3 gpl, and where the rate of change of thiosulfate concentration with time is negative, equation (28) is applicable.

$$\frac{-d\,(S_2O_3^{2-})}{dt} = k_1 \;;\; S_2O_3^{2-} > 0.5 \text{ gpl} \qquad (28)$$

under the constraint: $d/dt(S_2O_3^{2-}) < 0$

When the concentration of thiosulfate is below 0.5 gpl equation (29) adequately describes the experimental results.

$$\frac{-d\,(S_2O_3^{2-})}{dt} = k_2(S_2O_3^{2-})^2; \quad S_2O_3^{2-} < 0.5 \text{ gpl} \qquad (29)$$

The kinetic rate constants for Liquor C are:

k_1 = 0.15 gpl/min.
k_2 = 0.768 $(\text{gpl}\cdot\text{min.})^{-1}$

Equation (28) implies that the rate of oxidation is independent of concentration, above 0.5 gpl of thiosulfate. Below 0.5 gpl the rate decelerates to the point where a second order dependence on the concentration of thiosulfate is found (equation 29).

The values for k_1, were obtained by performing a linear least squares regression on four sets of replicate data for each of Liquors B and C. This procedure was also carried out for one set of oxidation data for Liquor A (Table 6). The initial datum used represented the maximum thiosulfate concentration obtained during the experiment. The last datum used corresponded to the point where curvature was first encountered (at approximately 0.5 gpl) in the thiosulfate concentration/time profile.

In the region where there is curvature, least squares estimates of rate constants for first and second order kinetic rate models (in thiosulfate concentration) were found. For all three liquors a second order model (with kinetic rate constant k_2) provided a better fit than did a first order model. The methods that were used to calculate k_1 and k_2 are given by Levenspiel (1972).

Figures 13 and 14 compare the model predictions with experimental data for Liquors B and C respectively. The transition from zero to second order kinetics is indicated by the intersection of the dotted lines. In both cases the experimental data are in reasonable agreement with the kinetic rate expressions. The model is not applicable in the region where the rate of change of thiosulfate concentration with time is positive. In this research the production of thiosulfate from unoxidized inorganic sulfur species is not being considered.

Rate constants for the three liquors are presented in Table 26. The rate of thiosulfate oxidation is largest for Liquor B (Fig. 13) and smallest for Liquor A (Fig. 12). This is in accordance with the experimentally observed trends which show that the thiosulfate residence time is the lowest for Liquor B and highest for Liquor A. The difference in kinetic rate constants between liquors indicates that the rate of oxidation is very highly dependent on the specific characteristics of the liquor. An explanation for this may be that of stable foam formation. The excellent mass transfer characteristics of foam promotes oxygen uptake into the liquor. Large volumes of foam were noted for all experiments with Liquor B and hence, more mass transfer area per liquor volume in this case. Liquor A, on the other hand, was the least foamy, indicating a low bubble surface area relative to the other two liquors.

4.2.6 Sulfate Kinetics

Obtaining a suitable kinetic model for sulfate was difficult because there were no obvious trends in the sulfate concentration data, that might indicate a simple type of rate mechanism. For low concentrations of thiosulfate or long residence times, the sulfate concentration/time profile is nearly flat (Figs. 11, 15). The rate of sulfate production is independent of all liquor species concentrations during this time. For large thiosulfate concentrations and short residence times, the production rate of sulfate is high. The concentration/time profile is not linear, however. This indicates that the exponent of the thiosulfate concentration term should be a non-zero integer during this period. A model was sought that could account for:

i) the shift in reaction order;

ii) provide an adequate statistical fit of the experimental data;

iii) provide some general applicability for all three liquors.

Some of the expressions that were tested as potential rate models are listed below. The concentrations of thiosulfate, sulfate, and trithionate are denoted by A, B, and C respectively. Kinetic powers are labelled n, m, and p, and kinetic rate constants by k_3, k_4, and k_5. Levenspiel (1972) noted that equations (30), (33), and (34) describe reactions of shifting reaction order.

$$\frac{dB}{dt} = \frac{k_3A^n}{1 + k_4A^m} \tag{30}$$

$$\frac{dB}{dt} = k_3A^n \tag{31}$$

$$\frac{dB}{dt} = k_3A^n + k_4C^m \tag{32}$$

$$\frac{dB}{dt} = \frac{k_3A^n}{(1 + k_4A)^m} \tag{33}$$

$$\frac{dB}{dt} = \frac{k_3A^n}{1 + k_4A^m} + k_5C^p \tag{34}$$

It is obvious that equations (31) and (32) do not satisfy the criteria of shifting reaction orders with time. They were investigated to examine the magnitude of the lack of fit with the more sophisticated model forms (equations 30, 33, 34).

To obtain the best estimates of the kinetic parameters in the rate expressions a Hooke & Jeeves computer subroutine, developed by Mackinnon (1986), was used. The program was set up to allow the user to input a postulated model form and the number of parameters to be estimated. Concentration/time data of all variables appearing in the rate expression, and experimental rate data (which were acquired previously by numerical differentiation of sulfate concentration data), were inputted at the same time. Initial parameter estimates, the number of iterations, and step sizes were also set.

The program searched for the best estimates of the specified parameters. This was done by minimizing the sum of squares residuals associated with the rate expression that was tested. A printout of the experimental rate data, the model rate data, least squares parameter estimates, and sum of squares residuals was obtained. If the postulated model form did not fit another form was tested. This trial and error procedure was continued until a satisfactory model was found. Appendix 5 documents the methods used to treat replicate data, and a sample calculation procedure for the results from Liquor C.

As expected, equations (31) and (32) displayed gross inadequacy of fit. Equation (33) was slightly better but was still inadequate. Equations (30) and (34), however, predicted the rate data well. Both of these forms were subsequently tested with experimental data from all three liquors.

The model prediction from equation (34) was slightly better than equation (30). It was discarded, however, because consistent values of the parameters k_3 and p could not be obtained from replicate experiments. This showed that the extra term was not warranted in light of the experimental error associated with the data. The physical interpretation of this result is that the kinetics of the trithionate hydrolysis reaction producing sulfate (Equation 26) are negligibly slow. Consequently, all models with the exception of equation (30), were eliminated from further consideration.

The average values obtained for the kinetic orders n and m from equation (30) were 2.1 +/- 0.3 and 3.1 +/- 0.4 respectively, from two sets of four replicate runs. It would be reasonable to state that the kinetic orders could be represented by the integers 2 and 3 for n and m respectively in view of the experimental errors associated with the data. The exact form of equation (30) is then known with exception of the kinetic rate constants. These were calculated by searching only for the least squares estimates of the constants corresponding to the integer powers specified above. These constants are given in Table 27.

The kinetic rate model for the sulfate production in BLOX can then be represented by equation (35).

$$\frac{d(SO_4^{2-})}{dt} = \frac{k_3(S_2O_3^{2-})^2}{1 + k_4(S_2O_3^{2-})^3} \qquad (35)$$

under the constraints:

$$\frac{d(S_2O_3{}^{2-})}{dt} < 0 \quad \& \quad (S_2O_3{}^{2-}) > 0 \, . \tag{36}$$

The values of the kinetic parameters k_3 and k_4 for Liquor C are:

$$k_3 = 0.30$$
$$k_4 = 0.99$$

where the concentration of thiosulfate is given in grams per liter.

The model predicts the sulfate concentration in the time period where the rate of change of thiosulfate concentration with time is negative. The time required for quantitative thiosulfate conversion is denoted by the dotted vertical lines in Figs. 11 and 15 for Liquors C and B respectively.

The model predictions are compared with experimental data from Liquor B in Figs. 10 and 15 at 4000 rpm and 2500 rpm respectively. When the concentration of thiosulfate is greater than zero, the predictions are within +/- 3% of the experimental data. The model underpredicts the sulfate concentration after quantitative conversion of thiosulfate because the contribution from the trithionate hydrolysis is not considered.

Rate constants for sulfate kinetics from Liquor B in Table 27 indicate that the yield of sulfate is enhanced with liquor turbulence. At 4000 rpm k_4 is 0.49 compared with 0.65 at 2500 rpm. The lower value of k_4 at 4000 rpm decreases the denominator in equation (30) and increases the sulfate production rate. Similarly, k_4 for Liquor C is 0.99, which means that the sulfate rate is lower than for Liquor B. This is in accordance with experimental results which show that the time of oxidation for Liquor C is longer than that for Liquor B.

To evaluate if the model has general applicability, the following criteria were considered:

i) The rate model should predict the sulfate concentration data within acceptable error limits for all three liquors;

ii) The model should predict the sulfate concentration data in the limits (ie. where thiosulfate is a) large, b) zero, or c) approaching zero.)

In case i), the sulfate concentration data are well predicted for all three liquors. This is demonstrated in Figs. 11, 12, and 15, for Liquors C, A, and B respectively. The validity, or lack thereof, of the second criterion can be established by considering each of the three cases in the sequence in which they are listed.

iia) In this case the concentration of thiosulfate is between 3 - 5 gpl so that $k_4A^3 >> 1$. The model predicts:

$$\lim_{\text{large } A} \frac{dB}{dt} = \lim_{\text{large } A} \frac{k_3A^2}{1 + k_4A^3}$$

$$= \frac{k_3}{k_4A}$$

This result indicates that a plot of dB/dt vs. 1/A at large A or small 1/A should be linear. Figs. vi, vii, and viii in Appendix 5 show that the relationship between dB/dt and 1/A is linear for all three liquors.

iib) In the second case, where the thiosulfate concentration is zero, it follows that the rate of sulfate production should also be zero. The model predicts

$$\left\{\frac{dB}{dt}\right\}_{A = 0} = \left\{\frac{k_3A^2}{1 + k_4A^3}\right\}_{A = 0}$$

$$= 0/1 = 0$$

which agrees with the expected result.

iic) In the third case the concentration of thiosulfate is small but not zero (0.2 - 0.5 gpl).

$$\lim_{A\to 0}\left\{\frac{dB}{dt}\right\}$$

$$= \lim_{A\to 0}\left\{\frac{k_3A^2}{1 + k_4A^3}\right\}$$

$$= (k_3A^2) / (1 + 0) = k_3A^2$$

This expression exhibits second order kinetics which is consistent with the rate model obtained for thiosulfate kinetics. Both rate expressions predict second order kinetics in the specified concentration range of thiosulfate.

From the above discussion it would be reasonable to conclude that equation (30) is an accurate representation of the experimental data for sulfate production during black liquor oxidation.

4.2.7 Effect of NaOH on Black Liquor Oxidation

The pH of black liquor drops progressively during BLOX because of consumption of caustic soda (NaOH) through several competing reactions. Some of these are given by equations (25), (38), and (39).

$$Na_2S_2O_3 + 2NaOH + 2O_2 \rightarrow 2Na_2SO_4 + H_2O \qquad (25)$$
$$f(\text{organics}) + xO_2 \rightarrow y(\text{organic acids}) + zH_2O \qquad (37)$$
$$a(\text{organic acids}) + bNaOH \rightarrow c(\text{Na salts}) + dH_2O \qquad (38)$$
$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (39)$$

Fig. 16 illustrates the decrease of pH for Liquor C from 13.05 before an experiment to about 9.6 after 45 minutes of oxidation. A constant pH of 9.6 +/- 0.1 is observed thereafter. At this point the thiosulfate is quantitatively oxidized from solution (Table 28).

Table 29 shows that a similar trend exists for the pH of Liquor B. It drops from 12.8 before an experiment to 9.7 after 60 minutes, where the concentration of thiosulfate is zero. The reproducibility of the pH data for replicates (Fig. 16), and between liquors (Tables 28, 29), is evidence that a primary source of consumption of sodium hydroxide in BLOX is from the oxidation of sodium thiosulfate.

The role of NaOH in BLOX reactions was further investigated with a series of three experiments in which different concentrations of NaOH were initially added to the unoxidized liquor ("SODABLOX"). The objective was to determine if the specific NaOH concentration affects the ultimate yields of sulfate and trithionate after BLOX. In addition, the effect of incremental additions of NaOH on the relative rates of oxidation was examined.

In the first of these experiments (SODABLOX1), 5 gpl of NaOH was added to the unoxidized liquor. Results from this study (Fig. 17) show that both sulfate and trithionate are produced in SODABLOX1. A mass balance on inorganic sulfur is closed to within an average deviation of 3.2% (Table 30). The sulfate yield is 64% of the total inorganic sulfur. This is practically identical with the 62% obtained for BLOX.

The kinetic rate of thiosulfate oxidation, k_1, decreased 39% from 0.15 gpl/min. to 0.091 gpl/min. with SODABLOX1. It is interesting that the kinetics of thiosulfate oxidation appear to be zero order even below 0.5 gpl. Unlike BLOX (no chemical addition) there is no visible shift in reaction order below 0.5 gpl.

When the initial incremental addition of NaOH concentration was increased to 15 gpl (SODABLOX2), the rate of thiosulfate oxidation decreased to 0.0459 gpl/min. or just 30.6% of the BLOX value. From Fig. 18 it is apparent that the kinetics of thiosulfate oxidation are zero order for the entire concentration range of thiosulfate. The zero order dependence at low $S_2O_3^{2-}$ for both SODABLOX runs suggests that the thiosulfate kinetics are highly influenced by the specific concentration of NaOH.

From equation (25) two hydroxyl ions are consumed for each thiosulfate ion that is oxidized.

$$Na_2S_2O_3 + 2NaOH + 2O_2 \longrightarrow 2Na_2SO_4 + H_2O \tag{25}$$

This large consumption of sodium hydroxide might affect the kinetics of thiosulfate oxidation at low $S_2O_3^{2-}$. When the concentration of thiosulfate is reduced to 0.5 gpl for instance it is possible that the hydroxyl ion concentration is not sufficiently large to maintain a high rate of reaction for BLOX. This could be the cause of the deceleration of oxidation rate, which is manifested by an increase of kinetic order from zero to two.

In the final SODABLOX experiment, 28 gpl NaOH was added to the unoxidized liquor (SODABLOX3). The rate of thiosulfate oxidation was further reduced to 0.021 gpl/min. or 14% of the rate found for BLOX. Even after 140 minutes the thiosulfate oxidation reaction was not complete (Fig. 19).

Table 31 examines the effect of incremental additions of NaOH on the rate of thiosulfate oxidation. For Liquor A, the oxidation rate is reduced 64% when 5 gpl NaOH is added. A steady rate decline with increasing NaOH is also evident for the results from Liquor C. When the initial concentration of NaOH is increased from 12 to 17 gpl, k_1 decreases from 0.15 gpl/min. to 0.091 gpl/min. Further rate reductions are observed with higher initial concentrations of sodium hydroxide.

The SODABLOX study demonstrates that NaOH is consumed rapidly in the BLOX reactions. Despite additions of 5 and 15 gpl NaOH, no significant increase of postoxidation pH value was noted in comparison with conventional BLOX (Table 31). When 28 gpl NaOH was added, the pH of the liquor after oxidation was only 10.65.

The lower kinetic rate of thiosulfate oxidation in SODABLOX allows a closer inspection of the concentration/time profile of trithionate during the initial stages of oxidation. Figs. 17, 18, and 19 show that most of the thiosulfate that reacts in the first 30 minutes of oxidation forms trithionate and not sulfate. For residence times greater than 40 minutes the concentration of trithionate is fairly constant ranging from 3.0 to 3.5 gpl. It is interesting that the sulfate production rate increases sharply after the concentration of trithionate has reached a relatively stable value of 3.0 - 3.5 gpl (Figs. 17, 18). This suggests that the formation of trithionate is favored when the concentration of thiosulfate is large (2.5 - 5.2 gpl), but that sulfate is the predominant oxidation product at lower concentrations ($S_2O_3^{2-}$ < 2.5 gpl).

Although SODABLOX decelerates the sulfate and trithionate production rates, the ultimate yields of these constituents are not significantly affected. Table 25 shows that the sulfate yields are 64% and 62% for 5 gpl and 15 gpl NaOH additions respectively. In comparison, a sulfate yield of 62% is attained without any NaOH addition. The balance of the inorganic sulfur is in the form of trithionate. The average deviation with the mass balance on inorganic sulfur is 1.7% when 15 gpl NaOH is added (Table 32), and 7.1% with an incremental addition of 28 gpl NaOH (Table 33).

4.3 Catalyst Screening

Fallavollita (1984) has noted that an underlying drawback of the Fluid Bed Recovery Concept for the gasification of kraft black liquor lies in the degree of volatile sulfur compounds produced during pyrolysis. To minimize emission of these gases in the FBR it may be necessary to further oxidize sodium thiosulfate - the principal product of conventional black liquor oxidation - to a less volatile species such as sulfate.

Fones and Sapp (1960) showed that it was possible to quantitatively oxidize sodium thiosulfate to sodium sulfate at the elevated temperatures and pressures found in the digester. The liquor organics are very severely degraded under these harsh process conditions, however, resulting in a substantial loss of thermal value. Process conditions used in conventional BLOX (80°C - 100°C, 1 atm. total pressure) prevent excessive oxidation of lignaceous organic compounds, but conversion of sodium thiosulfate is much more difficult under these milder conditions. Utilization of a suitable catalyst in a conventional type BLOX process may accelerate the kinetics of the thiosulfate oxidation, and prevent the excessive organic breakdown that accompanies high pressure oxidation.

With this in mind a suitable catalyst for the oxidation of thiosulfate in weak kraft black liquor was sought. A variety of chemicals were investigated for this purpose by adding concentrations of 10 gpl to unoxidized Liquor A. The effect of these chemicals on the rate of thiosulfate oxidation was investigated at 1500 rpm. Concentration/time data were generated for thiosulfate, sulfate, sulfite, and oxalate. Concentrations of the organic ion, oxalate ($C_2O_4^{2-}$) were closely monitored in all experiments to investigate if oxidation and/or chemical addition contributed to its formation in aqueous solution.

The first chemical investigated was cupric chloride ($CuCl_2$). Beychok (1973) stated that "the use of $CuCl_2$ as a catalyst permits 100% of the sulfides to be oxidized to sulfates" at an air pressure of 72 psi (4.9 atmospheres). Fig. 20 compares the rate of thiosulfate oxidation without catalysis (Table 2), with data obtained with 10 gpl $CuCl_2$ (Table 34). The maximum thiosulfate concentration observed with the addition of $CuCl_2$ is 2.72 gpl. This represents about half of the concentration observed for the noncatalytic oxidation (5.2 gpl). It is probable that the true maximum of approximately 5.2 gpl (Fig. 20) is not observed because of the rapid sequential oxidation of thiosulfate immediately after being formed from other inorganic sulfur species (S^o, S^{2-}, S_x^{2-}).

When the concentration of thiosulfate is reduced below 1.5 gpl, no further acceleration of the rate is observed. The residence time required to reduce the concentration of thiosulfate to 0.43 gpl is 70 minutes. This is about the same time as that required for the noncatalytic oxidation. There does not appear to be much catalytic activity for the thiosulfate oxidation with $CuCl_2$, during the last 40 minutes of oxidation. This could be the result of catalytic oxidation of the organic fraction occurring at the same time.

Most of the product of oxidation with $CuCl_2$ is not sulfate; its concentration does not increase at all during the first 40 minutes. Based on closure of the noncatalytic inorganic sulfur mass balance (demonstrated in Section

4.2.4), it is probable that the remaining product of oxidation is in the form of trithionate.

The concentration of oxalate ($C_2O_4^{2-}$) increases from 1.18 gpl before oxidation to 2.11 gpl after 55 minutes with the addition of the cupric chloride (Table 34). The concentration of sulfite is steady at 0.2 gpl regardless of the residence time.

There was some evidence of catalytic oxidation of thiosulfate right at the beginning of oxidation with 10 gpl $CuCl_2$. Consequently, a second experiment with 5 gpl $CuCl_2$ was performed. With the 5 gpl addition, the rate of thiosulfate oxidation is slower than that for noncatalytic oxidation (Fig. 21). The concentration of sulfate does not increase at all even after 70 minutes of oxidation (Table 35). This study confirms that $CuCl_2$ is not a catalyst for the oxidation of thiosulfate in black liquor under the experimental conditions (2.4 lpm O_2, 1500 rpm, 96°C). In fact, Fig. 21 indicates that the kinetics of inorganic sulfur oxidation are actually decelerated, probably because $CuCl_2$ catalyzes oxidation of the organic fraction.

This last point highlights the difficulty of obtaining a suitable catalyst for the oxidation of thiosulfate in kraft black liquor. It is not sufficient that a chemical catalyze the global oxidation rate of kraft black liquor. Rather, it is necessary that it selectively catalyze the inorganic sulfur fraction in the liquor. Cupric chloride may be a thiosulfate oxidation catalyst under other conditions as Beychok (1973) claims. It is not for the case of black liquor under these conditions, however, because of the ease with which the organics are oxidized.

Bhatia et al. (1975) have found that activated carbon is a catalyst for the oxidation of thiosulfate in pure solutions of the sodium salt. Fig. 22 compares the rate of noncatalytic oxidation of thiosulfate with that obtained after an addition of 10 gpl activated charcoal. The two rates are within the expected experimental error of each other. The concentration of thiosulfate is reduced to 0.70 gpl after 68 minutes of oxidation. During this period the sulfate concentration increases from 4.55 to 7.24 gpl (Table 36). There is no evidence of any catalysis for the oxidation of thiosulfate.

With hydroquinone, a known sulfide oxidation catalyst, the rate of oxidation of thiosulfate is very slow. The thiosulfate concentration/time profile at any time after 10 minutes is practically flat (Fig. 23). The concentration of oxalate increases steadily throughout the experiment from 1.01 gpl to 2.10 gpl after 80 minutes of oxidation (Table 37).

Fig. 24 shows the effect of adding 10 gpl iron filings to the black liquor (Table 38). The rate of oxidation is lower than for noncatalytic oxidation. This is presumably because the chemical is used for the selective oxidation of the organic fraction. Similar trends are observed for additions of manganese (Fig. 25), cobaltous chloride (Fig. 26), and manganese dioxide (Fig. 27). Chen (1970) stated that manganese and cobaltous chloride ($CoCl_2$), catalyze the oxidation of aqueous sulfides.

An interesting feature of the screening experiments is the effect of the chemical on the concentration of oxalate. When manganese is added (Table 39), the concentration of oxalate increases from 1.38 gpl to 2.54 gpl after 81.5 minutes of oxidation. With the addition of cobaltous chloride (Table 40), a steady increase from 0.99 gpl to 2.26 gpl after 80 minutes is observed. When MnO_2 is added (Table 41) the concentration of oxalate increases from 1.21 gpl to 3.18 gpl after 70 minutes of oxidation. The cause of the increase of the oxalate concentration is not known. However, its production seems to be favored when the oxidation of the inorganic sulfur species is not. The simultaneous rise of the concentration of oxalate with the lower rate of thiosulfate oxidation suggests that the relative production rate of oxalate could be correlated with the extent of organic oxidation.

Fig. 28 illustrates the effect of an addition of 10 gpl nickel aluminum alloy (NiAl) on the rate of thiosulfate oxidation. The residence time for conversion of the thiosulfate concentration to 0.5 gpl decreases from 72 minutes for noncatalytic oxidation, to 42 minutes with the NiAl alloy (Table 42). When 5 gpl NiAl is initially added to the unoxidized black liquor (Fig. 29), the residence time for conversion of the thiosulfate concentration to 0.54 gpl is 50 minutes (Table 43). This is a significant reduction over the 72 minutes required for noncatalytic oxidation. The residence time decrease for both concentrations of NiAl is impressive in light of the effects that other chemicals had on the oxidation rate. Based on this early finding, NiAl offered considerable promise for the catalytic oxidation of thiosulfate in kraft black liquor.

Another interesting result from the oxidation with 10 gpl NiAl is the apparent instability of the oxalate ion. Its concentration gradually increases from 0.76 gpl to 1.46 gpl at 31 minutes (Table 42). It drops to 0.97 gpl at 35.5 minutes but then increases steadily to 1.34 gpl at 56.5

minutes. Instability of $C_2O_4^{2-}$ with oxidation is also apparent with an addition of 5 gpl NiAl. Its concentration drops from 1.10 gpl at 4.5 minutes to 0.68 gpl at 6.5 minutes (Table 43).

From Table 42 it is apparent that very little of the product of thiosulfate oxidation with 10 gpl NiAl is sulfate. It was initially thought that most of the inorganic sulfur product was in the form of trithionate. This hypothesis was verified in Section 4.4.

The concentration of thiosulfate is initially just 0.50 gpl with an addition of 10 gpl NiAl. In comparison, the initial concentration of thiosulfate in noncatalytic oxidation is approximately 2.7 gpl (Tables 2 - 7). The decrease of the thiosulfate concentration shows up as a proportional increase of the sulfite concentration. The initial concentration of sulfite is 1.71 gpl; its steady-state concentration is 0.27 gpl (Table 42). The difference of the two values is 1.44 gpl. This additional concentration of sulfite (1.44 gpl) is 2.02 gpl when expressed as the "thiosulfate total equivalent". Added to the 0.5 gpl $S_2O_3^{2-}$ initially present in solution, the total concentration of the thiosulfate is 2.52 gpl. This is within the acceptable experimental error (6.7%) of the expected thiosulfate concentration (2.7 gpl).

noncat. $S_2O_3^{2-}$ = 2.7 gpl
catalytic $S_2O_3^{2-}$ = 0.5 gpl
difference = 2.2 gpl

steady-state SO_3^{2-} = 0.27 gpl
catalytic SO_3^{2-} = 1.71 gpl
difference = 1.44 gpl

amount of sulfite as thiosulfate:

$$= 1.44 \times \frac{112.2}{80.1} = 2.02 \text{ gpl}$$

sum of all accountable $S_2O_3^{2-}$ = 0.50 + 2.02
= 2.52 gpl

$$\% \text{ error} = \frac{(2.52 - 2.7)}{2.7} \times 100 = -6.7\%$$

The calculation supports the idea that the NiAl addition may cause a chemical breakdown of thiosulfate to sulfite and elemental sulfur as depicted by equation (41).

$$S_2O_3^{2-} \rightarrow SO_3^{2-} + S^0 \qquad (41)$$

Table 44 presents particle size distributions and surface area measurements of the NiAl catalysts used in this research. The chemical composition of both catalysts used was 50% nickel and 50% aluminum by weight. They were obtained from BDH Laboratory Reagents in England.

Catalyst I was used for all catalytic oxidation experiments with Liquor A. Catalyst II was used in experiments for both Liquors B and C. Most of the weight fraction (40 wt.% - 45 wt.%) falls in the range of 63 to 90 microns (particle size diameter). Less than 3% of the catalyst particle size diameter is greater than 90 microns. It is evident from the low surface area data for Catalyst I (0.56 +/- 0.02 m^2/g) and for Catalyst II (0.43 +/- 0.02 m^2/g), that the NiAl alloy that was used in this research is not a catalyst for commercial application in its present state. Kirk and Othmer (1969) have stated that precipitated catalysts can be made from nickel carbonate and nickel hydroxide. A supported nickel catalyst of the precipitated or of the impregnated type might be commercially viable for the catalytic oxidation of sodium thiosulfate in weak kraft black liquors.

4.4 Catalytic Oxidation

4.4.1 Closure of Inorganic Sulfur Balance

Table 45 shows the effect of catalyst concentration and residence time, on the total sulfur content for Liquor B. Before oxidation the concentration of total sulfur is 5.3 +/- 0.2 gpl. At 123 minutes, the concentration of total sulfur is 5.2 +/- 0.1 gpl based on an average of eight experiments. This result demonstrates that no appreciable amount of inorganic sulfur is volatilized during the course of catalytic oxidation. Qualitatively, this study was verified by noting that there was no smell of sulfur gases from the reactor during any of the experiments performed.

Table 46 shows that a mass balance on inorganic sulfur is closed to within an average deviation of 1.6% with Liquor B, at a catalyst concentration of 10 gpl. The products of the catalytic thiosulfate oxidation with the NiAl alloy are trithionate and sulfate.

Table 47 presents concentration/time data for sulfate, thiosulfate, and trithionate with Liquor C at a catalyst concentration of 5 gpl NiAl. The sulfur balance is closed to within an average deviation of -3.7%. The average deviations with the total inorganic sulfur balance from replicate experiments with 5 gpl NiAl are 2.2% (Table 48), -1.3% (Table 49), and -2.3% (Table 50). Hence, a sulfur balance between successive catalytic oxidation experiments with Liquor C at 5 gpl NiAl is achieved. The replicate experiments (Tables 48, 49, 50) also illustrate that good reproducibility of the trithionate and sulfate concentration data is obtained.

4.4.2 Effect of Catalyst Concentration and Liquor on Oxidation Rate

From Fig. 29. it is evident that a catalyst concentration of 5 gpl NiAl accelerates the rate of oxidation of thiosulfate for Liquor A. To investigate if a similar catalytic effect can be reproduced between liquors, an experiment with 5 gpl NiAl was done for Liquor C. The results are shown in Fig. 30. Noncatalytic thiosulfate oxidation data are obtained from Table 23 and catalytic oxidation data are taken from Table 49. The residence time required to reduce the concentration of thiosulfate to 0.2 gpl is reduced from 40 minutes in noncatalytic oxidation, to 25 minutes with the use of 5 gpl NiAl.

Most of the reaction product in the early stages of oxidation is trithionate and not sulfate. The concentration of trithionate is initially zero in the unoxidized liquor. It increases to 3.36 gpl at 10 minutes (Table 49) and reaches a steady-state concentration of approximately 3.5 gpl after 60 minutes of oxidation. The concentration of sulfate rises sharply after 10 minutes (Fig. 30), where the concentration of trithionate remains nearly constant.

Fig. 31 shows the reproducibility of the thiosulfate concentration/time data with 5 gpl NiAl. In all four experiments the concentrations of thiosulfate fluctuate arbitrarily during the first 10 minutes of oxidation (Tables 47 - 50). This behavior could be attributed to the fact that the thiosulfate may be reacting to form sulfate and trithionate simultaneous with its formation from sulfide, hydrosulfide, and elemental sulfur. Until all of these intermediate species are converted, the periodic consumption and regeneration of thiosulfate cause the peculiar trends which are observed.

Fig. 32 shows sulfate and trithionate concentration data from replicate experiments (Tables 47 - 50). The concentration of trithionate with catalytic oxidation (about 3.8 gpl) is higher than that for noncatalytic oxidation (about 3.0 gpl). A possible explanation for this result is that the sulfite produced from equation (41) reacts with thiosulfate to form polythionates ($S_3O_6{}^{2-}$, $S_4O_6{}^{2-}$) according to equation (42).

$$S_2O_3{}^{2-} \rightarrow SO_3{}^{2-} + S^0 \qquad (41)$$

$$xSO_3{}^{2-} + yS_2O_3{}^{2-} \rightarrow zS_nO_6{}^{2-} \qquad (42)$$

Equation (42) could account for the rapid disappearance of sulfite and the accelerated oxidation of thiosulfate without a corresponding increase of the production rate of sulfate.

A sequence of experiments with lower catalyst concentrations was investigated in experiments with Liquor A. With an addition of 3 gpl NiAl (Fig. 33), the noncatalytic and catalytic thiosulfate oxidation profiles are nearly superimposed. The concentration of thiosulfate is reduced to 0.4 gpl in 63 minutes (Table 51), compared to 72 minutes without catalysis.

Figures 34 and 35 compare the oxidation rates with additions of 1.0 gpl NiAl and 0.5 gpl NiAl respectively. From Fig. 35 there does not appear to be any evidence of catalytic activity at 0.5 gpl NiAl. The slight acceleration observed in Fig. 34 with 1 gpl NiAl (Table 53), may be due to experimental errors. It would appear that the minimum catalyst concentration for any significant reduction in residence time is 5 gpl NiAl.

Experimental evidence from all three liquors indicates that the sulfate yield decreases with catalyst concentration. In the case of Liquor A, the sulfate concentration is 5.70 gpl after conversion of thiosulfate (Table 42), with 10 gpl NiAl. The concentration of sulfate increases to 7.33 gpl with 5 gpl NiAl (Table 43), and to 8.02 gpl with 3 gpl NiAl (Table 51). There is a further rise to 8.49 gpl SO_4^{2-} obtained with 1 gpl NiAl (Table 52). For the noncatalytic oxidation under similar process conditions (Table 6), the sulfate concentration is 8.60 gpl.

Fig. 36 indicates that a similar trend exists for catalytic oxidation with Liquor B. The effect is not as pronounced as that observed for Liquor A, however. As the catalyst concentration is increased from 3 gpl to 7 gpl (Tables 54 - 58 inclusively), the sulfate concentration decreases from 8.7 gpl to 8.5 gpl, after conversion of thiosulfate. In comparison, the noncatalytic ultimate sulfate concentration is 9.4 gpl. Fig. 37 shows that the sulfate concentration data for catalytic oxidation is reproducible. This sequence of results for Liquors A and B confirms earlier speculation that the catalytic oxidation of thiosulfate increases the production of trithionate.

Table 25 shows that the sulfate yield for Liquor A decreases progressively from 64% of the total inorganic sulfur product in noncatalytic oxidation, to 54% with an addition of 5 gpl NiAl. With a catalyst concentration of 10 gpl NiAl, only 42% of the oxidation product of thiosulfate is in the sulfate form. In experiments with Liquor B the sulfate yield decreases from 70% in noncatalytic oxidation to 65% with an addition of 3 gpl NiAl. A further yield reduction to 62% is noted with a catalyst concentration of 10 gpl.

In oxidation experiments with Liquor C, the sulfate yield decreases from 62% (noncatalytic) to 54% when 5 gpl of NiAl is added. In comparison the sulfate yields for Liquor A are 64% (noncatalytic) and 54% (with 5 gpl NiAl). Clearly the oxidation products of the thiosulfate oxidation are independent of the characteristics of the liquor.

Table 25 shows that the yield of trithionate for catalytic oxidation ranges from 40% (10 gpl NiAl, Liquor B) to 44% (5 gpl NiAl, Liquor C). The reader is reminded that the yields of trithionate were measured experimentally and not obtained by difference. The total inorganic sulfur calculated is always within an acceptable margin of error (+/- 4%).

Figure 38 illustrates the effect of catalyst concentration on the rate of thiosulfate oxidation for Liquor B. With additions of 3 gpl NiAl (Table 54) and 5 gpl NiAl (Table 55), no decrease in residence time for the conversion of $S_2O_3^{2-}$ to 0.5 gpl was noted. With a 7 gpl NiAl addition (Table 56), however, the residence time decreased from 25 minutes to 20 minutes. There is good reproducibility of the thiosulfate concentration data with an addition of 7 gpl NiAl (Fig. 39). When 10 gpl of NiAl is added (Table 46), a slight increase of the rate of oxidation is observed, but the residence time for conversion of thiosulfate is not significantly reduced. It is evident from this sequence of experiments that catalysis exhibited by the NiAl alloy for the oxidation of thiosulfate is highly dependent on the specific characteristics of the black liquor.

The effects of liquor, catalyst concentration, and rpm on the residence time for thiosulfate oxidation are compared in Table 59. Without any chemical addition the concentration of thiosulfate can be reduced to 0.5 gpl in 72 minutes for Liquor A, 26 minutes for Liquor B, and 35 minutes for Liquor C. This result emphasizes the importance of the characteristics of the liquor on the overall rate of oxidation.

The reader may recall that the effect of impeller rpm on the rate of oxidation was discussed with regards to noncatalytic oxidation experiments with Liquor B in Section 4.2. It was stated there that the O_2 diffusional limitations are eliminated at 2500 rpm with a baffle. No further increase of the rate of oxidation is observed above 2500 rpm with the baffle. This result is shown in Table 59.

The effect of catalyst concentration on the rate of oxidation varies with the characteristics of the liquor. With 5 gpl NiAl, a decrease of residence time from 72 to 50 minutes (a reduction of 31%) is possible for Liquor A. The residence time for Liquor C is reduced 29% (from 35 minutes to 25 minutes), also with 5 gpl NiAl. For Liquor B, however, no decrease of residence time is noted with an addition of 5 gpl NiAl. The residence time for Liquor B is reduced only 20% (from 25 minutes to 20 minutes), even with a catalyst concentration of 10 gpl NiAl. In comparison, a 42% decrease of the residence time is noted for oxidation of Liquor A with 10 gpl NiAl. Clearly black liquor is the most important parameter governing the rate of oxidation of sodium thiosulfate.

It has been shown that the rate of oxidation of thiosulfate is O_2 diffusion limited at 800 rpm (Fig. 9). To determine if the NiAl catalyst has any influence on the rate of oxidation in the diffusion regime, two oxidation experiments (one catalytic with 5 gpl NiAl, one noncatalytic), were performed at 800 rpm. Noncatalytic oxidation data (Table 60) are compared with the catalytic oxidation (Table 61) in Fig. 40. After a 50 minute residence time there is essentially no difference between the thiosulfate curves for the two cases. It is evident that the rate of oxidation in an O_2 - starved environment is not accelerated in the presence of the catalyst. Clearly, the NiAl catalyst does not selectively catalyze the oxidation of the inorganic sulfur fraction in the black liquor. This is not surprising if one considers that the concentration ratio of organic carbon to total sulfur from Table 1 is 57.6 / 5.3 = 10.9 for Liquor B.

The production rate of sulfate without the addition of NiAl is slightly lower than for noncatalytic BLOX. This is expected, however, based on results presented earlier in this thesis (Table 25).

4.5 Postulated Inorganic Sulfur Reaction Pathway

Black liquor oxidation involves a complicated series of organic/inorganic reactions whose mechanisms are difficult to elucidate. Prior to this study, the inorganic sulfur oxidation reaction pathway was thought to involve the reaction sequence denoted by equations (42) and (43).

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH \qquad (42)$$

$$Na_2S_2O_3 + 2NaOH + 2O_2 \rightarrow 2Na_2SO_4 + H_2O \qquad (43)$$

Results from this research have shown that this reaction scheme is incomplete and can be quite misleading. Equation (43) shows that sodium thiosulfate can be quantitatively oxidized to sodium sulfate in the presence of sodium hydroxide. This is true at the elevated temperatures (>100°C) and pressures (> 10 atm. air pressure), as noted by Naito et al. (1970). It is invalid at the process conditions normally employed in commercial black liquor oxidation practice however (80 - 100°C, 1 atm. total pressure). In this research it was demonstrated that sodium trithionate ($Na_2S_3O_6$) is a major product of black liquor oxidation with and without catalysis under these milder conditions.

Tan and Rolia (1985) showed that in pure alkaline solutions thiosulfate is partially oxidized to sulfate by equation (46).

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \qquad (46)$$

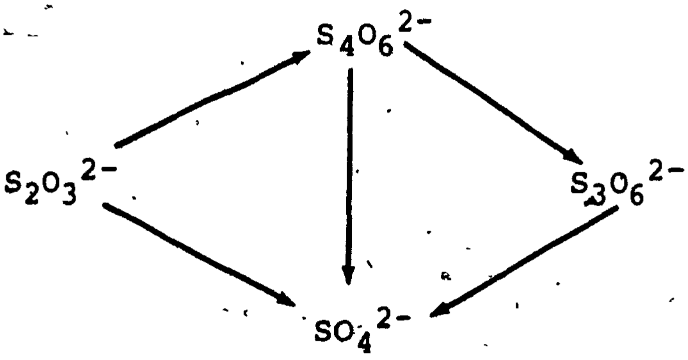
Equation (46) is interesting because it implies that NaOH is not directly reacting with thiosulfate as equation (43) suggests. Rather, the NaOH is depleted because it is consumed in the neutralization of acid generated with the thiosulfate oxidation. That is,

$$S_2O_3^{2-} + 2O_2 + H_2O \longrightarrow 2SO_4^{2-} + 2H^+ \qquad (46)$$
$$H^+ + OH^- \rightarrow H_2O \qquad (47)$$

The reaction mechanism which transforms thiosulfate to trithionate is not known. Oxidation of thiosulfate under standard BLOX process conditions may proceed through a complex series-parallel reaction network involving metastable sulfur oxyanions, including trithionate ($S_3O_6^{2-}$) and possibly tetrathionate ($S_4O_6^{2-}$). Chanda and Rempel (1985) studied the oxidation of thiosulfate by air at atmospheric pressure in pure salt solutions. They contend that the following reaction sequence is applicable for that reaction.

i) Tetrathionate and sulfate are directly produced from the oxidation of thiosulfate;
ii) Tetrathionate decomposes to form sulfate or trithionate;
iii) The trithionate could be further oxidized to sulfate given the right process conditions.

This reaction pathway is illustrated schematically as follows.



A similar reaction pathway may exist for the oxidation of thiosulfate in weak kraft black liquors. Rolia (1981) showed that trithionate ($S_3O_6^{2-}$) is stable in clear alkaline media, but tetrathionate ($S_4O_6^{2-}$) is not. Moreover, tetrathionate decomposes in seconds at pH > 10 to thiosulfate and trithionate through equation (47).

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad (47)$$

The validity of this observation was verified by Takizawa et al. (1973). This would suggest that the only resulting end products of the oxidation of thiosulfate in black liquor should be sulfate and trithionate. This was confirmed experimentally with consistent mass balances on inorganic sulfur, based on these two constituents, after conversion of thiosulfate. A possible reaction pathway governing the ultimate distribution of aqueous phase inorganic sulfur constituents after BLOX could then be given by the sequence of equations listed below.

$$S^{2-} + H_2O \rightarrow HS^- + OH^- \qquad (44)$$
$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \qquad (45)$$

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \qquad (46)$$

$$4S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 2S_4O_6^{2-} + 4OH^- \qquad (48)$$
$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad (47)$$
$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad (26)$$

The stoichiometry of equation (48) shows the oxidation of thiosulfate to produce tetrathionate. This reaction is given by Gilman et al. (1958).

Equations (44) and (45) show the oxidation of sulfide which is the predominant reaction in conventional BLOX. Equation (46) represents one of two paths for the production of sulfate. It is in parallel with the network of reactions denoted by equations (48), (47), and (26). These three reactions are in series with each other. They produce sulfate in parallel with equation (46), as the end product of the oxidation. That is,

i) thiosulfate reacts via equation (48) to produce tetrathionate;
ii) tetrathionate rapidly degrades to thiosulfate and trithionate in equation (47);
iii) hydrolysis of trithionate from equation (47) occurs in equation (26) to produce sulfate;
iv) thiosulfate produced in equation (47) can again react to produce sulfate directly in equation (46) or tetrathionate in equation (48);
v) this cycle continues until all the thiosulfate is depleted.

The ultimate product distribution is a function of the kinetic rate constants for each reaction, under the process conditions employed (temperature, agitation, catalyst concentration, and characteristics of the liquor).

4.6 Organic Oxidation

In this research the extent of organic oxidation was estimated on the basis of the thermal value (kJ / gram black liquor solids), and of the total organic carbon (TOC). Most of the decline of thermal value can be attributed to oxidation of the organic fraction to form a wide variety of acid forms. The energy value of these acidic derivatives is lower than the constituents from which they were formed. This results in a net reduction of the thermal value of the liquor.

Table 62 shows the effect of noncatalytic oxidation on thermal value for Liquor B after various extents of oxidation. Before oxidation, the thermal value is 12.5 +/- 0.4 kJ/g solids. It declines to 11.2 +/- 0.4 kJ/g after 26 minutes, where the concentration of thiosulfate is reduced to about 0.5 gpl. This decrease is 10.6 +/- 0.3% of the original heating value. The loss of thermal value from oxidation of inorganic sulfur species could not be calculated because of the complexity of the reaction pathway. After 117 +/- 4 minutes of oxidation, the thermal value is reduced to 10.7 +/- 0.1 kJ/g. This represents a relative decrease of 15.0 +/- 0.6%. After 180 minutes, the thermal value is reduced to 10.3 +/- 0.1 kJ/g, or by 17.6% of the original thermal value.

The effect of the catalytic oxidation with NiAl alloy on the loss of liquor thermal value is presented in Table 63. After conversion of thiosulfate at 28 minutes, the thermal value is 10.3 +/- 0.2 kJ/g. This is a 17.4 +/- 1.3% decrease of the original heating value. After 123 +/- 2 minutes of oxidation there is no change in thermal value. This indicates that the rate of organic oxidation is accelerated in the presence of the catalyst. It proves the validity of an earlier hypothesis that the NiAl catalyst is not selective for the oxidation of the inorganic sulfur fraction. The specific concentration of the catalyst does not seem to be significant in the decline of thermal value.

Table 64 shows the effect of oxidation with Liquor C on the concentration of the total organic carbon after various times. The effects of different initial chemical charges of catalyst and sodium hydroxide are also studied. Before oxidation the total organic carbon (TOC) is 64.8 +/- 1.5 gpl. After 122 +/- 2 minutes of noncatalytic oxidation the TOC is reduced to 63.8 +/- 0.9 gpl.

The concentration of carbonate increases from 18.1 +/- 0.5 gpl to 21.1 +/- 0.1 gpl after 122 +/- 2 minutes of noncatalytic oxidation. The carbonate may be formed from alkaline hydrolysis of unstable organic acids such as keto acids. These are produced during oxidation of carbohydrate degradation products, as given per equation (49).

$$RCOCOONa + NaOH \rightarrow RCHO + Na_2CO_3 \qquad (49)$$

Another possible explanation is that carbonate is produced from the reaction of CO_2 with NaOH given by equation (40).

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (40)$$

Caustic soda (NaOH) is initially present in a concentration of 12.0 +/- 0.1 gpl in the unoxidized liquor (Table 64). It decreases to 4.3 +/- 0.1 gpl after 122 +/- 2 minutes of noncatalytic oxidation. Part of the NaOH consumption may be from the reactions denoted in equations (49) and (40). The sodium hydroxide is also partially consumed in the neutralisation of various acids produced in the BLOX reactions.

For catalytic oxidation with 5 gpl NiAl, the TOC is reduced to 57.6 +/- 1.1 gpl after 124 +/- 4 minutes. The concentration of carbonate increases from 18.1 +/- 0.5 gpl to 22.1 +/- 0.1 gpl after oxidation. This does not fully account for the loss of organic carbon, however. The remainder of the carbon, probably exits with the off - gas as CO_2.

The presence of CO_2 in the off - gas was hypothesized based on observations from an oxygen analyzer, situated downstream of the reactor (Fig. 1). The difference between the $\%O_2$ registered and 100 (usually between 2 and 10%) is equal to the percentage of other gases liberated in the oxidation reactions. By a process of elimination, this gas is probably carbon dioxide because:

i) a total sulfur balance before and after oxidation is consistently closed (Tables 21, 45) indicating that it is not sulfur gas;

ii) the $\%O_2$ decreases with residence time (Fig. 41). This is probably because more CO_2 flows out of the reactor after longer reaction times, since less NaOH is left to retain it in solution.

From Table 65 the $\%O_2$ increased during the first 30 minutes of oxidation. This was the time required to completely flush the reactor and system lines of N_2 gas. The nitrogen was used to create an inert atmosphere above the liquor prior to the start of an experiment. After 30 minutes steady-state was attained; the $\%O_2$ noted there would also have been obtained during the first 30 minutes without the

N_2 flushing before an experiment. After 30 minutes the $\%O_2$ decreased, presumably because there was less sodium hydroxide remaining to retain the CO_2 in solution. More CO_2 was vented with the off - gas resulting in a lower $\%O_2$. After 70 to 80 minutes the $\%O_2$ value increased again. This was probably the time at which most of the organic oxidation was complete. This would result in less CO_2 formed, resulting in the larger $\%O_2$ that was observed.

As a check on the validity of the postulates made above, a sequence of three experiments at different initial concentrations of NaOH were performed (Table 64). As the concentration of initial NaOH added to the unoxidized liquor increased from 5 gpl to 28 gpl, the post-oxidation carbonate concentration increased from 23.0 gpl to 33.3 gpl. Despite additions of such large quantities of NaOH to the unoxidized liquor, very low concentrations of sodium hydroxide were found in the oxidized liquor products. This was evidence of an increased CO_2 retention effect when the alkalinity of the liquor was raised.

Fig. 41 compares the effects of noncatalytic oxidation, catalytic oxidation, and incremental caustic soda addition on the $\%O_2$ in the reactor off - gas. It is apparent that an increase of NaOH corresponds to an increased $\%O_2$ reading after a 30 minute residence time. This is to be expected because more CO_2 is retained in solution as carbonate.

In Section 4.3 of this thesis it was commented that a sudden decomposition of the organic ion oxalate ($C_2O_4^{2-}$) was found periodically during the course of oxidation. Figures 33 and 34, with additions of 3 gpl and 1 gpl NiAl respectively, show this phenomenon at approximately 25 minute residence times. It is possible that such behavior is observed because oxalate is oxidized to carbonate as shown in equation (50).

$$C_2O_4^{2-} + 2OH^- + [O] \longrightarrow 2CO_3^{2-} + H_2O \qquad (50)$$

Equation (50) would be a second explanation for the increase of the concentration of carbonate with the initial NaOH present in solution (Table 64).

5. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

5.1 Conclusions

In this research it was found that sodium trithionate ($Na_2S_3O_6$) is a major product of the oxidation of sodium thiosulfate in weak kraft black liquors. Based on trithionate as an intermediate the mass balance on inorganic sulfur, after conversion of thiosulfate, was closed. This is the first time in the published literature that closure of the mass balance on inorganic sulfur has been demonstrated after black liquor oxidation.

The oxidation of sodium thiosulfate was studied without catalysis (Section 4.2), with caustic soda addition (Section 4.2), and with catalysis (Section 4.4). It was shown for all three cases that quantitative oxidation of sodium thiosulfate is feasible with the current commercial BLOX conditions employed (80°C - 100°C, 1 atmosphere total pressure). Sodium trithionate accounts for between 25% and 35% of the oxidation product. The remainder (65% - 75%) is in the sulfate form. The precise distribution of these products depends on the specific characteristics of the liquor, agitation, and concentration of the catalyst. The product distribution is not affected by the concentration of the sodium hydroxide in solution.

A series of screening experiments showed that a nickel aluminum alloy (50% nickel, 50% aluminum), is an effective catalyst for the oxidation of thiosulfate in weak kraft black liquor. A catalyst concentration of 5 gpl can reduce the residence time for the thiosulfate oxidation between 30% and 40%. Catalytic oxidation of thiosulfate increases the production of trithionate.

The oxidation of thiosulfate is highly influenced by the characteristics of the liquor. Qualitatively, the rate of oxidation appears to increase with the amount of stable foam formation that is formed with agitation of the liquor. The global oxidation rate of black liquor changes from O_2 diffusion control to kinetic control above 1500 rpm.

Kinetic rate equations (obtained empirically) have been deduced for both the thiosulfate and sulfate constituents for noncatalytic oxidation at the process conditions employed in this research (94^oC +/- 2^oC, 1 atmosphere pressure). The forms of the rate models are not affected by the specific characteristics of the liquor.

The rate of oxidation of thiosulfate decelerates with an increase of the concentration of sodium hydroxide in the unoxidized liquor. When the concentration of NaOH is present in sufficient excess over stoichiometric requirement (equation 25), the kinetics of oxidation are adequately represented by equation (28) for the entire concentration range of thiosulfate.

$$Na_2S_2O_3 + 2NaOH + 2O_2 \rightarrow 2Na_2SO_4 + H_2O \qquad (25)$$

$$\frac{-d\,(S_2O_3^{\,2-})}{dt} = k_1 \qquad (28)$$

under the constraint: $d/dt(S_2O_3^{\,2-}) < 0$

If the initial concentration of NaOH is not in sufficient excess of the stoichiometric requirement (equation 25), then the rate of thiosulfate oxidation is decelerated below 0.5 gpl $S_2O_3^{\,2-}$. In that case the kinetics of thiosulfate oxidation are adequately represented by a second order dependence on thiosulfate concentration below 0.5 gpl $S_2O_3^{2-}$ (equation 29).

That is,

$$\frac{-d(S_2O_3^{2-})}{dt} = k_2(S_2O_3^{2-})^2 \qquad (29)$$

under the constraints:

$$\frac{d(S_2O_3^{2-})}{dt} < 0 \quad ; \quad S_2O_3^{2-} < 0.5 \text{ gpl}$$

The rate of sulfate production in kraft black liquor is adequately represented by equation (30).

$$\frac{d(SO_4^{2-})}{dt} = \frac{k_3(S_2O_3^{2-})^2}{1 + k_4(S_2O_3^{2-})^3} \qquad (30)$$

under the constraints:

$$\frac{d(S_2O_3^{2-})}{dt} < 0 \quad \& \quad (S_2O_3^{2-}) > 0$$

The concentration of the total organic carbon decreases after black liquor oxidation. This is because some of the carbon is oxidized to form carbon dioxide. This CO_2 can subsequently be reabsorbed by the alkaline black liquor to form sodium carbonate (equation 40).

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (40)$$

As a result, sodium hydroxide is consumed from the oxidation of inorganic sulfur species (equation 25) and from production of sodium carbonate (equation 40). Some sodium hydroxide is also consumed from neutralisation of a variety of organic based acids which are produced on oxidation. This results in a decline of the pH of the liquor from 13 to about 9.7 after conversion of thiosulfate.

Quantitative oxidation of thiosulfate in kraft black liquor results in a significant drain on the thermal value of the liquor. Without catalysis the decrease of the thermal value is about 11%; after catalytic oxidation the thermal value is reduced by about 18%. The nickel aluminum alloy would appear to be a catalyst for the global oxidation rate of black liquor. It is not selective for the inorganic sulfur fraction in the liquor.

5.2 Recommendations for Future Work

In this research it was shown that black liquor is the most important variable in the study of thiosulfate oxidation. The rates of oxidation of thiosulfate were quite variable between liquors. This was thought to be attributable to the extent of stable foam formation which is generated with agitation. Any future work in this area should therefore concentrate on the effects of physical parameters, such as surface tension, viscosity, and specific gravity, on the rate of thiosulfate oxidation. Intuitively, it would appear that the surface tension is a critical parameter in this regard.

The effect of surface tension on rates of oxidation could be investigated by adding different varieties and concentrations of surfactants to an unoxidized liquor. The effects of such surfactants on the kinetics and the product distribution of inorganic sulfur constituents could then be examined. A second sequence of experiments could focus on the relative effect of kraft black liquor from different mills on the rate of thiosulfate oxidation and the product yields of sulfate and trithionate.

Another area that could be explored is the effect of temperature and pressure on the yields of sulfate and trithionate. This could be studied for both noncatalytic and catalytic oxidation, with the NiAl alloy catalyst. Optimal process conditions for accelerating the oxidation kinetics of thiosulfate, maximizing the sulfate yield, and minimizing organic oxidation degradation, could then be identified.

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Table 1 : Properties of Hardwood Kraft Black Liquor before Oxidation[1]

Property	Liquor			Standard Deviation
	A	B	C	
Solids (wt. %)	17.0	15.9	16.6	0.2
Total sulfur (gpl)	5.4	5.3	5.1	0.2^p
Total sodium (gpl)	38.5	39.3	38.0	1.8^p
NaOH (gpl)	7.2	9.0	12.0	0.1
TOC[2] (gpl)	61.6	57.6	65.5	1.5
Total Calcium (mg/l)	NA	21.8	NA	4.7
S^{2-} (gpl)	0.5	NA	NA	<0.1
SO_4^{2-} (gpl)	4.6	4.6	4.0	0.2^p
CO_3^{2-} (gpl)	NA	14.3	18.1	0.5
pH	12.9	12.9	13.0	0.2^p

* NA data not available

** p represents pooled standard deviation estimates

1. Weak black liquor taken from brown-stock washers from Domtar's hardwood kraft mill in Cornwall, Ontario
2. Total organic carbon

Table 2 : Noncatalytic BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 100°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	0.27	4.58	1.06	2.71
2.5	0.20	4.62	1.08	4.45
4.5	0.17	4.58	1.10	5.20
5.0	0.17	4.54	1.10	5.09
5.5	0.27	4.57	1.14	4.81
7.0	0.29	4.57	1.20	4.82
9.5	0.28	4.66	1.25	4.85
11.5	0.35	4.81	1.35	4.55
14.0	0.36	4.81	1.38	4.39
17.0	0.36	4.91	1.43	4.29
20.0	0.39	4.93	1.44	4.09
23.0	0.38	4.92	1.46	3.75
26.5	0.38	5.07	1.48	3.45
35.5	0.36	5.53	1.59	2.83
43.0	0.28	5.93	1.20	2.25
52.0	0.21	6.63	1.24	1.29
64.0	0.20	7.50	1.38	0.64
72.0	0.20	7.62	1.41	0.48

* All ionic species concentrations in grams per liter (gpl)

Table 3 : Noncatalytic BLOX for Liquor A (2.4 lpm O_2, 2500 rpm, 95^{o}C)

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
2.0	0.17	4.80	4.00
7.0	0.16	4.50	4.00
10.5	0.17	4.60	4.00
13.5	0.18	5.10	4.25
26.0	0.18	5.40	3.45
41.0	0.19	7.00	2.45
53.0	0.14	7.30	1.35
62.0	0.14	7.30	1.10
71.0	0.14	7.80	0.55
108.0	0.14	8.10	nil

* All ionic species concentrations in grams per liter (gpl)

Table 4 : Noncatalytic BLOX for Liquor A (1.2 lpm O_2, 800 rpm, 100°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
0.0	0.18	4.95	2.75
0.5	0.18	4.99	2.81
2.0	0.19	4.47	3.80
13.0	0.22	4.55	4.90
16.0	0.22	4.61	4.91
19.0	0.22	4.72	5.03
26.0	0.23	4.75	5.05
33.0	0.22	4.86	4.92
57.0	0.21	4.31	4.56
96.0	0.22	4.59	4.64
141	0.21	4.70	4.35
164	0.21	4.75	4.16
189	0.21	5.57	3.93

* All ionic species concentrations in grams per liter (gpl)

Table 5 : Noncatalytic BLOX for Liquor A (1.2 lpm O_2, 1500 rpm, 100°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
0.0	0.16	4.90	2.65
2.5	0.17	4.60	2.95
4.5	0.18	4.60	3.05
6.5	0.14	4.60	3.90
8.0	0.18	4.70	5.20
9.0	0.13	4.60	5.35
10.0	0.15	4.60	5.30
11.5	0.20	4.60	5.20
15.5	0.18	4.60	4.90
24.0	0.20	4.80	4.45
28.0	0.22	4.85	3.95
33.5	0.20	5.10	3.50
44.0	0.21	6.80	1.85
63.0	0.16	8.20	0.50
73.0	0.18	8.60	0.35

* All ionic species concentrations in grams per liter (gpl)

Table 6 : Noncatalytic BLOX for Liquor A (1.2 lpm O_2, 2500 rpm, 100°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	0.15	4.58	1.31	2.72
3.0	0.15	4.63	1.32	3.81
5.0	0.15	4.60	1.33	5.06
7.8	0.15	4.39	1.30	5.06
10.8	0.15	4.69	1.46	5.25
14.0	0.15	4.77	1.55	5.17
17.8	0.15	4.81	1.63	5.02
23.5	0.15	4.95	0.80	4.62
29.5	0.15	5.05	0.83	4.19
35.8	0.15	5.48	2.04	3.50
41.5	0.15	5.85	2.07	2.90
46.5	0.15	6.47	2.22	2.14
52.3	0.15	7.22	2.36	1.46
57.8	0.15	7.90	2.50	0.98
70.0	0.15	8.30	1.08	0.68

* All ionic species concentrations in grams per liter (gpl)

Table 7 : Noncatalytic BLOX for Liquor A Replicate 1 (2.4 lpm O_2, 1500 rpm, 90°C)[1]

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
2.0	0.30	4.50	2.73
4.0	0.45	4.55	2.95
5.5	0.45	5.30	3.10
7.0	0.20	4.50	5.00
8.0	0.25	4.40	5.10
9.0	0.30	4.55	5.15
9.3	0.30	4.50	5.35
11.5	0.30	4.50	4.95
13.5	0.35	4.60	4.85
15.0	0.40	4.50	4.60
17.5	0.42	4.65	4.30
19.0	0.40	4.70	4.25
21.5	0.40	4.65	4.10
28.0	0.40	5.00	3.35
41.0	0.25	6.92	2.25
51.0	0.25	7.92	1.65

* All ionic species concentrations in grams per liter (gpl)

1. Replicate of Table 2

Table-8 : Noncatalytic BLOX for Liquor B (1.2 lpm O_2, 800 rpm, 95°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[1]	% diff.[2,3]
0.0	4.60	4.76	12.7	
1.6	4.58	4.91	13.0	
3.1	4.52	5.04	13.1	
5.0	4.53	5.21	13.5	
8.6	4.57	5.04	13.2	-2.3
12.3	4.92	5.05	13.6	0.8
15.3	4.66	4.91	13.1	-3.3
20.3	4.60	4.76	12.7	-5.6
26.1	4.68	4.73	12.8	-5.4
30.6	4.69	4.39	12.2	-9.7
35.4	4.66	4.29	12.0	-11.1
41.2	4.86	4.24	12.1	-10.3
46.1	5.04	4.13	12.1	-10.4
51.1	5.15	3.70	11.5	-15.0
55.7	5.17	3.74	11.6	-14.3
60.3	5.49	3.53	11.5	-14.6
70.8	5.51	3.12	10.8	-19.7
80.3	5.72	2.55	10.1	-25.3
95.2	6.35	2.01	9.8	-27.5

* All ionic species concentrations in grams per liter (gpl)

1. Total equivalent sulfate is the measured sulfate plus the measured thiosulfate as sulfate
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 9 : Noncatalytic BLOX for Liquor B Replicate 1 (1.2 lpm O_2, 800 rpm, 95^oC)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[2]	% diff.[3,4]
0.0	4.58	4.59	12.4	
1.6	4.60	5.20	13.5	
3.3	4.48	5.29	13.5	
4.8	4.45	5.36	13.6	
7.6	4.45	5.17	13.3	
15.9	4.49	4.81	12.7	-5.8
20.1	4.65	4.87	13.0	-3.9
30.2	4.78	4.59	12.6	-6.5
40.2	4.92	4.07	11.9	-12.0
50.1	5.15	3.49	11.1	-17.6
60.1	5.44	3.02	10.6	-21.5
70.6	6.22	2.96	11.3	-16.4
80.1	6.10	2.24	9.9	-26.4
95.8	6.28	1.62	9.1	-33.0

---

* All ionic species concentrations in grams per liter (gpl)

[1] Replicate of Table 8

[2] Inorganic sulfur expressed as sulfate (gpl)

[3] % deviation with inorganic sulfur balance on sulfate basis

[4] Expected inorganic sulfur as sulfate = 13.5 gpl

Table 10 : Noncatalytic BLOX for Liquor B-Replicate 2 (1.2 lpm O_2, 800 rpm, 95°C)[1]

time (min.)	SO_4^{2-} *	$S_2O_3^{2-}$ *	(SO_4^{2-}) total equivalent[2]	% diff.[3,4]
0.0	4.47	4.78	12.6	
1.8	4.43	5.09	13.1	
3.1	4.48	5.30	13.5	
7.6	4.37	5.02	13.0	
10.9	4.48	5.23	13.4	
15.3	4.42	4.95	12.9	-4.6
20.1	4.31	4.60	12.2	-9.8
31.3	4.65	4.28	12.0	-11.3
40.3	5.14	4.05	12.1	-10.6
50.3	4.98	3.58	11.1	-17.8
60.2	5.40	3.15	10.8	-20.1
70.3	5.72	2.94	10.7	-20.4
80.2	6.19	2.42	10.3	-23.5
99.3	6.32	1.71	9.2	-31.5

---

* All ionic species concentrations in grams per liter (gpl)

[1] Replicate 2 of Table 8

[2] Inorganic sulfur expressed as sulfate (gpl)

[3] % deviation with inorganic sulfur balance on sulfate basis

[4] Expected inorganic sulfur as sulfate = 13.5 gpl

Table 11 : Noncatalytic BLOX for Liquor B (1.2 lpm O_2, 1500 rpm, 94°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[1]	% diff.[2,3]
0.0	4.81	3.24	10.4	
1.8	4.62	4.75	12.7	
3.2	4.63	4.71	12.7	
4.4	4.78	4.58	12.6	-6.6
10.4	5.01	4.20	12.2	-9.7
20.2	5.85	2.43	10.0	-25.9
30.4	7.71	1.01	9.4	-30.1
40.2	8.46	0.29	9.0	-33.7
50.1	8.96			-33.6
60.8	8.72			-35.4
70.3	9.07			-32.8
80.4	9.01			-33.3
90.4	8.72			-35.4
100.1	8.73			-35.3
110.4	8.69			-35.6

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* All ionic species concentrations in grams per liter (gpl)

1. Inorganic sulfur expressed as sulfate (gpl)
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 12 : Noncatalytic BLOX for Liquor B (1.2 lpm O_2, 2000 rpm, 95°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[1]	% diff.[2,3]
0.0	4.60	2.77	9.4	—
1.8	4.63	4.80	12.8	
2.8	4.68	4.56	12.5	
4.2	4.41	4.75	12.5	-7.2
5.9	4.76	4.60	12.6	-6.5
15.3	5.10	3.33	10.8	-20.0
25.4	6.95	1.46	9.4	-30.0
37.0	8.35	0.20	8.7	-35.6
45.6	8.90			-34.1
55.2	8.95			-33.7
65.8	9.03			-33.1
75.5	8.77			-35.0
85.2	8.89			-34.1
95.3	8.89			-34.1
112.2	9.10			-32.6

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* All ionic species concentrations in grams per liter (gpl)

1. Inorganic sulfur expressed as sulfate (gpl)
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 13 : **Noncatalytic BLOX for Liquor B (1.2 lpm O_2, 2500 rpm, 95°C)**

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[1]	% diff.[2,3]
0.0	4.87	2.79	9.6	
1.6	4.43	4.88	12.8	
3.4	4.72	5.25	13.7	
4.9	4.70	4.62	12.6	-6.7
10.4	5.30	4.07	12.3	-9.2
20.2	6.73	2.23	10.5	-21.9
30.2	8.45	0.47	9.3	-31.5
40.9	8.64	0.25	9.1	-32.8
50.2	9.13			-32.4
60.3	8.73			-35.3
70.3	8.80			-34.8
80.2	9.01			-33.3
90.2	9.30			-31.1
100.4	9.70			-28.1
115.1	9.69			-28.1

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* All ionic species concentrations in grams per liter (gpl)

1. Inorganic sulfur expressed as sulfate (gpl)
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 14 : Noncatalytic BLOX for Liquor B (1.2 lpm O_2, 2500 rpm, baffle, 94°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[1]	% diff.[2,3]
0.0	4.42	2.79	9.2	
1.4	4.51	4.25	11.8	
2.6	4.67	4.36	12.2	
3.8	4.69	3.89	11.3	-16.1
5.5	4.75	3.69	11.1	-18.1
10.6	5.78	2.98	10.9	-19.4
15.2	6.94			
20.9	8.18	0.80	9.5	-29.3
25.9	9.16	0.34	9.7	-27.8
50.2	9.65			-28.5
80.5	9.61			-28.8
110.4	9.68			-28.3
140.1	9.65			-28.5
180.2	10.0			-25.9

* All ionic species concentrations in grams per liter (gpl)

1. Inorganic sulfur expressed as sulfate (gpl)
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 15 : Noncatalytic BLOX for Liquor B Replicate 1 (1.2 lpm O_2, 2500 rpm, baffle, 95°C)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[2]	% diff.[3,4]
0.0	4.62	4.81	12.8	
1.9	4.59	5.12	13.3	
3.6	4.79	4.80	13.0	
7.6	5.02	4.18	12.2	-9.9
11.2	5.48	3.59	11.6	-13.9
16.1	6.67	2.12	10.3	-23.7
20.1	7.73	1.45	10.2	-24.4
25.6	8.50	0.48	9.3	-31.0
30.3	8.73			-35.3
35.1	8.98			-33.5
40.0	9.15			-32.2
60.0	9.66			-28.4
80.8	9.16			-32.1
120.3	9.63			-28.7

* All ionic species concentrations in grams per liter (gpl)

1. Replicate 1 of Table 14
2. Inorganic sulfur expressed as sulfate (gpl)
3. % deviation with inorganic sulfur balance on sulfate basis
4. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 16 : Noncatalytic BLOX for Liquor B Replicate 2 (1.2 lpm O_2, 2500 rpm, baffle, 95°C)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[2]	% diff.[3,4]
0.0	4.65	4.05	11.6	
1.5	4.68	4.47	12.3	
3.1	4.74	4.07	11.7	
4.8	4.86	4.04	11.8	-12.8
8.8	5.25	3.62	11.4	-15.3
12.6	5.56	2.61	10.0	-25.8
16.0	6.39	1.98	9.8	-27.6
20.1	7.27	1.18	9.3	-31.2
25.2	8.29	0.46	9.1	-32.8
30.9	8.90	0.25	9.3	-30.9
40.3	9.23			-31.6
60.1	9.42			-30.2
84.4	9.44			-30.1
100.3	9.39			-30.4
121.6	9.62			-28.7

* All ionic species concentrations in grams per liter (gpl)

1. Replicate 2 of Table 14
2. Inorganic sulfur expressed as sulfate (gpl)
3. % deviation with inorganic sulfur balance on sulfate basis
4. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 17 : Noncatalytic BLOX for Liquor B Replicate 3 (1.2 lpm O_2, 2500 rpm, baffle, 94°C)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[2]	% diff.[3,4]
0.0	5.76	3.18	11.2	
1.9	4.82	4.86	13.1	
3.3	4.79	4.68	12.8	
4.8	4.75	4.40	12.3	-9.1
10.3	5.41	3.64	11.6	-13.8
15.2	6.86	2.06	10.4	-23.1
20.8	8.20	0.76	9.5	-29.6
25.2	8.85	0.35	9.4	-30.0
50.3	9.18			-32.0
70.1	9.37			-30.6
110.1	9.75			-27.8
130.1	9.76			-27.7
150.3	9.99			-26.0

* All ionic species concentrations in grams per liter (gpl)

1. Replicate 3 of Table 14
2. Inorganic sulfur expressed as sulfate (gpl)
~~3.~~ % ~~deviation~~ with inorganic sulfur balance on sulfate basis
4. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 18 : Noncatalytic BLOX for Liquor B (1.2 lpm O_2, 3200 rpm, baffle, 96°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	(SO_4^{2-}) total equivalent[1]	% diff.[2,3]
0.0	4.96	2.88	9.9	
2.3	5.19	5.21	14.0	
4.1	5.38	4.95	13.8	
6.1	5.45	4.45	13.1	-3.3
10.1	6.11	3.64	12.3	-8.6
14.2	6.69	2.64	9.3	-17.0
18.1	7.61	1.79	10.7	-21.0
22.4	8.70	1.13	10.6	-21.2
26.1	9.12	0.49	10.0	-26.2
40.0	9.96			-26.2
80.0	10.4			-23.0
120.1	10.3			-23.7

* All ionic species concentrations in grams per liter (gpl)

1. Inorganic sulfur expressed as sulfate (gpl)
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 19 : Noncatalytic BLOX for Liquor B (1.2 lpm O_2, 4000 rpm, baffle, 95°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[1]	%diff.[2,3]
0.0	4.48	4.01	NA	NA	NA
2.3	4.55	5.24	NA	NA	NA
4.5	4.90	4.53	NA	NA	NA
6.5	5.21	4.21	NA	NA	NA
10.3	5.71	3.38	NA	NA	NA
14.5	6.47	2.24	NA	NA	NA
18.3	7.79	1.29	NA	NA	NA
22.3	8.51	0.71	NA	NA	NA
26.4	8.67	0.55	NA	NA	NA
30.3	9.41	0.15	NA	NA	NA
60.4	9.66		2.65	13.6	0.7
90.6	9.83		2.50	13.6	0.7
120.1	9.60		2.19	12.9	-4.4
150.1	9.66		2.05	12.7	-5.9
180.1	9.80		1.96	12.7	-5.9
210.2	10.0		1.96	12.9	-4.4
240.6	10.3		1.88	13.1	-3.0
				ave.	-3.2

*All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Inorganic sulfur expressed as sulfate (gpl)
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 20 : Noncatalytic BLOX for Liquor C (1.2 lpm O_2, 2500 rpm, baffle, 96°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[1]	%diff.[2,3]
0.0	4.07	2.54	0	NA	NA
1.5	3.94	4.29	0	NA	NA
3.1	4.22	4.84	NA	NA	NA
4.6	4.06	4.47	NA	NA	NA
10.1	4.25	3.79	NA	NA	NA
15.0	4.48	3.33	2.25	13.5	4.7
20.6	5.08	2.70	1.64	12.2	-5.4
25.3	5.81	1.76	2.01	11.8	-8.5
35.4	7.14	0.48	2.47	11.7	-8.5
45.4	7.55	0.24	2.59	11.8	-8.5
55.3	8.22		2.44	11.9	-7.8
65.2	8.20		2.94	12.6	-2.3
75.6	8.15		2.11	11.3	-12.4
91.7	8.29		2.58	12.2	-5.4
123.3	8.44		2.33	11.9	-7.8
				ave.	-6.2

*All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Inorganic sulfur expressed as sulfate (gpl)
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 21: Effect of Noncatalytic Oxidation on Total Sulfur (1.2 lpm O_2, 2500 rpm, baffle, 95°C)

Sample[1]	Time (min.)	Total Sulfur (gpl)	$S_2O_3^{2-}$ (gpl)
1	0	5.14	2.63
2	0	5.26	
3	0	5.47	
4	0	5.28	
5	0	5.36	
6	0	5.36	
average	0	5.3 +/- 0.2	2.63
T	26	5.4	0.50
V	26	5.4	
average	26	5.4	0.50
K	112	5.7	0.00
L	115	5.7	
M	110	5.7	
P	120	5.5	
R	121	5.3	
S	120	5.2	
T	121	5.6	
V	120	5.4	
average	117 +/- 4	5.5 +/- 0.2	0.00
N	180	5.7	0.00

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[1] Black liquor samples taken from noncatalytic experiments at different times

Table 22 : Noncatalytic BLOX for Liquor C Replicate 1 (1.2 lpm O_2, 2500 rpm, baffle, 96°C)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[2]	%diff.[3,4]
0.0	3.89	2.63	0	NA	NA
1.5	3.96	4.40	NA	NA	NA
4.5	4.09	4.29	1.54	13.7	6.2
12.3	4.31	3.55	NA	NA	NA
17.1	5.10	2.75	1.82	12.5	-3.1
20.8	5.41	1.97	2.76	12.9	0.0
25.5	6.29	1.28	2.22	11.8	-8.5
30.3	6.89	0.59	3.38	13.0	0.8
35.3	7.27	0.45	3.18	12.8	-0.8
40.2	7.71	0.16	3.35	13.0	0.8
45.3	7.75		2.75	11.9	-7.8
50.1	7.87		2.79	12.1	-6.2
60.1	7.83		3.15	12.6	-2.3
82.5	7.72		2.99	12.2	-5.4
100.1	7.87		2.80	12.1	-6.2
142.5	8.27		2.96	12.7	-1.6
				ave.	-2.6

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*All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Replicate 1 of Table 20
2. Inorganic sulfur expressed as sulfate (gpl)
3. % deviation with inorganic sulfur balance on sulfate basis
4. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 23 : Noncatalytic BLOX for Liquor C Replicate 2 (1.2 lpm O_2, 2500 rpm, baffle, 96°C)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[2]	%diff.[3,4]
1.1	4.04	4.09	NA	NA	NA
2.1	4.01	5.23	NA	NA	NA
3.1	4.02	4.95	NA	NA	NA
4.1	4.08	4.78	1.10	13.9	7.8
5.5	3.95	4.19	0.92	12.5	-3.1
10.3	4.04	4.12	0.82	12.3	-4.7
15.1	4.33	3.65	2.20	13.9	7.8
20.3	5.19	3.20	0.64	11.6	-10.1
25.1	5.79	1.49	2.34	11.9	-7.8
30.1	6.50	0.82	3.08	12.5	-3.1
35.2	7.11	0.55	3.38	13.1	1.6
40.2	7.40	0.19	3.10	12.4	-3.9
45.3	7.57		3.58	12.9	0.0
50.0	7.68		2.90	12.0	-7.0
63.1	7.60		3.62	13.0	0.8
81.0	7.99		3.74	13.6	5.4
100.1	8.03		3.01	12.5	-3.1
120.5	8.32		3.01	12.8	-0.8
				ave.	-1.3

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* All ionic species concentrations in grams per liter (gpl)

1. Replicate 2 of Table 20
2. Inorganic sulfur expressed as sulfate (gpl)
3. % deviation with inorganic S balance on sulfate basis
4. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 24 : Noncatalytic BLOX for Liquor C Replicate 3 (1.2 lpm O_2, 2500 rpm, baffle, 96°C)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[2]	%diff.[3,4]
0.0	4.14	2.61	0	NA	NA
1.1	3.99	4.44	NA	NA	NA
2.1	4.09	4.87	NA	NA	NA
3.1	4.13	4.82	NA	NA	NA
4.1	4.40	5.01	NA	NA	NA
5.1	4.36	4.72	NA	NA	NA
10.7	4.78	3.96	NA	NA	NA
15.1	4.84	2.87	NA	NA	NA
20.1	5.40	1.88	3.10	13.3	3.1
25.3	6.35	1.13	3.01	12.8	-0.8
30.1	7.09	0.44	3.21	12.7	-1.6
40.0	7.65	0.17	3.42	13.1	1.6
45.3	7.58		3.16	12.3	-4.7
60.2	8.30		2.99	12.8	-0.8
80.9	8.02		2.84	12.3	-4.7
100.8	8.35		2.74	12.5	-3.1
123.1	8.45		2.72	12.5	-3.1
				ave.	-1.6

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* All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Replicate 3 of Table 20
2. Inorganic sulfur expressed as sulfate (gpl)
3. % deviation with inorganic S balance on sulfate basis
4. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 25 : Inorganic Sulfur Distribution after Oxidation[1]

Liquor	rpm	Chemical Added (gpl)	%Sulfur as SO_4^{2-}	%Sulfur as $S_3O_6^{2-}$	%Total Sulfur
A	1500	0	64		
B	1500	0	65		
B	2000	0	66		
B	2500	0	72		
B	2500^b	0	70		
B	3200^b	0	76		
B	4000^b	0	73	27	100
C	2500^b	0	62	34	96
C	2500^b	5 (NaOH)	64	39	103
C	2500^b	15 (NaOH)	62	34	96
A	1500	1 (NiAl)	63		
A	1500	3 (NiAl)	59		
B	2500^b	3 (NiAl)	65		
A	1500	5 (NiAl)	54		
B	2500^b	5 (NiAl)	65		
C	2500^b	5 (NiAl)	54	44	98
B	2500^b	7 (NiAl)	63		
A	1500	10 (NiAl)	42		
B	2500^b	10 (NiAl)	62	40	102

*. b represents with reactor baffle

[1] Experimentally measured; not obtained by difference

Table 26 : Thiosulfate Model Kinetic Rate Constants

Liquor	A	B	C
rpm	2500	2500^b	2500^b
k_1 (gpl/min.)	0.10	0.22	0.15
k_2 $(\text{gpl}\cdot\text{min.})^{-1}$	0.04	0.43	0.77

Table 27 : Sulfate Model Kinetic Rate Constants[1]

Liquor	A	B	B	C
rpm	2500^b	2500^b	4000^b	2500^b
k_3	0.09	0.35	0.30	0.31
k_4	0.32	0.65	0.49	0.99

* b represents with baffle

[1] concentration of $S_2O_3^{2-}$ in sulfate rate expression in gpl

Table 28 : Effect of Oxidation on pH for Liquor C (1.2 lpm O_2, 2500 rpm, baffle, 95°C)[1,2]

time (min.)	$S_2O_3{}^{2-}$ (gpl)	pH 1	pH 2	pH 3	pH 4
0.0	2.61	13.05	13.05	13.05	13.05
1.0	4.44	12.95	12.95	12.95	12.95
2.0	4.87			12.95	12.95
3.0	4.82	12.90		12.85	12.75
4.0	5.01	12.75	12.65	12.75	12.45
5.0	4.72			12.65	12.35
10.0	3.96	12.35	11.75	12.15	11.55
15.0	2.87	11.45	10.75	11.25	10.75
20.0	1.88	10.85	10.55	10.75	10.35
25.0	1.13	10.45	10.35	10.35	10.05
30.0	0.44		10.00	10.10	9.75
35.0		10.05	9.85	9.95	
40.0	0.17			9.75	9.75
45.0	0.00	9.75	9.65	9.70	9.55
50.0			9.65	9.60	
60.0		9.60	9.55	9.60	9.55
80.0			9.75	9.55	9.55
90.0		9.75			
100.0			9.65	9.55	9.55
120.0		9.75		9.65	9.65
140.0				9.75	

1. 1, 2, 3, 4 represent four replicate experiments
2. pH measured externally on withdrawn samples

Table 29: Effect of Oxidation on pH for Liquor B (1.2 lpm O_2, 2500 rpm, baffle, 95°C)[1]

time (min.)	$S_2O_3^{2-}$ (gpl)	pH
0.0	4.01	12.80
2.3	5.24	12.86
4.5	4.53	12.63
6.5	4.21	12.27
10.3	3.38	11.20
14.5	2.24	10.69
18.3	1.29	10.39
22.3	0.71	10.18
26.4	0.55	10.04
30.3	0.15	9.92
60.4	0.00	9.70
90.6		9.72
120.1		9.74
150.1		9.82
180.1		9.77
210.2		9.73
240.6		9.73

[1] pH measured externally on withdrawn samples

Table 30 : SODABLOX1 for Liquor C (1.2 lpm O_2, 2500 rpm, baffle, 5 gpl incremental NaOH, 95°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[1]	%diff.[2,3]
0.0	4.15	3.49	NA	NA	NA
2.0	4.06	4.60	NA	NA	NA
4.0	4.16	4.38	NA	NA	NA
10.0	4.41	3.96	NA	NA	NA
15.0	4.57	3.77	1.68	13.5	4.9
20.0	4.75	3.45	2.12	13.8	7.2
25.1	5.01	2.91	2.45	13.7	5.9
30.0	5.53	2.29	2.78	13.6	5.5
40.0	6.62	1.02	3.10	13.0	1.6
50.0	7.48	0.30	3.11	12.7	-1.6
60.0	8.06		3.22	12.9	0.0
70.1	8.06		3.78	13.7	6.2
80.0	8.20		3.14	12.9	0.0
90.0	8.20		3.33	13.2	2.3
100.0	8.55		3.05	13.1	1.6
125.0	8.49		3.36	13.5	4.7
				ave.	3.2

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* All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Inorganic sulfur expressed as sulfate (gpl)
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 31 : Effect of Incremental Caustic Addition on Thiosulfate Kinetic Rate

Liquor	Conc. NaOH Added (gpl)	pH after BLOX	k_1 (gpl/min.)	Total NaOH (gpl)
A^1	0		0.10	7.2
A^2	5		0.036	12.2
C^3	0	9.65	0.15	12.0
C^3	5	9.68	0.091	17.0
C^3	15	9.82	0.046	27.0
C^3	28	10.65	0.021	40.0

1. 1.2 lpm O_2, 2500 rpm, 100°C
2. 2.4 lpm O_2, 1500 rpm, 92°C
3. 1.2 lpm O_2, 2500 rpm, baffle, 95°C

Table 32: SODABLOX2 for Liquor C (1.2 lpm O_2, 2500 rpm, baffle, 15 gpl incremental NaOH, 95°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[1]	%diff.[2,3]
0.0	4.03	3.45	0.0	NA	NA
1.5	4.42	4.47	NA	NA	NA
2.7	3.97	4.31	NA	NA	NA
4.6	4.23	4.48	NA	NA	NA
10.1	4.25	4.21	NA	NA	NA
15.0	4.32	3.89	1.40	13.1	1.6
20.0	4.38	3.73	1.82	13.5	4.7
25.0	4.53	3.59	2.29	14.1	9.3
30.1	4.65	3.34	2.25	13.7	6.4
40.6	4.73	3.20	2.72	14.3	10.7
50.4	5.15	2.38	2.44	12.9	0.0
74.1	6.34	0.90	3.21	12.7	−1.6
102.9	7.73	0.12	3.19	12.7	−1.6
120.1	7.95		3.11	12.6	−2.3
150.6	7.91		2.74	12.0	−7.0
160.1	8.15		3.01	12.7	−1.6
				ave.	1.7

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* All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Inorganic sulfur expressed as sulfate (gpl)
2. % deviation with inorganic sulfur balance on sulfate basis
3. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 33 : SODABLOX3 for Liquor C (1.2 lpm O_2, 2500 rpm, baffle, 28 gpl incremental NaOH, 95°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[1]	%diff.[2,3]
0.0	4.02	3.68	NA	NA	NA
2.0	4.01	4.41	NA	NA	NA
4.1	3.73	3.89	NA	NA	NA
10.0	4.32	4.19	1.18	13.3	2.8
15.1	4.48	3.92	1.83	13.9	8.0
20.0	4.43	3.64	1.93	13.5	5.0
25.0	4.52	3.56	2.07	13.7	6.3
30.0	4.66	3.54	1.85	13.5	4.6
40.0	4.82	3.31	2.29	13.9	8.0
50.0	5.46	3.10	2.34	14.3	10.6
62.1	5.08	3.10	2.68	14.4	11.6
70.0	5.06	2.89	2.44	13.7	5.9
80.5	5.31	2.61	2.90	14.1	9.5
120.0	5.88	1.97	2.99	13.7	6.5
140.0	7.34	0.97	3.16	13.7	6.5
					ave. 7.1

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* All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Inorganic sulfur expressed as sulfate (gpl)

2. % deviation with inorganic sulfur balance on sulfate basis

3. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 34 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 10 gpl $CuCl_2$, 90°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	0.20	4.79	1.18	2.27
1.0	0.21	4.48	1.09	2.40
2.0	0.21	4.48	1.12	2.46
3.0	0.21	4.41	1.10	2.33
3.5	0.21	4.45	1.15	2.40
4.5	0.22	4.53	1.19	2.72
6.0	0.22	4.48	1.19	2.48
9.0	0.22	4.46	1.24	2.33
11.0	0.22	4.57	1.31	2.33
14.0	0.22	4.50	1.34	2.38
18.0	0.21	4.54	1.39	2.35
23.0	0.22	4.51	1.44	2.15
29.0	0.22	4.53	1.58	1.99
35.5	0.23	4.56	1.67	1.87
43.0	0.22	4.74	1.82	1.68
51.0	0.22	4.97	1.99	1.33
55.0	0.22	5.10	2.11	1.13
60.5	0.22	5.53	1.72	0.87
70.0	0.22	6.60	1.88	0.43

* All ionic species concentrations in grams per liter (gpl)

Table 35 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 5 gpl $CuCl_2$, 96°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	0.14	4.05	1.08	2.56
1.8	0.13	4.88	0.62	3.02
3.5	0.15	4.81	0.66	3.57
5.8	0.15	4.90	0.73	3.64
8.8	0.15	4.74	0.78	2.81
12.5	0.15	4.68	0.83	2.82
16.5	0.14	4.79	0.89	2.66
20.8	0.14	4.78	0.95	2.61
25.5	0.14	4.88	1.00	2.55
32.0	0.13	4.99	1.99	2.30
37.5	0.13	4.85	1.09	2.32
43.8	0.14	4.80	1.14	1.91
49.8	0.15	4.70	1.17	1.90
70.0	0.16	4.82	1.29	1.76

* All ionic species concentrations in grams per liter (gpl)

Table 36 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 10 gpl activated charcoal, 96°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
1.0	0.43	4.55	0.99	2.75
3.0	0.49	4.59	1.01	3.01
5.0	0.33	4.58	1.00	4.27
8.0	0.33	4.52	1.07	5.03
12.0	0.29	4.50	1.19	4.85
15.0	0.31	4.54	1.26	4.84
19.0	0.32	4.53	1.35	4.69
22.0	0.32	4.55	1.48	4.45
26.5	0.31	4.61	1.49	4.32
30.0	0.31	4.66	1.52	4.16
34.0	0.32	4.65	1.67	4.03
39.5	0.30	5.12	1.13	3.13
48.0	0.30	5.57	1.21	2.31
56.0	0.33	6.30	1.28	1.48
68.0	0.30	7.24	1.38	0.70

* All ionic species concentrations in grams per liter (gpl)

Table 37 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 10 gpl hydroquinone, 96°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	0.14	4.31	1.01	2.79
1.5	0.16	4.38	1.02	2.97
3.5	0.17	4.29	1.00	3.19
5.5	0.17	4.30	1.00	4.42
7.0	0.15	4.29	1.01	4.74
8.5	0.14	4.28	1.07	4.58
11.0	0.14	4.23	1.12	4.54
13.5	0.14	4.23	1.21	4.56
16.0	0.14	4.37	1.34	4.49
20.0	0.14	4.21	1.38	4.34
27.0	0.14	4.26	1.52	4.32
36.0	0.14	4.24	1.63	4.26
47.0	0.14	4.29	1.74	4.25
60.0	0.14	4.33	1.86	4.05
73.0	0.14	4.48	2.04	4.01
80.0	0.14	4.48	2.10	3.80

* All ionic species concentrations in grams per liter (gpl)

Table 38 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 10 gpl reduced iron powder, 90°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
1.5	0.59	4.05	1.20	2.88
3.5	0.41	4.43	1.27	2.81
5.0	0.54	4.32	1.28	3.39
7.5	0.54	4.37	1.29	4.82
10.0	0.54	4.37	1.34	5.23
12.5	0.33	4.25	1.35	5.16
15.0	0.34	4.37	1.46	5.16
18.0	0.34	4.36	1.52	5.19
25.0	0.34	4.25	1.60	4.74
30.0	0.34	4.31	1.70	4.76
37.0	0.34	4.39	1.82	4.42
45.0	0.40	4.60	2.01	3.92
52.0	0.40	4.74	2.09	3.43
60.5	0.38	5.01	1.50	2.99
71.0	0.35	5.43	1.57	2.61
81.0	0.35	5.67	1.62	2.07

* All ionic species concentrations in grams per liter (gpl)

Table 39 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 10 gpl manganese metal powder, 96°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
2.0	0.42	4.48	1.38	2.86
3.5	0.42	4.44	1.33	2.89
5.0	0.42	4.37	1.33	3.29
7.5	0.34	4.41	1.38	3.94
10.0	0.33	4.44	1.41	4.67
12.5	0.32	4.42	1.46	4.81
15.5	0.34	4.41	1.54	4.87
18.0	0.33	4.42	1.56	4.92
21.0	0.33	4.41	1.61	4.82
24.5	0.33	4.45	1.69	4.97
31.0	0.35	4.43	1.83	4.92
36.0	0.35	4.46	1.91	4.82
41.0	0.36	4.46	2.00	4.77
48.0	0.36	4.54	2.16	4.73
60.0	0.37	4.57	2.30	4.52
71.0	0.39	4.64	2.48	4.34
81.5	0.39	4.67	2.54	4.32

* All ionic species concentrations in grams per liter (gpl)

Table 40 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 10 gpl $CoCl_2$, 94°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	0.10	4.43	0.99	2.38
1.0	0.12	4.35	0.95	2.32
3.0	0.11	4.30	0.96	2.26
5.0	0.11	4.30	0.96	2.25
7.0	0.09	4.31	0.96	2.21
10.0	0.07	4.27	0.98	2.70
14.0	0.06	4.35	1.00	2.31
16.0	0.02	4.27	1.00	2.26
18.0	0.02	4.24	1.01	2.27
20.0	0.03	4.26	1.06	2.30
22.0	0.07	4.40	1.16	2.46
23.5	0.07	4.28	1.15	2.48
26.0	0.06	4.34	1.22	2.75
28.5	0.01	4.26	1.23	2.93
31.0		4.37	1.35	3.19
35.5		4.38	1.43	2.36
39.5		4.34	1.49	3.41
50.5		4.28	1.65	3.36
60.0		4.27	1.78	3.43
80.0		4.50	2.26	3.31

* All ionic species concentrations in grams per liter (gpl)

Table 41 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 10 gpl MnO_2, 92°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	0.28	4.55	1.21	2.98
1.5	0.28	4.44	1.23	2.99
3.0	0.28	4.50	1.30	3.43
4.5	0.28	4.50	1.34	4.02
6.5	0.27	4.39	1.36	4.20
9.0	0.27	4.48	1.52	4.23
12.5	0.28	4.50	1.64	4.25
15.5	0.28	4.48	1.73	4.24
17.5	0.30	4.50	1.85	4.28
20.0	0.28	4.44	1.89	4.34
22.5	0.30	4.51	2.03	4.23
25.0	0.30	4.40	2.03	4.20
28.0	0.30	4.47	2.15	4.08
33.0	0.28	4.46	2.26	3.84
40.0	0.28	4.58	1.65	3.90
49.5	0.28	4.84	1.87	3.75
59.5	0.31	4.83	2.02	3.53
70.0	0.31	5.07	3.18	2.79

* All ionic species concentrations in grams per liter (gpl)

Table 42 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 10 gpl NiAl, 92°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	1.71	4.24	0.76	0.50
4.5	0.52	4.05	0.75	2.63
5.0	0.50	4.03	0.79	2.88
6.0	0.59	4.34	0.81	2.93
7.0	0.59	4.39	0.87	2.83
7.5	0.59	4.33	0.87	2.66
9.5	0.52	4.34	0.90	2.41
15.5	0.31	4.40	1.01	2.07
20.0	0.28	4.42	1.14	2.17
25.0	0.28	4.48	1.27	1.58
27.0	0.30	4.60	1.40	1.68
31.0	0.29	4.61	1.46	1.08
35.5	0.27	5.10	0.97	0.76
42.0	0.27	5.11	1.07	0.49
50.0	0.27	5.41	1.24	0.24
56.5	0.29	5.70	1.34	0.19

* All ionic species concentrations in grams per liter (gpl)

Table 43 : Catalyst Screening BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 5 gpl NiAl, 96°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
1.0	0.46	4.65	1.12	2.06
2.5	0.18	4.58	1.15	3.19
4.5	0.18	4.17	1.10	3.65
6.5	0.32	4.71	0.68	3.62
12.5	0.26	4.75	0.76	3.31
15.5	0.25	4.87	0.79	3.13
18.5	0.25	4.93	0.84	3.26
25.0	0.24	5.30	0.92	2.71
31.5	0.23	5.79	0.99	2.15
37.0	0.24	6.09	1.03	1.57
43.0	0.18	6.80	1.08	1.10
50.0	0.17	7.22	1.11	0.54
55.5	0.17	7.33	2.12	0.33

* All ionic species concentrations in grams per liter (gpl)

Table 44 : Catalyst Particle Size Distribution

Particle Size Range (microns)	Catalyst I[*] weight % distribution	Catalyst II[**] weight % distribution
< 38	21.5	10.3
38 - 45	10.9	3.8
45 - 53	20.9	8.9
53 - 63	2.4	33.6
63 - 90	43.8	40.5
> 90	0.5	2.9
Total	100.0	100.0

[*] Surface area I = 0.56 +/- 0.02 m^2/g
[**] Surface area II = 0.43 +/- 0.02 m^2/g

Table 45: Effect of Catalytic Oxidation on Total Sulfur (1.2 lpm O_2, 2500 rpm, baffle, 95°C, catalyst)[1]

Catalyst Conc. (gpl)	Time (min.)	Total Sulfur (gpl)	$S_2O_3^{2-}$ (gpl)
0	0	5.14	2.63
0	0	5.26	
0	0	5.47	
0	0	5.28	
0	0	5.36	
0	0	5.36	
average	0	5.3 +/- 0.2	2.63
7	28	5.3	0.00
10	40	5.3	0.00
7	121	5.3	0.00
10	125	5.2	0.00
10	120	5.1	0.00
3	125	5.3	0.00
5	121	5.2	0.00
7	121	5.1	0.00
7	125	5.3	0.00
10	123	5.1	0.00
average	123 +/- 2	5.2 +/- 0.1	0.00

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1. Catalyst used was nickel aluminum alloy (NiAl)

Table 46: Catalytic BLOX for Liquor B (1.2 lpm O_2, 2500 rpm, baffle, 10 gpl NiAl, 95°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	SO_3^{2-}	%diff.[1,2]
0.0	5.02	0.40	NA	1.75	NA
2.1	5.20	2.49	NA	0.88	NA
4.4	5.40	2.75	NA	<0.20	NA
6.1	5.53	2.76	NA		NA
9.1	5.74	2.06	NA		NA
12.2	6.48	1.25	NA		NA
16.1	7.20	0.62	NA		NA
20.4	7.65	0.31	NA		NA
25.1	8.21		3.40		-1.5
40.4	8.51		3.77		4.9
60.2	8.53		3.75		4.9
80.1	8.12		3.60		0.0
102.7	8.49		3.90		6.2
123.1	8.34		3.01		-4.7
					ave. 1.6

*All ionic species concentrations in grams per liter (gpl)

**NA data not available

1. % deviation with inorganic sulfur balance on sulfate basis
2. Expected inorganic sulfur as sulfate = 13.5 gpl

Table 47 : Catalytic BLOX for Liquor C (1.2 lpm O_2, 2500 rpm, baffle, 5 gpl NiAl, 95°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[1]	%diff.[2,3]
0.0	3.95	1.19	NA	NA	NA
2.6	4.12	1.48	NA	NA	NA
3.5	4.14	1.27	NA	NA	NA
4.6	4.17	1.46	NA	NA	NA
6.1	4.21	1.70	NA	NA	NA
10.1	4.80	1.52	NA	NA	NA
15.1	5.05	1.57	2.77	11.9	-7.8
20.1	5.67	0.96	3.85	13.1	1.6
25.1	6.07	0.50	3.34	11.9	-7.8
30.1	6.62	0.21	4.17	13.2	2.3
40.1	6.75		3.76	12.4	-3.9
60.1	6.82		3.54	12.1	-6.2
80.1	6.94		3.69	12.5	-3.1
100.1	7.23		3.38	12.3	-4.6
				ave.	-3.7

---

*All ionic species concentrations in grams per liter (gpl)

** NA data not available

[1] Inorganic sulfur expressed as sulfate (gpl)

[2] % deviation with inorganic sulfur balance on sulfate basis

[3] Expected inorganic sulfur as sulfate = 12.9 gpl

Table 48 : Catalytic BLOX for Liquor C Replicate 1 (1.2 lpm O_2, 2500 rpm, baffle, 5 gpl NiAl, 95°C)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[2]	%diff.[3,4]
0.0	4.00	0.58	NA	NA	NA
1.1	4.11	1.13	NA	NA	NA
2.1	4.30	1.50	NA	NA	NA
3.1	4.32	2.01	NA	NA	NA
4.2	4.41	1.60	NA	NA	NA
7.3	4.65	1.13	NA	NA	NA
10.0	4.66	1.85	3.77	13.5	4.7
15.0	5.16	1.61	3.63	13.4	3.9
20.0	5.79	0.89	4.35	13.8	7.0
25.1	6.58	0.53	4.13	13.7	6.1
30.0	6.70	0.20	3.84	12.8	-0.8
40.0	6.83		3.64	12.3	-4.7
60.1	6.93		4.00	12.9	0.0
83.4	6.98		4.13	13.2	2.3
128.9	7.34		3.81	13.1	1.6
					ave. 2.2

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*All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Replicate 1 of Table 47
2. Inorganic sulfur expressed as sulfate (gpl)
3. % deviation with inorganic sulfur balance on sulfate basis
4. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 49 : Catalytic BLOX for Liquor C Replicate 2 (1.2 lpm O_2, 2500 rpm, baffle, 5 gpl NiAl, 95°C)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[2]	%diff.[3,4]
0.0	3.90	0.77	0.00	NA	NA
0.8	4.01	1.08	NA	NA	NA
2.1	4.18	1.23	NA	NA	NA
3.2	4.32	1.04	NA	NA	NA
4.1	4.42	1.77	NA	NA	NA
7.8	4.74	1.44	NA	NA	NA
10.0	4.85	1.80	3.36	13.0	0.8
15.2	5.72	0.88	3.68	12.7	-1.6
19.8	6.37	0.56	3.43	12.5	-3.1
24.9	6.72	0.23	3.94	13.0	0.8
30.0	6.73		4.62	13.7	6.2
40.0	7.03		3.85	12.8	-0.8
60.1	7.07		3.52	12.4	-3.9
80.6	7.00		3.62	12.4	-3.9
100.1	7.20		3.76	12.8	-0.8
120.1	7.41		3.11	12.1	-6.2
				ave.	-1.3

---

*All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Replicate 2 of Table 47
2. Inorganic sulfur expressed as sulfate (gpl)
3. % deviation with inorganic sulfur balance on sulfate basis
4. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 50 : Catalytic BLOX for Liquor C Replicate 3 (1.2 lpm O_2, 2500 rpm, baffle, 5 gpl NiAl, 96°C)[1]

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	(SO_4^{2-}) total equivalent[2]	%diff.[3,4]
0.0	3.98	1.45	NA	NA	NA
1.2	4.11	1.33	NA	NA	NA
2.1	4.11	0.85	NA	NA	NA
3.4	4.17	1.10	NA	NA	NA
4.4	4.32	1.81	NA	NA	NA
7.6	4.45	1.69	NA	NA	NA
10.3	4.66	1.88	3.51	13.1	1.6
15.0	5.00	1.46	3.53	12.8	-0.8
20.0	5.62	0.80	3.57	12.3	-4.7
25.0	6.29	0.36	3.47	12.1	-6.2
30.1	6.44	0.16	3.60	12.1	-6.2
35.1	6.50		3.83	12.2	-5.4
39.1	6.85		3.99	12.8	-0.8
60.0	6.84		3.67	12.3	-4.7
80.1	7.06		4.49	13.8	7.0
100.0	7.20		3.56	12.5	-3.1
				ave.	-2.3

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*All ionic species concentrations in grams per liter (gpl)

** NA data not available

1. Replicate 3 of Table 47
2. Inorganic sulfur expressed as sulfate (gpl)
3. % deviation with inorganic sulfur balance on sulfate basis
4. Expected inorganic sulfur as sulfate = 12.9 gpl

Table 51 : Catalytic BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 3 gpl NiAl, 95°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
1.0	<0.15	4.68	1.26	3.29
3.0	<0.15	4.52	1.25	4.30
5.0	<0.15	4.69	1.33	4.10
7.5	<0.15	4.73	1.38	3.93
10.5	<0.15	4.75	1.42	3.67
13.5	<0.15	4.91	1.48	3.67
16.8	<0.15	4.98	1.51	3.67
20.0	<0.15	5.14	1.58	3.58
25.3	<0.15	5.23	1.63	3.34
30.3	<0.15	5.64	0.86	3.08
35.3	<0.15	5.84	0.90	2.96
40.8	<0.15	6.15	0.93	2.46
45.8	<0.15	6.59	2.13	2.12
50.5	<0.15	6.69	2.01	1.48
56.0	<0.15	7.34	2.29	1.03
63.25	<0.15	8.02	2.33	0.44

*All ionic species concentrations in grams per liter (gpl)

Table 52 : Catalytic BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 1 gpl NiAl, 96°C)

time (min)	$SO_3{}^{2-}$	$SO_4{}^{2-}$	$C_2O_4{}^{2-}$	$S_2O_3{}^{2-}$
0.0	<0.15	4.85	1.24	2.67
2.8	<0.15	4.80	1.22	3.31
5.3	<0.15	4.84	1.27	5.05
8.0	<0.15	4.78	1.33	4.79
11.5	<0.15	4.97	1.49	4.54
14.5	<0.15	4.98	1.57	4.33
17.8	<0.15	5.08	1.66	4.07
21.8	<0.15	5.34	0.89	3.71
27.5	<0.15	5.79	0.92	3.02
34.0	<0.15	6.63	2.17	2.24
44.5	<0.15	7.85	2.39	0.89
50.8	<0.15	8.49	2.56	0.48

* All ionic species concentrations in grams per liter (gpl)

Table 53 : Catalytic BLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 0.5 gpl NiAl, 97°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	<0.15	4.74	1.33	2.89
2.8	<0.15	4.64	1.29	3.44
5.0	<0.15	4.64	1.30	4.48
8.0	<0.15	4.75	1.37	5.42
10.8	<0.15	4.77	1.45	5.29
14.0	<0.15	4.90	1.55	5.07
17.8	<0.15	4.89	1.64	4.62
20.0	<0.15	5.05	0.82	4,65
25.5	<0.15	5.45	0.89	4.23
30.0	<0.15	5.59	2.01	3,65
35.0	<0.15	5.91	2.13	3.43
40.0	<0.15	5.96	1.99	2.93
45.0	<0.15	6.52	2.24	2,65
50.3	<0.15	6.84	2.33	2.01
60.0	<0.15	7.52	2.31	1.16

* All ionic species concentrations in grams per liter (gpl)

Table 54 : Catalytic BLOX for Liquor B (1.2 lpm O_2, 2500 rpm, baffle, 3 gpl NiAl, 95°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
0.0	0.94	5.01	1.33
2.1	0.44	5.02	3.55
4.1	<0.20	5.21	3.74
6.5		5.59	3.38
9.0		5.73	2.78
12.4		6.55	2.05
16.1		7.44	1.21
20.1		7.78	0.69
25.1		8.43	0.42
40.1		8.71	
60.1		8.73	
80.1		8.39	
100.1		9.07	
125.1		8.74	

* All ionic species concentrations in grams per liter (gpl)

Table 55 : Catalytic BLOX for Liquor B (1.2 lpm O_2, 2500 rpm, baffle, 5 gpl NiAl, 95°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
0.0	1.14	4.67	1.03
2.1	0.56	5.56	2.88
4.1	<0.20	4.89	3.13
6.1		5.18	3.11
9.2		5.28	3.06
12.6		5.88	2.10
16.1		6.56	1.59
20.1		7.63	0.73
25.1		8.29	0.41
40.1		8.44	
60.1		8.68	
80.1		9.26	
100.1		8.76	
121.2		8.86	

* All ionic species concentrations in grams per liter (gpl)

Table 56 : Catalytic BLOX for Liquor B (1.2 lpm O_2, 2500 rpm, baffle, 7 gpl NiAl, 94°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
0.0	1.51	5.15	0.73
2.1	0.90	5.12	2.84
4.1	0.72	5.15	2.62
6.1	<0.20	5.23	2.59
9.1		5.53	2.56
12.1		6.31	1.80
16.1		7.25	0.89
20.1		7.70	0.44
25.1		8.18	<0.10
40.3		8.51	
60.1		8.56	
80.1		8.23	
100.1		8.41	
121.3		8.59	

* All ionic species concentrations in grams per liter (gpl)

Table 57 : Catalytic BLOX for Liquor B Replicate 1 (1.2 lpm O_2, 2500 rpm, baffle, 7 gpl NiAl, 94°C)[1]

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
0.0	1.78	4.82	0.44
2.1	0.91	5.04	2.50
4.1	<0.20	5.11	2.65
6.2		5.20	2.23
8.2		5.38	2.19
12.1		5.85	1.87
16.1		6.60	1.07
20.1		7.25	0.51
25.1		7.45	0.16
40.1		8.55	
60.1		8.11	
80.1		8.09	
100.4		8.45	
120.9		8.41	

* All ionic species concentrations in grams per liter (gpl)

1. Replicate 1 of Table 56

Table 58 : Catalytic BLOX for Liquor B Replicate 2 (1.2 lpm O_2, 2500 rpm, baffle, 7 gpl NiAl, 95°C)[1]

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
0.0	1.29	5.17	0.83
2.1	0.57	5.15 *	2.36
4.1	<0.20	5.23	2.63
6.1		5.38	2.63
8.1		5.42	2.71
12.1		5.83	2.45
16.1		6.48	1.50
20.1		7.20	0.77
25.1		8.07	0.44
40.2		9.34	
60.1		8.51	
80.1		8.60	
100.4		8.53	
125.3		8.90	

* All ionic species concentrations in grams per liter (gpl)

1. Replicate 2 of Table 56

Table 59: Effect of Liquor, Catalyst Concentration, and Impeller rpm on Thiosulfate Residence Time

Liquor	Catalyst[1] Conc. (gpl)	rpm	Residual $S_2O_3^{2-}$ (gpl)	Oxidation Time (min.)
A	0	1500	0.5	72
A	10	1500	0.5	42
A	5	1500	0.5	50
A	3	1500	0.4	63
A	1	1500	0.5	51
B	0	800	1.7	96
B	0	1500	0.3	40
B	0	2000	0.2	37
B	0	2500	0.25	41
B	0	2500^b	0.5	26
B	0	3200^b	0.5	26
B	0	4000^b	0.55	26
B	10	2500^b	0.3	20
B	7	2500^b	0.5	20
B	5	2500^b	0.4	25
B	3	2500^b	0.4	25
C	0	2500^b	0.5	35
C	5	2500^b	0.5	25

*b represents with reactor baffle

1. Catalyst used was nickel aluminum alloy (NiAl)

Table 60 : Noncatalytic BLOX for Liquor B (2.4 lpm O_2, 800 rpm, 94°C)

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$
0.0	4.50	2.63
1.6	4.82	2.94
3.1	4.83	3.93
5.0	4.71	4.72
8.3	4.58	4.58
14.2	4.59	4.58
20.3	4.62	4.31
33.0	4.95	4.10
43.0	5.08	3.63
54.9	5.22	3.49
69.8	5.43	3.06
85.9	5.95	2.97
100.1	5.92	2.16
115.1	6.33	1.93
130.3	6.56	1.66

*All ionic concentrations in grams per liter (gpl)

Table 61 : Catalytic BLOX for Liquor B (2.4 lpm O_2, 800 rpm, 5 gpl NiAl, 96°C)

time (min)	SO_3^{2-}	SO_4^{2-}	$S_2O_3^{2-}$
0.0	1.05	4.81	1.19
1.6	0.43	4.93	2.09
3.9	<0.20	4.51	2.13
5.5		4.69	2.28
10.1		5.12	2.47
16.9		4.87	2.67
25.1		4.61	3.09
38.3		4.67	2.89
47.8		4.64	3.90
60.2		4.74	3.24
70.1		4.83	3.29
80.1		5.06	2.92
90.3		5.29	2.67
100.2		5.52	2.34
115.2		5.68	1.97
130.5		5.95	1.76

* All ionic species concentrations in grams per liter (gpl)

Table 62: Effect of Noncatalytic Oxidation on Thermal Value, Liquor B (1.2 lpm O_2, 2500 rpm, baffle, 95°C)

Sample	Time (min.)	Thermal Value (kJ/g)	Relative% Decrease
1	0	12.8	
2	0	12.5	
3	0	13.0	
4	0	12.6	
5	0	12.0	
6	0	12.1	
average	0	12.5 +/- 0.4	
T	26	11.1	10.9
V	26	11.2	10.3
average	26	11.2 +/- 0.1	10.6 +/- 0.3
K	112	10.6	15.4
L	115	10.6	15.5
M	110	10.7	14.6
P	120	10.8	13.9
R	121	10.7	14.6
S	120	10.6	15.4
T	121	10.6	15.4
V	120	10.6	15.4
average	117 +/- 4	10.7 +/- 0.1	15.0 +/- 0.6
N	180	10.3	17.6

Table 63: Effect of Catalytic Oxidation on Thermal Value, Liquor B (1.2 lpm O_2, 2500 rpm, baffle, catalyst, 95^oC)[1]

Catalyst Concentration (gpl)	Time (min.)	Thermal Value (kJ/g)	Relative % Decrease
0	0	12.8	
0	0	12.5	
0	0	13.0	
0	0	12.6	
0	0	12.0	
0	0	12.1	
average	0	12.5 +/- 0.4	
7	28	10.3	17.6
10	40	10.4	16.6
7	121	10.3	17.6
10	125	10.6	15.4
10	120	10.4	16.6
3	125	10.2	18.7
5	121	10.5	16.4
7	121	10.1	19.2
7	125	10.4	16.6
10	123	10.2	18.7
average	123 +/- 2	10.3 +/- 0.2	17.4 +/- 1.3

1. Catalyst used was nickel aluminum alloy (NiAl)

Table 64: Oxidation of Liquor Organics, Liquor C (1.2 lpm O_2, 2500 rpm, baffle, 95°C)

Res. Time (min.)	Chemical Charge (gpl)	TOC (gpl)	CO_3^{2-} (gpl)	NaOH (gpl)
0	0	62.5	17.8	12.0
0	0	65.5	18.4	12.0
0	0	65.5	18.6	12.0
0	0	65.5	17.6	
ave.	0	64.8 +/- 1.5	18.1 +/- 0.5	
123	0	62.9	21.1	4.3
120	0	64.7	21.0	4.3
123	0	63.7	21.1	4.3
122 +/- 2	0	63.8 +/- 0.9	21.1 +/- 0.1	
142	0	62.1	20.2	
120	5 (NiAl)	57.2	22.1	4.5
129	5 (NiAl)	57.6		
120	5 (NiAl)	56.5		
125	5 (NiAl)	59.0	22.1	
124 +/- 4		57.6 +/- 1.1	22.1	
125	5 (NaOH)	59.8	23.0	5.5
160	15 (NaOH)	58.1	27.4	6.7
140	28 (NaOH)	56.0	33.3	9.3

Table 65: Effect of Oxidation, Residence Time, and Chemical Addition on %O_2 in Reactor Off-Gas, Liquor C[1]

Time (min.)	no addition to liquor	5 gpl NiAl	5 gpl NaOH	15 gpl NaOH	28 gpl NaOH
		%O_2 in reactor off-gas			
0	0.0	0.0	0.0	0.0	0.0
10	49.6	94.4	94.8	88.3	87.8
20	89.7	98.2	99.4	97.9	96.6
30	95.1	98.1	100.0	99.5	98.4
35	94.8	97.4	100.0	100.0	98.6
40	93.9	96.6	100.0	100.0	98.8
45	92.7		99.5	100.0	98.9
60	90.0	93.7	97.4	99.6	99.0
70	88.3	94.2	95.0	99.4	99.0
80	89.2	94.7	94.6		99.1
100	89.6	94.9	94.1	97.3	99.1
120	90.9	94.1	95.1	95.5	99.1
140					99.0
150				94.9	
160				95.9	

1. Chemicals studied were NiAl catalyst and NaOH in varying concentration

Table 66 : SODABLOX for Liquor A (2.4 lpm O_2, 1500 rpm, 5 gpl NaOH, 92°C)[1]

time (min)	SO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$	$S_2O_3^{2-}$
0.0	0.23	4.57	1.13	3.13
2.5	0.41	4.67	1.15	2.83
5.5	0.48	4.62	1.15	3.72
7.5	0.21	4.59	1.17	4.75
10.0	0.21	4.53	1.22	4.71
12.5	0.26	4.76	1.37	5.13
16.5	0.30	4.67	1.45	4.97
22.5	0.30	4.57	1.55	4.71
29.0	0.35	4.61	1.77	4.51
33.0	0.35	4.31	1.82	4.51
38.0	0.39	4.61	2.04	4.54
45.5	0.43	4.72	2.20	4.26
53.0	0.44	4.86	2.39	4.18
62.0	0.43	5.13	1.74	3.44
73.0	0.39	5.73	1.93	2.90
81.0	0.39	6.17	1.97	2.45

* All ionic species concentrations in grams per liter (gpl)

1. With NaOH addition

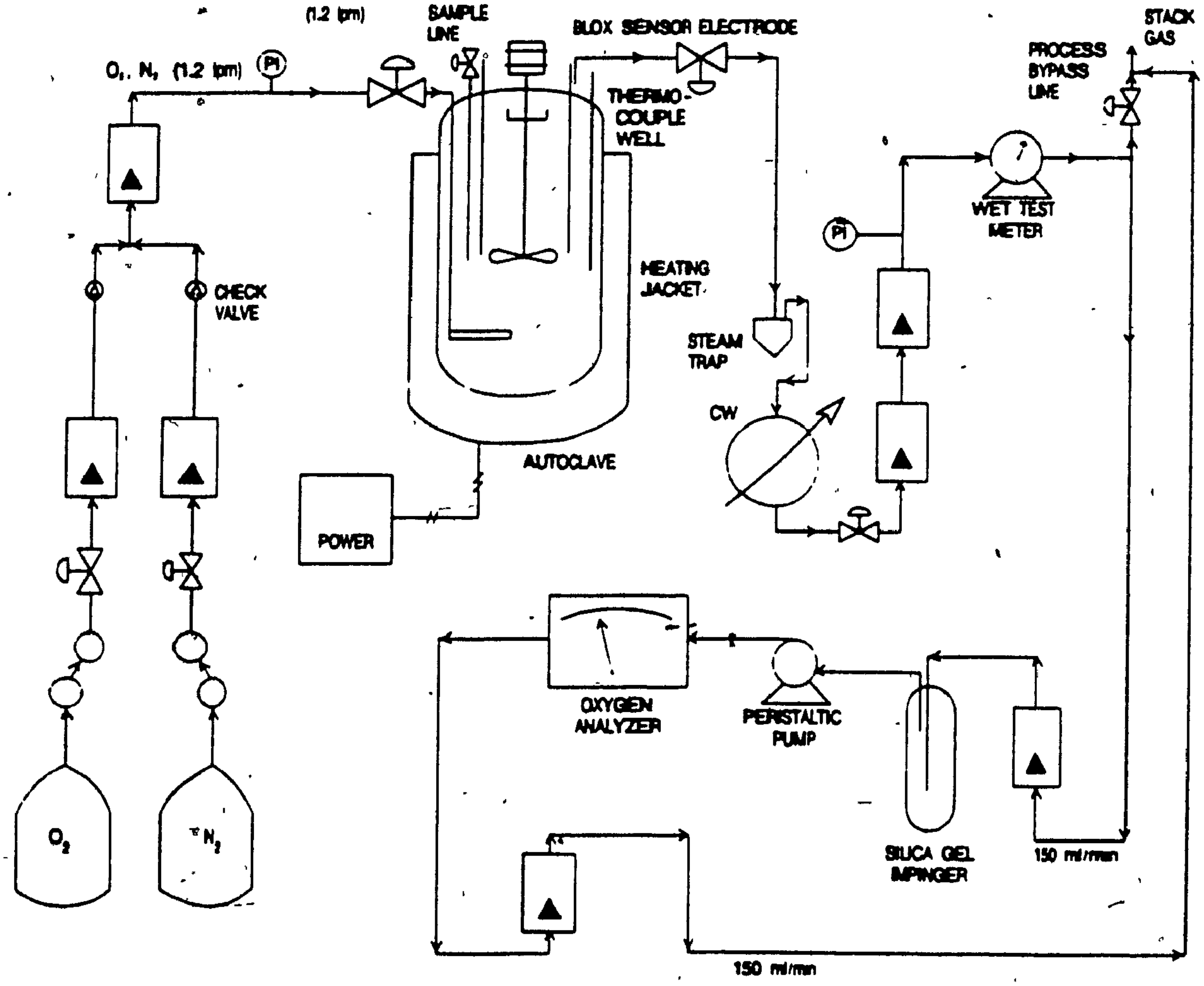

Figure 1. Process flowsheet.

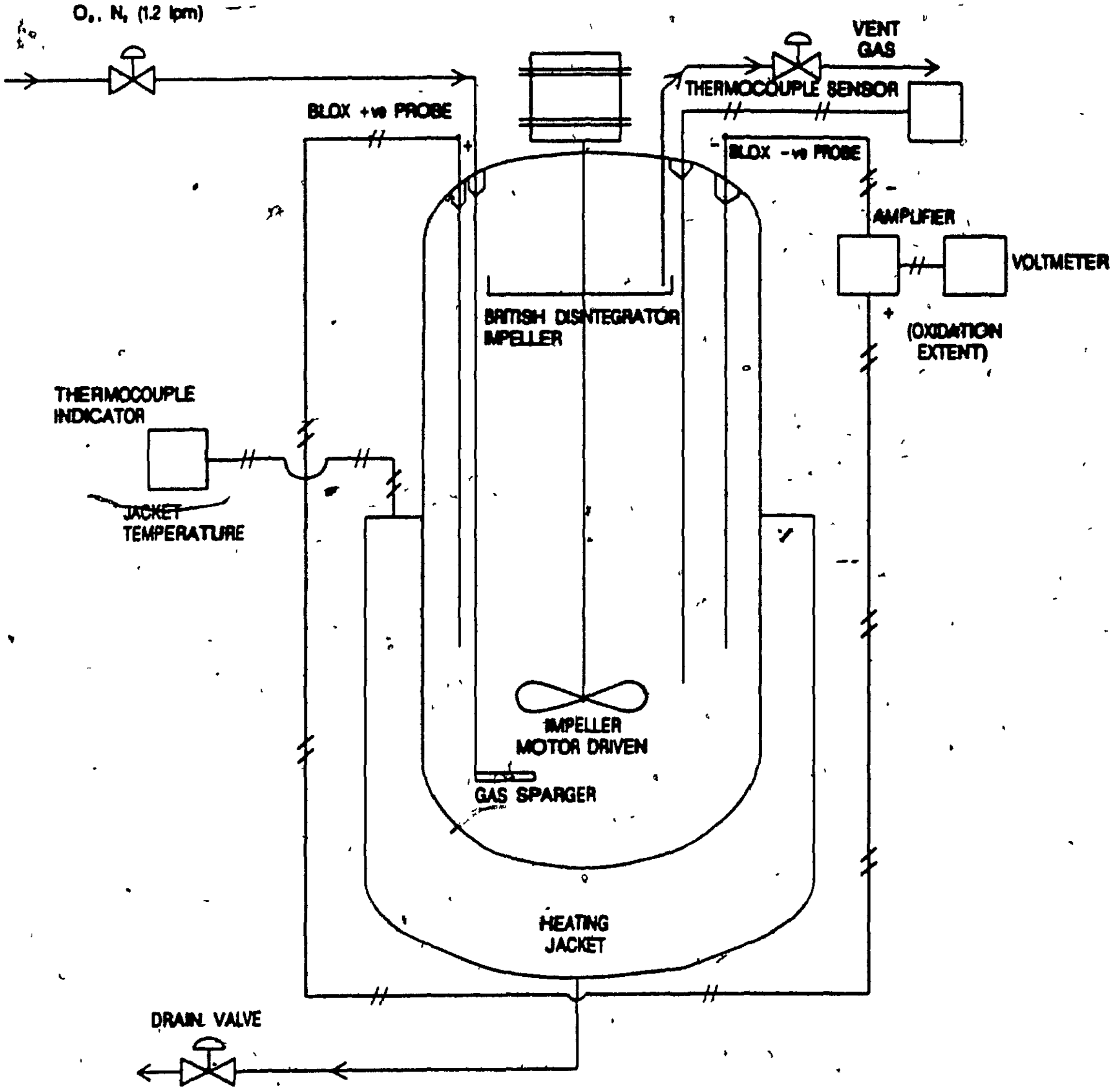

Figure 2. Ancillary equipment.

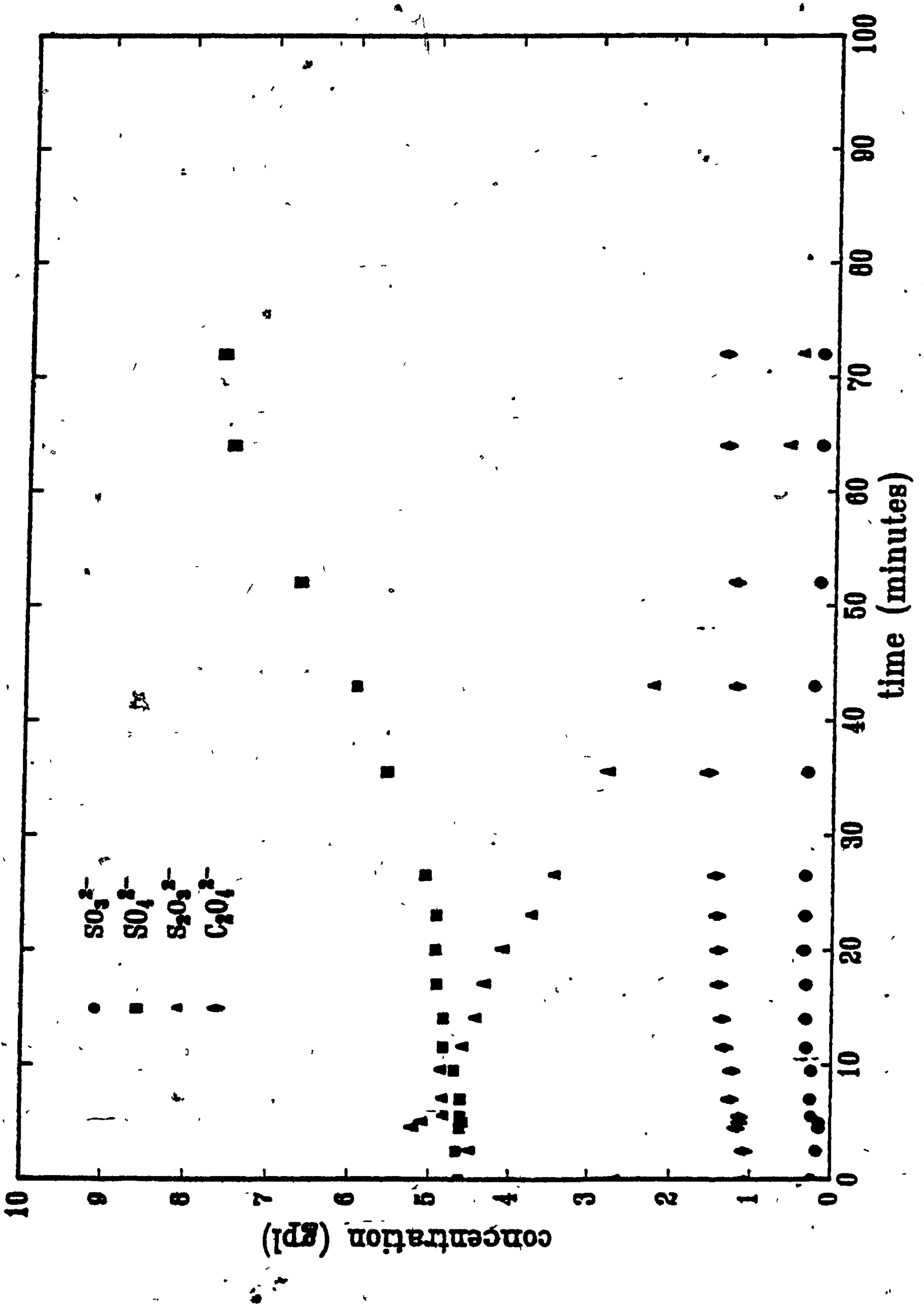

Figure 3. Noncatalytic BLOX for Liquor A at 2.4 lpm O_2 and 1500 rpm.

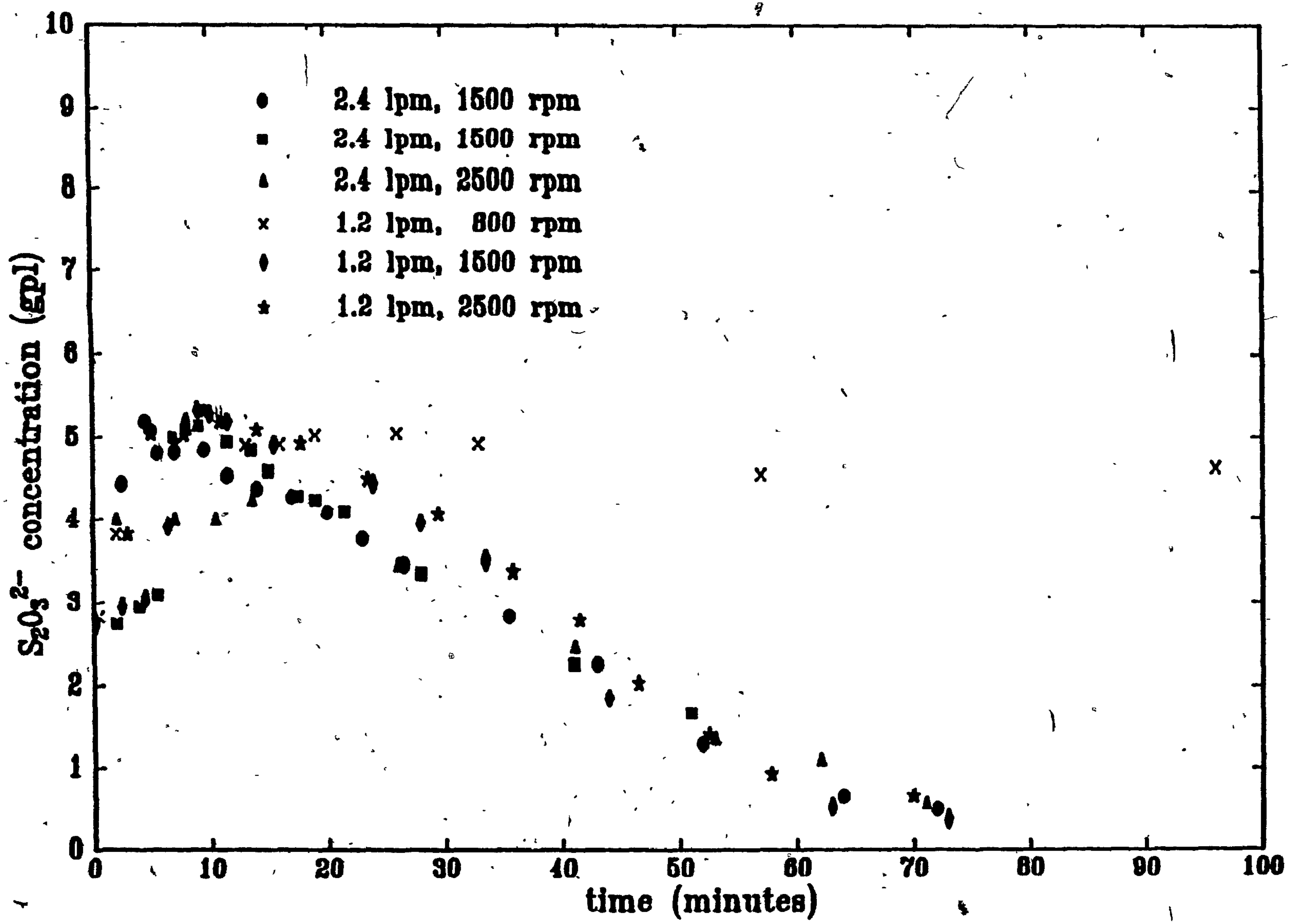

Figure 4. Effect of impeller rpm and O_2 flowrate on thiosulfate oxidation for Liquor A.

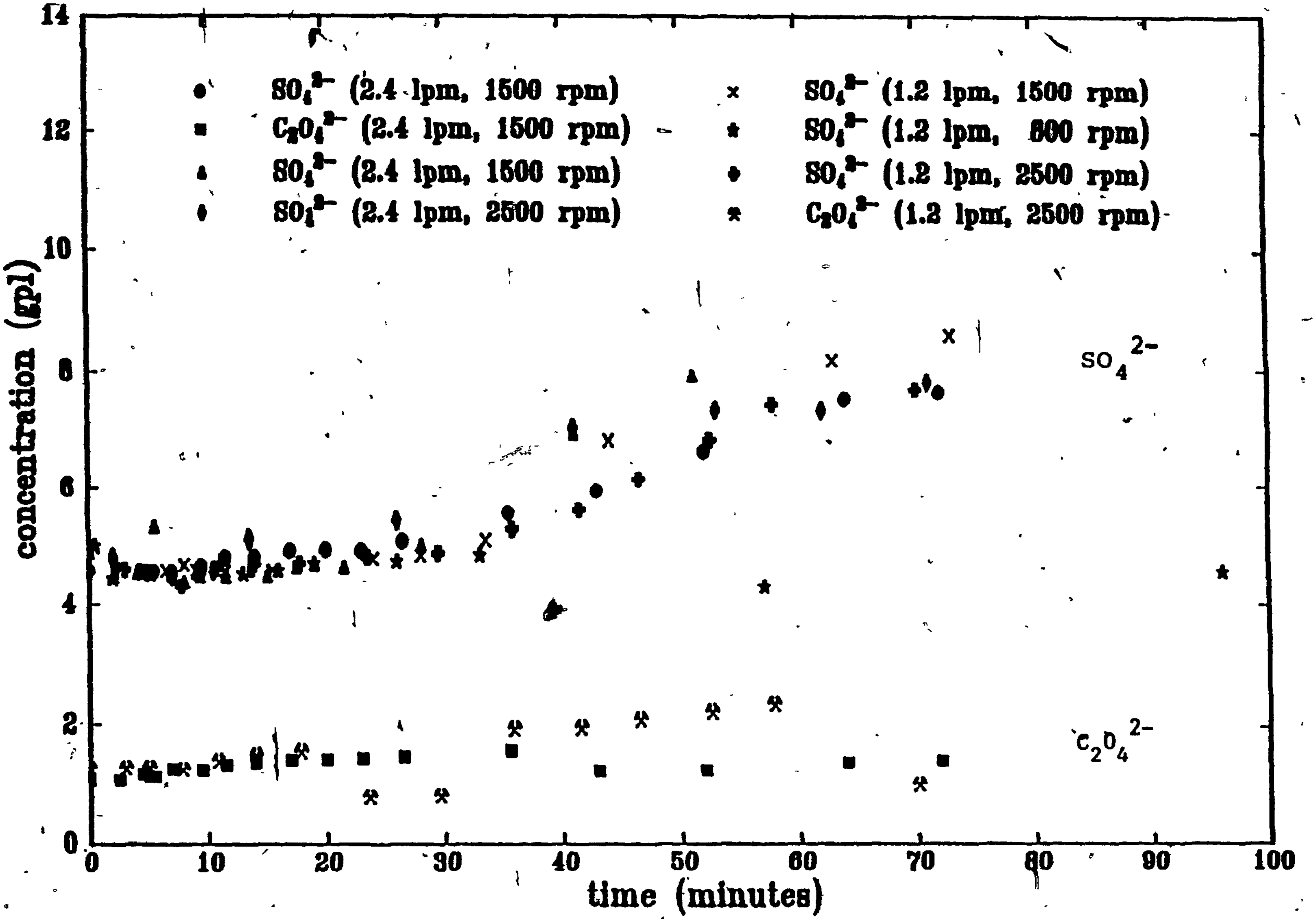

Figure 5. Effect of impeller rpm and O_2 flowrate on sulfate and oxalate production for Liquor A.

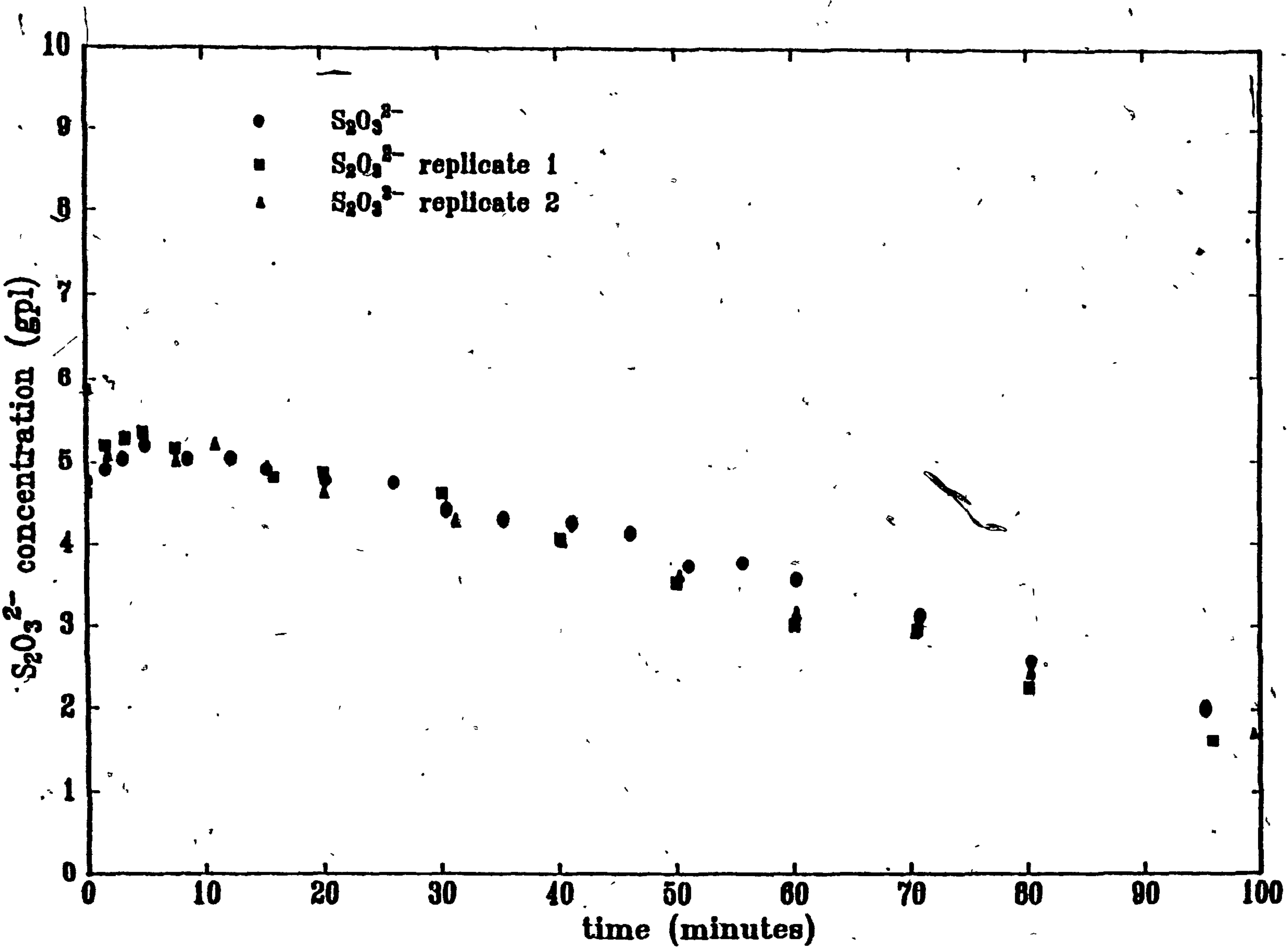

Figure 6. Experimental reproducibility of noncatalytic thiosulfate oxidation for Liquor B at 1.2 lpm O_2 and 800 rpm.

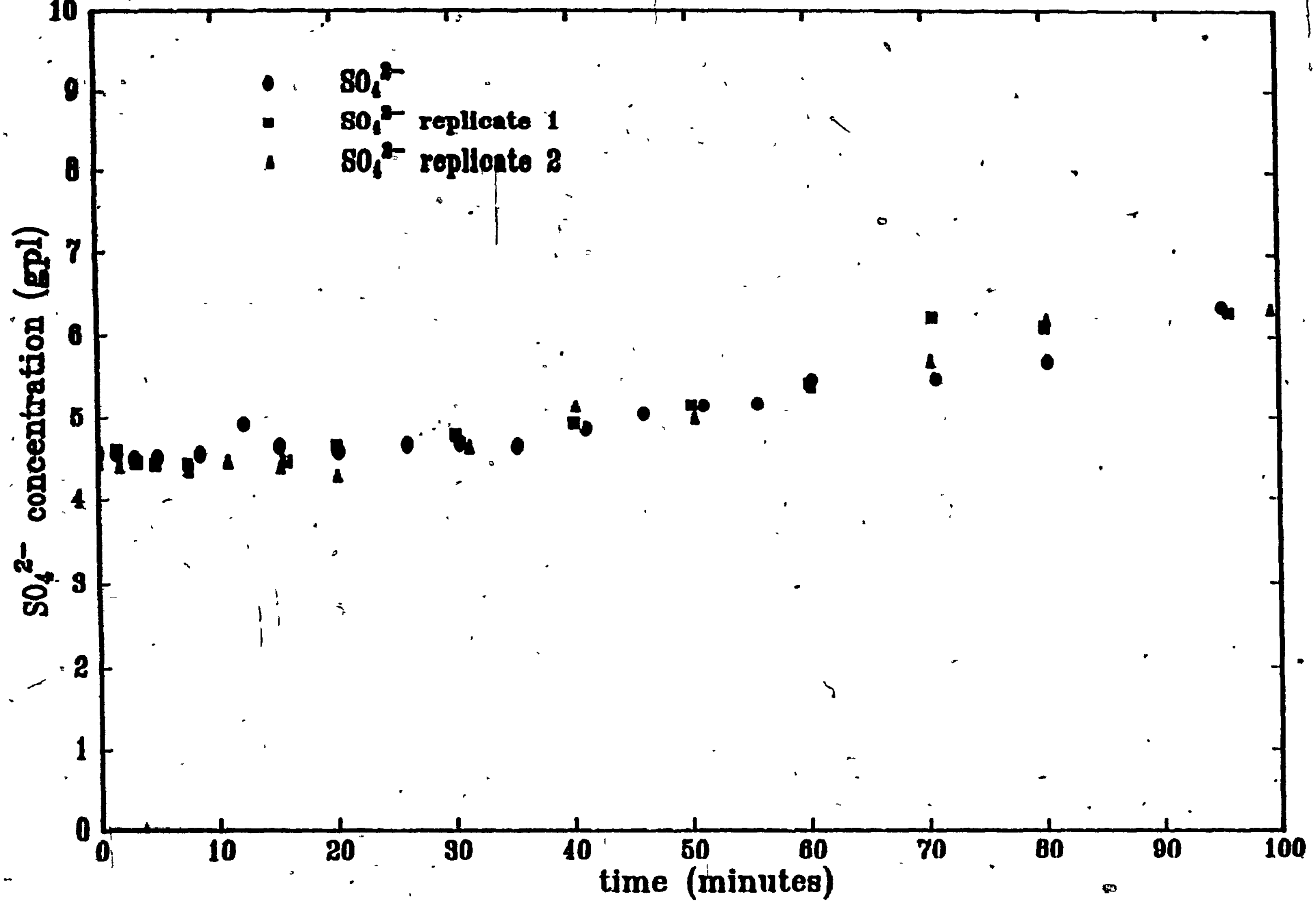

Figure 7. Experimental reproducibility of noncatalytic sulfate data for Liquor B at 1.2 lpm O_2 and 800 rpm.

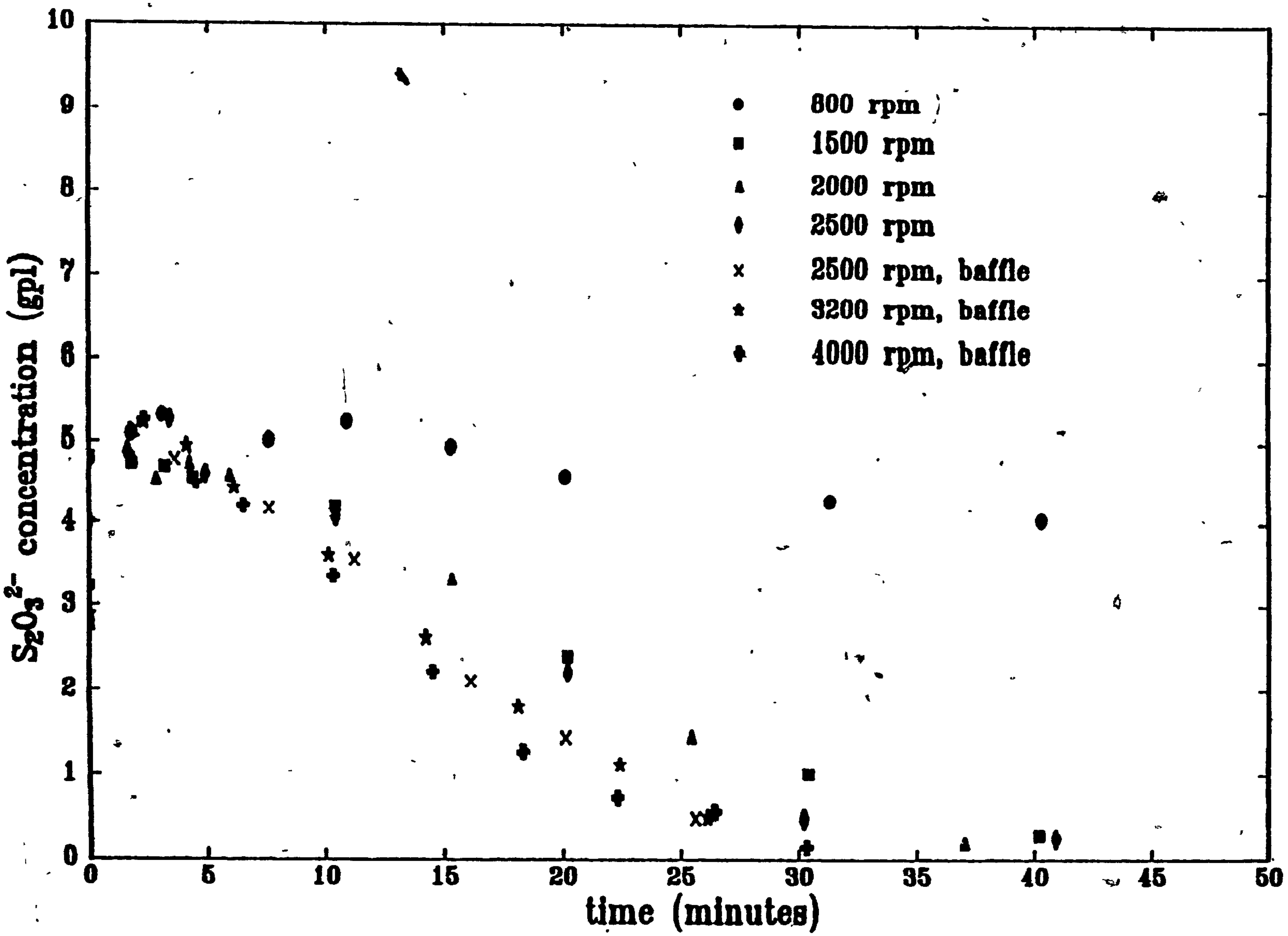

Figure 8. Effect of impeller rpm on noncatalytic thiosulfate oxidation for Liquor B at 1.2 lpm O_2.

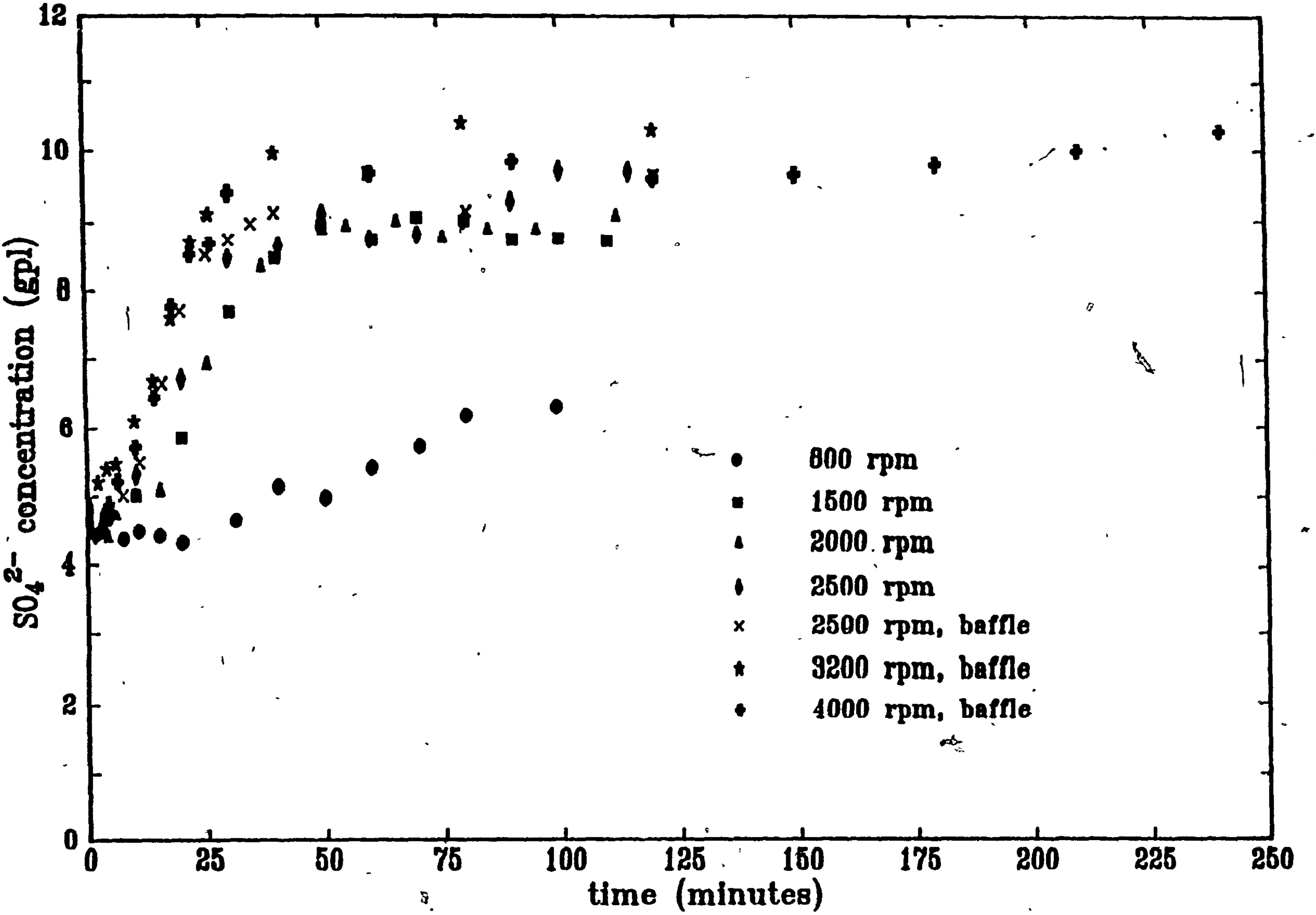

Figure 9. Effect of impeller rpm on noncatalytic sulfate production for Liquor B at 1.2 lpm O_2.

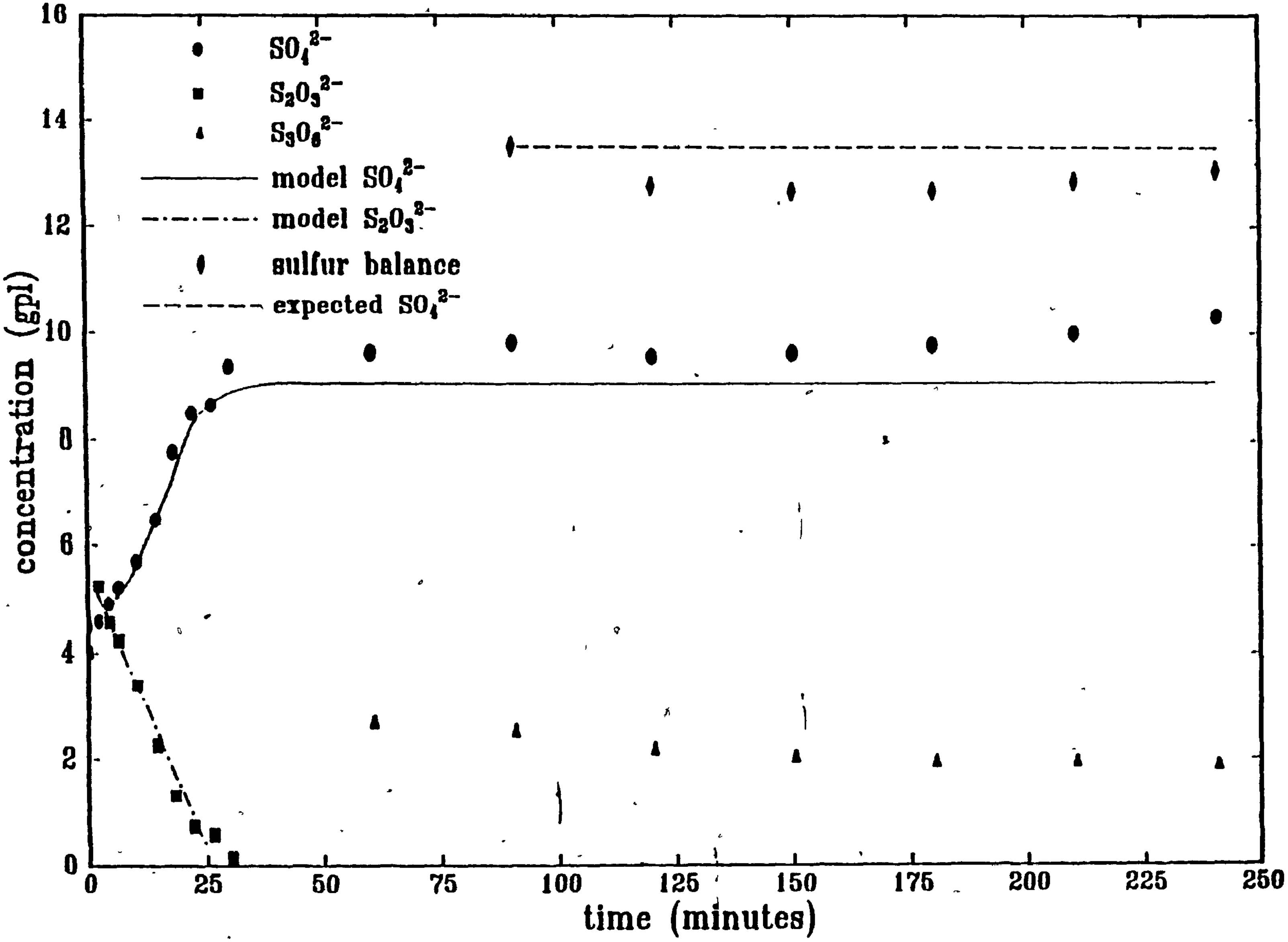

Figure 10. Noncatalytic inorganic sulfur balance for Liquor B at 1.2 lpm O_2, 4000 rpm, with baffle.

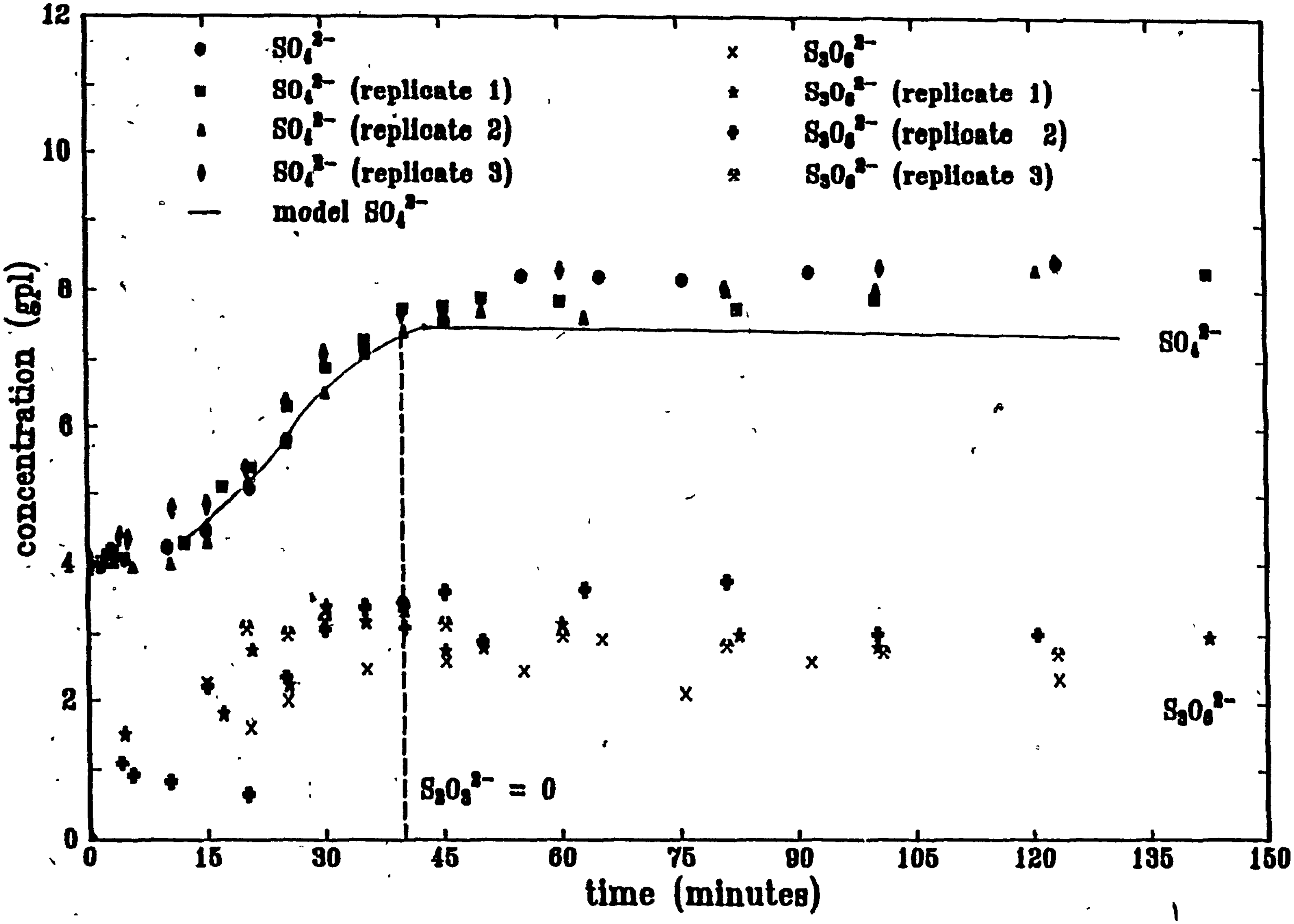

Figure 11. Experimental reproducibility of noncatalytic sulfate and trithionate production for Liquor C at 1.2 lpm O_2 and 2500 rpm with baffle.

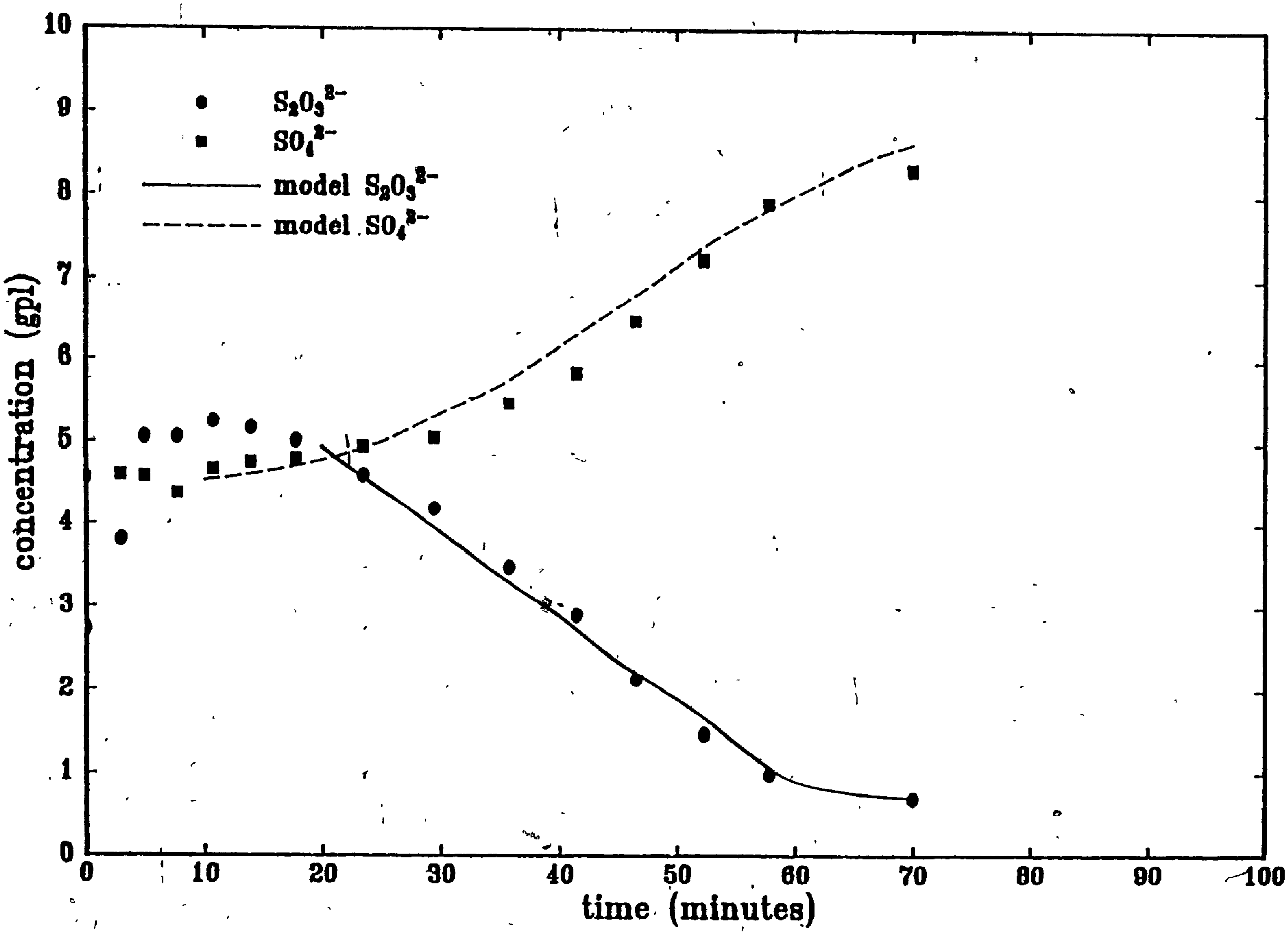

Figure 12. Evaluation of models for SO_4^{2-} and $S_2O_3^{2-}$ kinetics for Liquor A.

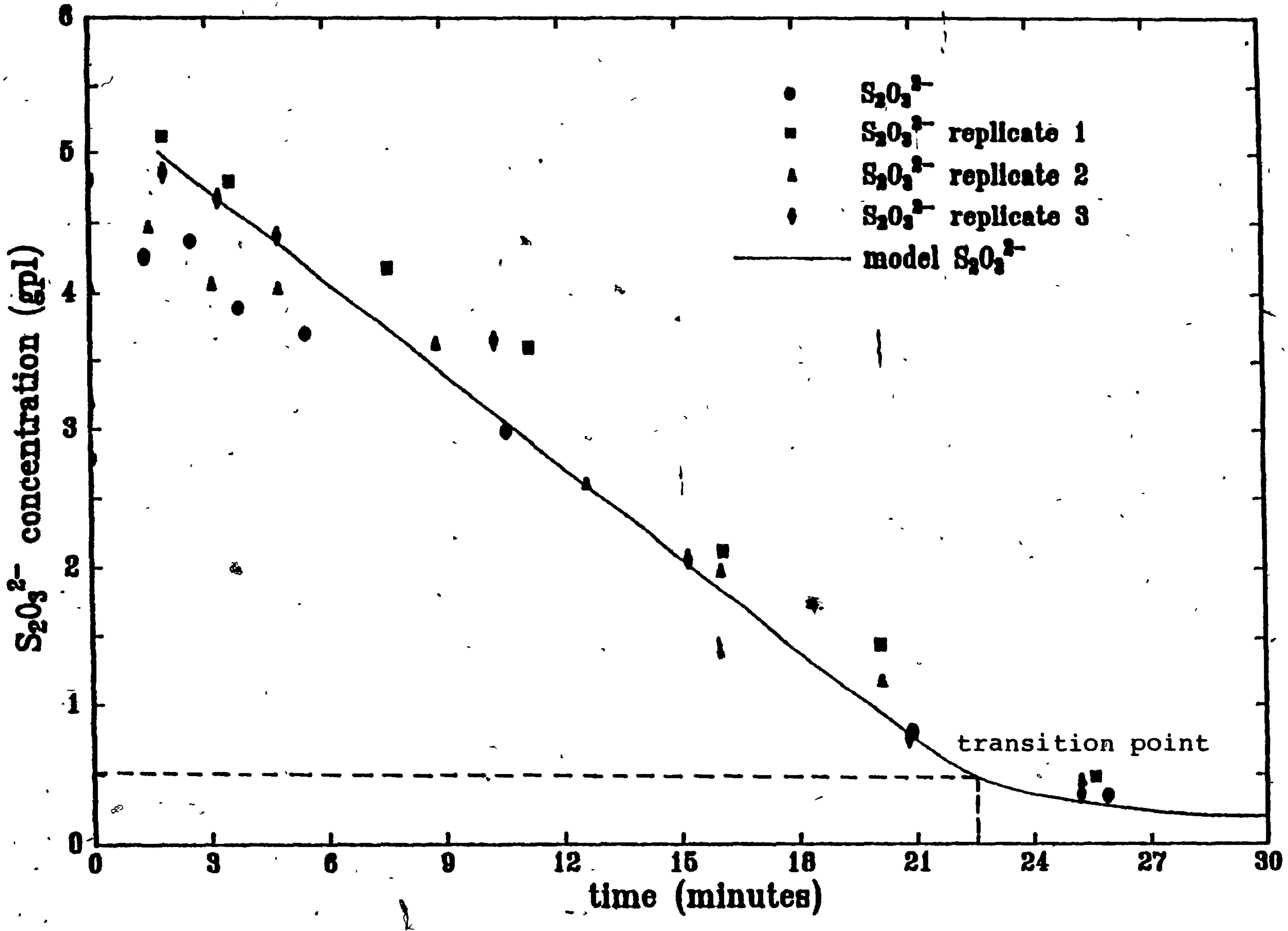

Figure 13. Experimental reproducibility of noncatalytic thiosulfate oxidation for Liquor B at 1.2 lpm O_2 and 2500 rpm with baffle.

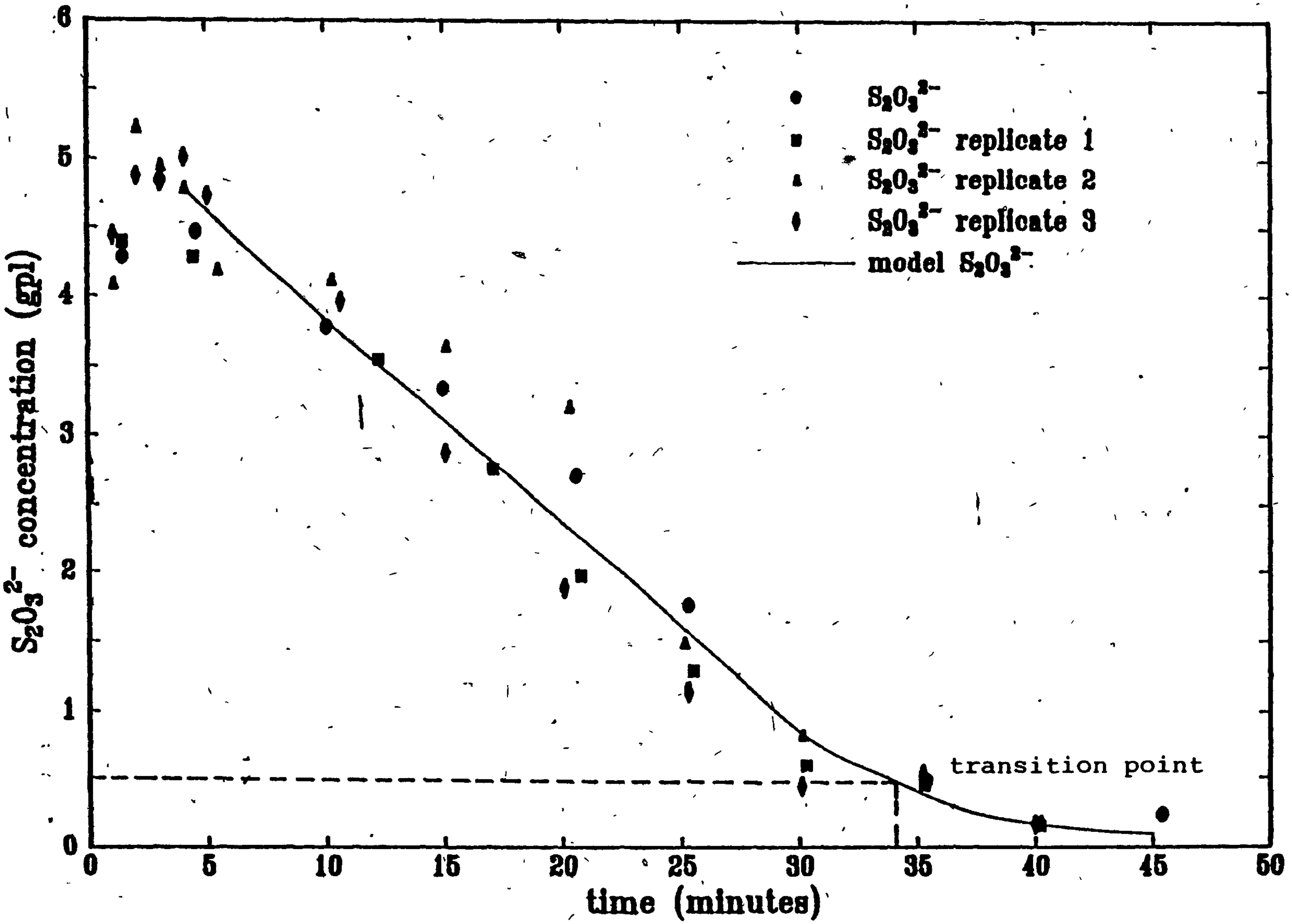

Figure 14. Experimental reproducibility of noncatalytic thiosulfate oxidation for Liquor C at 1.2 lpm O_2 and 2500 rpm with baffle.

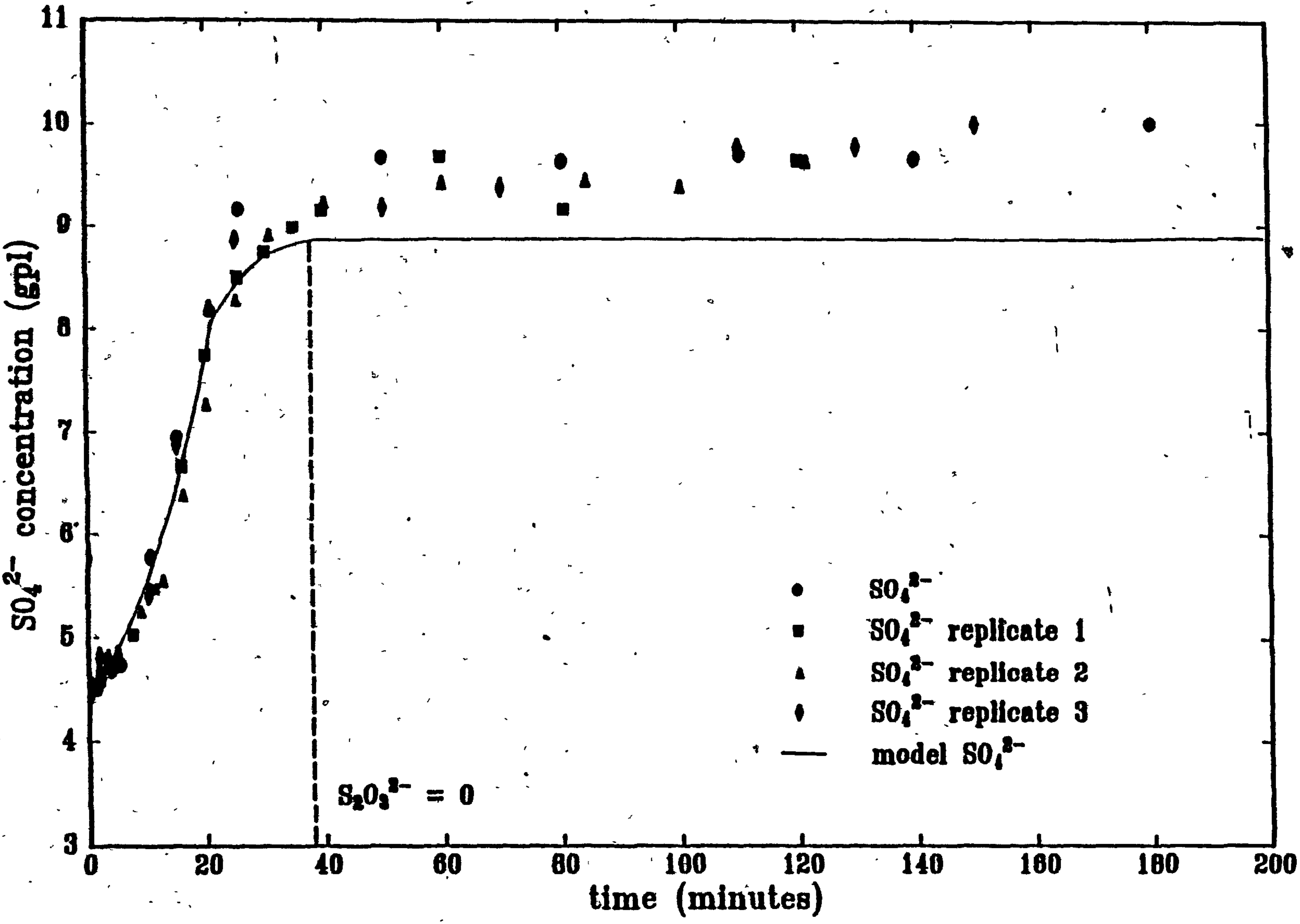

Figure 15. Experimental reproducibility of noncatalytic sulfate production for Liquor B at 1.2 lpm O_2 and 2500 rpm with baffle.

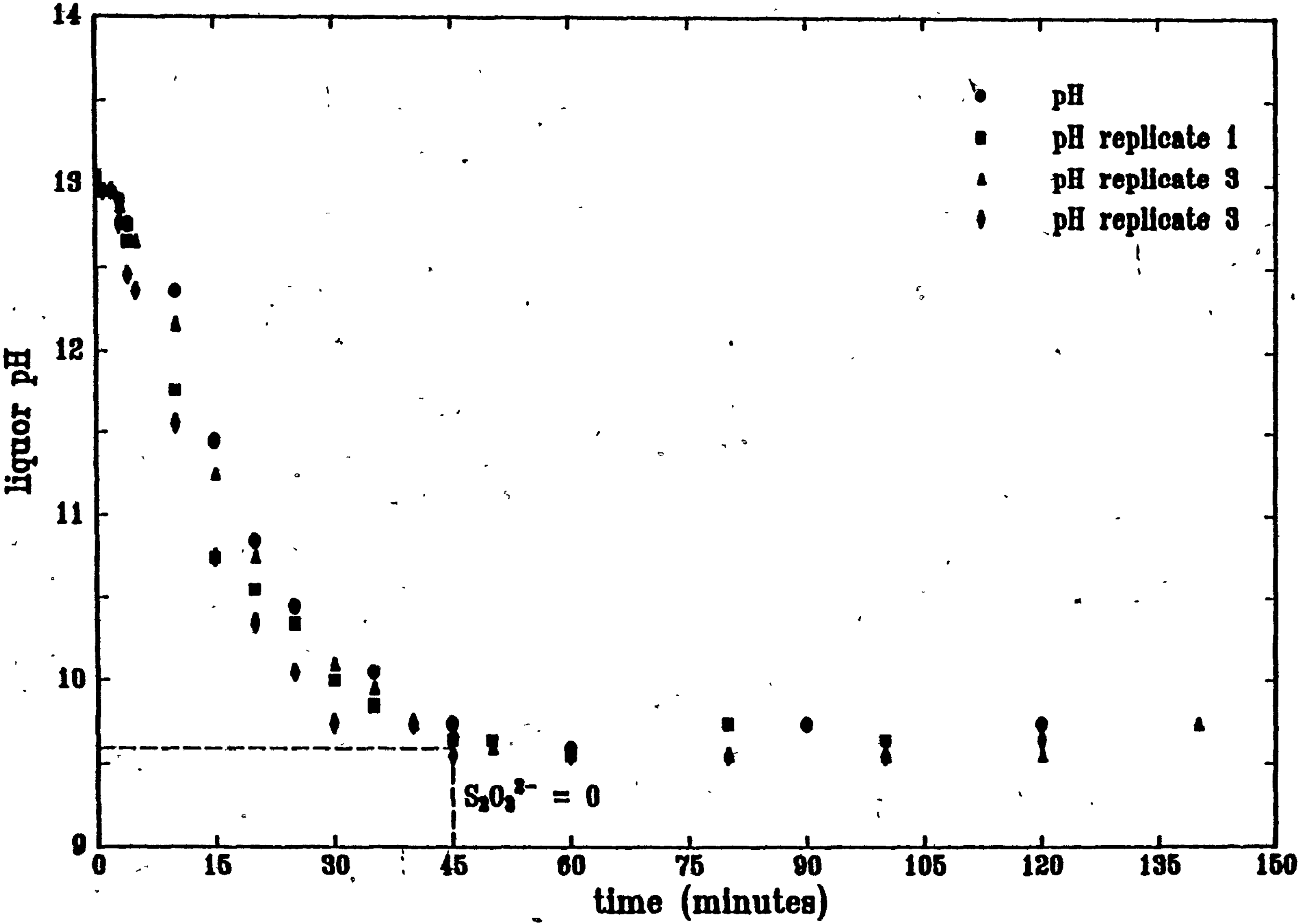

Figure 16. Experimental reproducibility of Liquor pH at 1.2 lpm O_2, 2500 rpm, and with baffle.

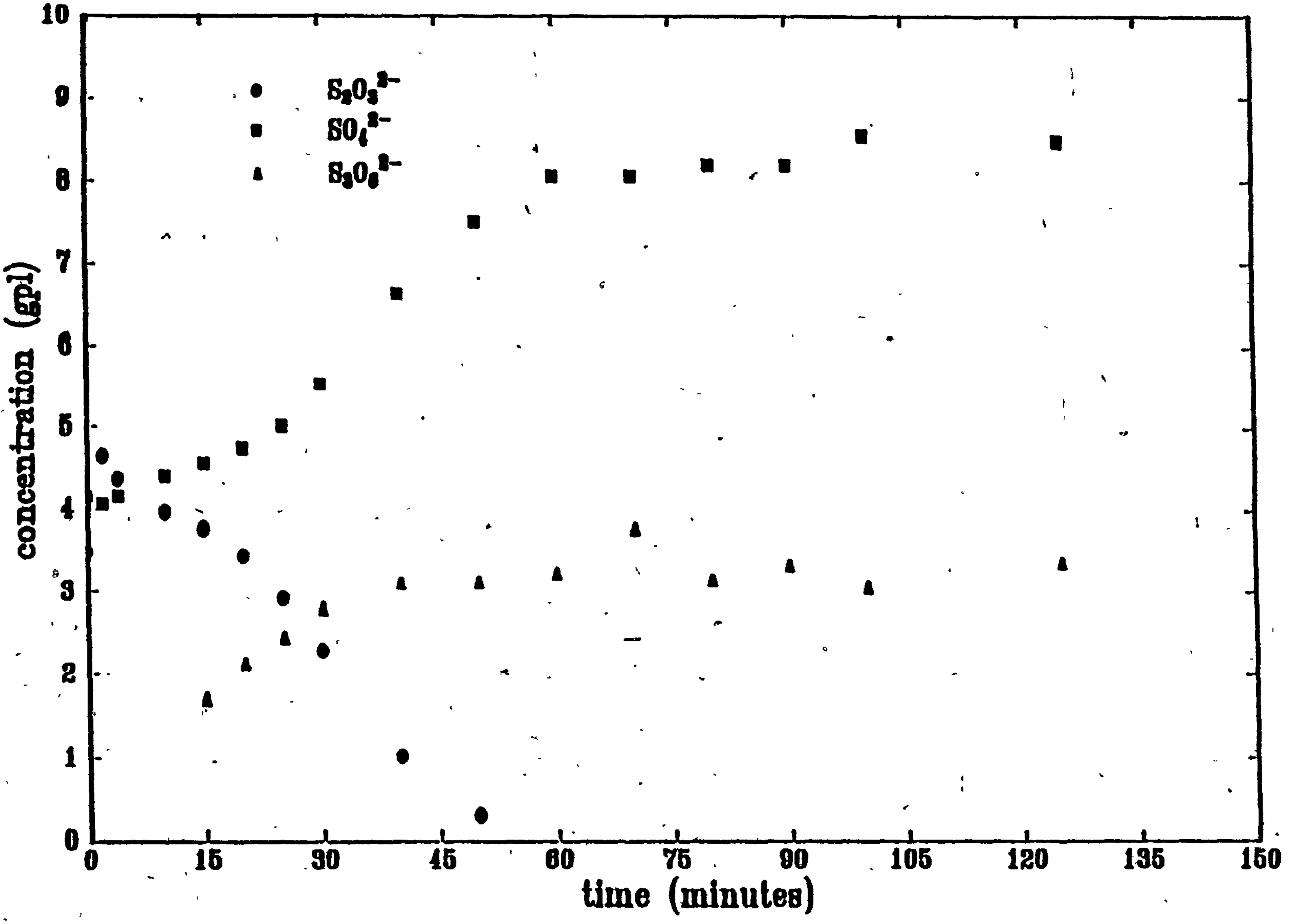

Figure 17. SODABLOX1 : Effect of 5 gpl NaOH addition on oxidation at 1.2 lpm O_2 and 2500 rpm with baffle.

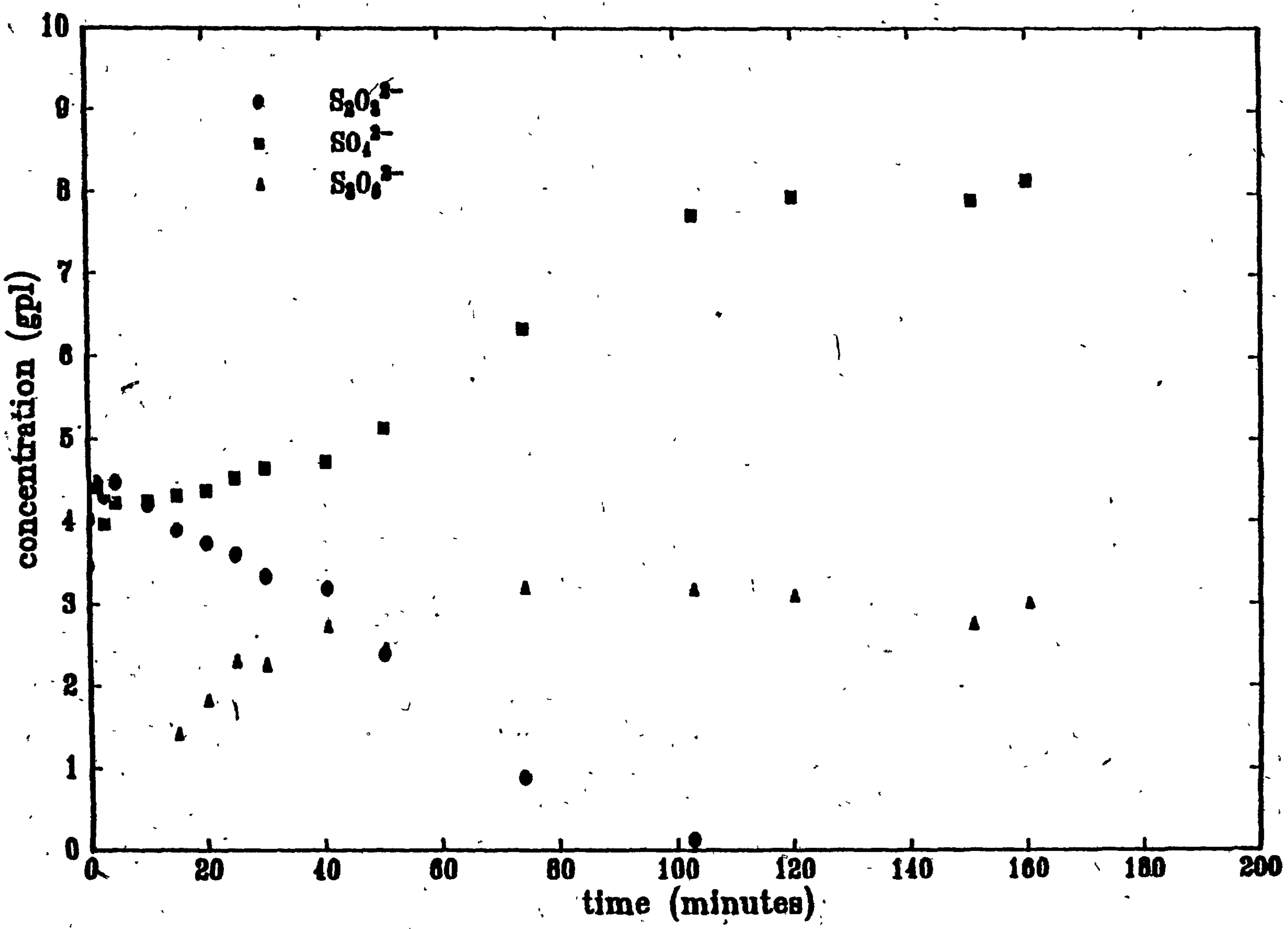

Figure 18. SODABLOX2 : Effect of 15 gpl NaOH addition on oxidation at 1.2 lpm O_2 and 2500 rpm with baffle.

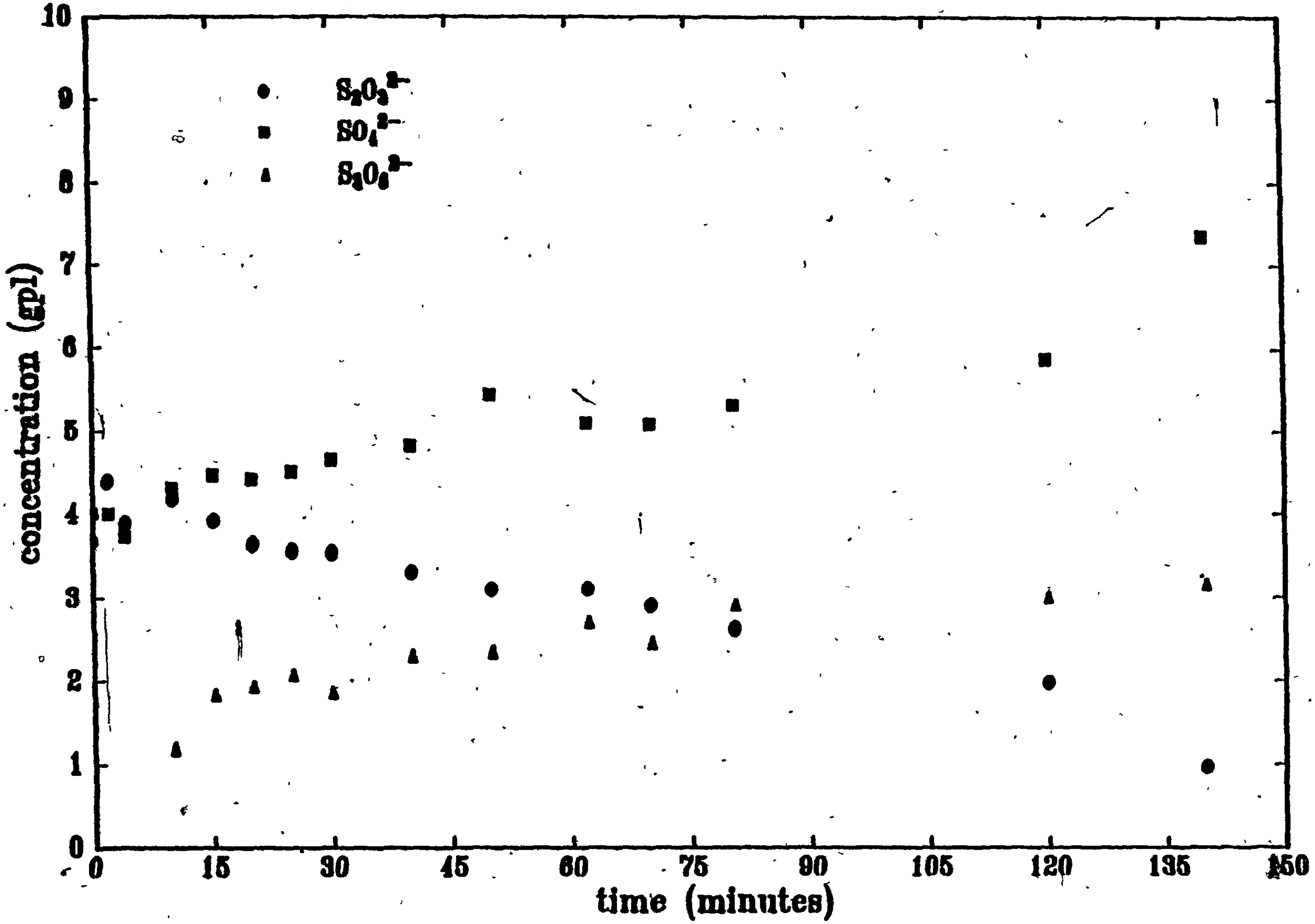

Figure 19. SODABLOX3 : Effect of 28 gpl NaOH addition on oxidation at 1.2 lpm O_2 and 2500 rpm with baffle.

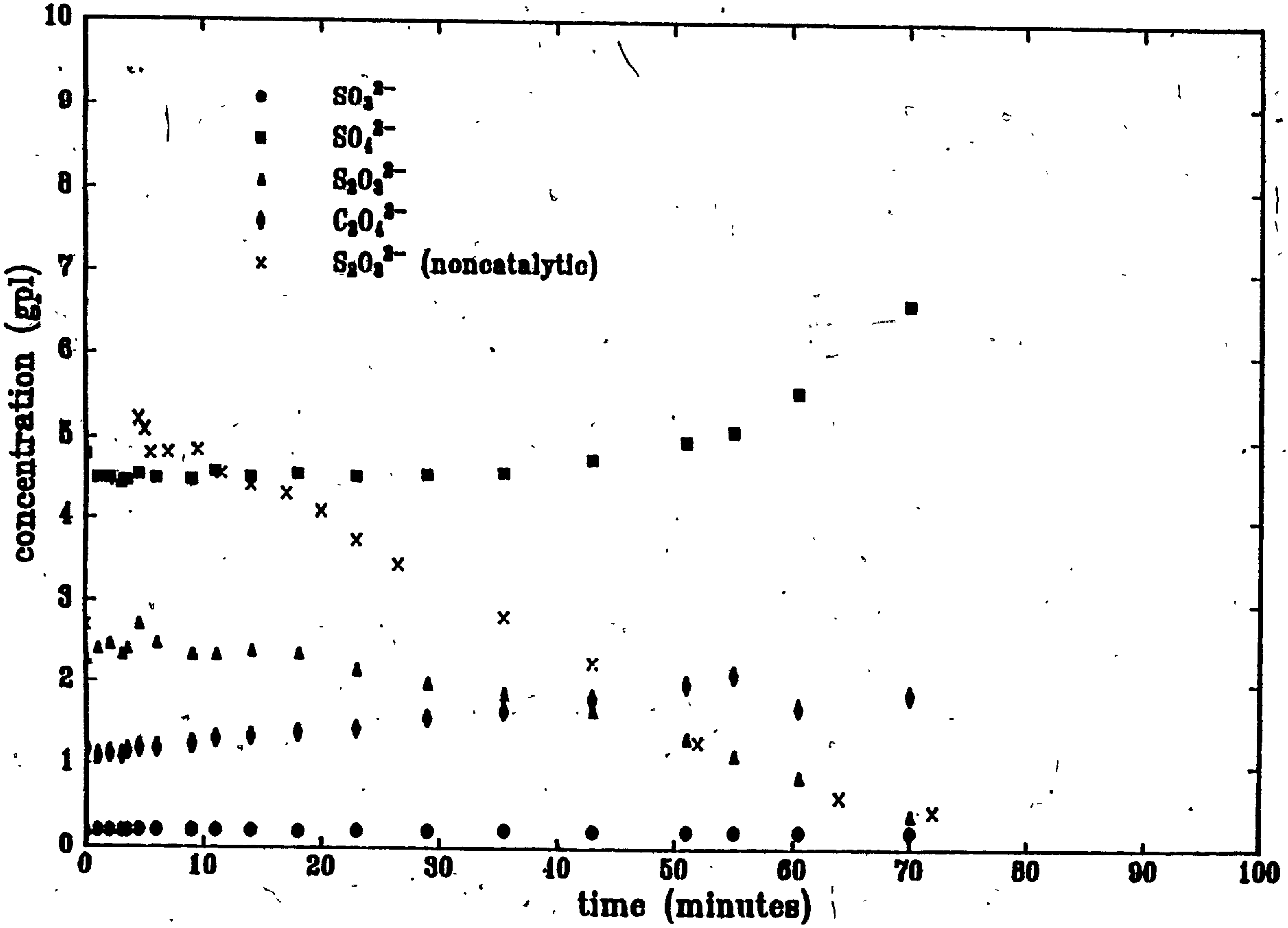

Figure 20. Effect of 10 gpl $CuCl_2$ addition on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

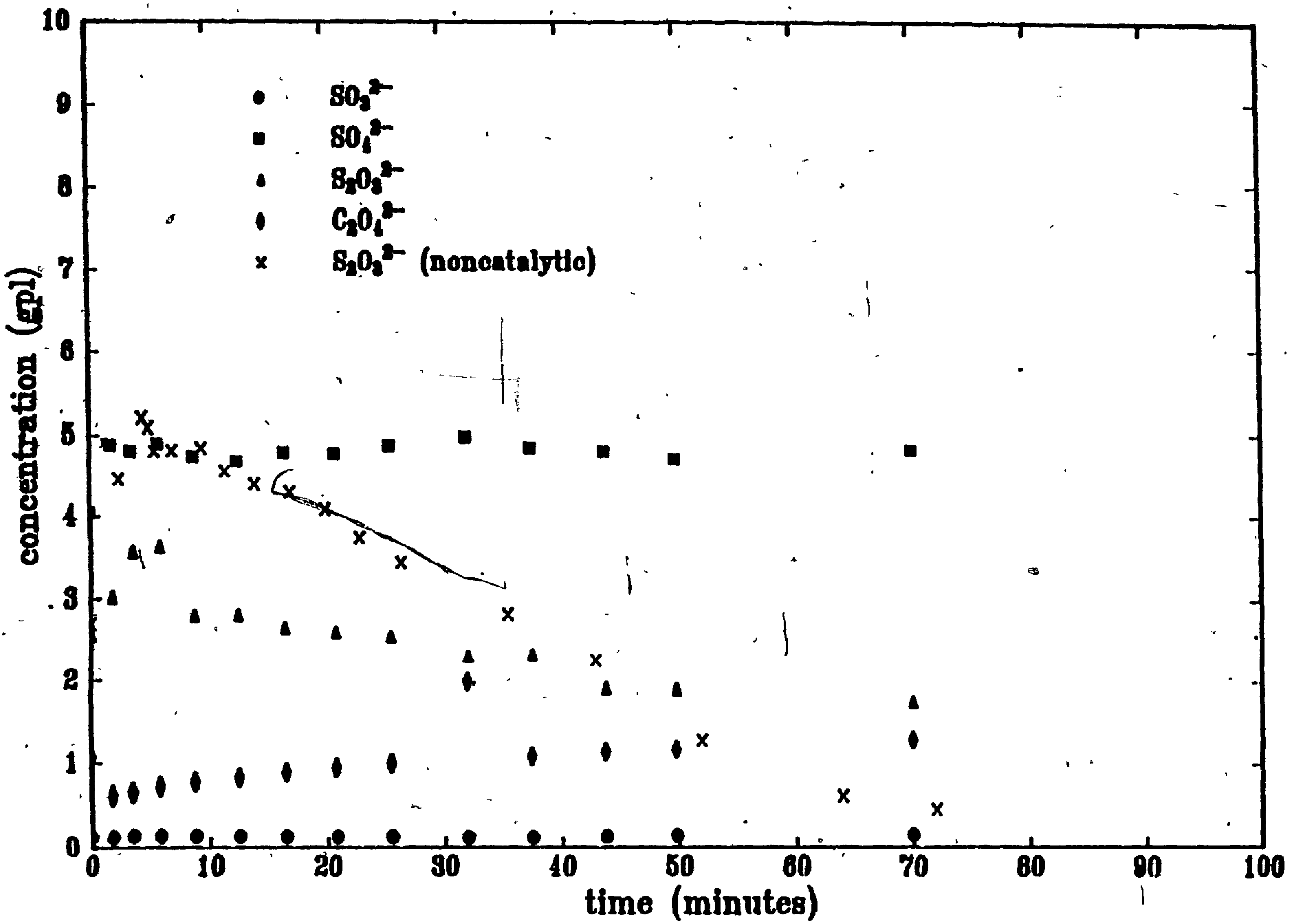

Figure 21. Effect of 5 gpl $CuCl_2$ addition on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

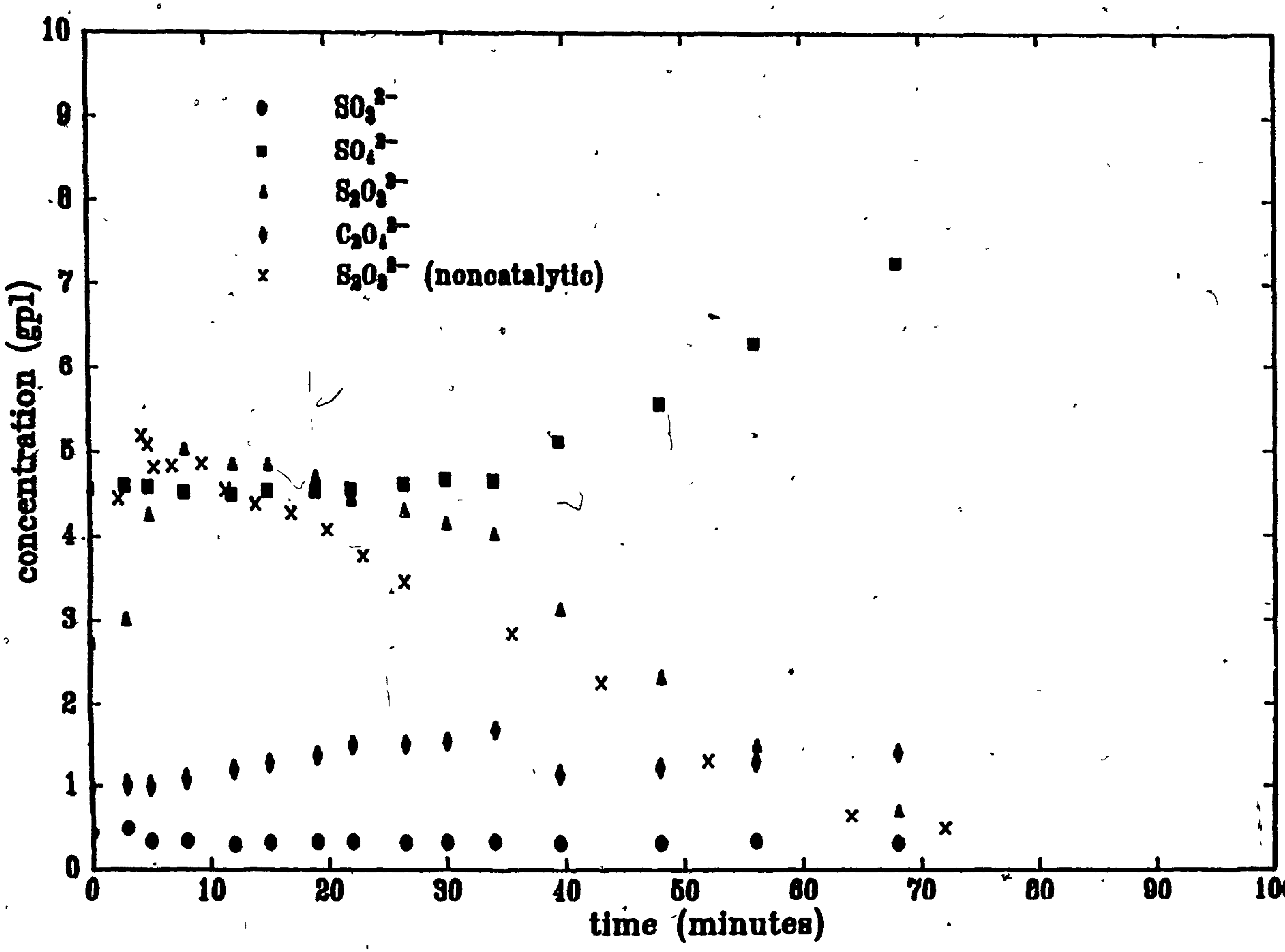

Figure 22. Effect of 10 gpl activated charcoal addition on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

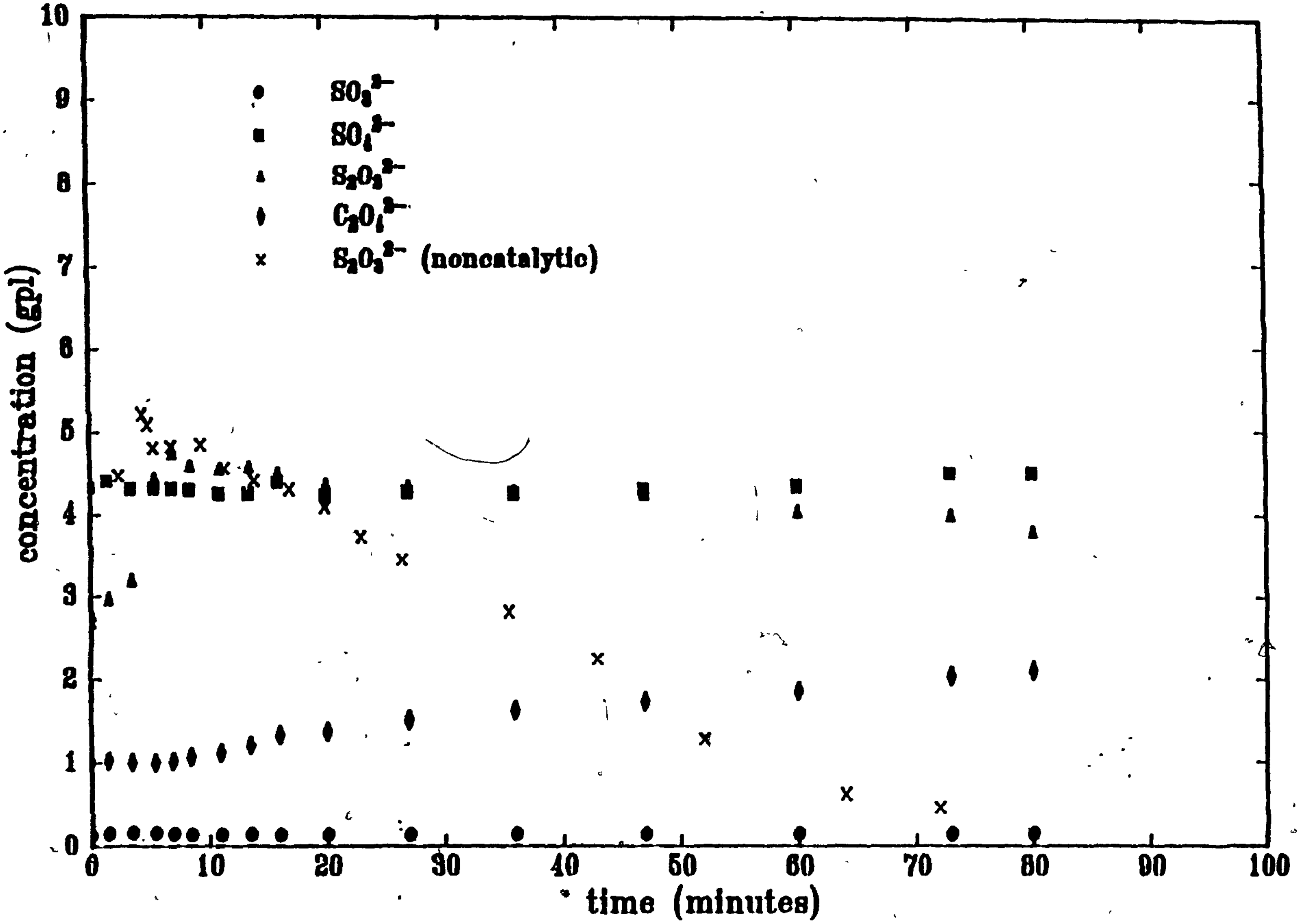

Figure 23. Effect of 10 gpl hydroquinone addition on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

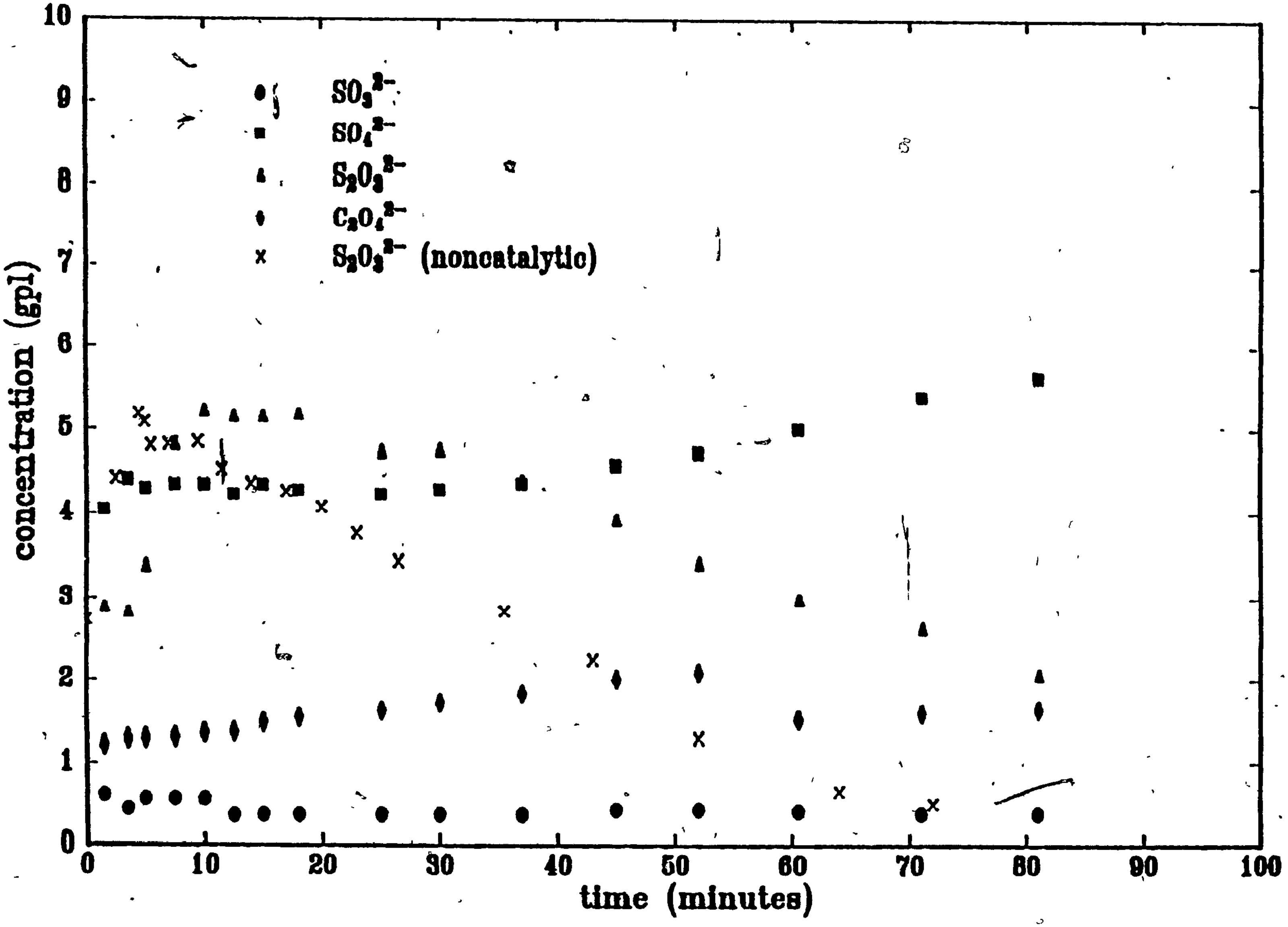

Figure 24. Effect of 10 gpl reduced iron filings on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

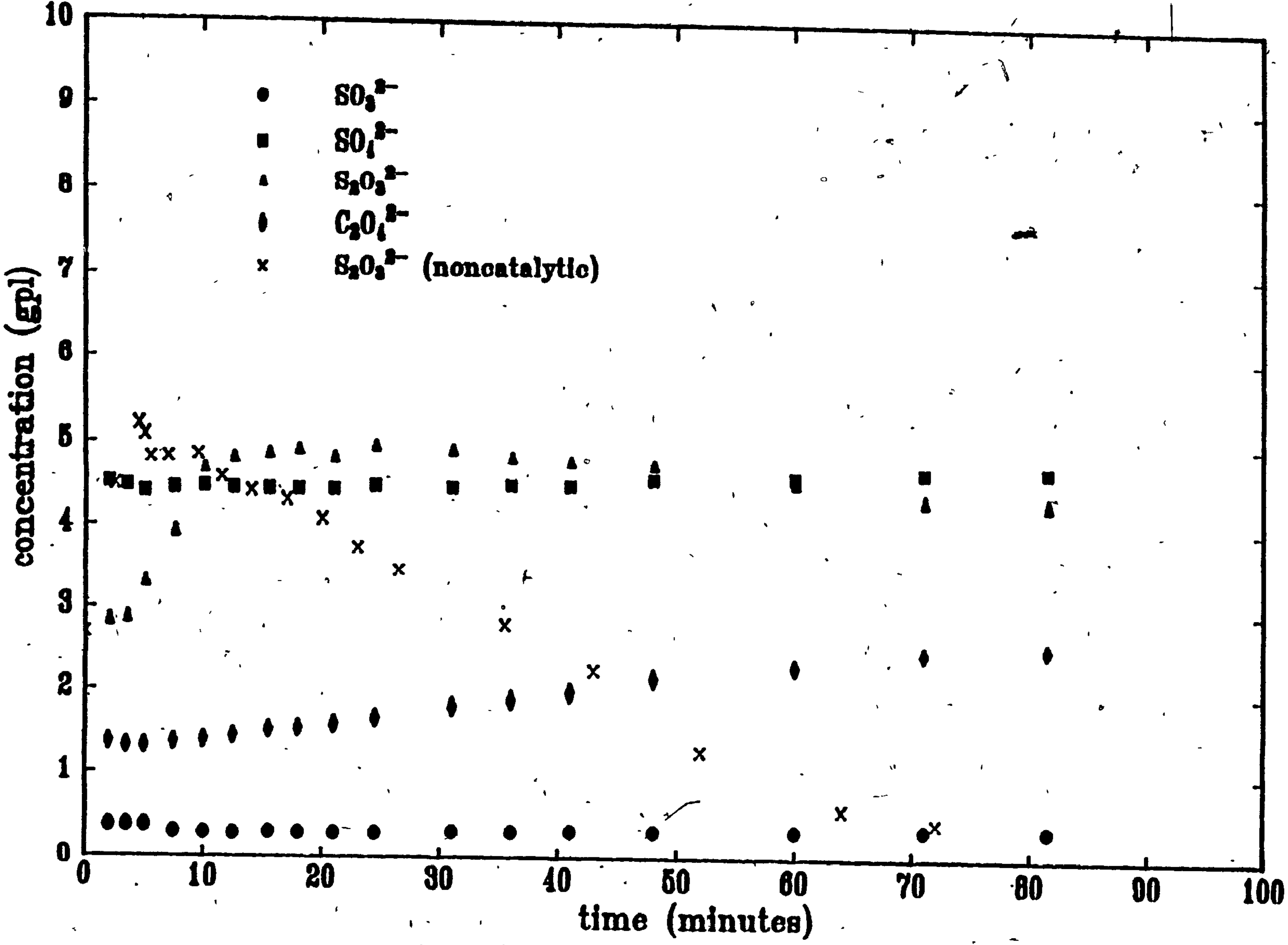

Figure 25. Effect of 10 gpl manganese on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

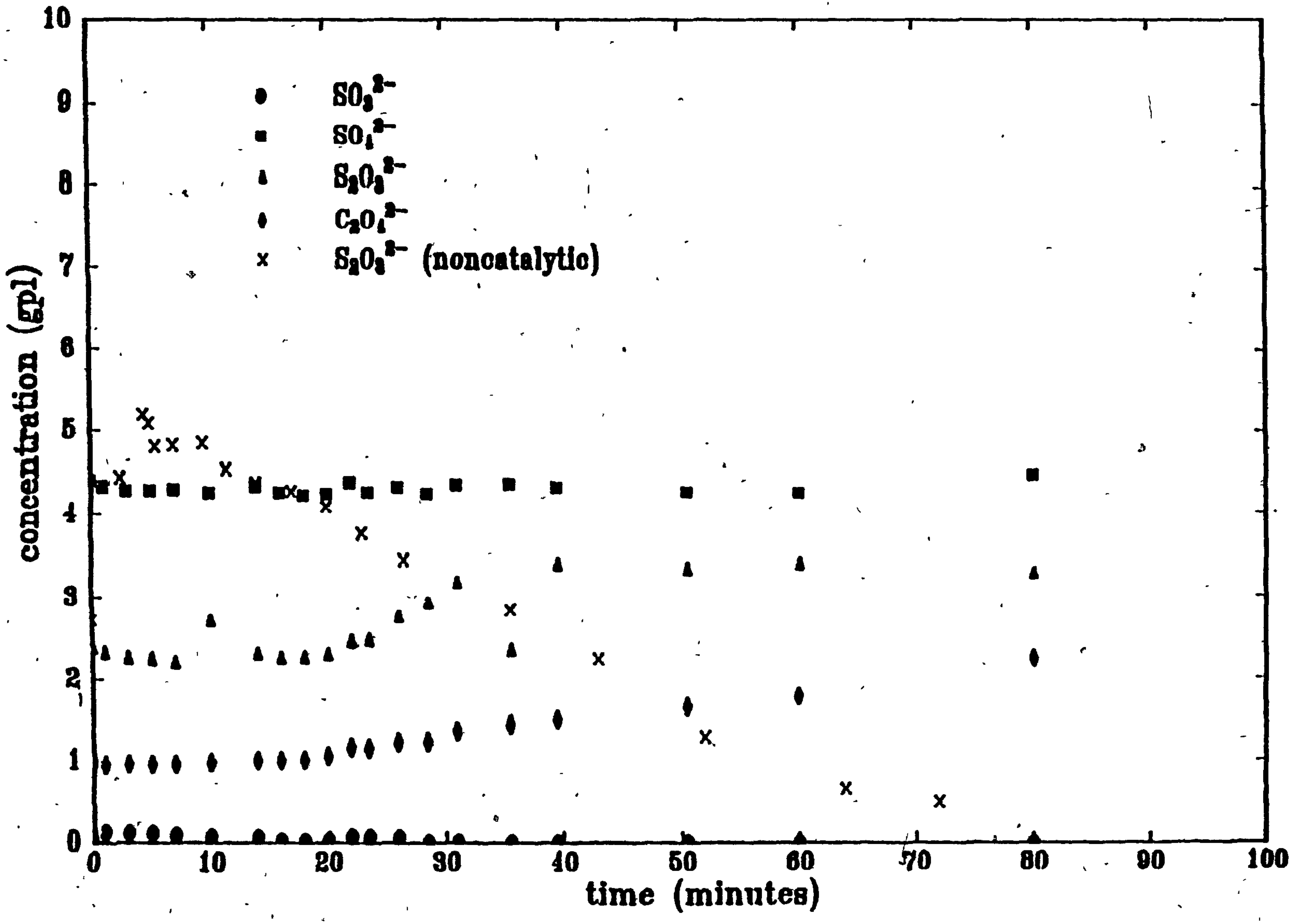

Figure 26. Effect of 10 gpl $CoCl_2$ addition on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

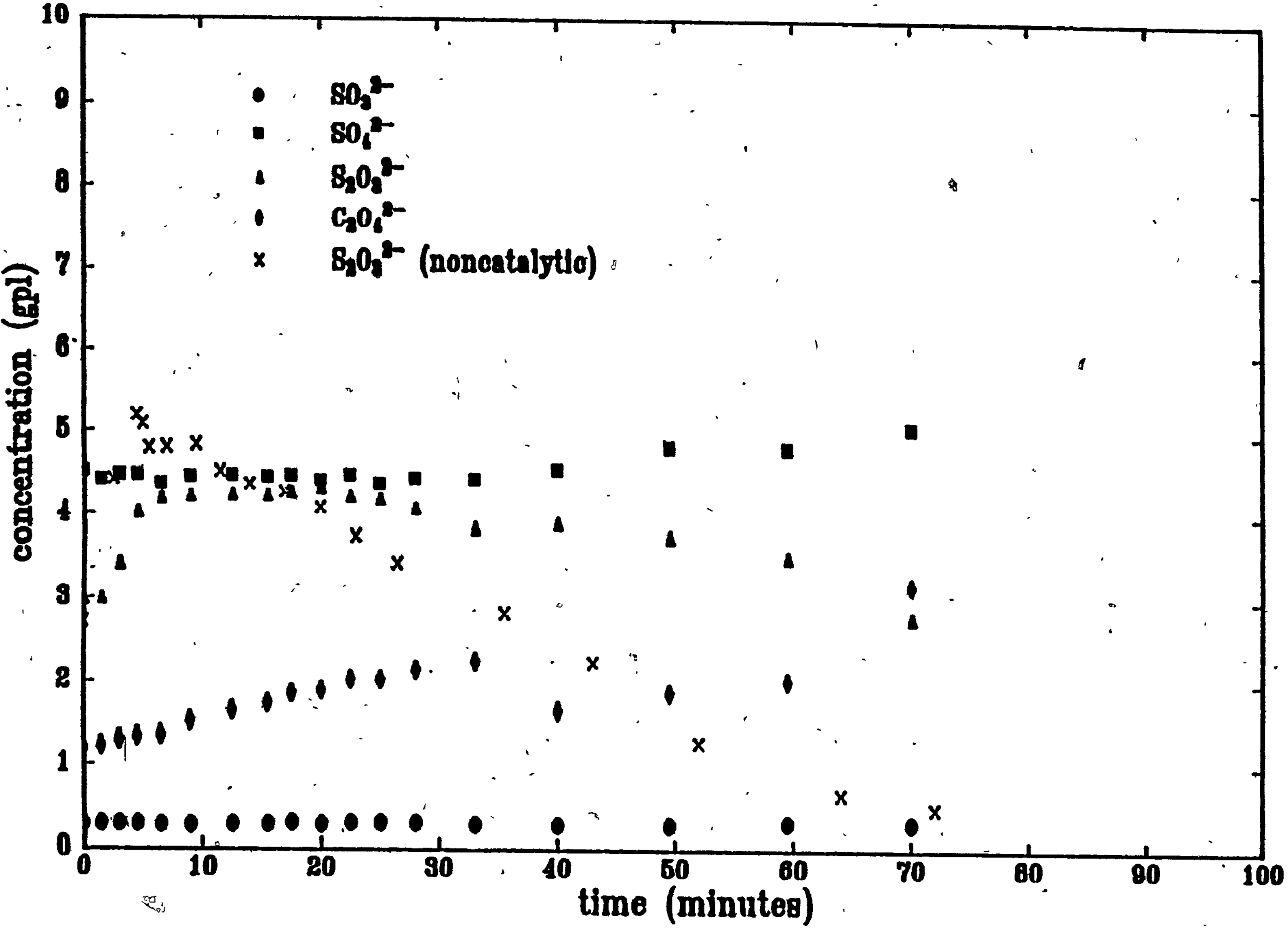

Figure 27. Effect of 10 gpl MnO_2 on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

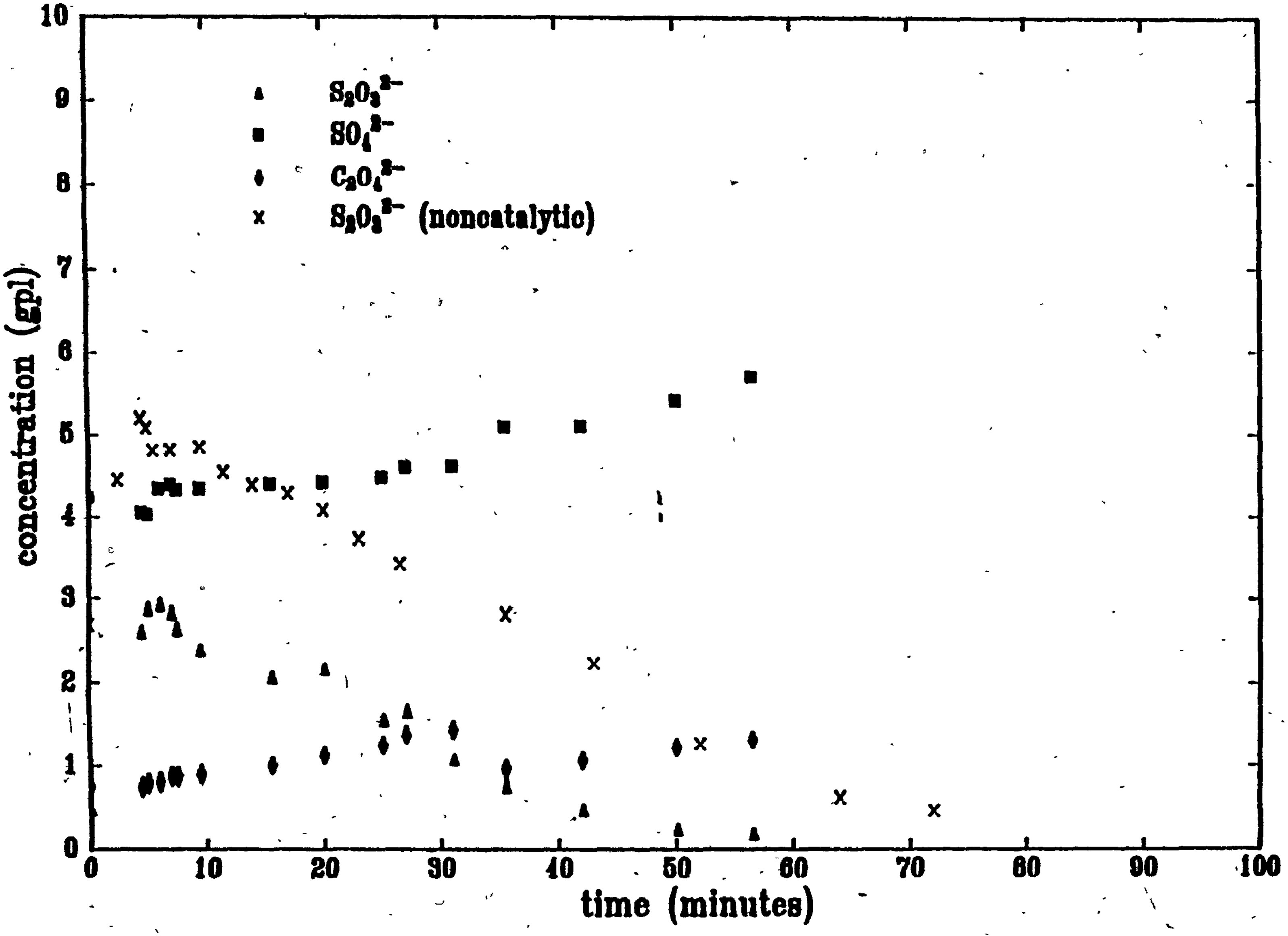

Figure 28. Effect of 10 gpl NiAl on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

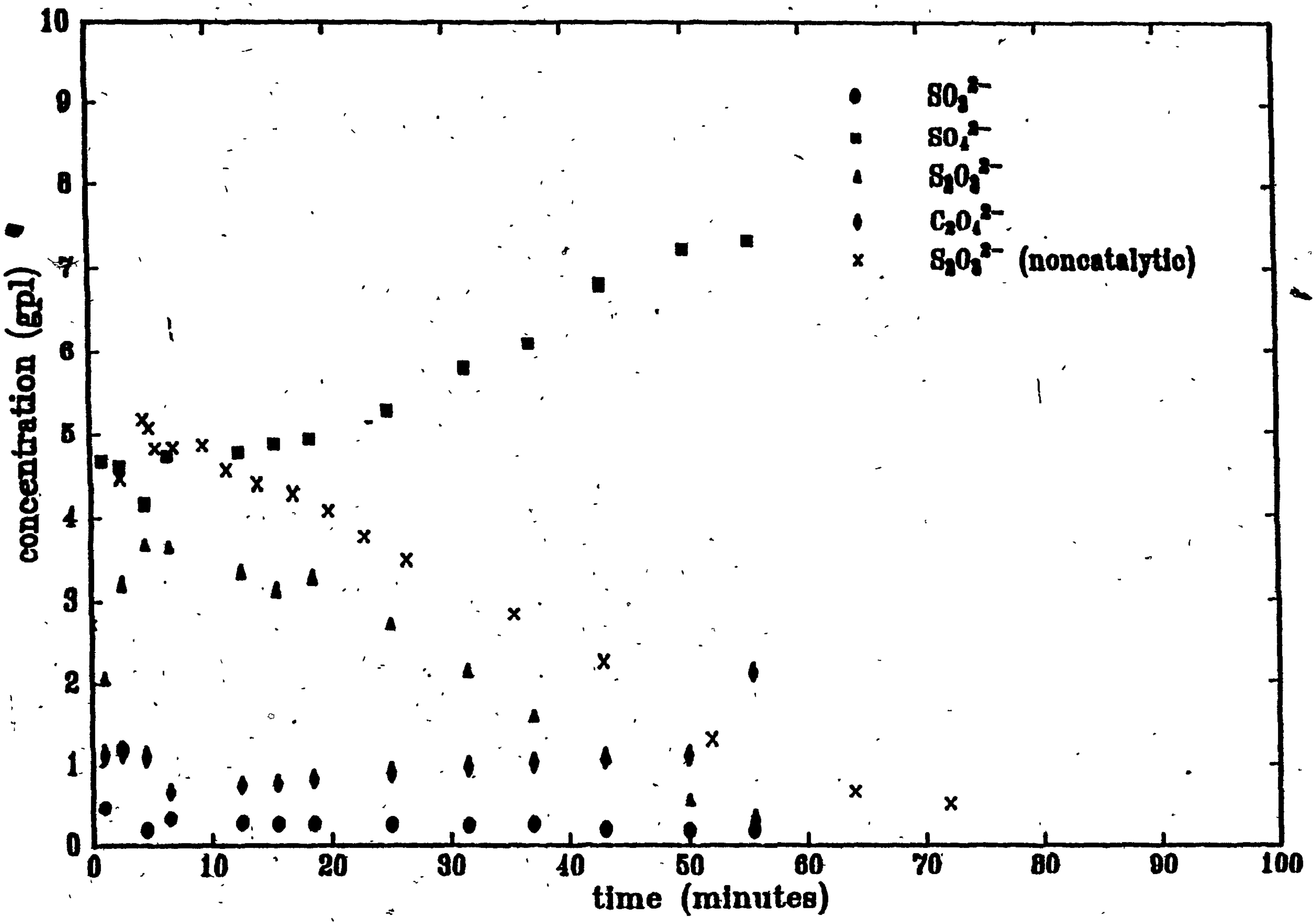

Figure 29. Effect of 5 gpl NiAl on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

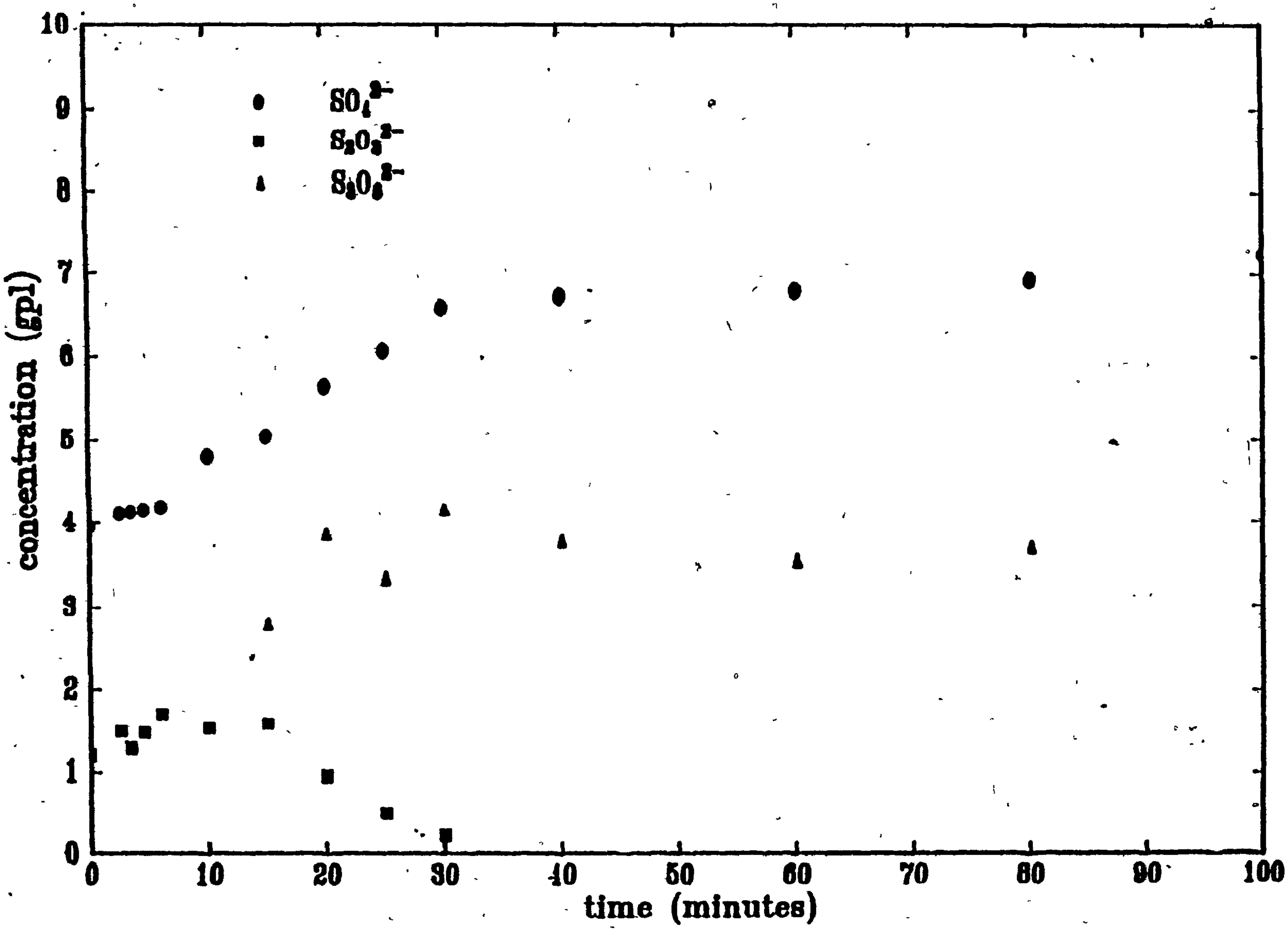

Figure 30. Effect of 5 gpl NiAl on oxidation for Liquor C at 1.2 lpm O_2 and 2500 rpm with baffle.

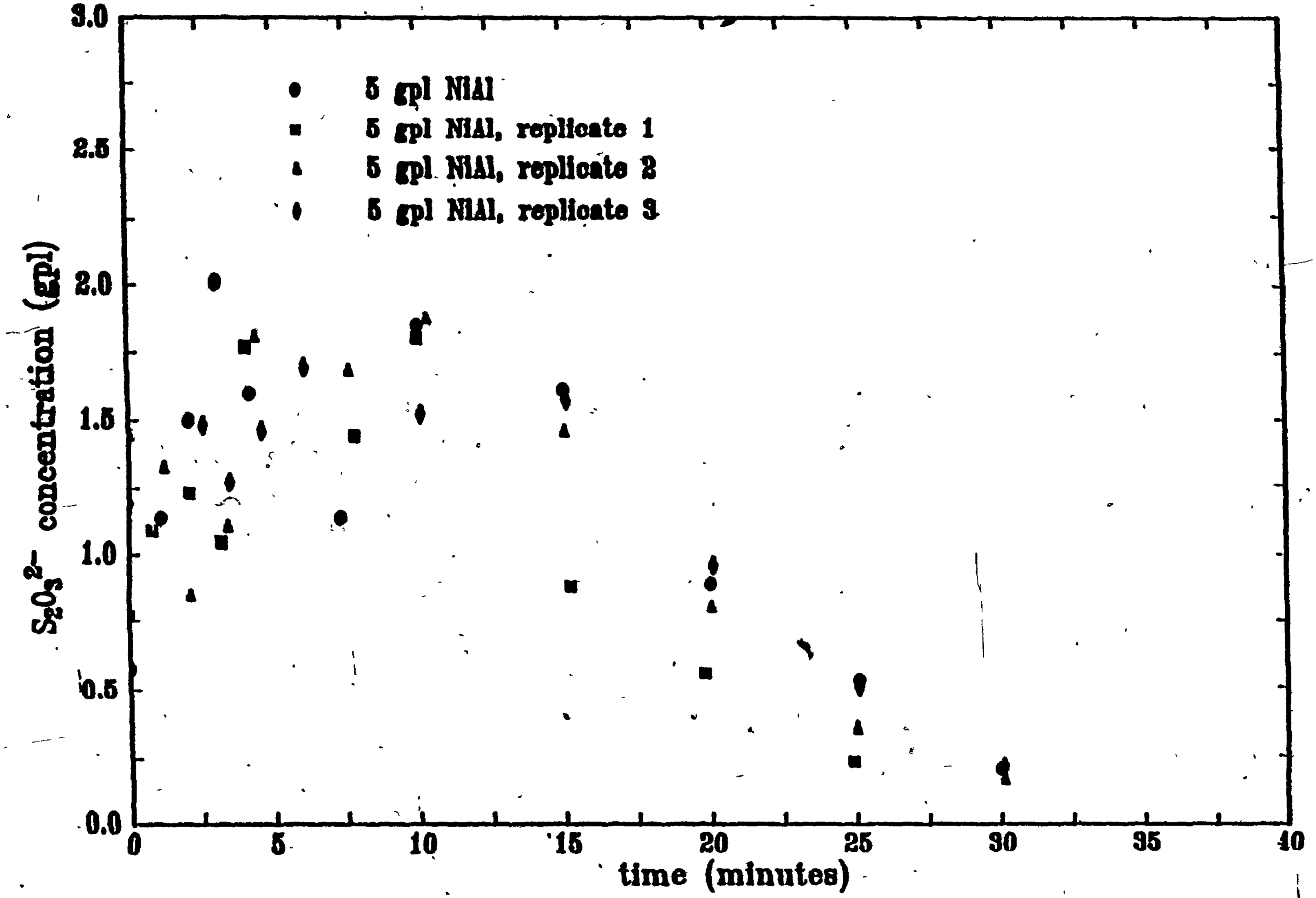

Figure 31. Experimental reproducibility of catalytic thiosulfate oxidation for Liquor C with 5 gpl NiAl at 1.2 lpm O_2 and 2500 rpm with baffle.

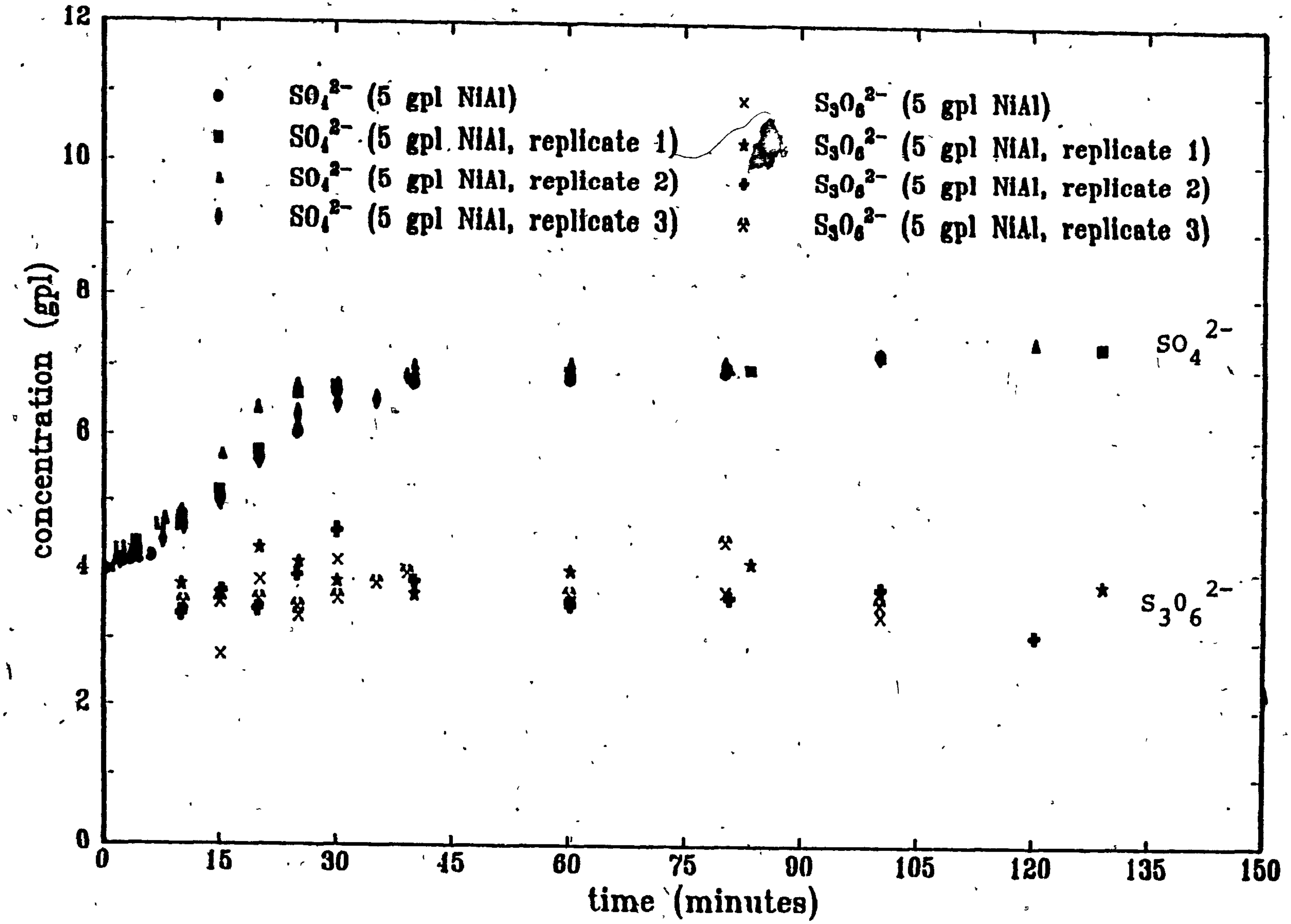

Figure 32. Experimental reproducibility of catalytic oxidation on sulfate and trithionate production for Liquor C with 5 gpl NiAl at 1.2 lpm O_2 and 2500 rpm with baffle.

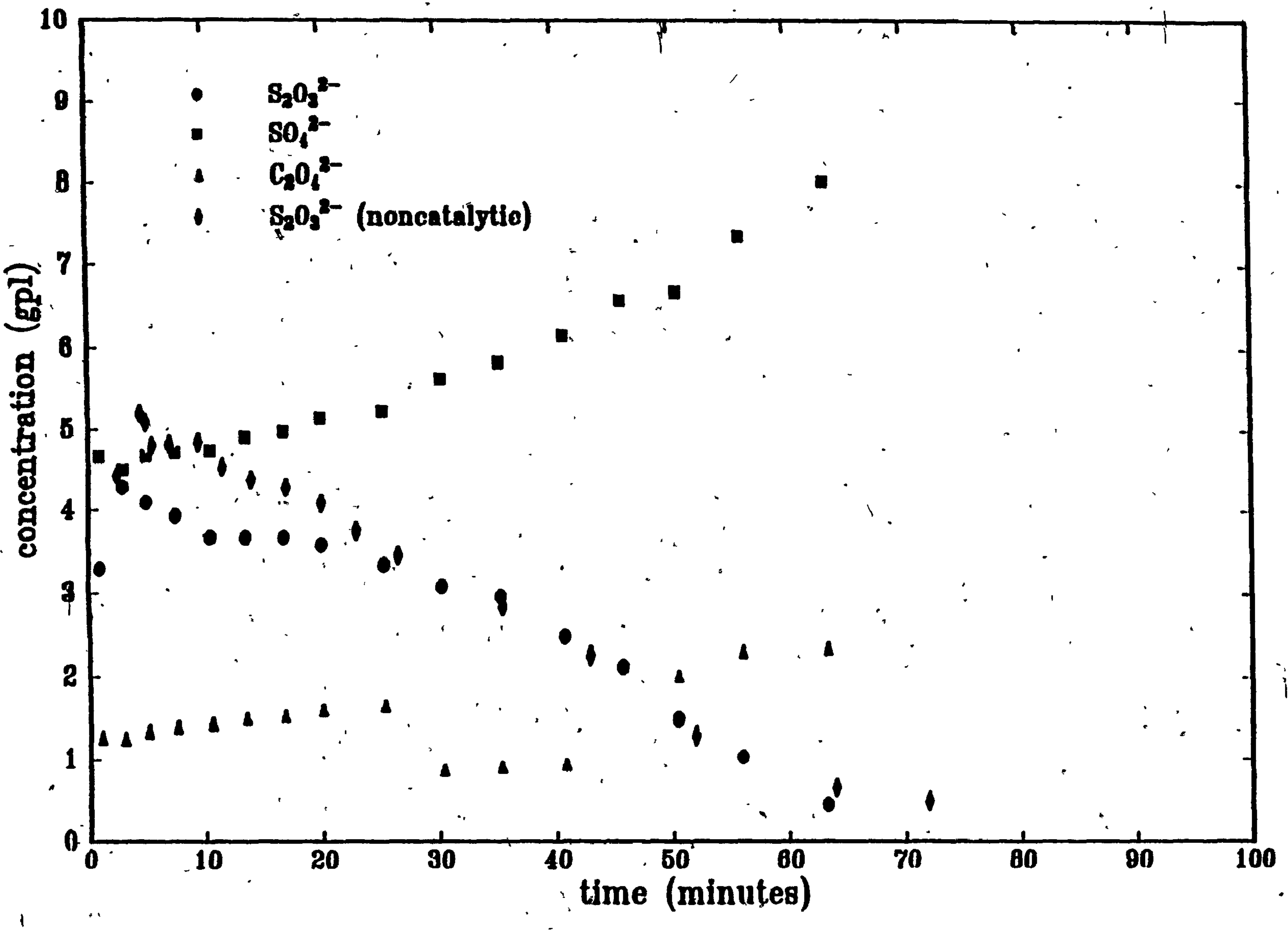

Figure 33. Effect of 3 gpl NiAl on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

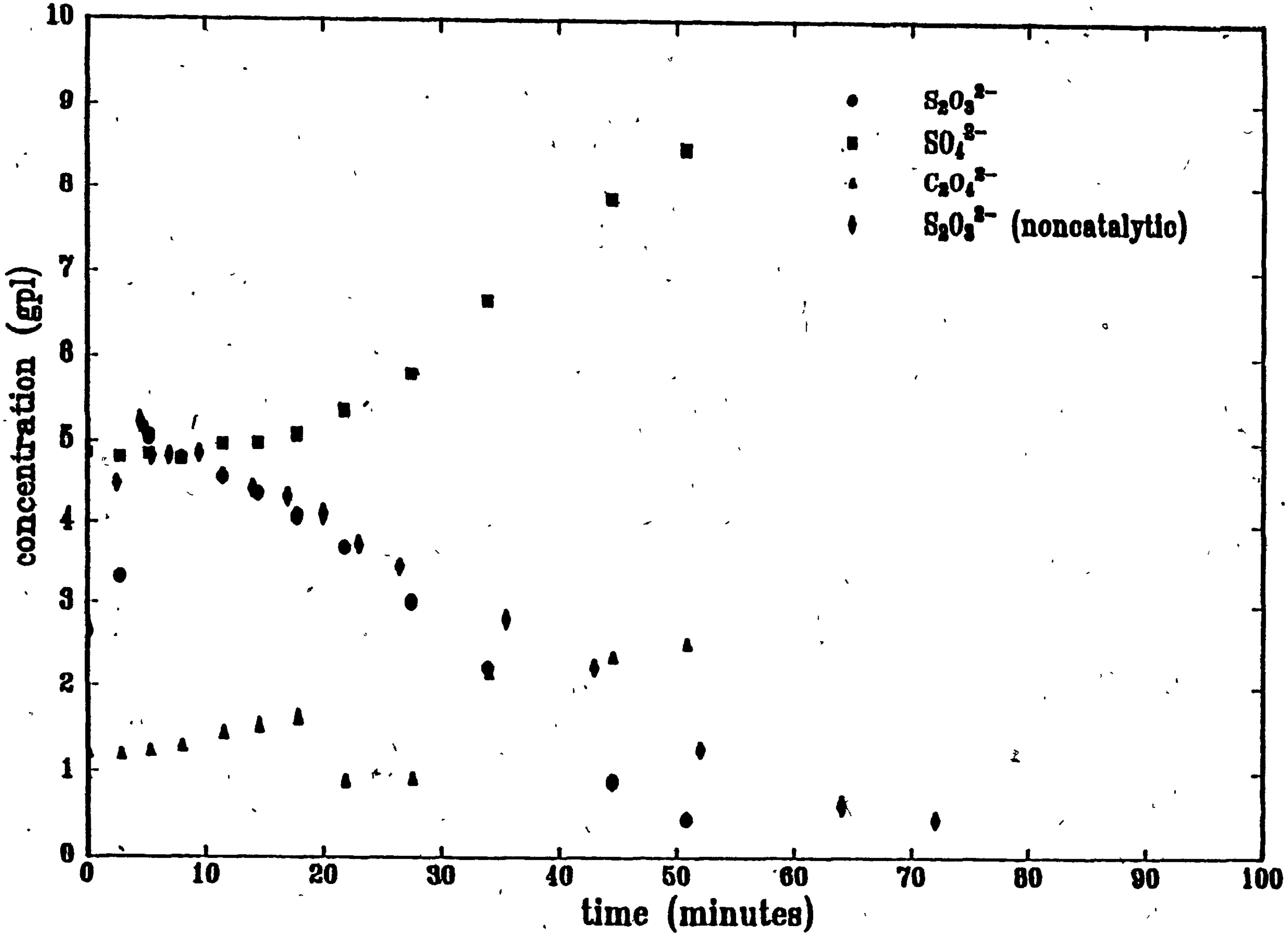

Figure 34. Effect of 1 gpl NiAl on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

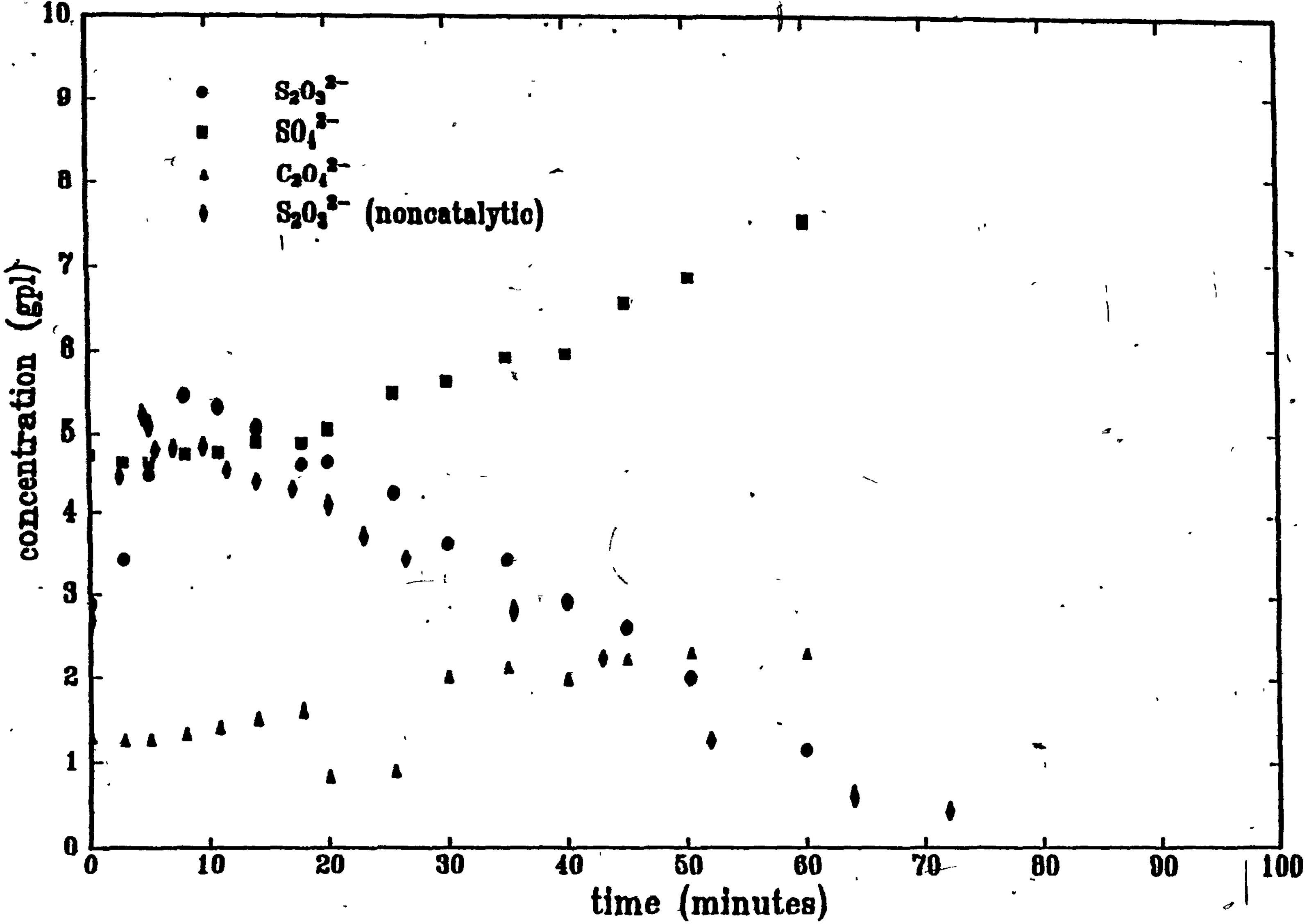

Figure 35. Effect of 0.5 gpl NiAl on oxidation for Liquor A at 2.4 lpm O_2 and 1500 rpm.

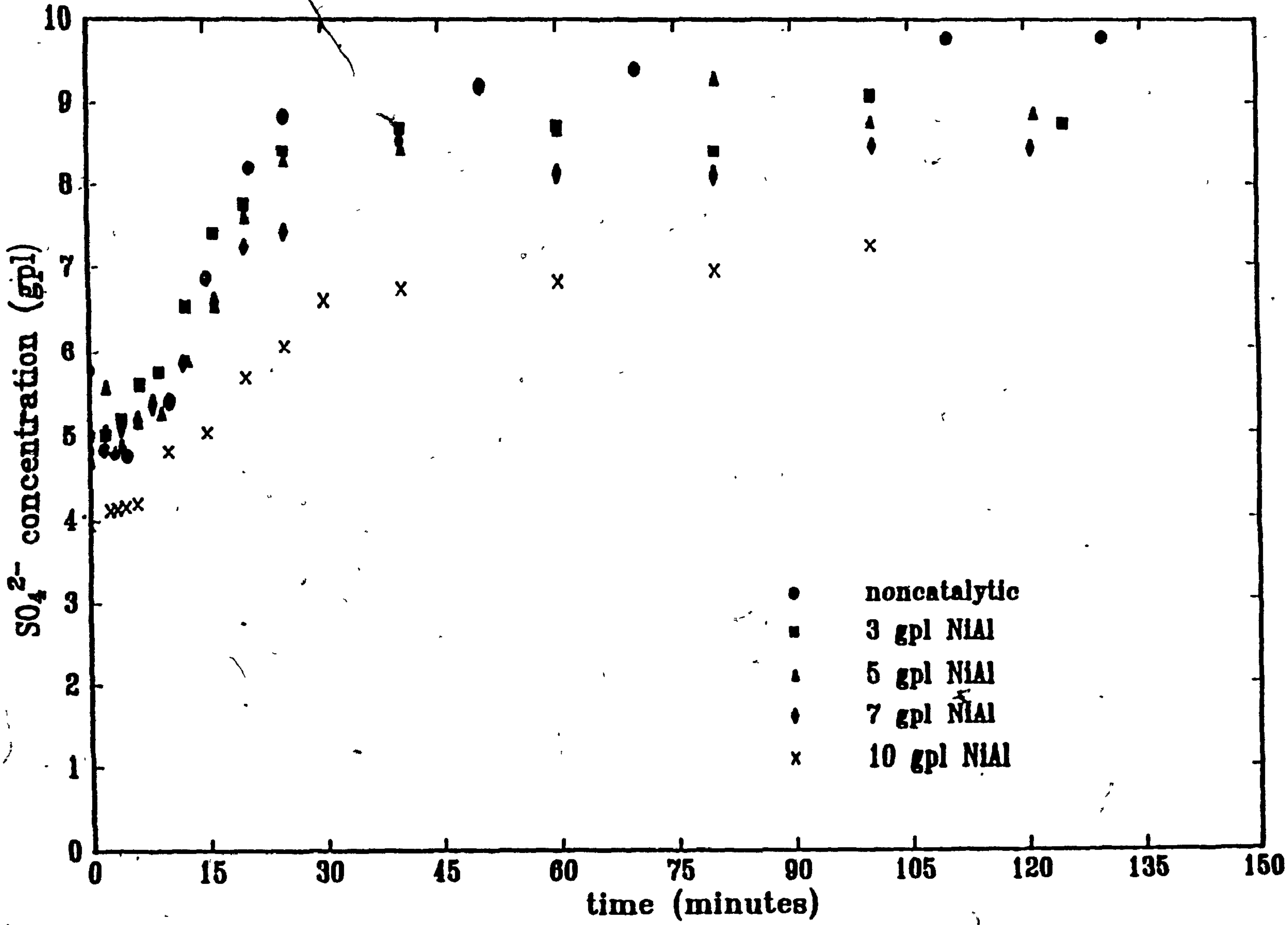

Figure 36. Effect of catalyst concentration for Liquor B at 1.2 lpm O_2 and 2500 rpm with baffle.

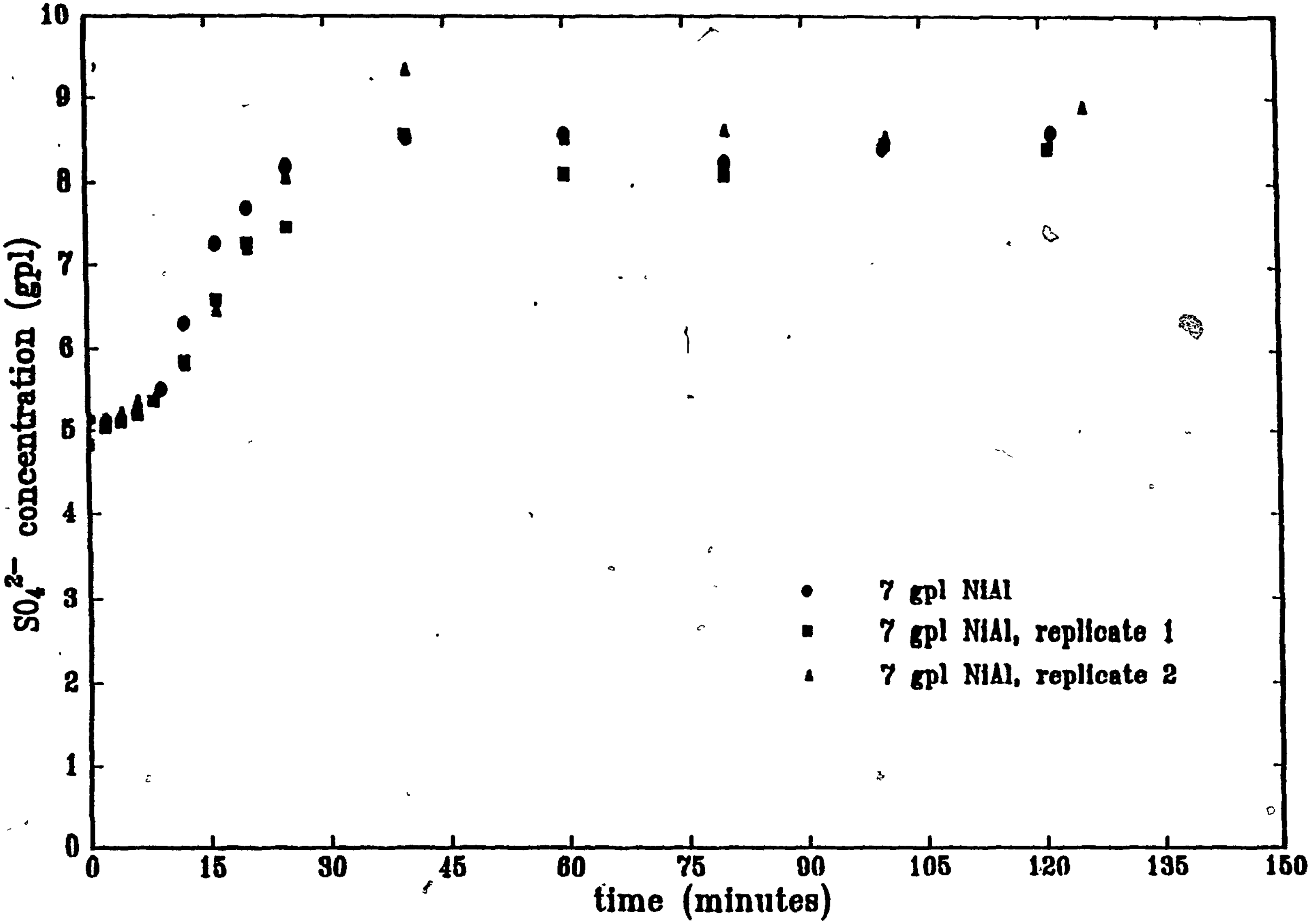

Figure 37. Experimental reproducibility of catalytic oxidation on sulfate production for Liquor B at 1.2 lpm O_2 and 2500 rpm with baffle.

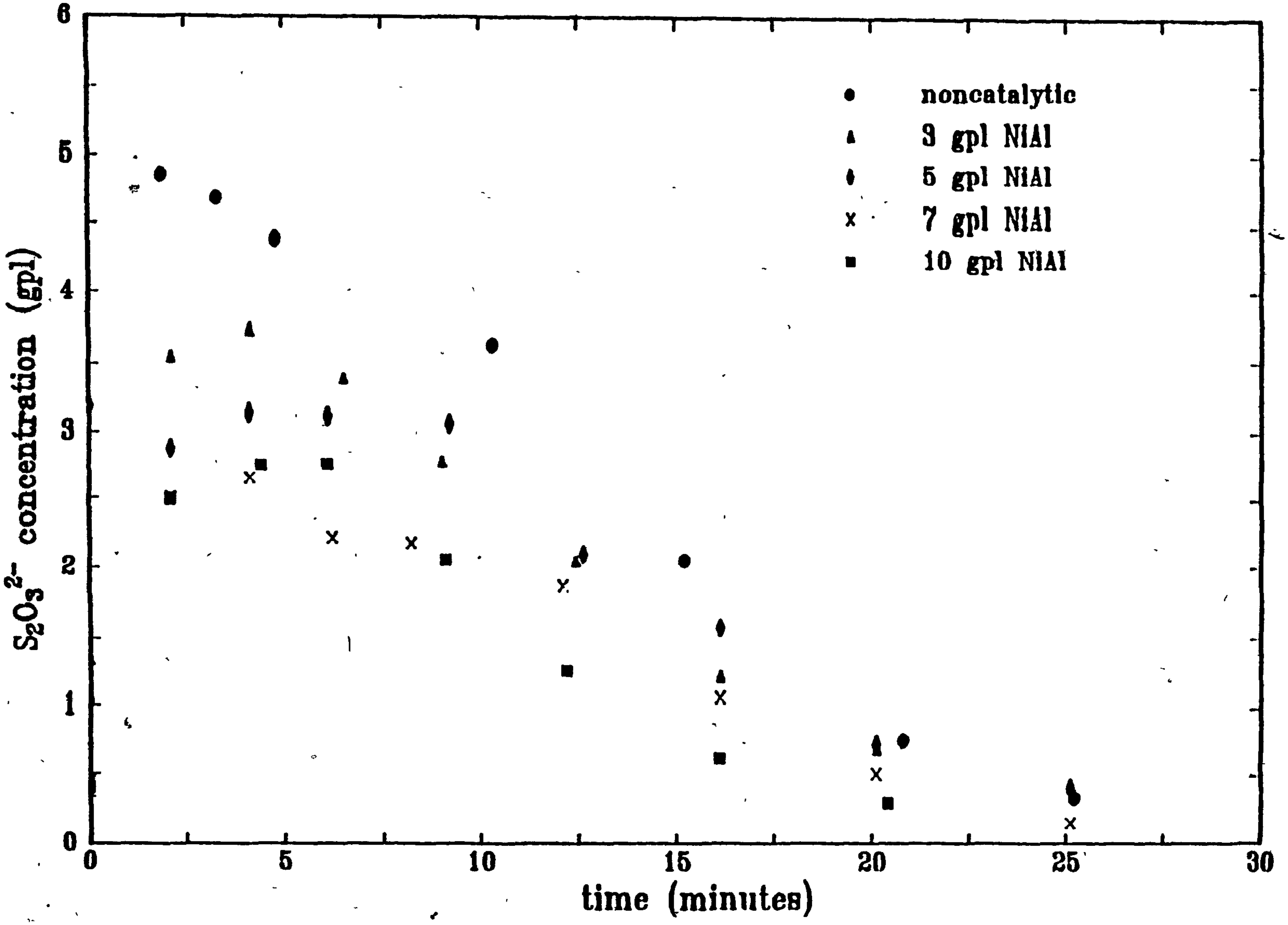

Figure 38. Effect of NiAl alloy catalyst loading on $S_2O_3^{2-}$ oxidation for Liquor B at 1.2 lpm O_2 and 2500 rpm with baffle.

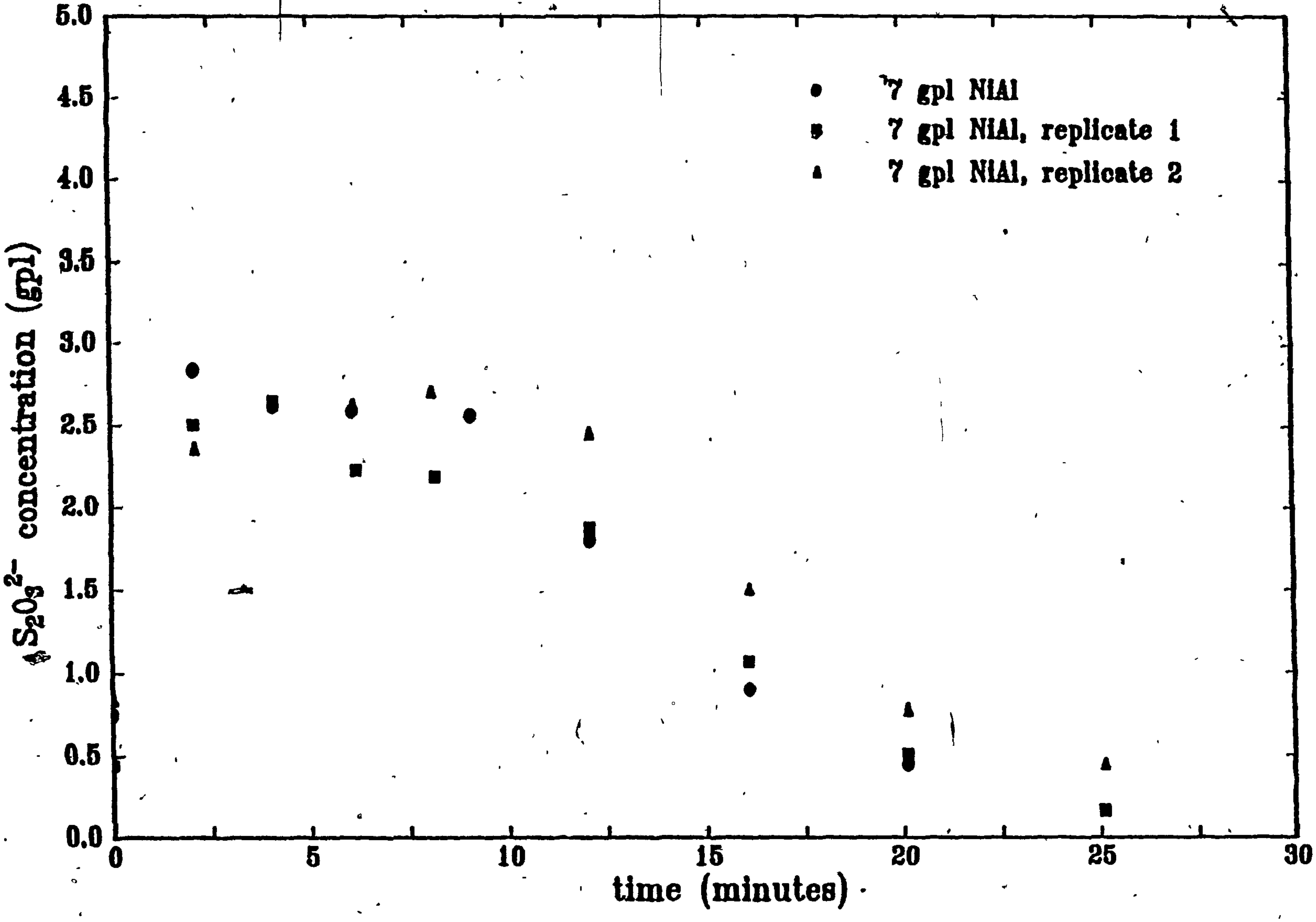

Figure 39. Experimental reproducibility of 7 gpl catalyst loading on thiosulfate oxidation rate for Liquor B at 1.2 lpm O_2, 2500 rpm, and with baffle.

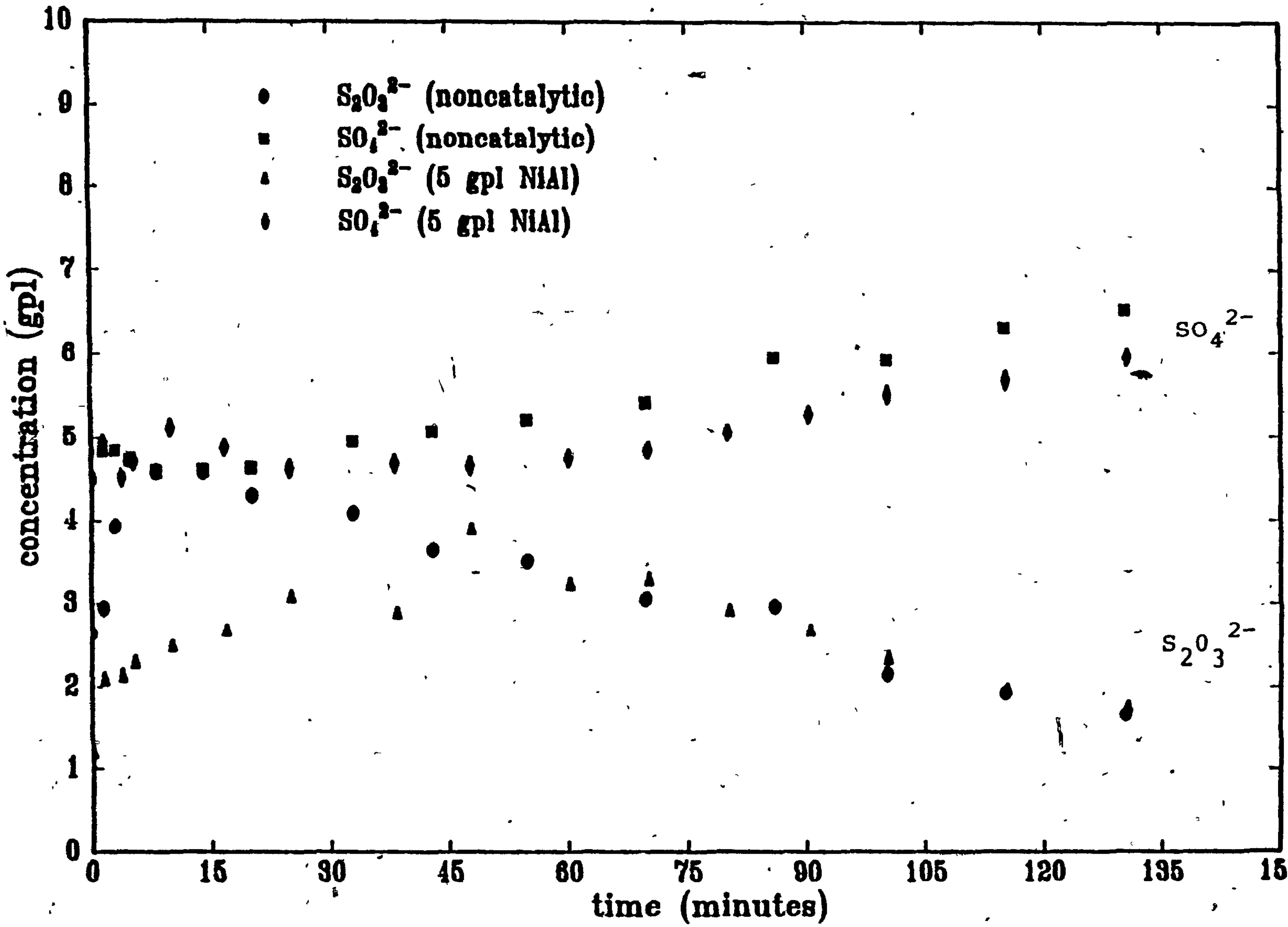

Figure 40. Comparison between noncatalytic and catalytic BLOX with 5 gpl NiAl for Liquor B at 2.4 lpm O_2 and 800 rpm.

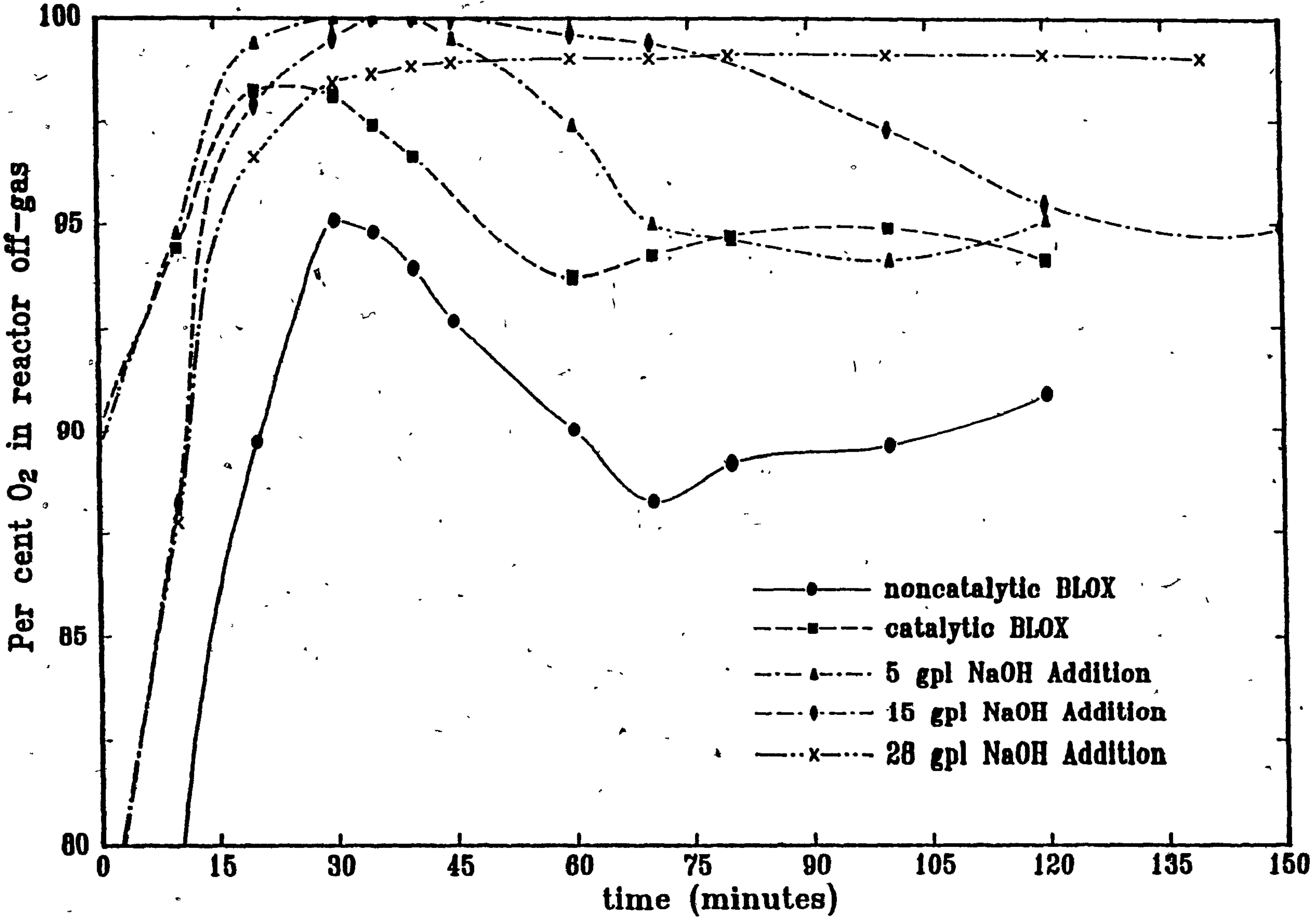

Figure 41. Effect of reactor residence time on $\%O_2$ in reactor off-gas.

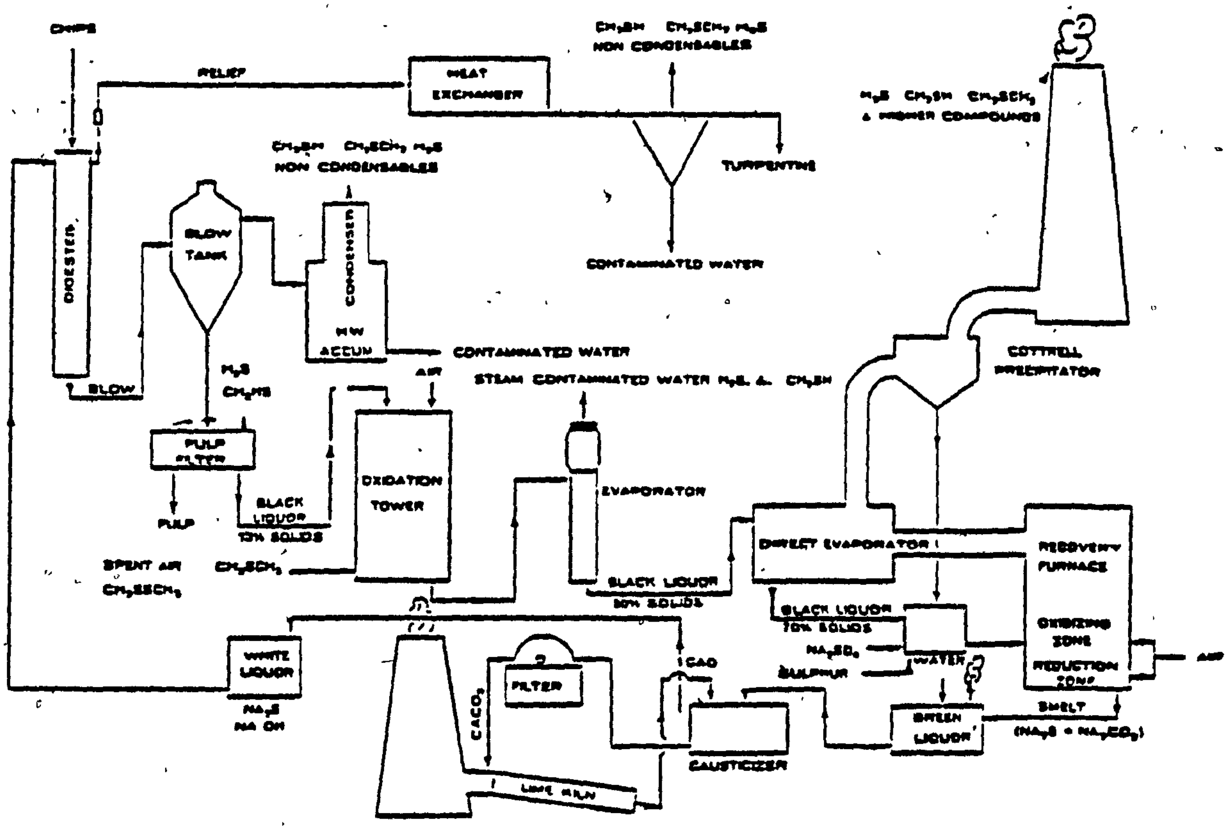

Figure I. Process flowsheet of kraft chemical/energy recovery cycle (Ref.7).

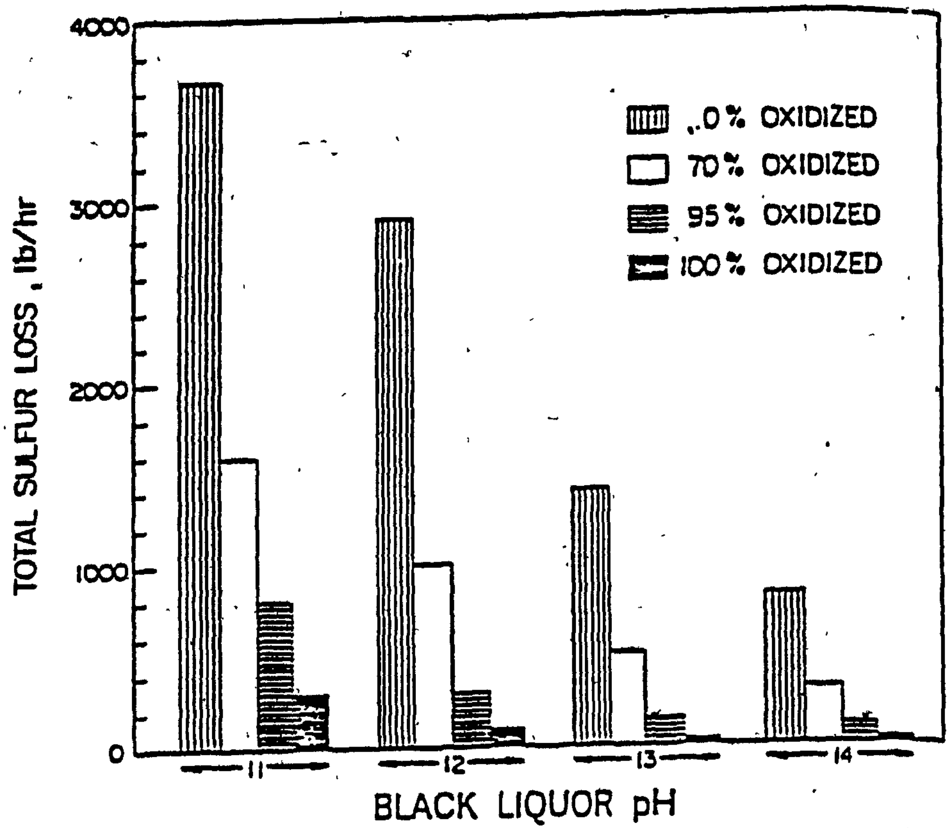

Figure II. Effect of oxidation and liquor pH on volatile sulfur emissions (Ref. 62).

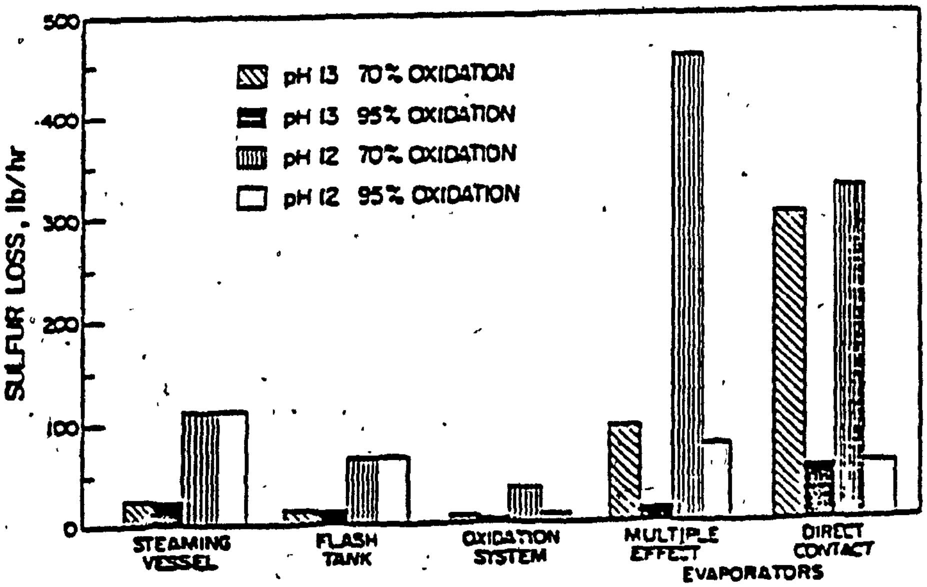

Figure III. Volatile sulfur emissions from various points in a kraft mill (Ref. 62).

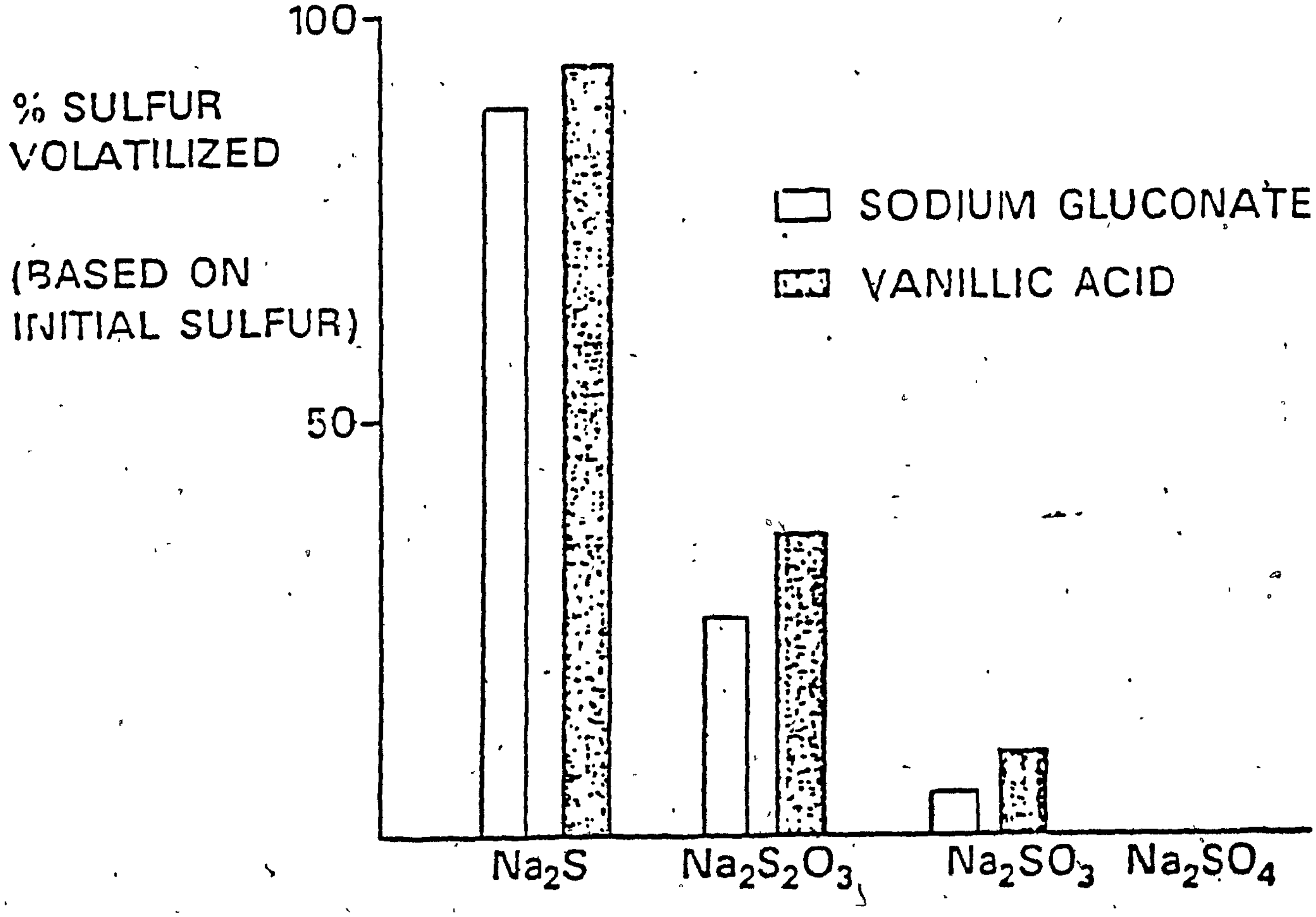

Figure IV. Effect of inorganic sulfur compound type on amount of sulfur volatilized during pyrolysis (Ref. 55).

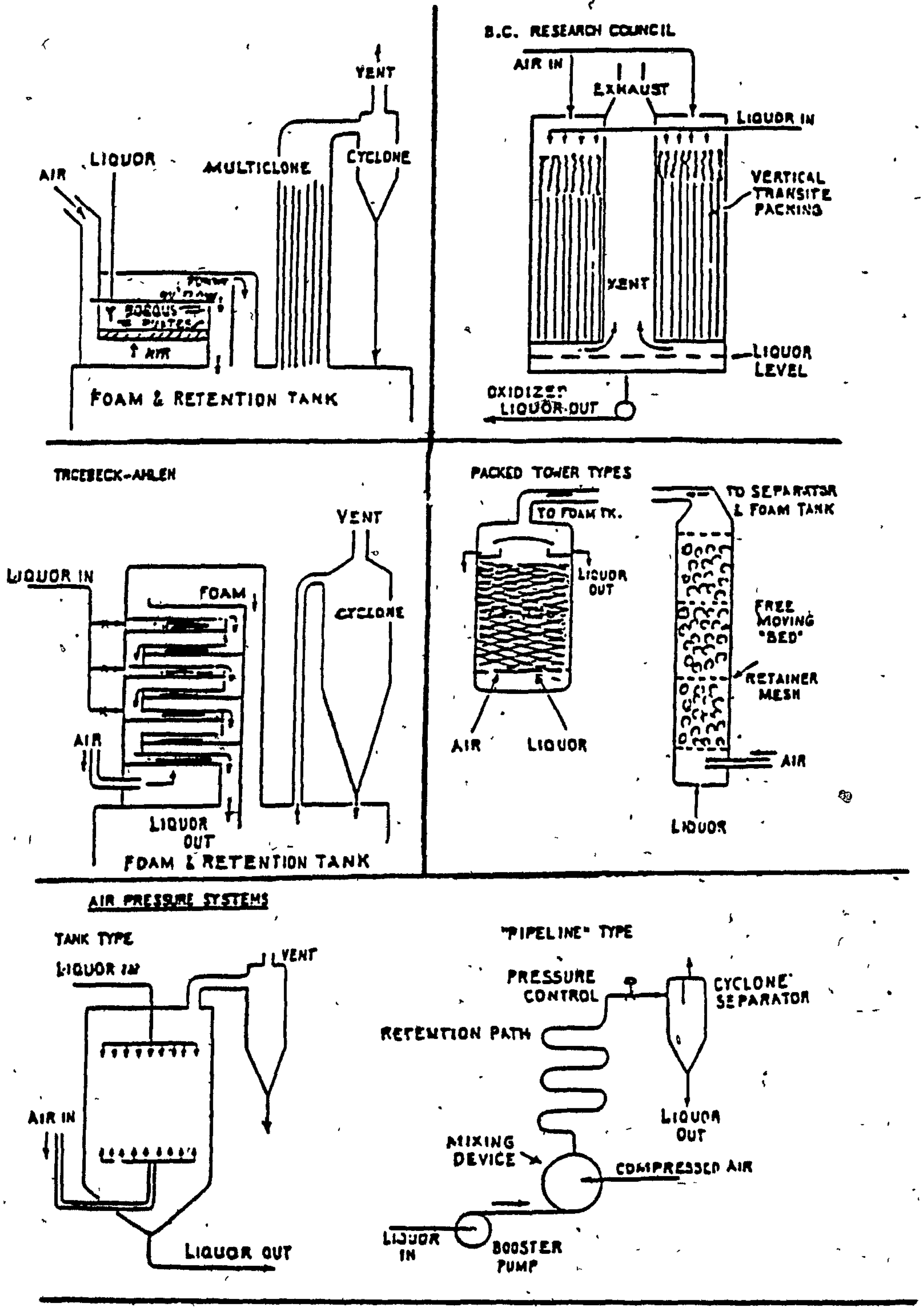

Figure V. Schematics of common oxidation technology (Ref. 26).

APPENDIX 2 : IC COMMISSIONING RESULTS

Table I : IC Commissioning I

Species	Other Species Present	# runs	% change	elapsed time (hrs.)
sulfite	—	44	2.0	0.0
sulfate	—	38	1.3	0.0
thiosulfate	—	39	2.8	0.0
sulfite	sulfate thiosulfate thionates	7	6.0	4.0
sulfate	thiosulfate sulfite thionates	7	2.1	4.0
thiosulfate	sulfate sulfite thionates	7	0.9	4.0
sulfite	thiosulfate sulfate	7	13.7	24.0
sulfate	thiosulfate sulfite	7	3.0	24.0
thiosulfate	sulfite sulfate	7	2.9	24.0

APPENDIX 2 : IC COMMISSIONING RESULTS

Table II : IC Commissioning II

Species	Output Range (microsiemens)	Linear Concentration Range (ppm)	Integration Method
sulfite	30	0-35	peak height
	10	0-7	peak height
sulfate	30	0-25	peak height
	10	0-7	peak height
thiosulfate	30	0-50	peak area
	10	0-7	peak area
	3	0-3	peak area

APPENDIX 2 : IC COMMISSIONING RESULTS

Table III : IC Commissioning III

Species	Typical Range (gpl)	Dilution Factor of Black Liquor Sample	Output Range (microsiemens)
sulfate	4-6	1000x	10
thiosulfate	2-5	1000x	10
sulfite	0.15-0.30	1000x	10
sulfate	6-10	2000x	10
thiosulfate	0-2	2000x	3
sulfite	0-0.15	2000x	10
sulfate	>10	5000x	10
thiosulfate	<0.5	5000x	NA
sulfite	0	5000x	10

APPENDIX 3 : ESTIMATION OF EXPERIMENTAL ERROR

Table IV : Experimental Uncertainty Estimates I*

ionic species	Method	Number Data Points	Average relative %error	Standard Deviation (gpl)
sulfite (SO_3^{2-})	IC	5	15	0.03^p
sulfate (SO_4^{2-})	IC	50	4	0.20^p
thiosulfate ($S_2O_3^{2-}$)	IC	32	3	0.15^p
trithionate ($S_3O_6^{2-}$)	titration	19	4	0.22^p
oxalate ($C_2O_4^{2-}$)	IC	15	8	0.12
carbonate (CO_3^{2-})	IC	4	3	0.48
hydroxide	titration	6		

* "p" represents pooled standard deviation estimates

APPENDIX 3 : ESTIMATION OF EXPERIMENTAL ERROR

Table V : Experimental Uncertainty Estimates II*

ionic species	Method	Average relative %error	# points	Standard Deviation
Total solids	oven drying	2	6	0.2 (wt.%)
Total sulfur	wet combustion	2	6	0.11 (gpl)
Thermal value	bomb calorimetry	3	6	0.39 (kJ/g)
TOC	Technicon Autoanalyzer	3	4	1.5 (gpl)
Calcium	Atomic Absorption	19	4	4.7 (mg/l)
Sodium	Atomic Absorption	3	9	1.8^p (gpl)
pH	pH meter	1	43	0.19^p

* "p" represents pooled standard deviation estimates

APPENDIX 3 : ESTIMATION OF EXPERIMENTAL ERROR

Table VI : Computation Of Pooled Standard Deviation For Sulfate Data From Replicate Runs.

Time (min.)	run	SO_4^{2-} (gpl)	m-1	$\hat{s}_i^2$	$(m-1)\hat{s}_i^2$
0	AB	4.17	3	0.0169	0.0506
	AC	3.89			
	AD	4.00			
	AE	4.14			
1.1	AD	4.04	1	0.0125	0.00125
	AE	3.99			
1.5	AB	3.94	1	0.0002	0.0002
	AC	3.96			
2.1	AE	4.09	1	0.0032	0.0032
	AD	4.01			
3.1	AB	4.22	2	0.005	0.01
	AD	4.08			
	AE	4.13			
4.1	AD	4.08	1	0.0512	0.0512
	AE	4.40			
4.5	AB	4.06	1	0.00045	0.00045
	AC	4.09			

Table VI cont'd

Time (min.)	run	SO_4^{2-} (gpl)	m-1	$\hat{s}_i^2$	$(m-1)\hat{s}_i^2$
10.2	AB	4.25	1	0.0221	0.0221
	AD	4.04			
15.1	AB	4.48	2	0.0687	0.1374
	AD	4.33			
	AE	4.84			
20.3	AD	5.19	3	0.0263	0.079
	AE	5.40			
	AC	5.41			
	AB	5.08			
25.3	AB	5.81	3	0.0908	0.2724
	AC	6.29			
	AD	5.79			
	AE	6.35			
30.2	AC	6.89	2	0.09	0.18
	AD	6.50			
	AE	7.09			
35.3	AB	7.14	2	0.0072	0.0145
	AC	7.27			
	AD	7.11			

Table VI cont'd

Time (min.)	run	SO_4^{2-} (gpl)	m-1	$\hat{s}_i^2$	$(m-1)\hat{s}_i^2$
40.2	AC	7.71	2	0.027	0.0541
	AD	7.40			
	AE	7.65			
45.3	AB	7.55	3	0.00856	0.0257
	AC	7.75			
	AD	7.57			
	AE	7.58			
50.0	AC	7.87	1	0.0181	0.0181
	AD	7.68			
60.2	AE	8.30	1	0.11	0.11
	AC	7.83			
81.0	AC	7.72	2	0.0273	0.0546
	AD	7.99			
	AE	8.02			
100.1	AC	7.87	2	0.0597	0.1195
	AD	8.03			
	AE	8.35			

Table VI cont´d

Time (min.)	run	SO_4^{2-} (gpl)	m-1	$\hat{s}_i^2$	$(m-1)\hat{s}_i^2$
123	AC	8.27	3	0.0765	0.0229
	AB	8.44			
	AD	8.33			
	AE	8.45			
10.5	N	5.78	1	0.0685	0.0685
	P	5.41			
15.2	N	6.94	1	0.0032	0.0032
	P	6.86			
16.1	S	6.67	1	0.0392	0.0392
	R	6.39			
20.1	S	7.73	1	0.1058	0.1058
	R	7.27			
20.8	N	8.16	1	0.0008	0.0008
	P	8.20			
25.8	N	9.16	1	0.2178	0.2178
	S	8.50			
40	S	9.15	1	0.0032	0.0032
	R	9.23			

Table VI cont'd

Time (min.)	run	SO_4^{2-} (gpl)	m-1	$\hat{s}_i^2$	$(m-1)\hat{s}_i^2$
50	N	9.65	1	0.1104	0.1104
	P	9.18			
60	S	9.66	1	0.0288	0.0288
	R	9.42			
80	N	9.61	2	0.0516	0.1033
	S	9.16			
	R	9.44			
110	N	9.68	1	0.0245	0.0245
	P	9.75			
120	S	9.63	1	0	0
	R	9.62			
					1.9327

$$\hat{s}_p^2 = \frac{\sum_{i=1}^{\ell}(m-1)\hat{s}_i^2}{\sum_{i=1}^{\ell}(m-1)} = \frac{1.9327}{50} = 0.0387$$

so that, $s_p = 0.20$ gpl

APPENDIX 4 : CALCULATION OF TRITHIONATE CONCENTRATION FROM MERCURIC CHLORIDE TITRIMETRIC METHOD

Nomenclature:

V_A : volume of acid (ml)
V_B : volume of base (l)
N_A, N_B : normalities of acid, base (N)
V_s : equivalent base for thiosulfate reaction (ml)
V_{KI} : equivalent base for for KI induced alkalinity (ml)
V_{eff} : equivalent base for polythionate reaction (ml)
V_T : total base required for sum of all reactions (ml)
bl : black liquor

In this case the experimentally measured parameters from titrations are:

V_A = 2.00 ml
V_B = 23.50 ml = 0.02350 l
N_A = 0.00492 N
N_B = 0.00816 N

All other parameters are calculated values.
To calculate the concentration of trithionate in the presence of thiosulfate and sulfate, consider the concentration data (gpl) at 15 minutes in Table 50 for sulfate, thiosulfate, and trithionate.

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	$S_3O_6^{2-}$	% diff.
15	5.00	1.46	3.53	-0.8

Recall that the stoichiometric equations for trithionate and thiosulfate from Section 3.5.2 are:

$2S_3O_6^{2-} + 3HgCl_2 + 4H_2O \longrightarrow HgCl_2 \cdot 2HgS + 8H^+ + 4Cl^- + 4SO_4^{2-}$
......(21)

$2S_2O_3^{2-} + 3HgCl_2 + 2H_2O \longrightarrow HgCl_2 \cdot 2HgS + 4H^+ + 4Cl^- + 2SO_4^{2-}$
......(22)

1. Trithionate Stoichiometric Relation

To calculate the concentration of trithionate get from stoichiometry equation (21)

$1\ S_3O_6^{2-} \equiv 4H^+$

since $1\ OH^- \equiv 1H^+$

then $1\ S_3O_6^{2-} \equiv 4OH^-$

since mol. wt. $S_3O_6^{2-} = 192.2$

sample size (black liquor) = 2.00 ml = 0.00200 l

therefore, $S_3O_6^{2-} = (V_BN_B x\ 0.25) \times 192.2$ g/mol x 1/0.002 l

so that,

$S_3O_6^{2-} = (24025V_BN_B)$ gpl (i)

2. Similarly for tetrathionate get:

$S_4O_6^{2-} = (28050V_BN_B)$ gpl (ii)

3. Thiosulfate Correction

$1\ S_2O_3^{2-} \equiv 2H^+$

so $1\ S_2O_3^{2-} \equiv 2OH^-$

since mol. wt. $S_2O_3^{2-}$ = 112.2
normality of base = N_B = 0.00816 N
sample volume size = 2.00 ml = 0.00200 l

then the volume of base corresponding to a known thiosulfate concentration in gpl for a 2 ml black liquor aliquot is equal to:

$$V_s = \frac{g\ S_2O_3^{2-}}{\text{liter (bl)}} \times \frac{1\ \text{mole}}{112.2\ gS_2O_3^{2-}} \times 2 \times \frac{1\ \text{liter}}{0.00816\ \text{mol}} \times 0.002\ l$$

so that,

$$V_s = 0.00437\ S_2O_3^{2-}\ (l) = 4.37\ S_2O_3^{2-}\ (ml)$$

$$V_s = 4.37\ S_2O_3^{2-}\ (ml) \qquad \text{(iii)}$$

4. KI Alkalinity Correction

Proceeding directly to step 9 Section 3.5.4 the equation for equivalent alkalinity from KI is given by,

$$V_{KI} = \frac{N_A V_A}{N_B} \qquad \text{(iv)}$$

From iv get

$$V_{KI} = \frac{(0.00492)(2.00)}{(0.00816)} = 1.21\ ml$$

5. Calculation of Total Equivalent NaOH

The total base required is the sum of equivalent NaOH from both titrations (step 10) so,

$$V_T = V_B + V_{KI} \quad \text{(v)}$$

so $V_T = 23.50 + 1.21 = 24.71$ ml

6. Calculation of Base Used in Thiosulfate Oxidation

From step 11, Section 3.5.4 and equation iii calculate base used in thiosulfate reaction.

$$V_s = (4.37)(1.46) = 6.38 \text{ ml}$$

so $V_{eff} = 24.71 - 6.38 = 18.33$ ml

7. Calculation of Trithionate Concentration

From i

$$S_3O_6^{2-} = (24025)(18.33 \times 10^{-3})(0.00816)$$
$$= 3.59 \text{ gpl}$$

Correcting for water evaporation from the liquor during an experiment (a factor of 0.982 in this case),

$$S_3O_6^{2-} = 3.59 \times 0.982 = 3.53 \text{ gpl}$$

8. Calculation of Tetrathionate Concentration

Calculated as $S_4O_6^{2-}$ get from ii

$$S_4O_6^{2-} = (28050)(18.33 \times 10^{-3})(0.00816)$$
$$= 4.20 \text{ gpl}$$

Correcting for water evaporation during an experiment,

$$S_4O_6^{2-} = 4.20 \times 0.982 = 4.12 \text{ gpl}$$

9. Equivalent Trithionate Sulfur as Sulfate

To obtain equivalent amount of sulfur as sulfate from trithionate multiply by appropriate molecular weight ratios to first convert to sulfur and then to sulfate.

Note: molecular weights:
32.1 for S^o
96.1 for SO_4^{2-}
192.2 for $S_3O_6^{2-}$
112.2 for $S_2O_3^{2-}$

For illustration use step 7 result for trithionate.

therefore, $SO_4^{2-} = 3.53 \times 96.3/192.2 \times 96.1/32.1$
$= 3.53 \times 1.5$
$= 5.29$ gpl SO_4^{2-}

10. Equivalent Thiosulfate Sulfur as Sulfate

Calculate sulfate sulfur from thiosulfate in a similar way as done for trithionate in 9):

$SO_4^{2-} = S_2O_3^{2-} \times 64.2/112.2 \times 96.1/32.1$
$= 1.71\ (S_2O_3^{2-})$ (vi)
$SO_4^{2-} = (1.71)(1.46) = 2.50$ gpl

11. Sulfur Balance Calculation on Sulfate Basis

To obtain sulfate in black liquor if all thionate and thiosulfate had been converted to sulfate, add sulfate from steps (9) and (10) respectively to sulfate concentration from IC measurement.

ie. $(SO_4^{2-})_{tot.} = (SO_4^{2-})_{IC} + (SO_4^{2-})_{step\ 9} + (SO_4^{2-})_{step\ 10}$
$= 5.00 + 5.29 + 2.50 = 12.8$ gpl

12. Calculation of Expected Sulfur as Sulfate

Calculate the expected sulfate assuming quantitative thiosulfate conversion from its peak value. The expected value can be estimated by taking the maximum thiosulfate value obtained in noncatalytic oxidation, converting it to equivalent sulfur as sulfate, and adding to initial sulfate concentration; That is, from vi get:

$$(SO_4^{2-})_{exp} = (SO_4^{2-})_{initial} + 1.71(S_2O_3^{2-})_{max}$$
$$= 4.00 + (1.71)(5.2) = 12.9 \text{ gpl}$$

The value of 5.2 gpl thiosulfate was obtained as the average value peak for thiosulfate from a series of noncatalytic oxidation runs. Note that this maximum thiosulfate concentration cannot be obtained from a catalytic run because of the rapid sequential decomposition of thiosulfate to trithionate which masks the true peak.

13. Calculation of % Deviation with Balance

Calculate % difference with the expected value if polythionate species is presumed to be trithionate.

$$\% \text{ difference} = \frac{(12.8 - 12.9)}{12.9} \times 100 = -0.8\%$$

14. Sulfur Imbalance Based on Tetrathionate

If the polythionate was tetrathionate then from steps 8 and 11

$$(SO_4^{2-})_{tot.} = 5.00 + (1.71)(4.12) + 2.50$$
$$= 14.5 \text{ gpl}$$

$$\% \text{ difference} = \frac{(14.5 - 12.9)}{12.9} \times 100 = 12.4\%$$

From this calculation it appears that the thionate species present is trithionate.

✓

APPENDIX 5: TREATMENT OF EXPERIMENTAL DATA FOR SULFATE KINETIC RATE MODEL

The ensuing procedure was used to formulate databases from the replicate experiments.

1. For each liquor the thiosulfate (A), and sulfate (B) concentration data from all replicate sets were statistically averaged at the various times they were taken during an experiment;
2. Average sulfate and thiosulfate data points were plotted vs. time and smooth curves were drawn;
3. Sulfate and thiosulfate concentrations were interpolated from the smoothed curves at predetermined time intervals;
4. Time and interpolated sulfate, thiosulfate data were tabulated;
5. From the smoothed sulfate curves rate data was obtained at regular time intervals by numerical computer differentiation to ensure maximum possible accuracy ;
6. Time (t), thiosulfate (A), sulfate (B), and sulfate rate data (dB/dt) were tabulated and entered into the program;
7. Whenever a new rate expression was tested, a program line stipulating the new expression was inserted into the program replacing the old one;
8. The program was run yielding the least squares estimates of the rate constants, powers, and sum of squares residuals;
9. In the case where the powers were set to 2 and 3, least squares estimates of rate constants were given for these fixed values of the powers;
10. Model rate data was compared with experimental rate data; if the fit was bad it was discarded;

11. If the rate data was a good approximation to experimental, predicted sulfate values were found by plotting model rate data (dB/dt) vs. t and numerically integrating the area under the curve at the chosen time intervals. Note that the area under the curve is given by:

$$\text{Area} = \int_0^T \frac{dB}{dt}\, dt = \int_0^T dB = B(T) - B(T_0) \qquad \text{(vii)}$$

12. These values, $B(T) - B(T_0)$, were added to the initial sulfate present in the black liquor before oxidation, $B(T_0)$ to obtain $B(T)$ so that the general expression is denoted by:

$$B(T) = B(T_0) + \int_0^T \left\{\frac{dB}{dt}\right\} dt \qquad \text{(viii)}.$$

13. After obtaining all the model sulfate data, it was plotted with the experimental data and the goodness of fit was inspected visually;

14. % difference between predicted and experimental data was also calculated and the model was considered satisfactory if the prediction was consistently within a 5% maximum error limitation.

APPENDIX 5 : SULFATE KINETIC RATE MODEL

Table VII : Database for Liquor C for Predicted Sulfate Concentration from Integration

time (min.)	D´ (expt.) (gpl/min.)	D´(calc./interp.) (gpl/min.)	SO_4^{2-} (gpl)
10	0.063	0.079	4.15
12	0.074	0.085	4.31
14	0.102	0.092	4.49
16	0.114	0.1	4.68
18	0.117	0.11	4.89
20	0.129	0.121	5.12
22	0.152	0.134	5.38
24	0.165	0.148	5.66
26	0.162	0.16	5.97
28	0.15	0.162	6.29
30	0.112	0.14	6.59
32	0.1	0.104	6.84
34	0.09	0.068	7.01

Table VIII: Liquor C Database For Sulfate Model *

time (min.)	SO_4^{2-}	$S_2O_3^{2-}$	D′ (gpl/min.)
10	4.15	3.87	0.063
12	4.3	3.57	0.074
14	4.46	3.27	0.102
16	4.68	2.97	0.114
18	4.90	2.67	0.117
20	5.18	2.37	0.129
22	5.45	2.07	0.152
24	5.75	1.77	0.165
26	6.08	1.47	0.162
28	6.42	1.17	0.15
30	6.68	0.87	0.112
34	7.04	0.50	0.09
36	7.20	0.18	0.075
40	7.48	0.16	0.062
45	7.80	0.00	0.00

*All ionic species concentrations are in grams per liter (gpl)

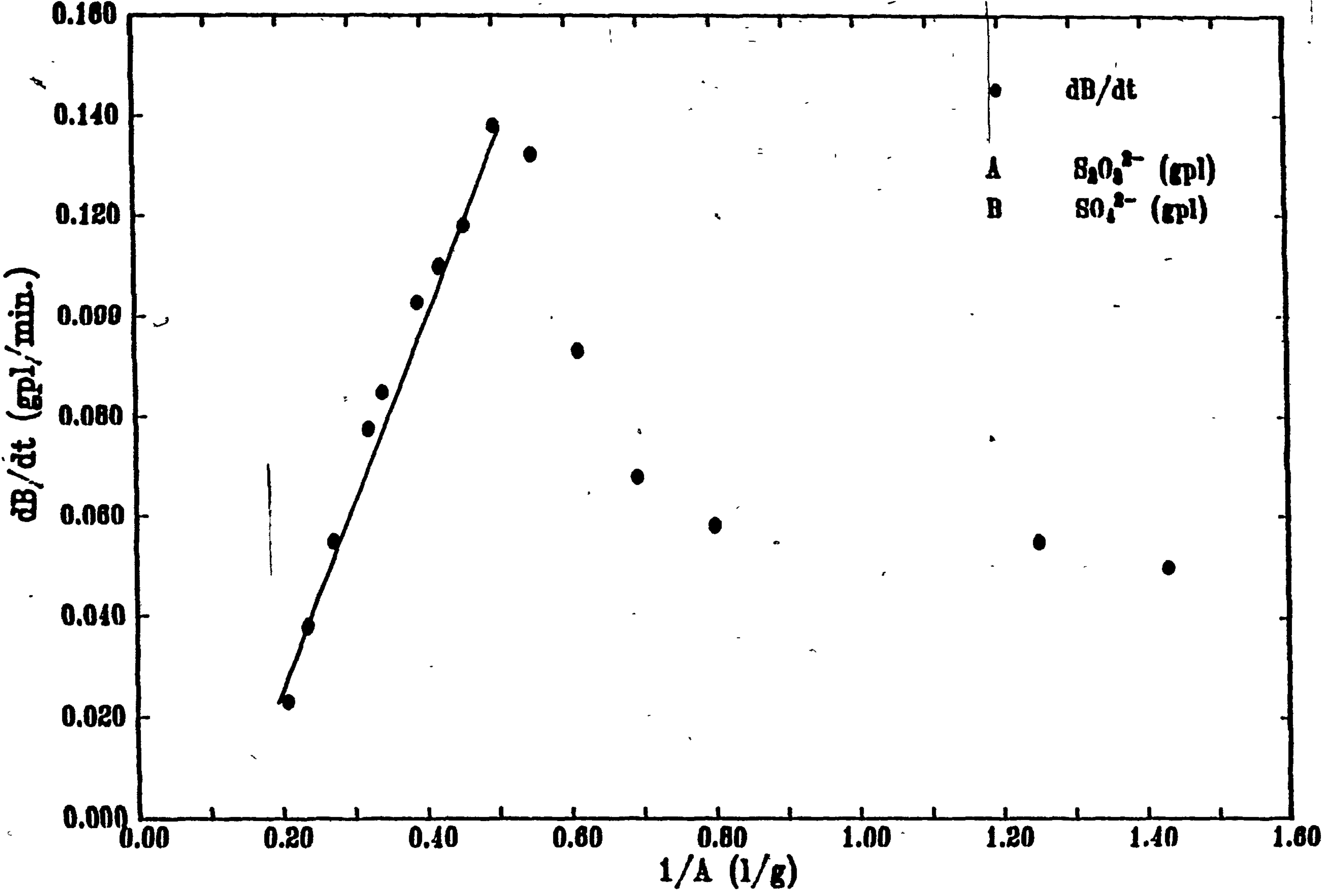

Figure VI. Test of sulfate model adequacy for Liquor A.

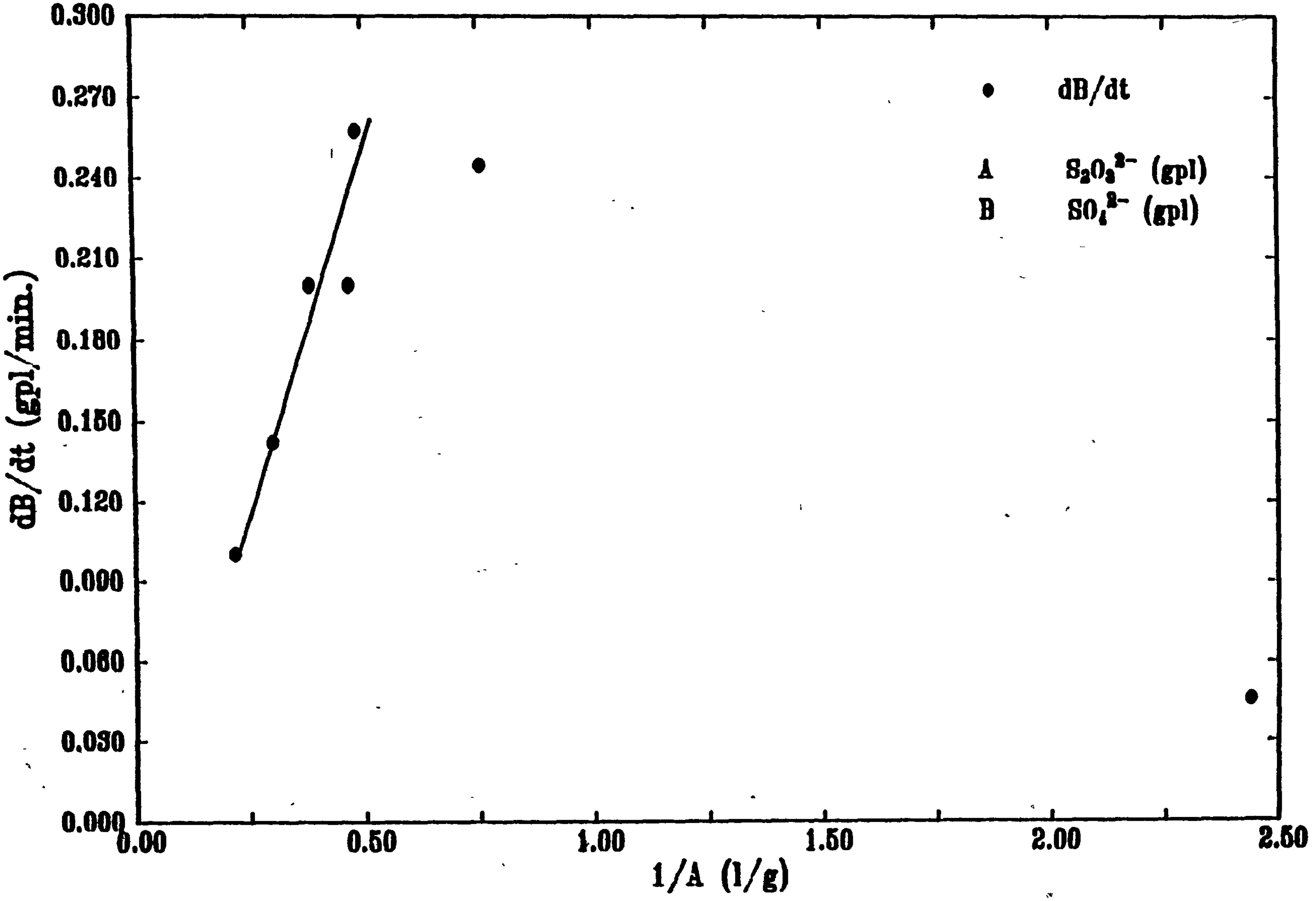

Figure VII. Test of sulfate model adequacy for Liquor B.

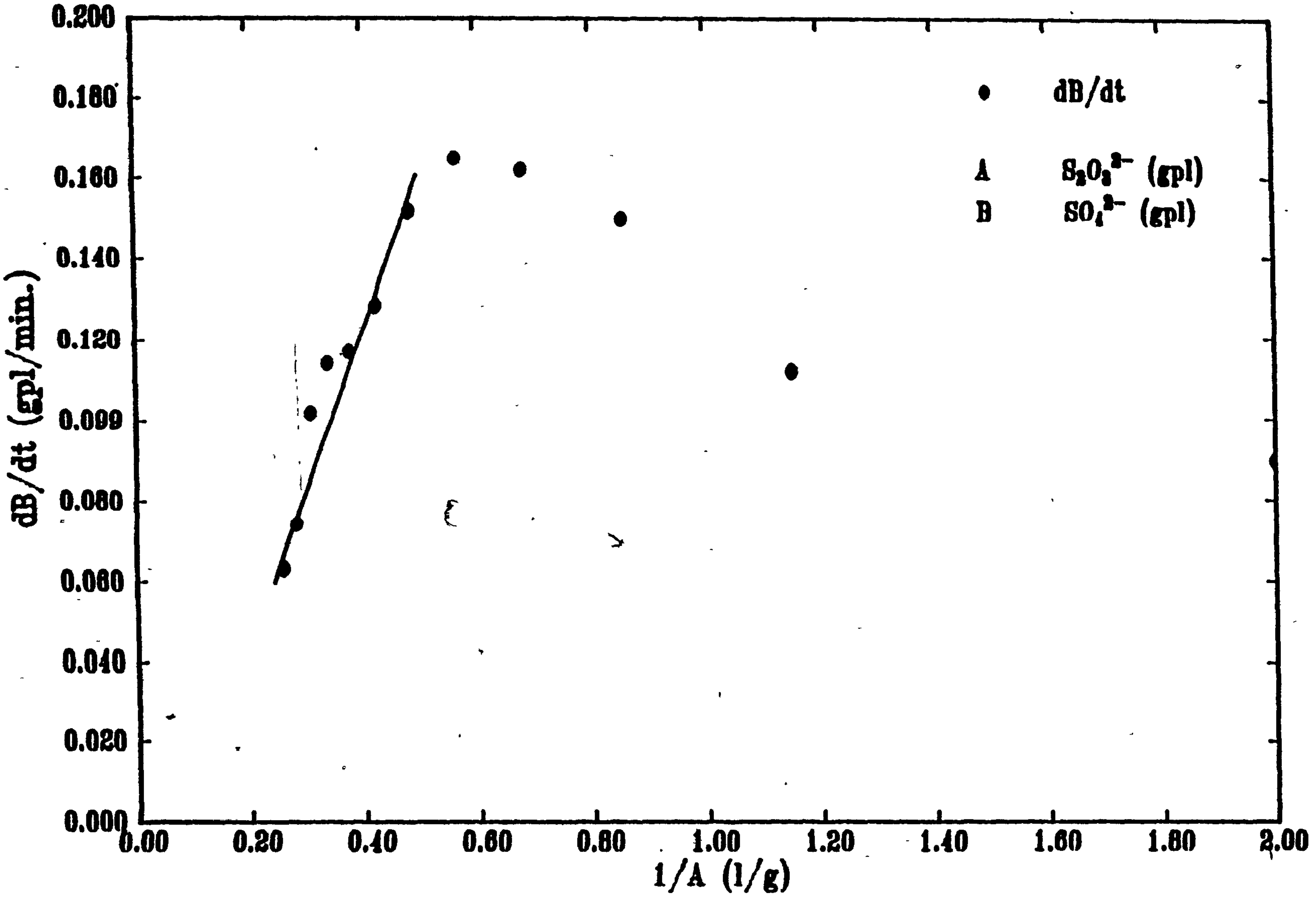

Figure VIII. Test of sulfate model adequacy for Liquor C.