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BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN IN A PLUG FLOW REACTOR

by

HAL BLUFORD HARRISON COOPER, JR.

A dissertation submitted in partial fulfillment

of the requirements for the degree of

DOCTOR OF PHILOSOPHY

UNIVERSITY OF WASHINGTON

1972

Approved by August T. Perano Jr

Department Civil Engineering

Date August 18, 1972

UNIVERSITY OF WASHINGTON

Date: August 1, 1972

We have carefully read the dissertation entitled "Black Liquor Oxidation with Molecular Oxygen in a Plug Flow Reactor"

submitted by Hal Bluford Harrison Cooper, Jr. in partial fulfillment of the requirements of the degree of Doctor of Philosophy and recommend its acceptance. In support of this recommendation we present the following joint statement of evaluation to be filed with the dissertation.

The dissertation involved experimental investigation of oxygen mass transfer, reaction kinetics, and chemistry of weak and strong black liquor oxidation with molecular oxygen in a pilot scale plug flow reactor. The purpose of the study was to develop design criteria for subsequent installation of full scale systems used to oxidize sodium sulfide for Kraft mill odor control.

Results indicated molecular oxygen to be feasible for oxidation of sodium sulfide in weak black liquor with molecular oxygen, but only for polishing to counteract reversion in strong black liquor. Sodium sulfide oxidation increased with increasing temperature, pH, pressure, and decreasing thiosulfate and solids concentrations. Sodium sulfate formation in weak liquor increased with temperature and pH. Design criteria for weak liquor systems included liquid Reynolds numbers above 40,000, pH's between 12.0 and 12.6, temperatures of 170 to 190°F, and retention times of 15 to 30 minutes. Strong black liquor oxidation was limited by incomplete oxygen mass transfer, black liquor cooling, lignin oxidation, prolonged retention time, excess oxygen consumption, and sulfide reversion.

Significance of the research was that it provided information necessary for design of two stage plug flow reactor systems employing consecutive weak and strong black liquor oxidation with oxygen at minimum capital cost. Black liquor oxidation with molecular oxygen would facilitate compliance with air pollution regulations without the necessity for substantial capital investment associated with replacement of direct contact evaporators.

The Candidate's research effort is of considerable importance to air resources, and was carried out in a comprehensive and scholarly manner. His dissertation represents a significant contribution to knowledge.

DISSERTATION READING COMMITTEE: Kyosti V. Sarkanen

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Signature Hal B. H. Cooper, Jr.

Date August 18, 1972

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I. INTRODUCTION

A. Problem

1. Legal

Kraft pulp mills constitute a major potential industrial source of malodorous and other sulfur gas emissions to the atmosphere in the United States. The recovery furnace and associated direct contact evaporator is perhaps the greatest single potential source of these malodorous sulfur gas discharges in the Kraft pulping process. The tendency towards more widespread and increasingly stringent air pollution standards at the Local, State and Federal levels of government necessitates the development of methods for controlling these sulfur gas emissions. Source emission standards are currently in effect to regulate malodorous sulfur gas emissions from recovery furnaces and other Kraft mill sources in Humboldt County, California. Regulations enacted by the States of Oregon and Washington specify maximum total reduced sulfur emission levels from Kraft recovery furnaces for 1972 and 1975 as 2.0 and 0.5 pounds of sulfur per ton of pulp, respectively. More stringent standards for total reduced sulfur emissions from Kraft pulp mills are being considered by other States and by the Federal government. The new chemical recovery systems which eliminate direct contact of black liquor with recovery furnace flue gas to minimize total reduced sulfur emissions also increase the potential for release of sulfur oxides and particulate emissions from Kraft recovery furnaces.

2. Process

Oxidation of sulfur compounds present in the spent pulping liquid (called black liquor) provides a potentially effective means for controlling malodorous and other sulfur gas emissions from Kraft recovery furnaces

employing direct contact evaporation of black liquor with furnace flue gas. Oxidation of the potentially odorous sulfur compounds present in the black liquor (particularly sodium sulfide and sodium mercaptide) to innocuous products by contact with air has proven successful for both weak and strong black liquor streams at mills pulping relatively nonresinous wood species, particularly in the Northwestern United States.

Oxidation of weak black liquor with atmospheric oxygen (air) has met with only limited success at Kraft pulp mills pulping highly resinous woods such as yellow pines in the Southeastern United States because of excessive foaming associated with the presence of certain high molecular weight organic compounds in the wood (known as tall oil). The problems associated with foaming have resulted in the primary use of strong black liquor oxidation with air at Kraft mills pulping extensive quantities of pine wood species, but certain benefits associated with weak black liquor oxidation are then eliminated. Molecular oxygen provides an alternative to atmospheric oxygen for black liquor oxidation in Kraft pulp mills where considerable amounts of highly resinous pine wood species are being pulped. Molecular oxygen provides a means for stabilizing the sulfur compounds present in black liquor to reduce malodorous sulfur gas emissions without the excessive foaming associated with air oxidation.

B. Objectives

The overall purpose of the research project is the development of rational engineering design criteria for plug flow reactor systems used for oxidation of potentially odorous sulfur compounds in Kraft black liquor with molecular oxygen. The present research has several specific objectives in attempting to further the knowledge regarding the mass transfer, kinetics, chemistry and economics of black liquor oxidation with molecular oxygen as a

prospective means of Kraft pulp mill odor control. Primary emphasis is to be placed upon the chemistry and kinetics of the oxidation reactions of sodium sulfide and other inorganic sulfur compounds present in the black liquor.

1. Mass Transfer

It is desired to determine the conditions favoring maximum rate of absorption and subsequent utilization of oxygen in the black liquor with a minimum of retention time and increased resistance to liquid flow. Several specific areas of mass transfer are to be investigated. First, it is desired to determine the effects of oxygen and liquid flow rates, plus tube diameter, upon the resultant oxygen bubble sizes in simulated clear liquid solutions flowing through transparent pipes. The effect of liquid Reynolds number on the dispersion of oxygen gas into the liquid phase is important for a design of subsequent systems where molecular oxygen is to be injected into black liquor in a plug flow reactor. Second, it is desired to determine the respective effects of gas and liquid flow rates, liquid temperatures and solids concentrations, oxygen total and partial pressures, pipe diameters and contactor configuration upon the rate of oxygen absorption into actual weak and strong black liquor streams. Third, the effects of respective gas and liquid flow rates, and pipe diameters upon two phase flow configuration are to be investigated. It is desired to determine possible increases in fluid resistance to flow as a possible indicator of additional liquid pumping requirements in full scale installations.

2. Reaction Kinetics

Studies of the reaction kinetics for oxidation of sodium sulfide and mercaptide in black liquor are made to determine the reaction rate constants for subsequent extrapolation of the results of pilot scale experiments to

the design of full scale systems. Minimum and maximum liquor retention times are to be determined in the plug flow reactor and any associated liquor storage facilities. The liquid retention time in the system must be sufficient to provide for effective oxidation of sodium sulfide and sodium mercaptide, but not so great as to cause reversion of the sulfide and mercaptide ions, cause other undesirable effects, or result in excessive capital investment for storage facilities.

There are three main objectives for the studies of reaction kinetics. First, it is desired to determine the effects of inlet concentrations, liquid temperatures, liquid pH, solids concentrations and oxygen addition rates upon the respective reaction rate constants for oxidation of sodium sulfide and sodium mercaptide. Second, it is desired to carefully delineate the effects of reaction times upon the respective reaction rate regimes for oxidation of sodium sulfide and sodium mercaptide in black liquor to determine retention time requirements for high degree oxidation. Third, the effects of liquid temperature and pH on the relative rates of competing side reactions are to be investigated. Of particular concern are the conversion of the intermediate sodium thiosulfate to sodium sulfate and oxidation of lignin in terms of excess oxygen consumption.

3. Reaction Chemistry

The chemistry of black liquor oxidation involves considerations of both the inorganic and organic sulfur compounds, plus organic materials such as lignins and resinous organic acids. Determining factors favorable to maximum conversion of sodium sulfide to sodium thiosulfate in black liquor is of particular importance from an economic standpoint. Primary emphasis is to be placed upon the reactions of the inorganic sulfur compounds present in the black liquor.

Several areas of the chemistry of black liquor oxidation are to be investigated. First, the effects of liquid temperature, liquid pH, inlet concentrations, and oxygen input rate upon the selectivity and degree of completeness of the respective oxidation reactions of sodium sulfide and sodium mercaptide are to be investigated. Second, the effects of addition of controlled amounts of sodium hydroxide and hydrochloric acid for pH adjustment, and sodium thiosulfate upon the reaction products and the degree of completeness of the oxidation reactions are to be investigated. Third, the effects of maintaining an aerobic environment during storage is to be investigated in terms of possible retardation of the "reversion" to re-form sodium sulfide in oxidized black liquor. Fourth, the effects of black liquor oxidation upon the possible oxidation of lignin materials present and potential losses in black liquor heating value are to be investigated. Fifth, the possible effects of black liquor oxidation upon tall oil yield is to be investigated.

4. Process Economics

A major consideration regarding the ultimate usefulness of molecular oxygen for black liquor oxidation in Kraft pulp mills involves the potential economic feasibility of the process. The operating costs with using molecular (tonnage) oxygen must be sufficiently low to make it economically competitive with alternative methods for controlling malodorous sulfur gas emissions from Kraft recovery furnaces. First, an economic analysis of the effect of black liquod oxidation upon the Kraft process is to be made in terms of process operating costs, both in terms of variable oxygen costs and process credits. Second, an analysis of the potential markets for molecular oxygen is to be made for Kraft pulp mills in the United States. Third, if possible, it is desired to make estimates of the relative economics of black liquor

oxidation with molecular oxygen as an alternative to other methods for odor control in Kraft pulp mills.

C. Significance

1. Paper Industry

Black liquor oxidation with molecular oxygen provides a means for reducing malodorous sulfur gas emissions from Kraft recovery furnaces to meet existing or proposed air pollution regulations. The process can be installed in existing mills at a minimal capital investment without the necessity for replacing existing systems employing direct contact evaporation of black liquor, or the installation of additional particulate control facilities. The capital investment for a system employing black liquor oxidation with molecular oxygen is minimal because the system can normally be installed within the piping of an existing mill and requires only minimum liquor storage facilities. The major operating cost of the system involves the cost of purchasing the oxygen for on-site injection. The alternatives would be to replace these existing direct contact evaporators with new indirect contact evaporation systems and additional particulate control facilities, construction of new recovery furnaces employing indirect contact evaporation of black liquor, or oxidation of strong black liquor with atmospheric oxygen. The cost of replacing existing direct contact evaporators with new indirect contact evaporation systems would probably exceed 200 million dollars for the pulp and paper industry as a whole. The capital costs for systems using molecular oxygen would be much less than those using air as the source of oxygen in the process.

Molecular oxygen is particularly suitable for black liquor oxidation at large Kraft pulp mills in the Southeastern United States. A primary

reason is that oxygen can be utilized in sufficient quantities to obtain relatively low prices because of economies of scale. The process can be installed within the piping of an existing mill without major alterations so that the capital cost is minimized. The foaming problems associated with air when pulping the highly resinous Southern yellow pines can be alleviated with oxygen because the nitrogen diluent medium is absent. Molecular oxygen can be used for weak black liquor oxidation in Southern Kraft pulp mills without excessive foaming, while air normally cannot. Additional benefits of weak black liquor oxidation with molecular oxygen are reduced scaling and corrosion in multieffect evaporators, reduced sodium sulfate and lime chemical makeup requirements, increased cooking liquor sulfidity, improved tall oil yield, improved evaporator condensate water quality, plus reduced malodorous sulfur gas emissions from evaporator noncondensable and tall oil vent gases.

2. Research Project

The significance of the present research is that it is the first direct comprehensive evaluation of the parameters affecting the mass transfer, kinetics, and chemistry of black liquor oxidation using molecular oxygen in a tubular plug flow reactor for both weak and strong black liquor. The present research will provide quantitative information regarding rational design criteria for plug flow reactors and subsequent storage facilities used for oxidation of sodium sulfide and sodium mercaptide in Kraft black liquor. Quantitative information regarding black liquor oxidation phenomena is to be obtained from dynamic studies on an actual pilot scale continuous flow plug flow reactor. The purpose of using the pipeline reactor is to facilitate the extrapolation of pilot scale results to design of full-scale field installations.

Particular contributions of the present research are as follows. First, it is desired to determine the rate of oxygen absorption into black liquor, and the respective reaction rate constants for oxidation of sodium sulfide and sodium mercaptide at varying concentration rate regimes. Second, of particular concern in terms of potential air pollution problems are the determination of conditions favoring essentially complete oxidation of sodium sulfide and sodium mercaptide within the plug flow reactor and subsequent storage facilities. Third, studies of the respective rates of oxidation for sodium sulfide and sodium mercaptide in both weak and strong black liquor are to be made. Fourth, studies of the respective rates of sodium thiosulfate conversion to sodium sulfate, and possibly lignin oxidation, as competing side reactions are to be investigated.

Fifth, studies of molecular oxygen in two phase gas-liquid flow are to be made in terms of flow configuration to determine factors favoring maximum oxygen transfer into the liquid phase, possible increases in liquid resistance to flow, and the effects of contactor configuration on possible increases in retention time resulting from "holdup" phenomena. Sixth, the resultant two phase gas-liquid flow configurations and oxygen gas bubble sizes when dispersed into a transparent liquid as functions of gas flow rate, tube diameter, and liquid Reynolds number are to be evaluated as design aids for black liquor systems.

Factors affecting the economics of using molecular oxygen for weak and strong black liquor oxidation are to be given particular attention. First, studies are to be made of operating conditions favoring maximum utilization of oxygen for the selective oxidation of sodium sulfide and sodium mercaptide in black liquor. Second, factors affecting the competing side reactions of

conversion of sodium thiosulfate to sodium sulfate, and organic lignin to oxidation products are to be evaluated in terms of potential oxygen consumption. Third, the effect of operating conditions upon possible reductions in liquor heating value from lignin oxidation are to be investigated. Fourth, the effect of operating conditions upon potential increases in tall oil yield are to be investigated.

D. Approach

1. Experiments

The approach of the present research is experimental in nature, and will be devoted to laboratory and field studies in three major areas. First, laboratory studies are to be made regarding the rates of absorption of oxygen into solutions of simulated and actual black liquor samples, and also oxidation studies in black liquor with molecular oxygen. The purpose of these studies is to determine potential retention time requirements for the system, and the relative occurrences of potentially competing side reactions. Second, field studies are to be made of factors affecting the mass transfer of oxygen into plain water flowing through a transparent tube by means of visual observation and high speed photography. The purpose is to provide prospective design data for subsequent construction of a pilot scale plug flow reactor for black liquor oxidation. Third, variables affecting the mass transfer, kinetics, and chemistry of oxidation of sodium sulfide and other constituents in black liquor are to be investigated with a pilot scale plug flow reactor.

2. Predictions

Results of the above experiments can be used to make a series of predictions regarding the design and operation of full-scale installations.

First, engineering design criteria can be developed from the experimental results to facilitate the design of full-scale installations where black liquor is to be oxidized with molecular oxygen at either new or existing Kraft pulp mills. Second, potential operating problems can be predicted from experimental results for full-scale systems to facilitate either process modification or operating changes. Third, an economic analysis can be made of the potential feasibility for application of molecular oxygen for black liquor oxidation at Kraft pulp mills in the United States. Of particular interest are predictions of net mill operating costs when using the system, and the potential market for oxygen sales to the pulp and paper industry.

II. BACKGROUND INFORMATION

A. Kraft Pulping

1. Paper Industry

The pulp and paper industry is one of the largest in the United States, with total annual sales of approximately 20 billion dollars, and mills located in nearly every state. Paper manufacture involves harvesting of the wood raw material from forests, chipping and digestion of wood to recover cellulose fibers in the form of pulp, followed by formation of the pulp fibers into sheets of paper on a paper machine for subsequent sale. Pulp mills are normally located in geographical areas where adequate supplies of water and timber raw material are available. The pulp produced is normally shipped to paper mills located adjacent to large metropolitan areas, to be processed into finished products for subsequent marketing.

a. Pulp Production

The three major types of pulping processes are mechanical, semi-chemical, and chemical. These processes provide varying degrees of removal of cellulose fibers from the wood for conversion to paper and other related products. The chemical pulping methods employed are the Sulfite and Kraft processes, respectively. The Kraft process accounts for approximately 60 percent of the total pulp production in the United States, with approximately 24,000,000 tons of Kraft pulp produced in 1968 (1). Market projections indicate that Kraft pulp production will nearly double by 1980, with the major portion of this increase at Kraft pulp mills in the Southeastern United States, as shown in Figure 1.

b. Mill Locations

In 1968, there were a total of 116 Kraft pulp mills in the United States with a total production capacity of 88,000 tons per day (1). Approximately 75 percent of the total Kraft pulp production is in the Southeastern part of the United States, with about 15 percent being located in the Pacific Northwest. The remaining 10 percent of the Kraft pulping capacity is approximately evenly divided between the upper Midwest and New England sections of the country. The location of Kraft pulp mills in the United States is illustrated in Figure 2, and listed in detail in the Appendix.

The Southeastern region of the United States contains 78 of the 116 Kraft pulp mills in the country. It is the location of 25 of the 28 Kraft mills in the United States with pulp production capacities of greater than 1,000 tons per day. Primary wood species in the Southeastern United States are the highly resinous yellow pines such as Loblolly, Longleaf, Shortleaf, and Slash. Large pulping capacities and pine wood species make the large Southeastern Kraft pulp mills particularly suitable for black liquor oxidation with molecular oxygen because of economies of scale for oxygen production and possible increased chemical byproduct recovery.

2. Kraft Process

The Kraft process employs the use of sodium sulfide and sodium hydroxide for delignification of wood chips to facilitate separation of cellulose fibers, which are then refined and made into paper. The spent cooking liquid, containing the inorganic sulfur and other compounds, plus lignin and other organic materials dissolved from the wood, is known as black liquor. The black liquor is separated from the pulp fibers by washing, concentrated by successive operations of multiple effect indirect contact

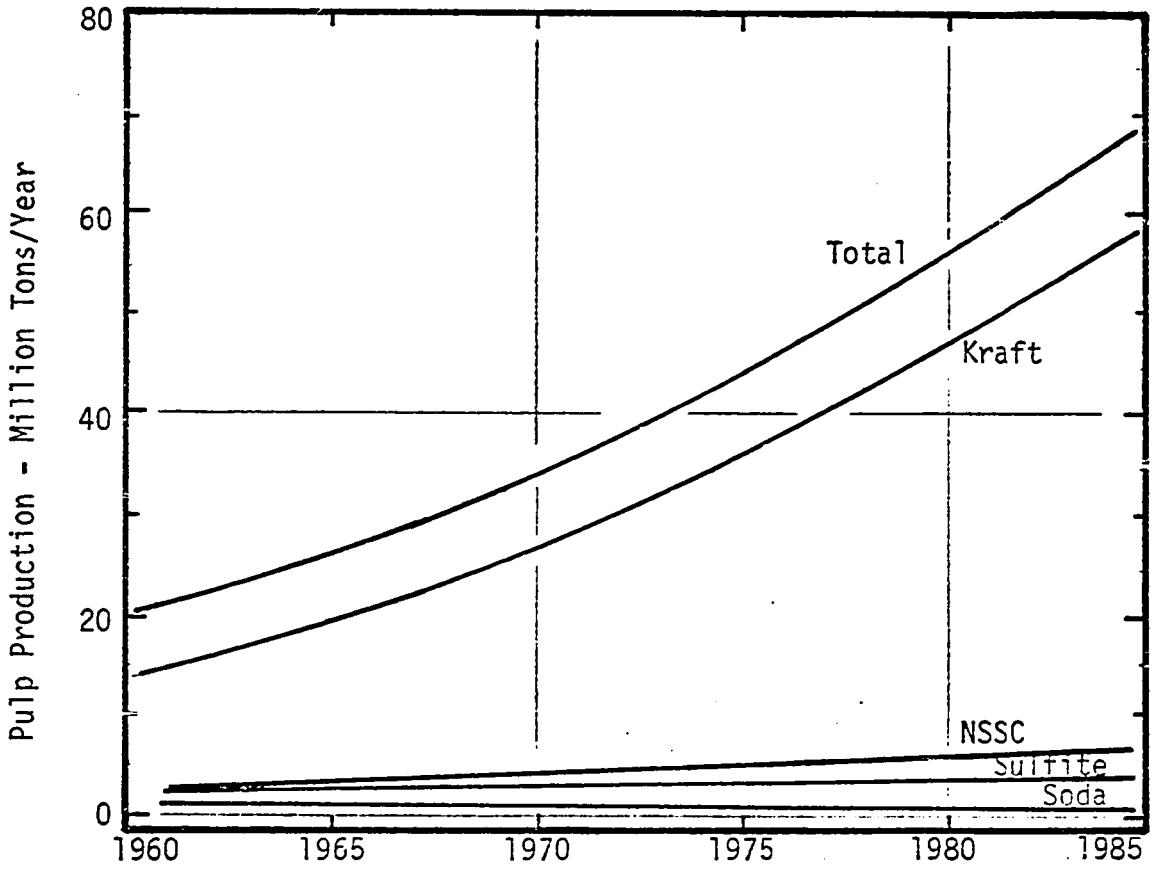


FIGURE 1. CHEMICAL PULP PRODUCTION IN THE UNITED STATES

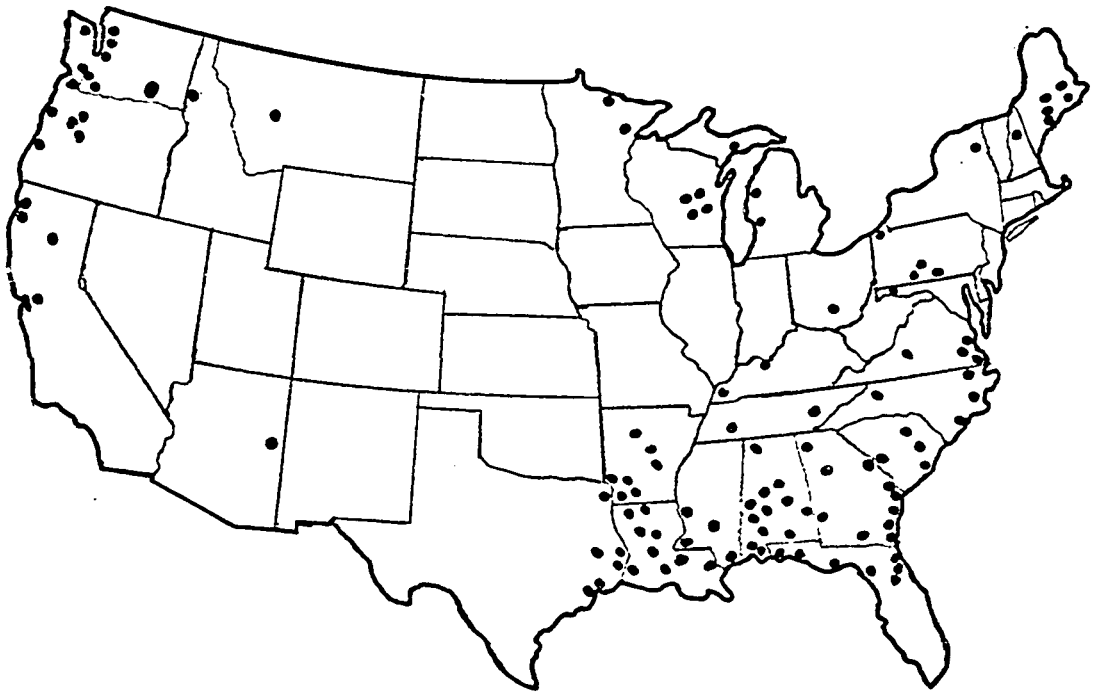


FIGURE 2. LOCATION OF KRAFT PULP MILLS IN THE UNITED STATES.

evaporation with steam followed by direct contact evaporation with hot flue gas. Tall oil is often separated from the black liquor by flotation and acidulation at an intermediate stage during the multiple effect evaporation process.

Sodium sulfate is then added as a makeup chemical to the black liquor after direct contact evporation. The concentrated black liquor is then burned in a specially designed furnace for heat and chemical recovery, with the flue gases being used for final concentration of the black liquor. The inorganic sulfur compounds are reduced to sodium sulfide in the lower part of the recovery furnace and subsequently dissolved into water in the smelt dissolving tank. The sodium carbonate salts formed in the recovery furnace are reconstituted by causticizing with calcium hydroxide to regenerate the initial sodium hydroxide, and the resulting white liquor is recirculated to the digester. The calcium carbonate formed during the causticizing step by the reaction between sodium carbonate and calcium hydroxide is then washed and burned in a lime kiln to regenerate calcium oxide. The lime is then slaked in water for return to the causticizing system as calcium hydroxide. A schematic diagram of a typical Kraft pulp mill is illustrated in Figure 3.

B. Odor Control

1. Process Sources

The addition of sodium sulfate as a makeup chemical and the formulation of sodium sulfide as a delignification aid provides for the possible formation of malodorous sulfur gases such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide, plus sulfur dioxide and sulfur trioxide. Major potential emission sources for malodorous sulfur gases include the digester blow and relief gases, the brown stock washer vent gases, the multiple effect evaporator noncondensable gases, the tall oil vent

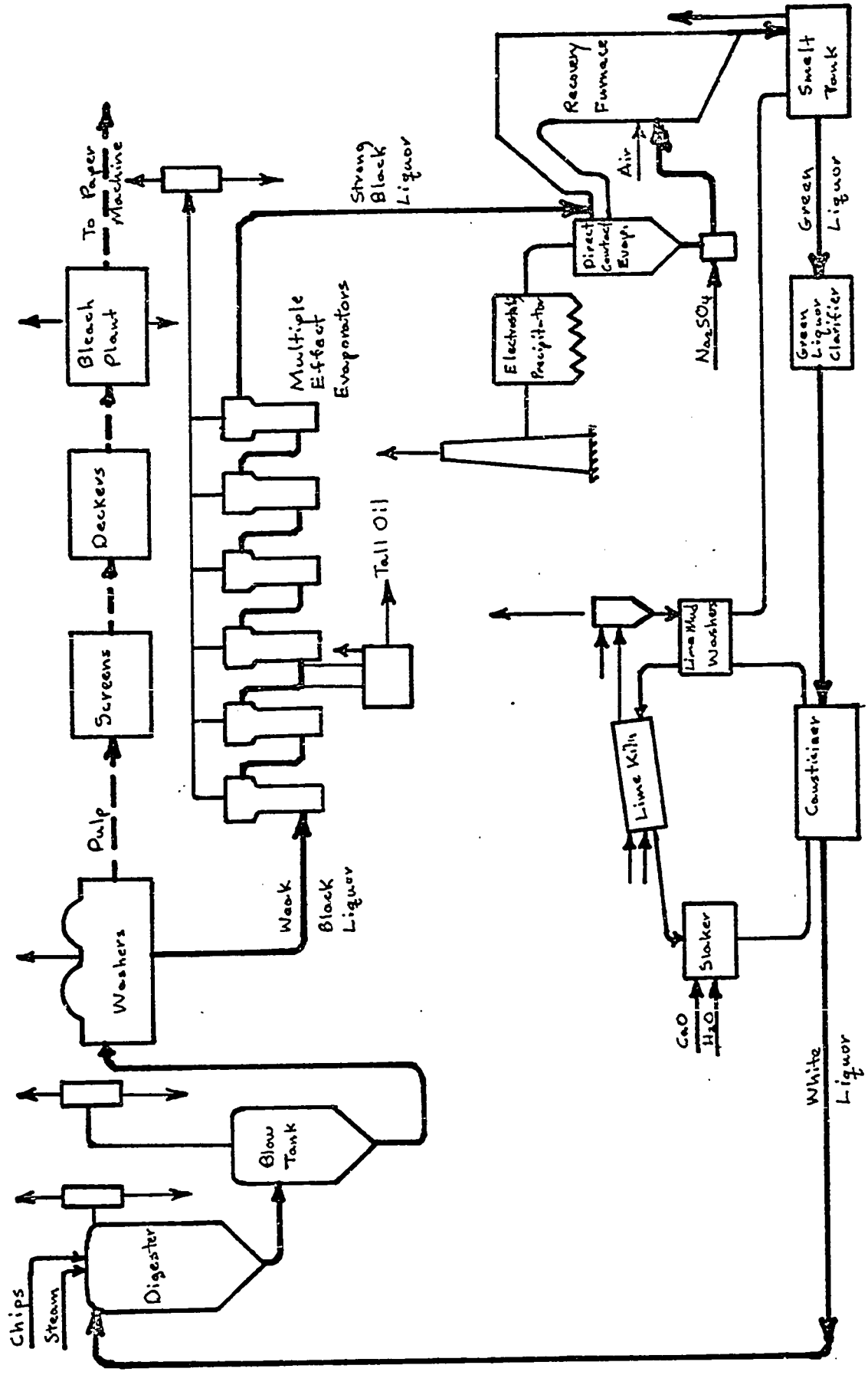


FIGURE 3. FLOW DIAGRAM FOR A KRAFT PULP MILL.

gases, the recovery furnace flue gases, the smelt tank and lime kiln exit gases, plus waste water treatment operations (2). The major potential sources of malodorous sulfur gas emissions affected by black liquor oxidation are the multiple effect evaporator, tall oil recovery units, and the recovery furnace following direct contact evaporation of black liquor.

a. Multiple Effect Evaporator

The concentration of black liquor by passage through a series of multiple effect evaporators by countercurrent contact with steam results in the release of considerable quantities of evaporated water and volatile gases. The gas stream is then passed through either a jet or surface condenser to facilitate heat recovery. The gaseous effluent is a relatively low volume, high concentration evaporator noncondensable gas stream while the liquid effluent is the contaminated evaporator condensate water. Principal mechanisms of release of odorous gases from the multiple effect evaporators are thermal degradation of sodium sulfide and mercaptide to produce hydrogen sulfide and mercaptans, plus volatilization of organic sulfur compounds by heating, evaporation, and turbulent mixing. Major process variables are inlet concentrations, black liquor pH, liquid temperature increase, and degree of agitation.

b. Tall Oil Recovery

Tall oil is a valuable by-product from certain wood species (such as Southern yellow pines) containing high molecular weight organic acids. It is recovered by acidulation of the black liquor with sulfuric acid followed by flotation of the raw tall oil at an intermediate step during multiple effect evaporation. The major potential source of odorous gases is a high concentration, low volume stream of hydrogen sulfide upon acidulation of the tall oil, and is either batch or continuous in nature, depending on the process.

Major variables affecting hydrogen sulfide release are inlet sodium sulfide concentration in the black liquor, liquid pH change, and the degree of liquid agitation. Major methods of control of tall oil vent gas emissions are alkaline scrubbing and oxidation of the weak black liquor.

c. Direct Contact Evaporation

The concentrated black liquor emerging from the multiple effect evaporators is then further concentrated so as to support its own combustion in the Kraft recovery furnace. At most North American Kraft pulp mills this additional concentration is performed by direct contact between the black liquor and flue gas from the recovery furnace, which is also a potential source of large quantities of malodorous sulfur gas emissions. It is a low concentration, high volume, continuous flow source, which tends to make exhaust gas control difficult. The amounts of malodorous sulfur gas emissions vary with the inlet liquid concentrations, the black liquor pH and alkalinity, and the degree of gas-liquid contact. Principal mechanisms of control are adjustment of the furnace firing rate, caustic addition to increase black liquor pH, and either weak or strong black liquor oxidation. Alternative Scandanavian practice employs use of additional stages of indirect contact evaporation (usually forced circulation) to provide for additional concentration of the black liquor.

d. Black Liquor Oxidation

Black liquor oxidation with air provides a means for reducing odorous sulfur gas emissions from multiple effect and direct contact evaporation. It may also provide an additional source of odorous gas discharges, primarily by stripping of volatile organic sulfur gases, where the emission rate depends on inlet concentration and gas-liquid contact. The source joins increasing relative importance as the recovery furnace emissions are reduced.

One means of control is thermal incineration by addition to the inlet combustion air of the Kraft recovery furnace. The problems associated with malorodour sulfur gas emissions from air oxidation units may be alleviated or eliminated by the use of molecular oxygen as an alternative source of oxygen because the nitrogen diluent gas is no longer present.

2. Control Technology

Several recent reviews of Kraft pulp mill odor control technology have been published. A comprehensive review of odor control practices at Kraft pulp mills in Europe and North America has recently been compiled by Sarkanen, Hrutfiord, Johanson, and Gardner (3). Recent governmental publications on Kraft pulp mill emission control practices have been published in the United States (1) and Sweden (4). Recent descriptions of European Kraft pulp mill odor control methods have recently been presented by Adams (5) and Banciu (6). Hendrickson (7) edited the proceedings of a recent international conference on sulfate pulping held at Sanibel Island, Florida, in 1966. Other reviews of emission control technology have been prepared by Wright (8), Shah (9), Kenline and Hales (10), Harding and Landry (11) and Landry and Longwell (12). Black liquor oxidation practices are described in varying degrees in all of the above references.

a. Direct Contact Evaporation

Most existing Kraft pulp mills in the United States employ direct contact evaporation of black liquor for the final concentration step prior to burning in the recovery furnace. Direct contact evaporation can be performed in a high pressure drop venturi scrubber with strong black liquor as the liquid medium, where the venturi system serves the dual functions of water evaporation and particulate removal. The venturi-type evaporators are gradually being replaced because of their inability to meet particulate air

pollution source emission standards. The cascade and cyclone-type direct contact evaporators are low pressure drop gas-liquid contact devices used for concentration of strong black liquor by evaporation. Electrostatic precipitators located downstream of the direct contact evaporator provide particulate emission control and chemical recovery.

The direct contact evaporator serves several functions besides the concentration of black liquor from 50 to 60-65 percent solids. It provides several benefits upon the Kraft recovery system as follows: 1) it improves the thermal efficiency of heat transfer from the gaseous to the liquid phase as compared to indirect contact evaporation because no intermediate metal surfaces are involved; 2) it reduces the inlet gas temperature to the electrostatis precipitator, where the lower gas temperature results in a reduced volumetric gas flow rate, which allows a smaller precipitator to be constructed at a lower capital cost; 3) it reduces the inlet particulate loading to the electrostatic precipitator by 20 to 40 percent by weight, primarily by scrubbing of large particles emitted from the furnace, as reported by Hisey (13); 4) direct contact evaporation of the alkaline black liquor can result in absorption of approximately 75 percent of the sulfur dioxide emitted from the recovery furnace (14)(15), and nearly all of the sulfur trioxide (16); 5) under conditions of high black liquor pH and low sodium sulfide concentration in the strong black liquor, the direct contact evaporator can actually absorb hydrogen sulfide emitted from the recovery furnace, as observed by Blosser and Cooper (17), Murray and Rayner (18), plus Walther and Amberg (19).

Direct contact evaporation also has the potential for liberation of substantial amounts of malodorous sulfur gases from the black liquor, particularly hydrogen sulfide from acidification of sodium sulfide in the

incoming black liquor. Major variables affecting the emission rate of malodorous sulfur gases are inlet sodium sulfide and mercaptide concentrations, liquor pH and alkalinity, and degree of gas-liquid contact. Murray (18) observed that increasing the black liquor pH causes a substantial decrease in hydrogen sulfide emissions from recovery furnaces following direct contact evaporation.

Black liquor oxidation provides a useful means for controlling malodorous sulfur gas emissions at most North American Kraft pulp mills practicing direct contact evaporation of black liquor. Oxidation of the sodium sulfide and mercaptide to innocuous products in either weak black liquor upstream of, or strong black liquor downstream of the multiple effect evaporators provides the opportunity for providing substantial reductions in malodorous sulfur gas emissions, particularly from the multiple effect evaporator, noncondensable gases, tall oil vent gases, and recovery furnace flue gases, plus the evaporator condensate waters. Substantial reduction in sulfur gas emissions from direct contact evaporation is a particular benefit of black liquor oxidation, as shown in Table 1 (1):

TABLE 1. EFFECT OF BLACK LIQUOR OXIDATION ON SULFUR GAS EMISSIONS DURING DIRECT CONTACT EVAPORATION (10).[1]

Gas	Unoxidized Liquor	Oxidized Liquor
Hydrogen Sulfide	5.0-30.0	0.1-2.0
Methyl Mercaptan	0.3-2.0	0.05-0.20
Dimethyl Sulfide	0.05-0.15	0.01-0.05
Dimethyl Disulfide	0.10-0.30	0.01-0.15

Note 1: Emission rate in lb. sulfur emitted per air-dried ton of pulp produced.

b. Indirect Contact Evaporation

Indirect contact evaporation is used to concentrate black liquor from 50 to 60-65 percent solids to eliminate the possibility of odorous gas release during direct contact evaporation. Two proprietary systems employing indirect contact evaporation are now being installed at new Kraft mills in the United States. The former involves the conventional Scandanavian system where the liquor is concentrated by forced circulation evaporators for subsequent feeding to the recovery furnace (20). The latter involves preheating air by indirect contact with recovery furnaces flue gas in a rotating, laminaire heat exchanger. The preheated air is then used to concentrate the strong black liquor in a conventional cascade evaporator. The air and black liquor are both then fed separately to the recovery furnace (21).

Indirect contact evaporation eliminates a potentially large source of malodorous sulfur gas emissions resulting from direct contact evaporation. The technique has proven successful from extensive experience in Scandinavia (4) and more limited experience in the United States (13). Indirect contact evaporation provides a potential means for virtually eliminating the recovery furnace as a source of malodorous gas emissions. It is then only necessary to operate the recovery furnace so as to minimize malodorous sulfur gas generation. The system employing forced circulation evaporation also has a lower moisture content in the exit gases from the recovery furnace than following direct contact evaporators, thus reducing possible plume opacity problems. The air cascade evaporation system may have potential problems with corrosion and particulate plugging of the rotary heat exchanger.

Indirect contact evaporation also eliminates a potential air pollution control device. The direct contact evaporator reduces the particulate loading

of the recovery furnace flue gases entering the precipitator. The result is that the electrostatic precipitator can then be smaller because of the lower inlet loading. The alkaline black liquor also is a good scrubbing agent for sulfur oxides, and under certain conditions, reduced sulfur gases. The thermal efficiency of the process is also somewhat lower because the recovery flue gas temperature is normally higher than following direct contact evaporators.

C. Oxygen Production

1. Gas Separation

The molecular oxygen used for black liquor oxidation is manufactured by separation of ambient air into its respective components. The two main methods employed for oxygen production include cryogenic fractional distillation and molecular sieve adsorption. The cryogenic system employs compression of the inlet air to a liquir state at 450 psig pressure, followed by passage through a reversing heat exchanger and moisture removal in gel traps. The liquified air is then passed into a double column rectification unit for selective fractional distillation of nitrogen followed by its removal as a waste product. The oxygen at approximately 99.5 percent by volume purity is then heated and removed for either storage as a liquid, or shipped as a gas via pipeline (22). The cryogenic system is normally used for large oxygen production facilities of greater than 100 tons per day.

The molecular sieve adsorption system employs compression and passage of air through a series of molecular sieve absorption columns. The air is compressed to 30 to 60 psig and is consecutively passed through four adsorption columns in parallel, each of which selectively adsorbs carbon dioxide, water vapor, hydrocarbons, and most of the nitrogen. The oxygen is not adsorbed and passes through the column along with the argon. The

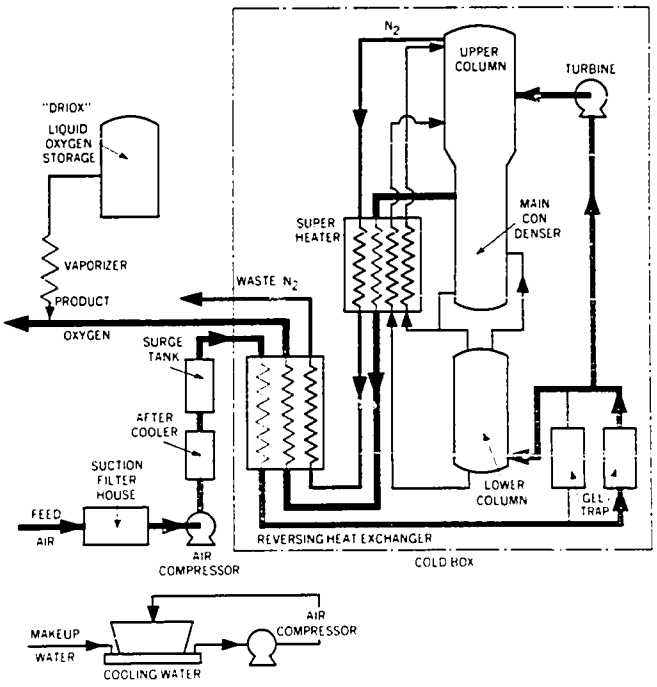
resulting gas stream is approximately 90 to 95 percent oxygen by volume, with the remainder argon and small amounts of nitrogen. Each column is periodically regenerated by reducing the pressure to allow nitrogen and the other gases to be bled off as a waste gas stream (23). Molecular sieve adsorption systems are normally used for small on-site oxygen plants of between 25 and 100 tons per day capacity where extremely high purity oxygen is not required. Both systems are illustrated in Plate I.

2. Market Economics

Oxygen gas is finding increasing use for industrial applications in the United States and elsewhere. The major markets to date are for the manufacture of steel and chemical industry applications, particularly certain petrochemical operations. Additional markets exist in welding, medical, aerospace, and metallurgical applications. A relatively new application is the use of oxygen for waste water treatment applications as a modification to the activated sludge process. There is a potential market or perhaps 20 to 40 million dollars per year for municipal waste water alone, with additional industrial applications as well. Large new potential markets for oxygen use may also develop for production of synthetic natural gas by coal gasification (24), oxygen pyrolysis of solid wastes as a replacement for incineration with air (25), and the manufacture of pulp and paper (26). Location of other manufacturing facilities using substantial quantities of oxygen or nitrogen which are adjacent to pulp and paper mills can substantially enhance its potential economic attractiveness. A listing of annual oxygen sales for 1966 is presented in Table 2 (25).

A particularly important variable affecting oxygen use is its unit cost, which can vary from seven dollars per ton for large uses to 35 dollars for small uses of 50 tons per day or less. For small users it is often less

a. Cryogenic Fractional Distillation:



b. Molecular Sieve Adsorption:

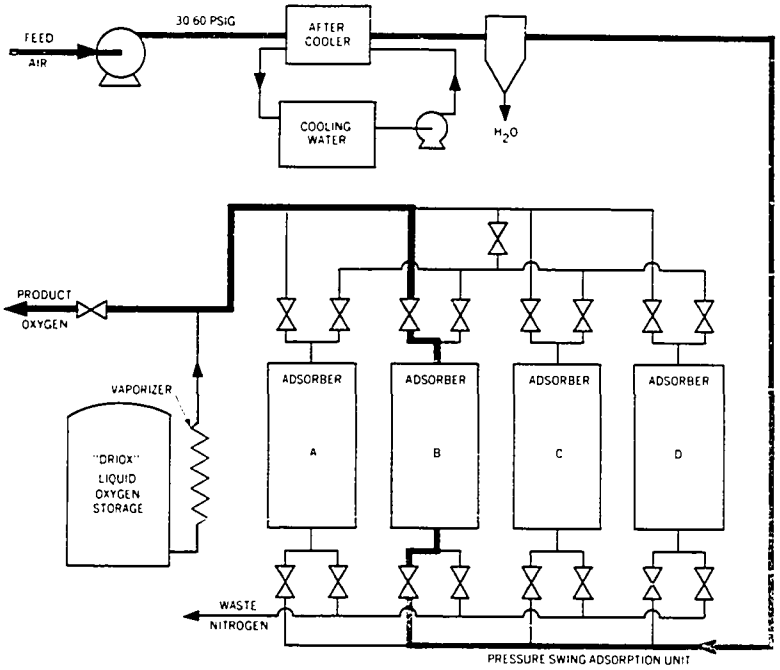


PLATE I. SYSTEMS FOR PRODUCING MOLECULAR OXYGEN.

TABLE 2. ANNUAL OXYGEN CONSUMPTION IN THE UNITED STATES FOR 1966 (27).

Application	Annual Consumption 10^6 SCF	Annual Consumption 10^3 Tons
Steel Manufacture	155,000	6,460
Other Metallurgical	13,900	580
Chemical Industry	63,700	2,660
Aerospace	10,200	425
Medical and Other	24,200	1,020
Total	367,000	11,145

expensive to have the oxygen brought in from a central facility and stored, while an on-site plant is normally more desirable when larger quantities are involved. For extremely large quantities of oxygen where a number of customers are involved, pipelines provide a feasible means for supplying oxygen at a low unit cost (28).

For on-site plants to be located at mills, either cryogenic or molecular sieve plants can be used, depending upon the oxygen requirements. For the cryogenic units operated at plants with greater than 100 tons per day capacity, electric power cost is a particularly important variable because of the high power requirements for gas compression. Recent reports by the U. S. Bureau of Mines (29) and the Federal Water Quality Administration (30) provide information regarding unit costs of oxygen at on-site plants. The selling price of cryogenic oxygen is primarily dependent upon the electric power cost and the quantity produced, as shown in Figure 4 (29). The cost of molecular oxygen produced at molecular sieve adsorption plants depends primarily on the purity desired and the quantity used, as discussed by Hall and Singman (31). Recent studies indicate that oxygen of 60 percent purity

can be produced for as low as 15 dollars per ton of oxygen (32). A third alternative is the use of liquid oxygen shipped from a central plant. The cost is dependent on distance from the plant, and is feasible only for small quantity uses. The effect of oxygen consumption rate and means of supply is illustrated in Figure 5 (30).

D. Related Applications

The economic desirability of using molecular oxygen for black liquor oxidation increases as its selling price is reduced. The unit cost of oxygen is lowered as the degree of consumption increases because of economies of scale, thus providing an economic incentive to find additional uses for oxygen in Kraft pulp mills. Several additional uses for oxygen include oxygen pulping, oxygen bleaching, recovery furnace and lime kiln augmentation, and waste water treatment. A summary of the approximate ranges for oxygen consumption in the Kraft process are presented in Table 3 (33).

1. Pulping Process

a. Oxygen Bleaching

Use of oxygen for pulp bleaching is now in the process of becoming commercially feasible for new and existing Kraft pulp mills. The first installation in the United States is now being constructed at the West Point, Virginia, Kraft pulp mill of the Chesapeake Corporation (34). The technique provides a means for increasing the brightness of pulps and replacing acidic chlorination and caustic extraction bleaching stages. The effect is to reduce the potential water pollution problems associated with these latter processes, particularly the highly colored effluents resulting from alkaline extraction bleaching stages (35).

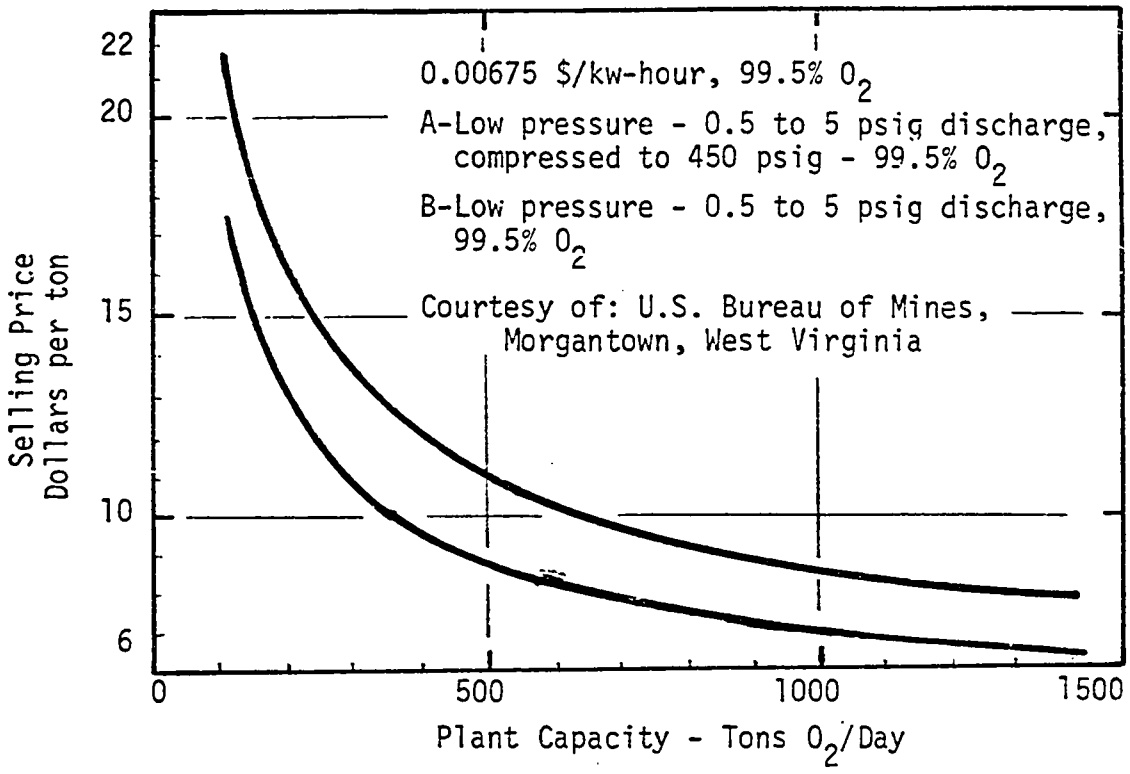


FIGURE 4. EFFECT OF PRODUCTION CAPACITY ON SELLING PRICE FOR CRYOGENIC OXYGEN PLANTS

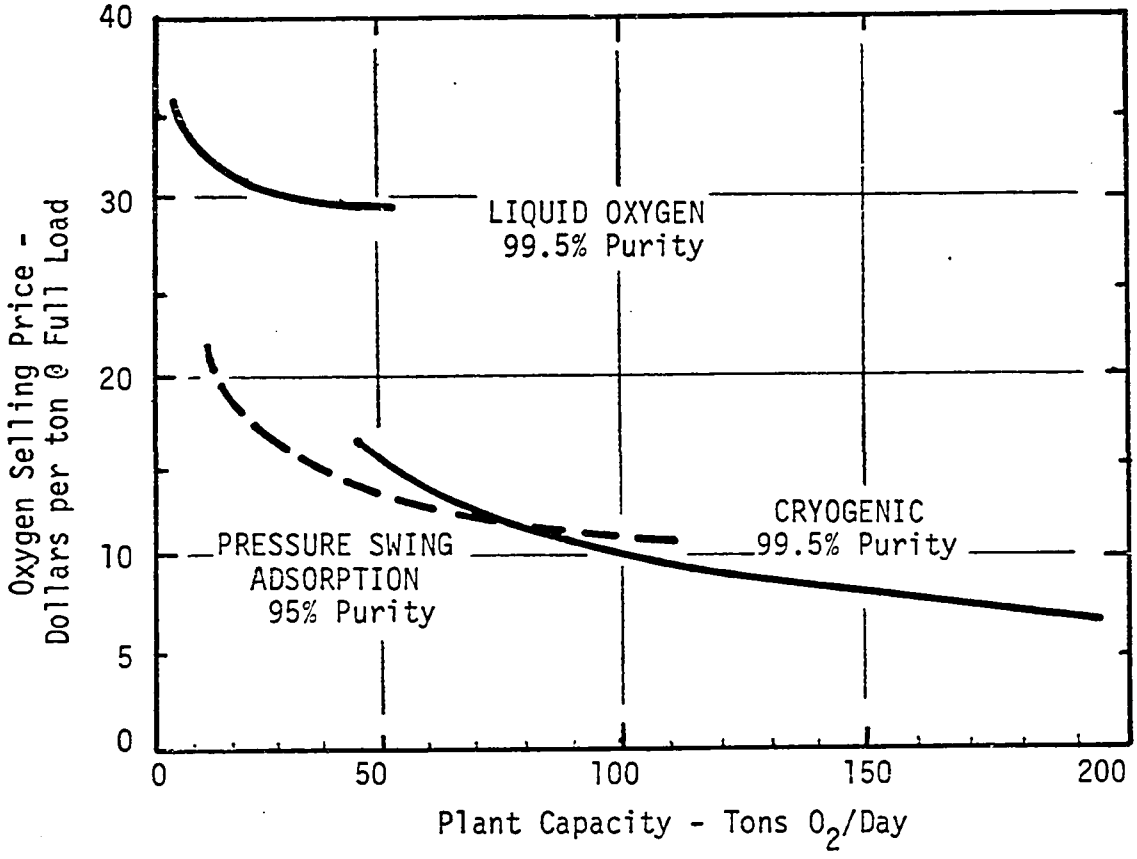


FIGURE 5. EFFECT OF OXYGEN CONSUMPTION RATE ON SELLING PRICE AND SUPPLY METHOD.

TABLE 3. POTENTIAL OXYGEN CONSUMPTION IN KRAFT PULP MILLS.

Usage	Consumption - lb O_2/Ton Pulp Average	Range
Odor Control		
Black Liquor Oxidation	75	50-100
Recovery Furnace Addition	25	0-50
Lime Kiln Addition	5	0-10
Waste Water Treatment	35	20-50
Total	140	70-210
Pulping Process		
Oxygen Bleaching	50	40-70
Oxygen Pulping	200	150-250
Total	250	190-320

b. Oxygen Pulping

Use of oxygen for pulping provides a means for elimination of sulfur from the pulping process, and elimination of the present Kraft mill odor problem. The techniques would replace the present Kraft process, but would employ consumption of large quantities of oxygen in a two stage process employing both oxygen treatment and alkaline extraction (36). However, oxygen pulping techniques are still in the developmental stage.

2. Odor Control

a. Recovery Furnace Addition

Addition of oxygen with the combustion air of existing recovery furnaces can be used as a means for controlling hydrogen sulfide emissions, particularly in heavily overloaded furnaces. The oxygen addition must be done in such a way that there is effective mixing and combustion of the sulfur, but without

subsequent problems with furnace overheating, chemical reduction efficiency decrease, or potential explosion hazards. The oxidation of sulfur must be sufficiently selective to minimize the degree of oxygen consumption, and combustion conditions controlled so as to minimize the formation of oxides of nitrogen. Recent work by Kolberg (37) indicates that the technique is useful for controlling hydrogen sulfide emissions from Kraft recovery furnaces, controlling smelt bed height, and releasing additional heat from combustion. However, the oxidation process is relatively nonselective, so that large quantities of oxygen may be required to control malodorous sulfur gas emissions from heavily overloaded furnaces. An alternative technique may provide for modification of existing Kraft recovery furnaces to provide for separate pyrolysis of the black liquor with molecular oxygen.

b. Lime Kiln Addition

Oxygen may also be added to the combustion zone of lime kilns to control malodorous sulfur gas emissions in a manner similar to recovery furnaces. Precautions should be taken to assure effective mixing and to prevent potential kiln overheating. The technique may allow greater lime mud throughout rates for through existing kilns with increased production. There is no known field experience to date with the technique.

3. Waste Water Treatment

Molecular oxygen finds several potential applications for waste water treatment in the pulp and paper industry. These include use of oxygen for activated sludge aeration in place of air, increasing dissolved oxygen levels in aerated stabilization basins, pipeline effluent oxidation treatment, and oxygenation of receiving waters to maintain suitable dissolved oxygen levels for aquatic life. The use of oxygen for waste water treatment enhances its economic attractiveness for other paper industry applications.

a. Activated Sludge Oxygenation

It is possible to use molecular oxygen in place of air as the source of oxygen for activated sludge aeration. The technique has proven successful for municipal secondary waste treatment in a recent study at Batavia, New York (30). Grader, South, and Djordjevic (38) report the successful use of a modified activated sludge system for the treatment of unbleached Kraft pulp mill effluent on a pilot scale. The system used employs four completely mixed oxygenation chambers arranged in series, with both oxygen gas and liquid effluent in cocurrent flow. The functions of oxygen bubble dispersion and liquid mixing are performed by turbine aerators placed in each chamber. The exhaust gas in each chamber is consecutively recirculated by means of compressors through the aerators. Following the oxygenation step, the activated sludge from the clarifier is returned to the inlet of the aeration system.

Results of the pilot studies indicate that the activated sludge system is consistently able to produce reductions in biochemical oxygen demand of 90 percent or greater with oxygen utilization efficiencies of greater than 90 percent. The system is able to operate at relatively high mixed liquor solids concentrations of 5,000 to 7,000 milligrams per liter, and high dissolved oxygen levels of five milligrams per liter or greater can be maintained because of the absence of nitrogen in the inlet gas. Sludge setting and thickening properties are superior to conventional air systems, and less waste sludge is produced than for comparable air activated sludge units. It is possible to have smaller aeration and clarifier tanks with the oxygen system because of reduced aeration retention time requirements and increased sludge concentrations. Lower nutrient requirements because of lower gas flow rates, and reduced odor emissions because of the enclosed

aeration tanks are also advantages of the process. However, pH and temperature controls may be required at specific installations, necessitating additional operating costs.

b. Pipeline Oxidation System

Stoyer (39) describes a system where municipal waste water can be oxidized in a plug flow reactor by injection of either air or molecular oxygen under pressure into a pipeline with the liquid effluent. The co-current flow system employs removal and activation of the primary sludge by aeration upstream of the pipeline reactor. The pressurized gas (either oxygen or air) and the activated primary sludge are injected into the effluent flowing through the pipeline reactor and allowed to flow for at least two to three miles. The secondary sludge produced is then removed from the liquid effluent by sedimentation, and may be either returned to the inlet of the reactor or disposed of by landfill or incineration, as shown in Figure 6.

Results obtained during a three week field trial with air indicate the system is able to reduce the biochemical oxygen demand by more than 90 percent, and reduce the tendency for odorous gas generation. The technique may be applicable for the treatment of pulp and paper mill waste waters, particularly as a pretreatment device for existing waste water treatment facilities to reduce the inlet loading. It also may be used for oxidation of the more easily reactive volatile compounds which might produce potential odor problems. Molecular oxygen may prove superior to air because no nitrogen is present, resulting in increased oxygen solubility, enhanced reaction rates, reduced liquid foaming, and lessened tendency to evolve volatile gases by stripping.

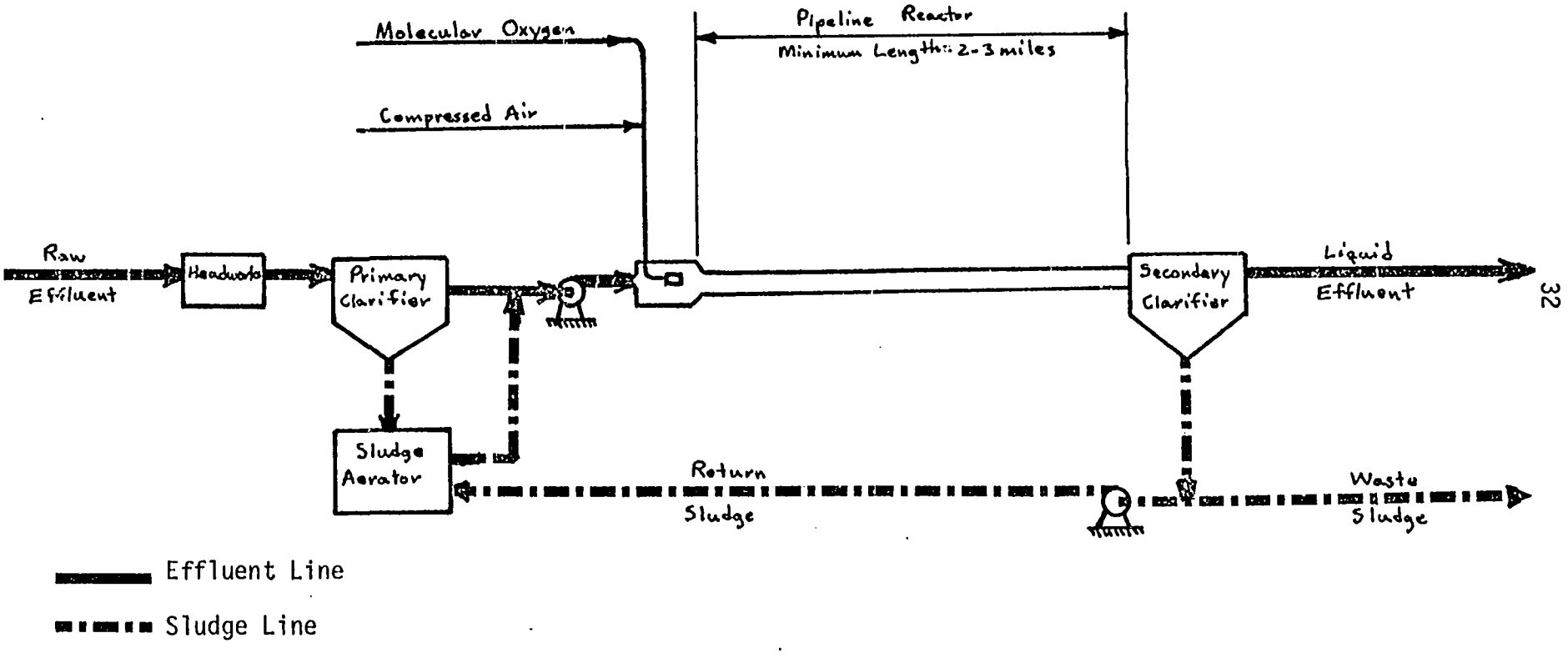


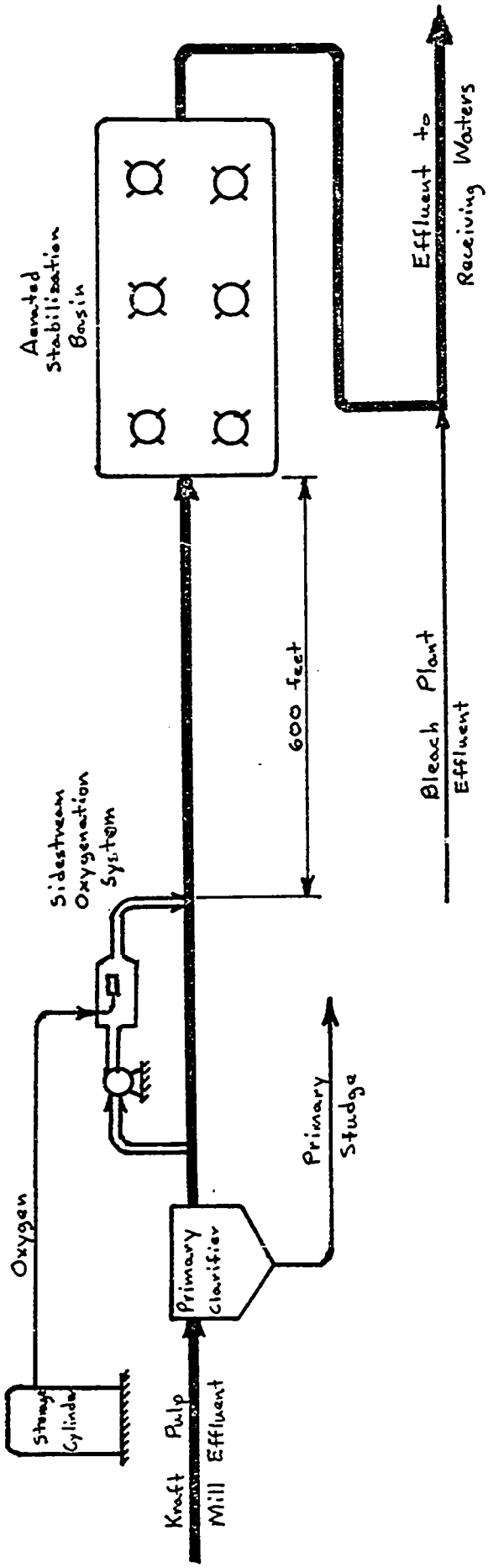
FIGURE 6. PIPELINE REACTOR SYSTEM FOR WASTE WATER TREATMENT (39).

c. Sidestream Oxygenation

An additional use of molecular oxygen for waste water treatment is introduction directly into the effluent or into the receiving water by means of oxygenation into a small portion of the liquid stream to reduce pumping costs. The purposes of the oxygen addition step are to increase the dissolved oxygen concentrations and reduce the incoming biochemical oxygen demand of either waste waters effluents or receiving waters, respectively. A potential process for sidestream oxygenation, called "Lindox," has been developed for oxygen addition into either liquid effluents or receiving waters (40).

The Brewton, Alabama, mill of Container Corporation of America employs a sidestream oxygenation system for addition of molecular oxygen to Kraft mill effluent to upgrade the performance of an existing aerated stabilization basin (41). The system employs removal of a portion of the pulp mill effluent following primary treatment, addition of oxygen to supersaturation conditions under pressure, and return to the main liquid effluent line. The oxygen is then in contact with the full liquid effluent for approximately ten seconds in a 600 foot pipe upstream of the basin, as shown in Figure 7. The oxygen absorption efficiency for the system is greater than 90 percent, and the system uses between one and five tons per day of oxygen, depending on the time of year. The technique also serves to reduce potential odor problems associated with the waste water treatment operations.

An additional use of oxygen is the reaeration of receiving waters with molecular oxygen to increase dissolved oxygen levels. The technique is generally used in the late Summer period of low stream flow, low dissolved oxygen levels, and high liquid temperatures, when excessive waste discharges may have a particularly severe effect on receiving water quality in terms of



Courtesy of: Union Carbide Corporation, Tarrytown, New York, 1972.

FIGURE 7. OXYGEN ENRICHMENT OF KRAFT MILL EFFLUENT BY SIDESTREAM OXYGENATION.

dissolved oxygen level. Amberg (42)(43) reports on two installations where molecular oxygen is added to receiving waters adjacent to pulp and paper mills to augment dissolved oxygen levels during Summer periods of high temperature and low stream flows. The systems are both of the sidestream oxygenation type where small portions of the river flow are pumped through the system and oxygen added at supersaturation conditions. Power turbines are used for the oxygen dispersion into water, and absorption efficiencies of 40 to 55 percent can be obtained. The technique is able to increase the dissolved oxygen concentration in receiving waters by from one to three milligrams per liter.

4. Nitrogen Utilization

The economic feasibility of using molecular oxygen for black liquor oxidation or other applications in the pulp and paper industry is substantially enhanced if possible uses for nitrogen can be found. Three possible uses are as follows: 1) inert gas supply for mill process instrumentation; 2) pressure flotation of tall oil to avoid oxidation with air; 3) possible stripping of condensate waters to facilitate water reuse. Applications for nitrogen at adjacent manufacturing facilities such as frozen food processing, ammonia synthesis, inerting systems for petrochemical manufacture, and others may also enhance the economic attractiveness of using oxygen, which would then otherwise be a waste product from the above operations.

III. LITERATURE REVIEW

A. Previous Investigations

1. Early Developments

The first known mention in the literature of subject material relating to black liquor oxidation phenomena for Kraft pulping was made by Klason and Segerfelt (44) in 1911. They observed that the sodium sulfide content of black liquor appeared to decrease with time during storage for extended periods when exposed to air. These findings were verified in subsequent studies by Heath, Bray, and Curran (45), who also found that the sodium sulfide concentration of black liquor decreased upon storage when exposed to air. However, they attributed this concentration decrease to reaction of sodium sulfide with organic constituents in the black liquor because it was not possible to observe a simultaneous increase in liquid pH or alkalinity. In addition, Basberg (46)(47) found that when black liquor was stored in an air-tight container at room temperatures, its concentration did not change during several weeks of storage.

Staidl and Schmitt (48) were perhaps the first to recognize the true nature of and potential usefulness of oxidizing black liquor for chemical fixation of the sulfur compounds present. They presented a series of observations regarding aeration of Kraft black liquor at a Superintendent's meeting in Madison, Wisconsin in 1938, the full text of which was never published. They observed that during the Kraft chemical recovery furnace operation that adding sodium sulfate as a makeup chemical resulted in a loss of 12 percent of the sodium input but 46 percent of the sulfur. The disproportionately high losses of the sulfur (over and above particulate losses as sodium sulfate) were believed to result from emissions of gaseous

sulfur compounds, primarily hydrogen sulfide resulting from thermal instability of sodium sulfide present in black liquor. The proposed method for reducing the excessive sulfur losses from the recovery system was to aerate the black liquor to reduce the chemical makeup requirements by oxidizing the sodium sulfide present.

2. Laboratory Studies

Several early studies led to the subsequent development and use of black liquor oxidation systems, initially with air. Bergstrom and Trobeck (49) made what was perhaps the first comprehensive laboratory study chemistry of black liquor oxidation, which was initially reported in 1939. They observed that the sodium sulfide concentration in black liquor at elevated temperatures decreased rapidly upon exposure to air, and that sodium thiosulfate was the major reaction product. Their results were later used to develop commercial-scale systems for black liquor oxidation at Kraft pulp mills in Scandanavia. They also studied the kinetics of the reaction between sodium sulfide and molecular oxygen, which will be discussed in a later section.

Tomlinson (50) reported in 1946 on a series of pilot scale experiments where black liquor was oxidized with air in a packed bed absorption tower. Primary emphasis was devoted to measuring the rate of sodium sulfide concentration decrease as an indicator of oxygen mass transfer from air into weak black liquor. Results indicated that five times the stoichiometric air requirement was necessary for effective conversion of sodium sulfide to sodium thiosulfate in the black liquor. The optimum rate of sodium sulfide oxidation was found to occur at a temperature of approximately 70°C (158°F), and that the initial oxidation rate was very rapid.

Bialkowsky and DeHaas (51)(52) reported on a series of laboratory and field studies of black liquor oxidation with air on a wetted wall cocurrent flow column in 1951. They had initially noted that there was a substantial decrease in the sodium sulfide concentration of black liquor upon contact with air in passing through brown stock pulp washing. Laboratory studies of black liquor oxidation with air on the wetted wall column yielded several findings. First, the oxidation of sodium sulfide was catalyzed by the presence of organic compounds present in the black liquor, thus increasing the rate of the oxidation reactions. Second, more oxygen was absorbed into the black liquor than necessary for the stoichiometric oxidation of sodium sulfide to sodium thiosulfate, indicating that constituents other than sodium sulfide in the black liquor were being oxidized. Third, no increase in sodium hydroxide concentration of the black liquor was noted, possibly because of the buffering action of the carbonate and other constitutents present.

They also made studies of the effect of temperature upon the oxidation of sodium sulfide and its reaction products. First, increasing the temperature at which the black liquor was oxidized decreased the potential for foaming but increased the oxygen consumption. Second, evaporation of black liquor to dryness at 300°F resulted in substantial liberation of hydrogen sulfide from unoxidized black liquor, but virtually none from oxidized liquor. Third, when black liquor was evaporated to dryness at temperatures above 500°F, hydrogen sulfide was liberated from both unoxidized and oxidized black liquor. These findings indicated that hydrogen sulfide emissions from direct contact evaporation could be minimized by black liquor oxidation, but not during combustion in the recovery furnace.

Wright (53)(54) reported on a series of laboratory studies regarding the kinetics of black liquor oxidation performed by the British Columbia

Research Council in 1952. The rate of sodium sulfide oxidation with air was measured over a temperature range from 40°C to 90°C (105°F to 195°F) by using a specially designed respirometer, and several conclusions were drawn. First, the oxidation of sodium sulfide proceeded in two successive well-defined reaction rate regimes limited by oxygen mass transfer and chemical reaction rate, respectively. Second, the rate of oxygen mass transfer was limiting only at the higher sodium sulfide concentrations, so that gas-liquid contact beyond a certain point was unnecessary. Third, the author mistakenly stated that the oxidation of sodium sulfide and mercaptide was complete within two to three minutes, a finding not supported by the data.

Fourth, the oxidation of sodium sulfide was accelerated by the presence of organic catalytic materials in the black liquor as compared to alkaline solutions alone, verifying the previous findings of Bialkowsky and DeHaas. Fifth, the complete oxidation of sodium sulfide with air required two to five moles of oxygen per mole of sodium sulfide oxidized, indicating possible incomplete mass transfer, and competing side reactions. Sixth, the rate of sodium sulfide oxidation did not appear to increase with temperature above 60°C (140°F). Seventh, the amount of oxygen consumed per unit amount of sodium sulfide oxidized increased with temperature. These two findings indicated that increasing black liquor temperature to increase sodium sulfide oxidation rate would probably not be beneficial.

3. Field Studies

Several early field investigations of black liquor oxidation with air yielded particularly useful information regarding the potential usefulness of the technique for Kraft pulp mill odor control. Brauns (55) described the INKA (Industrikemiska Aktiebolaget) system of combined multiple effect and direct contact evaporation of black liquor developed in Sweden during

World War II. The system employed condensation of water from the recovery furnace flue gases to heat black liquor indirectly by passing the liquor repeatedly over a series of perforated plates over which air was blown. In recirculating the liquor approximately 20 times the sodium sulfide content was reduced by approximately 80 percent in concentrating the liquid. It was noted that a substantial amount of air was added to achieve this level of oxidation, indicating that concentrating the black liquor might have an inhibitory effect on oxygen transfer into the liquid phase. One possible reason that the system only achieved an 80 percent oxidation of sodium sulfide was that there was a relatively limited black liquor retention time.

Tomlinson (56)(57) reported on the results of the installation of full scale black liquor oxidation units at two Kraft pulp mills in Canada, which began operating in 1943 and 1944, respectively. The air oxidation systems were both of the countercurrent flow, multiple sieve tray type, and were installed for weak black liquor oxidation. Stack gas analyses showed that substantial quantities of hydrogen sulfide were liberated from unoxidized black liquor during direct contact evaporation by the action of acidic components such as carbon dioxide and sulfur dioxide present in the recovery furnace flue gas. Oxidation of the weak black liquor with air substantially reduced its sodium sulfide concentration, the amount of hydrogen sulfide liberated during multiple effect and direct contact evaporation, and the rate of metal corrosion of these evaporator surfaces.

Hisey (58) reported on the operation of a Tomlinson-type recovery system employing black liquor oxidation at a Kraft pulp mill in Springs, South Africa, in 1951. A countercurrent flow packed tower was used for the weak black liquor oxidation step where the inlet air was the exhaust from the brown stock washer hood vents, and the exhaust from the oxidation

tower added to the combustion air of the recovery furnace. The average oxidation efficiency of the system was found to be approximately 85 percent for sodium sulfide. However, oxidation of the black liquor with air for as long as 48 hours did not result in complete oxidation of the sodium sulfide present. The black liquor oxidation system appeared to cause a reduction in hydrogen sulfide concentration in the recovery furnace flue gas by absorption across the direct contact evaporator.

Two early studies in Scandanavia provided information regarding potential problems with black liquor oxidation. Tahtinen (59) described experiences of weak black liquor oxidation with air at a Kraft pulp mill in Finland pulping substantial quantities of pine wood species. The system was found to have serious operating problems caused by excessive foaming which could not be readily rectified. Sylwan (60) reported on a somewhat more successful air oxidation system of a design similar to the one used by Tahtinen. Foaming problems associated with air oxidation of weak black liquor could be substantially reduced by removal of the soap materials from the liquor upstream of the oxidation tower. Benefits noted for black liquor oxidation were reductions in salt cake and lime chemical makeup requirements, fuel consumption, and multiple effect evaporator corrosion rate.

B. Previous Reviews

1. Collins Reviews

A number of literature reviews regarding black liquor oxidation practices were prepared by Mr. T. T. Collins covering the period from 1948 to 1962, which extensively covered developments in the field. In 1948, Collins and Collins (61)(62) noted that hydrogen sulfide emissions from a Kraft recovery furnace following direct contact evaporation were substantially reduced when processing oxidized black liquor as compared to

unoxidized liquor. In 1949, Collins and West (63)(64) reported that in addition to reduced hydrogen sulfide and sulfur dioxide emissions, that the partial oxidation of sodium sulfide in black liquor resulted in decreased corrosion rates for multiple effect evaporator tubes and cyclone evaporator internals, plus increased green and white liquor sulfidities.

Collins (65) prepared an extensive review of the chemistry of black liquor oxidation in 1950. First, he reported that when weak black liquor at 180°F was oxidized with air for three hours, the sodium sulfide concentration was reduced by approximately 90 percent. The major portion of the sodium sulfide was oxidized to sodium thiosulfate, but a small percentage was converted further to sodium sulfate, as listed in Table 4 (65).

TABLE 4. EFFECT OF BLACK LIQUOR OXIDATION ON CHEMICAL COMPOSITION (65).

Component	Units	Oxidation	After Oxidation
Na_2S	gm/liter	9.01	1.02
$Na_2S_2O_3$	gm/liter	4.07	11.78
Na_2SO_3	gm/liter	0.18	0.00
Na_2SO_4	gm/liter	3.97	5.48
Total Sulfur			
Addition	gm/liter	6.29	6.42
Analysis	gm/liter	6.56	6.45
Total Solids	%	19.7	----

Second, studies of the thermal stabilities of sulfur compounds present in black liquor indicated that sodium sulfite and sodium sulfate were stable at temperatures of 300°C (600°F) or higher. However, the heating of sodium

thiosulfate to 300°C resulted in its partial decomposition with sulfur dioxide as a product, indicating the potential for release from oxidized black liquor. Sodium sulfide decomposed upon heating to 150°S (300°F) to release hydrogen sulfide gas and form sodium hydroxide. Third, sodium thiosulfate underwent partial decomposition at liquid pH's of 4.0 or lower to form sodium sulfite and liberate sulfur dioxide, a potential problem in tall oil acidulation, and also for analytical techniques for thiosulfate ion measurements. Fourth, sodium peroxide was found to be an effective oxidizing agent for sodium sulfide, but its estimated cost was a prohibitive 100 dollars per ton of pulp produced.

Collins (66) second review in 1950 dealt with the potential benefits of black liquor oxidation on the Kraft recovery system. A series of tests indicated that high degree black liquor oxidation could reduce hydrogen sulfide emissions from multiple effect and direct contact evaporation by as much as 90 percent. Other benefits listed included increased white liquor sulfidity, reduced lime makeup requirements, reduced corrosion in multiple effect and direct contact evaporators, and more uniform multiple effect evaporator operation.

Collins (67)(68) published an additional literature review in 1953 listing an additional benefit of black liquor oxidation as improved evaporator condensate water quality. The reason for the improvement in the condensate water quality was that the evaolution of hydrogen sulfide from black liquor was substantially reduced by the oxidation process.

Collins (69) reported on additional developments regarding black liquor oxidation in 1955, which included the design and operating features of a pilot scale oxidation unit. The system employed passage of weak black liquor over a porous carbon diffuser through which air was being blown, where the

foam formed was reconstituted in a deaeration tank. Particularly severe foaming problems were observed for black liquors resulting from pulping of pine wood species.

Collins (70) prepared an additional review of black liquor oxidation practices in 1962, and reported conflicting experiences regarding weak black liquor oxidation with air at two Southern Kraft pulp mills. One mill employed a packed tower, but the system could not be made operable because of excessive foaming. The other mill employed a porous black diffuser, and reported intermittent success during a six month trial period employed both mechanical foam breaking and liquid defoamer addition. Black liquor oxidation was suggested as a means of increasing tall oil yield as a potential process benefit. The use of strong black liquor oxidation to alleviate foaming problems associated with weak black liquor oxidation for mills pulping substantial quantities of pine wood species was also mentioned.

2. Landry Review

Landry (71) prepared an extensive review of weak and strong black liquor oxidation systems at Kraft pulp mills in the United States. Advantages cited for weak black liquor oxidation upon multiple effect evaporator operation included reduced corrosion, increased heat transfer, reduced hydrogen sulfide concentration in the evaporator noncondensable gases, improved evaporator condensate water quality, reduced steam requirements because of a slight liquor concentration. The weak black liquor oxidation systems operated with relatively low horsepower, but normally required a large capital investment for equipment.

Landry studied the effects of contactor configuration, foam breaking devices, and defoamer addition on the relative ability to control foaming when oxidizing pine weak black liquor with air. Results indicated that the

non-foam generating falling film wetted wall contactors generated much less foam than the foam generating bubble tray porous diffuser contactors, but also produced lower sodium sulfide oxidation efficiencies. It was noted that black liquor oxidation improved the degree of tall oil separation. Mechanical, sonic, and thermal defoaming devices all proved ineffective for controlling foam from Southern pine black liquor. Chemical defoaming liquids and kerosene proved to be effective for controlling foam, but the operating costs were a prohibitive $1.50 to $3.00 per ton of pulp.

Landry also mentioned the possible future use of molecular oxygen for weak black liquor oxidation at Southern Kraft mills. Use of oxygen instead of airprovided a potential means of alleviating the foaming problems associated with pulping of highly resinous pine wood species because of the absence of the nitrogen diluent medium.

3. Hendrickson Review

Hendrickson and Harding (72) reviewed black liquor oxidation practices at several Kraft pulp mills in the Southeastern and Northwestern United States, the benefits of black liquor oxidation, and the special problems associated with oxidation of black liquor with air in Southern Kraft pulp mills pulping substantial quantities of pine. The installation of either weak or strong black liquor oxidation systems at existing mills resulted in reductions of malodorous sulfur gas emissions from recovery furnaces following direct contact evaporation of 80 to 95 percent. Sulfur savings in mills where weak black liquor oxidation systems were employed averaged 43 pounds per ton of pulp, as compared to no oxidation. Sulfur savings in mills practicing strong black liquor oxidation averaged 32 pounds per ton of pulp as compared to no oxidation. Results indicated a potential sulfur loss during multiple effect evaporation of approximately 10 pounds

per ton of pulp. It was not clear from the article whether these losses were as sulfur or sodium sulfate, but were probably the latter.

4. NCASI Review

Blosser and Cooper (73) compiled a summary review of black liquor oxidation systems using air at Kraft pulp mills in the United States. Data was compiled regarding the design and operating characteristics of existing weak and strong black liquor oxidation systems on stream in 1968. The major types of units surveyed included packed towers, bubble tray towers, plus agitated and unagitated air sparged units. Several major findings were deduced from the survey of existing black liquor oxidation systems.

First, the efficiency of sodium sulfide oxidation for all of the units was a function of the product of the amount of oxygen supplied relative to the stoichiometric requirement and the liquid retention time. A summary of approximate loading factor requirements to achieve given levels of sodium sulfide oxidation efficiency on an overall basis is listed in Table 5 (73).

TABLE 5. EFFECT OF OXYGEN-LIQUOR LOADING FACTOR ON SODIUM SULFIDE OXIDATION EFFICIENCY FOR BLACK LIQUOR OXIDATION SYSTEMS USING AIR (73).

Na_2S Oxidation Efficiency %	Loading Factor - minutes[1]	
	Weak Liquor	Strong Liquor
80	200	250
90	250	325
95	300	400
98	350	600
99	400	800
100	500	1000+

Note 1: Loading Factor = $\frac{\text{lb } O_2 \text{ Actual}}{\text{lb } O_2 \text{ Theor.}} \times$ Liq. Ret. Tim - min.

The higher values required for the strong black liquor may reflect the increased difficulties involved with oxygen mass transfer into the more viscous strong black liquor.

Second, the efficiency of sodium sulfide oxidation was found to increase with air flow rate and liquid retention time for given systems at constant liquor flow rate, but decreased with increasing sodium sulfide concentration beyond a certain point. Third, the rate of sodium sulfide oxidation appeared to be more rapid in black liquors at mills pulping substantial quantities of hardwoods such as oak than softwoods such as pine or fir. Fourth, an extensive series of studies at one mill showed that increasing the efficiency of sodium sulfide oxidation in weak black liquor from 85 to 100 percent substantially reduced the hydrogen sulfide emissions from the recovery furnace following direct contact evaporation. Even at 100 percent efficiency, hydrogen sulfide emissions were noted, indicating either formation in the furnace or "reversion" of oxidized liquor to sodium sulfide during multiple effect evaporation.

5. Foreign Reviews

A limited amount of work on black liquor oxidation has been performed in Eastern Europe. Laszkiewicz (74) and Zielinski (75) have reviewed black liquor oxidation practices in Poland. Among the benefits listed for black liquor oxidation were that it increased white liquor sulfidity and heat recovery, and reduced lime and salt cake makeup requirements, plus substantially reducing the emissions of malodorous sulfur gases. The viscosity of black liquor was raised by oxidation at temperatures below 60°C (140°F).

Several recent papers described experiences with black liquor oxidation in the Soviet Union. Grabovskii and Maksimov (76) performed a series of laboratory experiments on a modified wetted wall column, and found that the sodium sulfide oxidation efficiency was 93.5 to 98.0 percent at an air flow

rate of 290 cubic meters of air per cubic meter of black liquor (39 cubic feet of air per gallon of black liquor) and a black liquor temperature of 90°C (194°F). Malyshkin (77) studied black liquor oxidation in a pilot-scale packed tower reactor. Results indicated that an air flow rate of 300 to 350 cubic meters of air per cubic meter of black liquor (40 to 47 cubic feet of air per gallon of black liquor) resulted in a sodium sulfide oxidation efficiency of 93 to 95 percent. Sulfur losses in a full-scale Kraft recovery system could be reduced by approximately 50 percent by using weak black liquor oxidation. Alferova and Titova (78) performed an extensive study of the chemistry of black liquor oxidation, and also found that the odor of evaporator condensate waters could be substantially reduced by weak black liquor oxidation.

C. Air Oxidation

A number of systems have been employed for the oxidation of both weak and strong black liquor using air as the source of oxygen. Weak black liquor oxidation with air has been extensively practiced at Kraft pulp mills in the Pacific Northwest where foaming has not been a major problem. Strong black liquor oxidation with air has come into increasing use at Kraft pulp mills in the Southeastern United States where foaming of weak black liquor has been a severe problem. It has also been applied at mills practicing weak black liquor oxidation for polishing to counteract reversion to sodium sulfide.

1. Weak Liquor Systems

a. Equipment

The major types of systems which have been employed to date for weak black liquor oxidation with air include the following: 1) packed absorption

towers (50)(51)(79)(80); 2) bubble tray towers (69)(81)(82); 3) agitated air spargers (83); 4) rotating fluid contactors (84)(85); 5) other systems, including pressurized vessel reactors (86) and wetted wall columns (87). Blosser and Cooper (73) extensively reviewed the design and operating features of existing weak black liquor oxidation systems. They reported that consistently high levels of sodium sulfide oxidation efficiency could be obtained with the porous plate diffuser (Collins) and sieve tray tower (Trobeck-Ahlen or Lundberg) bubble tray-type weak black liquor oxidation systems, provided that sufficient surface contact area and air flow rates were employed. Less effective performance was noted for packed tower systems, possibly because of inadequate liquor retention times, and the agitated air spargers because of frequent mechanical breakdowns.

b. Problems

Most of the existing weak black liquor oxidation systems using air installed to date have been located at Kraft pulp mills in the Pacific Northwest and Northeastern sections of the United States. Pine has not been the predominant wood species in these mills so that the severe foaming problems associated with Southern pines have been circumvented. Blosser and Cooper (73) reported several major problems which inhibited the success of weak black liquor oxidation with air. These problems include the following: 1) excessive foaming resulting from highly resinous wood species such as pine; 2) inability to achieve high degrees of sodium sulfide oxidation resulting from underdesign of systems; 3) system overload caused by increased production without expansion of existing units, resulting in decreased liquid retention time; 4) inability to achieve effective oxygen mass transfer from air into the black liquor.

2. Strong Black Liquor

The problems associated with foaming when air was used for oxidation of weak black liquor at mills pulping substantial quantities of pine led to the development of strong black liquor oxidation at Kraft pulp mills in the Southeastern United States. Strong black liquor oxidation could act to reduce potential emissions of malodorous sulfur gases from the direct contact evaporator and counteract reversion to sodium sulfide. It would not affect sulfur gas emissions during multiple effect evaporation or produce the other benefits associated with weak black liquor oxidation.

a. Systems

The major type of strong black liquor oxidation system employed to date has been the unagitated air sparger, or Champion system. Other devices have also been used, including agitated air spargers, rotating fluid contactors, and plug flow reactors.

Hawkins (88)(89) reported the development of a strong black liquor oxidation system employing an aeration tank followed by a deaeration tank in series, where the single stage aeration tank employed an unagitated radial pipe nozzled sparger for contacting air with black liquor. The system was consistently able to produce a sodium sulfide oxidation efficiency of 97 to 98 percent, resulting in a reduction of hydrogen sulfide emissions from the recovery furnace from 500 to 50 parts per million by volume. Padfield (90) reported on modification of the system by addition of a second aeration tank in series with the first to upgrade overall system performance. The sodium sulfide oxidation efficiency of the system was increased to 99.95 percent by the modifications, resulting in reduction of hydrogen sulfide emissions from the recovery furnace following direct contact evaporation from fifty to two parts per million by volume.

The two other systems employed have displayed less successful performance that unagitated air spargers for strong black liquor oxidation with air. The agitated air sparging system was employed at one mill, but suffered severe maintenance problems caused by frequent breakdown of the agitator on the turbine aerator and the mechanical foam breakers (73). The Ashbrook rotating fluid contactor (84) has seen limited use for polishing of strong black liquor with air in series with existing units. Caron (91) reported that the system produced incomplete sodium sulfide oxidation because of incomplete oxygen mass transfer and insufficient liquid retention time.

b. Evaluation

Blosser and Cooper (73) reported the successful use of strong black liquor oxidation at a number of mills in the Southeastern United States. They found substantial differences in sodium sulfide oxidation rates at different mills, depending on the wood species being pulped. They reported the necessity for use of deaeration tanks following the oxidation towers for removal of entrained air to facilitate liquid pumping, and to remove tall oil during multiple effect evaporation to alleviate potential foaming problems. Kerosene, fuel oil, and chemical agents proved effective for foam control, but mechanical foam breakers did not. Morgan (92) reported that the efficiency of strong black liquor oxidation increased with air flow rate, liquor height, and retention time. The rate of sodium sulfide oxidation increased with increasing inlet sodium sulfide concentration, and decreasing liquor height and retention time.

At a recent National Council symposium on black liquor oxidation held in Atlanta, Georgia, the use of two stage strong black liquor oxidation systems were described (93). Storage of oxidized strong black liquor for longer than two hours resulted in substantial reversion, so that oxidation towers should

be located following storage facilities. Increasing the black liquor solids concentration above 52 percent resulted in considerably increased resistance to oxygen mass transfer because of the high liquid viscosity. Black liquor oxidation also appeared to increase the tall oil yield, but the quality of the material recovered was decreased.

c. Plug Flow Reactors

Tobias and Robertson (94) described the recent development of an agitated cocurrent plug flow reactor for oxidation of strong black liquor with air, using a system similar to that proposed for the present research. The primary purpose of the system was to polish strong black liquor with air following multiple effect evaporation to counteract the "reversion" to sodium sulfide of oxidized weak black liquor in an existing system. The system employed location of one oxidation unit on the exit pipe of the strong black liquor storage tank, and one on the strong black liquor recirculation line, as shown in Figure 8. Each reactor was located so that a pipe with a central, axially-located baffle formed two mixing chambers, each with an agitator. Two parallel pipes were located immediately upstream of the agitators in both chambers, with holes drilled so as to obtain a fanning "air curtain" effect. The air bubbles were sheared into smaller bubbles by the rotating action of the agitators to facilitate maximal gas-liquid interfacial contact area, turbulence and mixing.

Preliminary results indicated that the sodium sulfide oxidation efficiency for the system was virtually 100 percent with both units operating at inlet concentrations of three grams per liter or less. The oxidation efficiency was essentially 100 percent with the system on the storage tank exit line alone at sodium sulfide concentrations of 1.3 grams per liter or less. The system also appeared to have higher oxygen utilization efficiencies

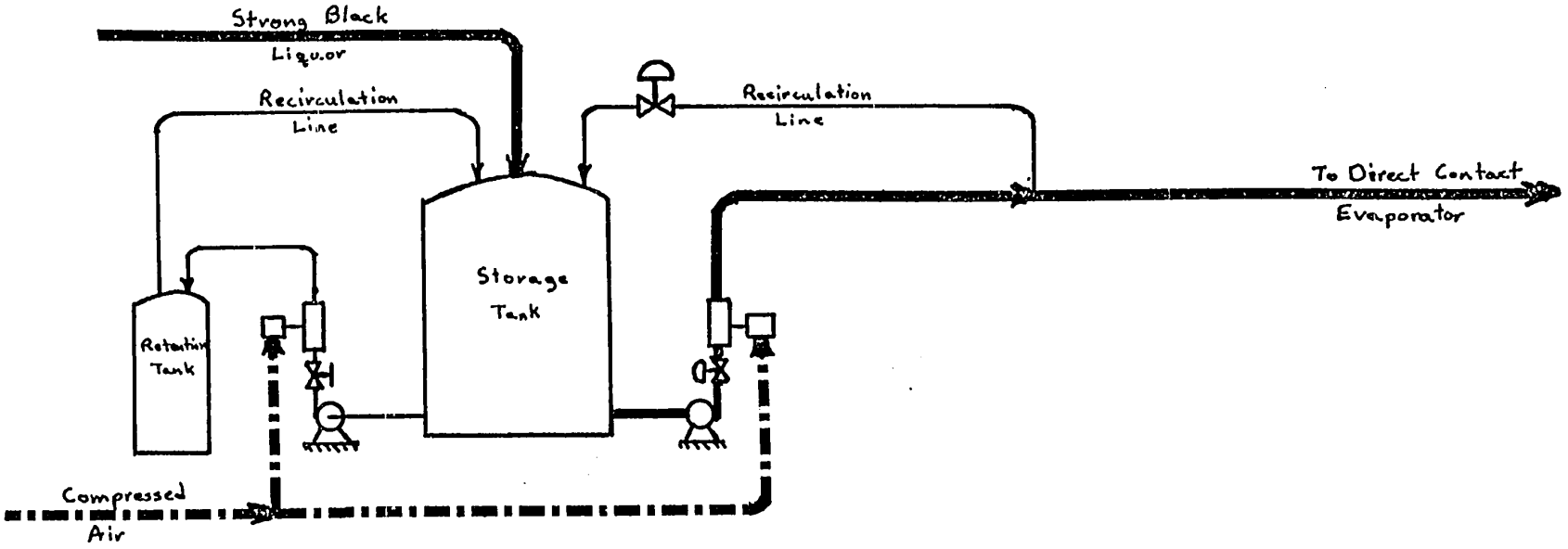


FIGURE 8. PIPELINE OXIDATION SYSTEM FOR STRONG BLACK LIQUOR OXIDATION WITH AIR.

than conventional air sparged units. No major problems with foaming were observed, but the wood furnish of the mill was primarily oak hardwoods. The two phase flow system reduced liquor line plugging but also caused substantial line vibrations, requiring secure fastening of the pipes. When the system was installed at a second mill, the operation of the recovery furnace bed became unstable, possibly because of sulfate formation with resultant pH reduction and subsequent lignin precipitation from the black liquor.

3. Combination Systems

Two recent papers have been devoted to describing use of weak and strong black liquor oxidation in series to counteract problems associated with "reversion" to sodium sulfide of oxidized weak black liquor during multiple effect evaporation. Tobias and Robertson (94) developed an agitated plug flow reactor for oxidation of strong black liquor at a mill which also had a porous plate diffuser type weak black liquor oxidation system. The system proved effective for oxidation of sodium sulfide with polishing operations to counteract reversion. It was probably not suitable for treating unoxidized strong black liquor because of the two phase gas-liquid flow problems associated with excessive air-to-liquid flow ratios.

Martin (95) also developed a system for polishing of strong black liquor following multiple effect evaporation after high degree weak black liquor oxidation in an existing Collins porous plate diffuser system. The system employed injecting air into the bottom of an existing storage tank through a series of eight pipes connected to a central header. Results indicated that the sodium sulfide concentration of the strong black liquor could be maintained at below 0.01 grams per liter with the system when the inlet concentration was below 1.5 grams per liter.

D. Molecular Oxygen

The severe foaming problems associated with oxidation of weak black liquor with atmospheric oxygen (air) at Kraft mills in the Southeastern United States pulping pine wood species led to consideration of use of molecular oxygen as an alternative source of oxygen. The foaming problems of air oxidation could be alleviated with molecular oxygen because the inert nitrogen diluent medium was no longer present. The major drawback to use of oxygen for black liquor oxidation to date has been its excessive cost, but recent trends have been towards lower oxygen prices, thus making it a more competitive alternative. Additional trends were the possible future uses of oxygen for pulp bleaching, chemical pulping, waste water treatment, and addition to recovery furnace firing zones for odor control. The above applications may result in reduced oxygen prices because of the economies of scale associated with greater oxygen consumption at a given mill site.

1. Laboratory Studies

a. Bergstrom and Trobeck

Several laboratory investigations were made of the potential use of molecular oxygen for black liquor oxidation. Bergstrom and Trobeck (49) reported in 1939 on a study of black liquor oxidation with oxygen. They used an enclosed batch absorption system for measuring the rate of oxygen uptake into weak black liquor, and found that the absorption of oxygen into black liquor took place in three well-defined reaction rate regimes, as shown in Figure 9.

The oxidation of sodium sulfide took place in the initial phase and there appeared to be no net oxidation of organic materials present as long as sulfide ion was present in the black liquor. The oxidation of sodium

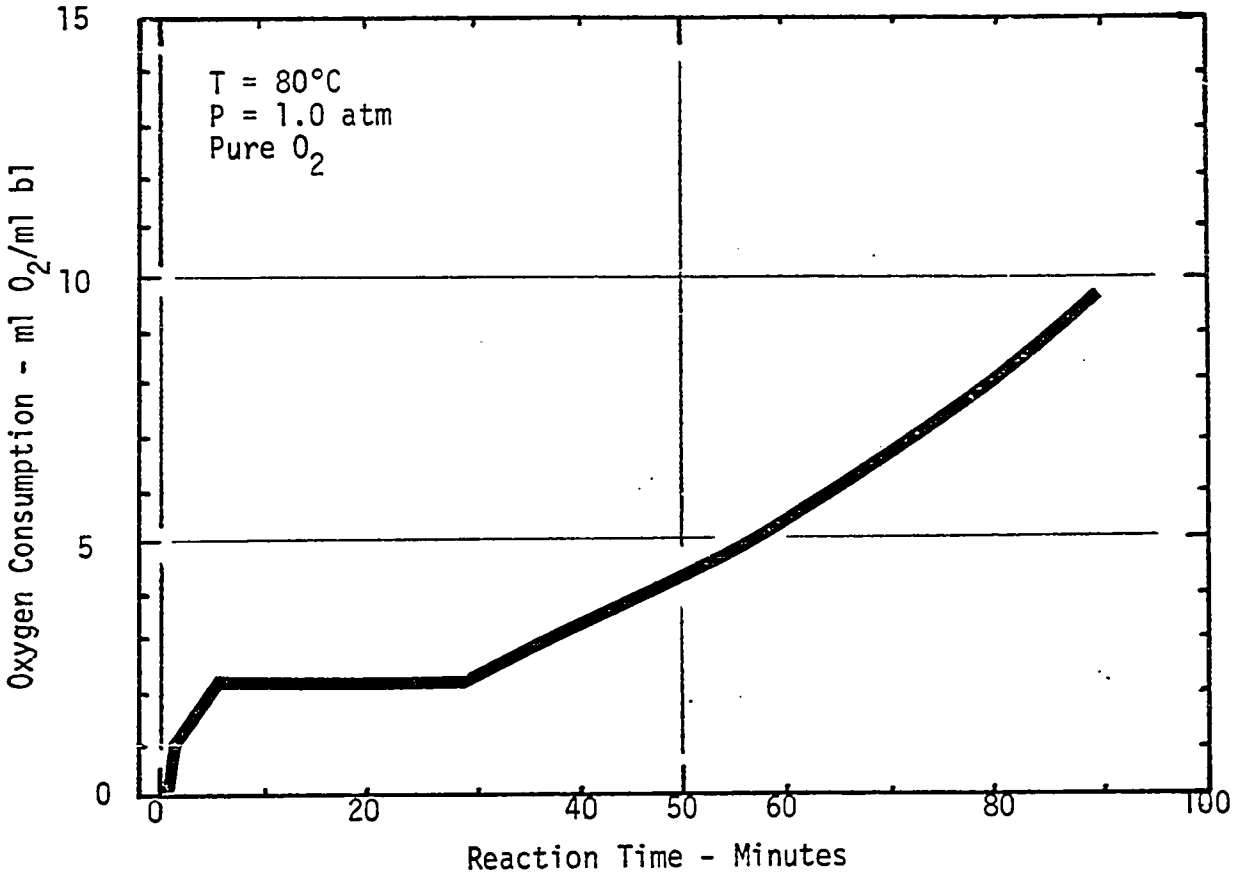


FIGURE 9. OXYGEN ABSORPTION INTO WEAK BLACK LIQUOR IN A BATCH REACTOR (49)

sulfide was found to take place in two different stages within the first five minutes of absorption, indicating that the reaction sequence of sodium sulfide oxidation proceeded in two separate steps with differing rate-limiting processes. The second region from five to thirty minutes displayed virtually no oxygen uptake, and was characterized by the absence of sodium sulfide. The third regime after thirty minutes was characterized by a relatively slow rate of oxygen uptake and a loss of liquor heating value, which was believed to be caused by oxidation of organic constituents in the black liquor. The study indicated that the oxidation of sodium sulfide was relatively rapid in weak black liquor, and was sufficiently selective so that competing side reactions did not cause the consumption of excessive quantities of oxygen.

b. Venemark Study

Venemark (96) reported on the results of a laboratory study of weak black liquor oxidation with pure oxygen in a batch reactor in 1956. He found that the rate of sodium sulfide oxidation during the initial reaction period was independent of the sodium sulfide concentration, and was primarily dependent on the rate of oxygen mass transfer. The rate of sodium sulfide oxidation was catalyzed by the presence of organic materials in the black liquor where the primary reaction product of sodium sulfide oxidation was sodium thiosulfate. When samples of weak black liquor were oxidized with pure oxygen to varying degrees of sodium sulfide oxidation efficiency, complete oxidation of the sodium sulfide required substantially more oxygen than for the stoichiometric conversion to sodium thiosulfate, as shown in Table 6.

TABLE 6. EFFECT OF SODIUM SULFIDE OXIDATION EFFICIENCY ON TOTAL OXYGEN CONSUMPTION (96).

Sodium Sulfide Data		Oxygen Addition[2]
Concentration grams/liter	Efficiency %	Actual/Stoich. %
10	0	0
2	80	130
1	30	160
0	100	200
0[3]	100 (Total)	350

Notes: 1. Based on amount of sodium sulfide oxidized.

2. Stoichiometric oxygen requirement based on reaction:
$2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$

3. Point where no more oxygen could be absorbed into the liquor.

TABLE 7. EFFECT OF BLACK LIQUOR OXIDATION WITH PURE OXYGEN ON LIQUID CHEMICAL COMPOSITION (96).

Na_2S gm/liter	$Na_2S_2O_3$[1] gm/liter	Na_2SO_4 gm/liter	Na_2CO_3 gm/liter	NaOH gm/liter	pH
11.4	0.1	9.3	14.2	0.32	11.90
3.4	0.0	10.0	14.3	-	-
1.3	0.6	10.1	15.1	0.21	11.72
0.07	3.1	10.3	15.8	0.10	11.40
0.00	1.5	11.3	16.0	0.02	10.80

Notes: 1. Increase above initial sodium thiosulfate concentration.

2. Reaction conditions:

T = 91°C (196°F)
S = 19.6% Solids

The above findings pointed to the occurrence of oxygen-consuming reactions in the black liquor other than the oxidation of sodium sulfide to sodium thiosulfate. Oxidation of weak black liquor for extended periods resulted in increased sodium sulfate concentrations, decreased sodium thiosulfate levels, and reduced black liquor pH, as shown in Table 7. A possible reason for these phenomena was the reaction of sodium thiosulfate with oxygen to form sodium sulfate, with a net consumption of sodium hydroxide and a resultant drop in liquid pH. Further studies also indicated that the amount of sodium sulfate formed increased slightly with temperature. An additional possible cause of the lowered pH was the oxidation of phenolic lignin and other organic constituents present in the black liquor, ultimately to carbon dioxide and water; a slight increase in sodium carbonate concentration was noted as the degree of oxidation increased. The significance of the above findings was that competing side reactions could cause consumption of additional quantities of oxygen. The drop in liquid pH could cause lignin precipitation with resultant plugging of evaporator surfaces.

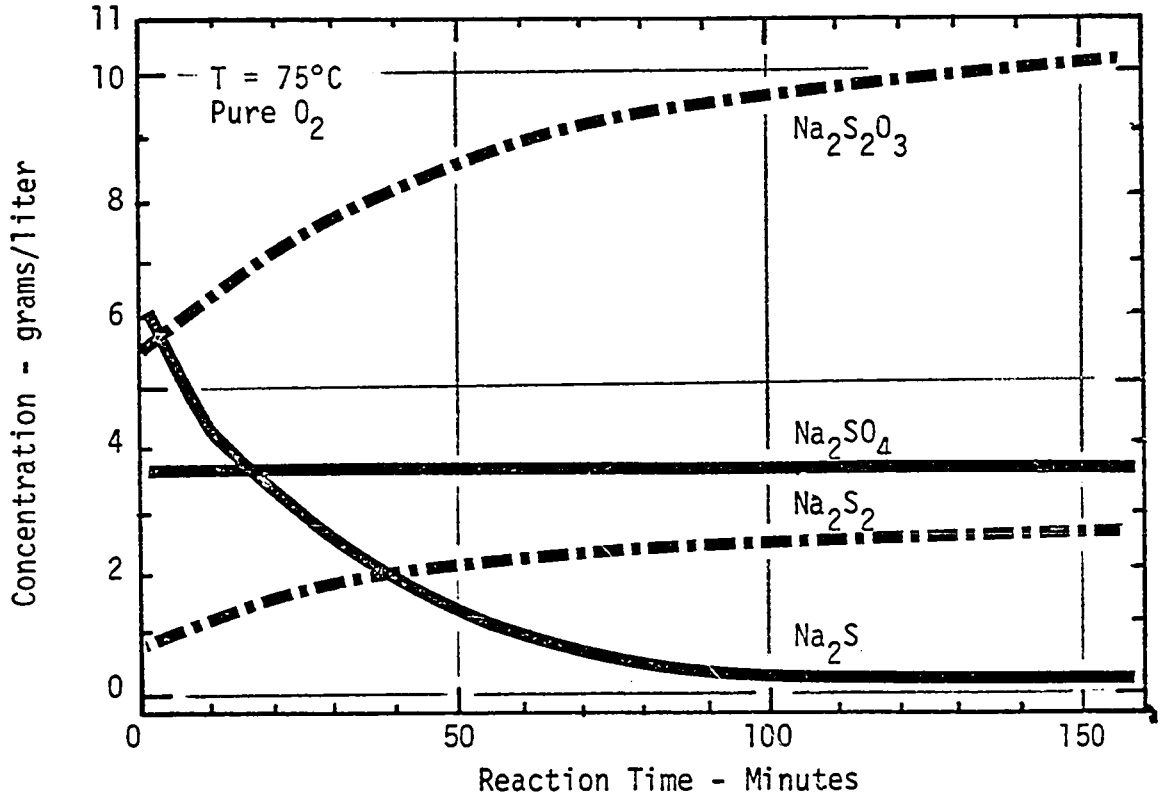
c. Ricca Study

Ricca (97) reported in 1962 on the results of an additional laboratory study of factors affecting weak black liquor oxidation with molecular oxidation. An enclosed, completely mixed batch reactor with a continuous oxygen feed was used to perform the oxidation studies. He found that the oxidation of sodium sulfide to sodium thiosulfate proceeded rapidly, but that it was more difficult to oxidize the organic sulfur compounds with oxygen in black liquor. The results indicated the emissions of hydrogen sulfide could be reduced during multiple effect and direct contact evaporation, but not the organic sulfur compounds. No major increases in sodium sulfate concentration were observed during the study indicating that the oxygen-consuming side

reaction of thiosulfate to sulfate was not a major problem, at least in the batch reactor. Ricca also observed that sodium polysulfide concentration increased during the reaction period, that oxidation temperatures below 60°C (140°F) favored the formation of elemental sulfur, and that storage of oxidized black liquor resulted in the "reversion," or re-formation of sodium sulfide. The effect of reaction time on the chemical composition of weak liquor during one oxidation study has been illustrated in Figure 10.

Riccan made several conclusions regarding the kinetics of the black liquor oxidation reactions. The oxidation of sodium sulfide proceeded in two distinct steps where the oxygen was initially absorbed into the black liquor, and then reacted with the sodium sulfide present. The oxidation of sodium sulfide appeared to be catalyzed by the presence of organic constituents in the black liquor, when compared to an alkaline solution of sodium sulfide without the presence of dissolved organic materials, as shown in Figure 10. The rate of the sodium sulfide oxidation increased with liquid temperature up to 75°C (167°F), with the optimum range between 60°C and 75°C. The amount of oxygen consumed per unit amount of sodium sulfide oxidized increased substantially when the liquid temperature increased beyond 60°C, probably because of the occurrence of competing side reactions such as oxidation of organic materials present. Use of ozone as the source of oxygen in addition to molecular oxygen did not appear to increase either the rate or degree of sodium sulfide oxidation in weak black liquor. Ricca proposed the use of a two stage reaction system for carrying out the black liquor oxidation with molecular oxygen employing a pipeline reactor and liquid storage tank in series.

a. Change in Chemical Composition (97)



b. Effect of Organic Catalysis (97)

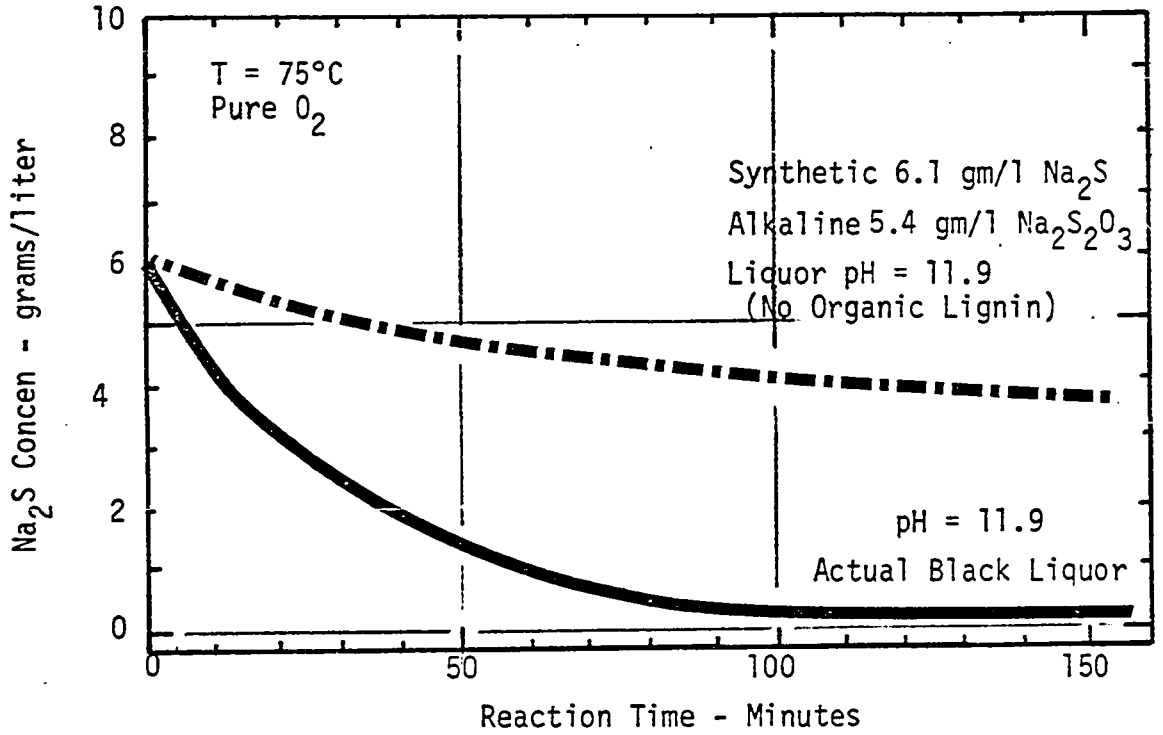


FIGURE 10. CHEMICAL COMPOSITION CHANGE DURING BATCH WEAK BLACK LIQUOR OXIDATION WITH OXYGEN

d. Sakhuja and Basu

Sakhuja and Basu (98) reported on the results of a recent study of black liquor oxidation in India, where black liquor from the pulping of bamboo was oxidized with air and molecular oxygen in a batch reactor. Results indicated that the rate of the sodium sulfide oxidation reaction was substantially increased by the addition of organic phenolic catalysts such as hydroquinone. The major portion of the sodium sulfide oxidized was converted to sodium thiosulfate (82 percent), and a small additional portion was converted to sodium sulfate (4 percent). However, 14 percent of the sulfur could not be accounted for by either of these ions, indicating that other constituents such as polysulfide, polythionate, and sulfite ions, and elemental sulfur may have been formed.

2. Digester Addition

One possible point of introducing oxygen to the Kraft recovery system was at the digester to oxidize the sodium sulfide and mercaptide at the end of a cook to prevent their release. The technique had the advantages of performing the oxidation in an enclosed re-ctor to assure complete utilization of the oxygen added, and performing the operation at high temperatures to assure maximum reaction rates and minimal possibilities for reversion to sodium sulfide. Problems that might be encountered were possible digester corrosion, excessive oxygen consumption because of competing side reactions such as sulfate formation and lignin oxidation, and potential degradation in pulp quality. Two recent studies have involved addition of molecular oxygen to Kraft mill digesters at the ends of cooks to oxidize the sodium sulfide and mercaptide persent in the black liquor.

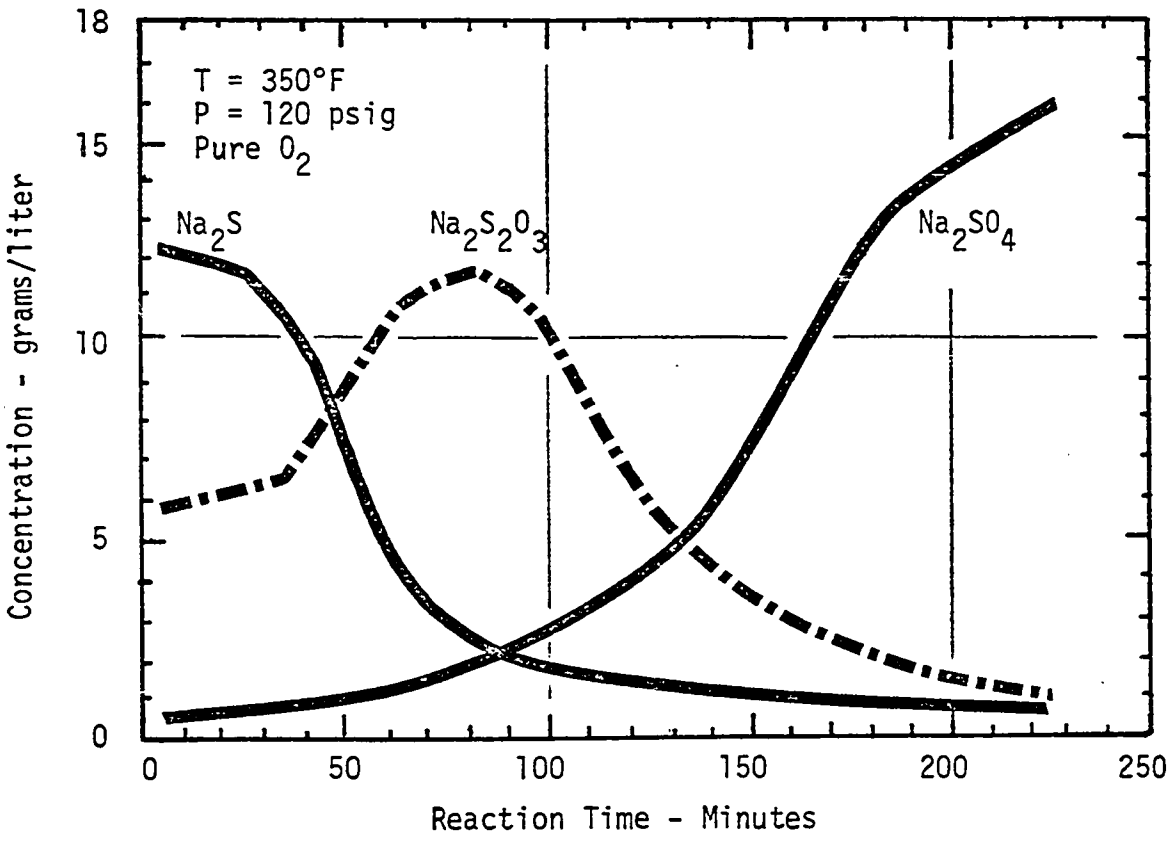
a. Fones and Sapp

Fones and Sapp (99) reported on the use of oxygen addition to a Kraft digester for oxidation of black liquor in 1960. Oxygen was added at the ends of successive cooks to a pressure vessel containing pulp alone, black liquor alone, and a mixture of pulp and black liquor. For the test cook with pulp alone, the lignin content of the pulp was reduced by oxidation and its brightness increased.

When oxygen was injected into a digester containing both pulp and black liquor at the end of the cook, the sodium sulfide was rapidly and completely oxidized. The high reaction temperatures and pressures resulted in the formation of substantial quantities of sodium sulfate, with a resultant drop in liquid pH and a dramatic increase in the amount of oxygen consumed. In addition, the oxidation process also reduced the bursting strength and brightness of the pulp, and an increase was noted in its lignin content. Oxidation of the black liquor with oxygen at the end of the cook proved to be uneconomical because of the excessive oxygen requirements, and the detrimental effects upon pulp quality.

Tests were also made to determine the effect of oxygen addition to a pressurized vessel containing only black liquor on the oxidation of sodium sulfide. Oxygen was added to black liquor alone in a digester at 100 psig and 150°C in a series of stages to recirculated black liquor. The oxygen then reacted with the sodium sulfide and other constituents present until the pressure returned to its initial value. The process was continued for nearly four hours, with the resultant changes in chemical composition and liquid pH as shown in Figure 11. Results indicated that the initial reaction product was sodium thiosulfate, but substantial quantities of sodium sulfate were found after oxidation for an extended period, with a resultant drop in

a. Effect on Chemical Composition (99)



b. Effect on Liquid pH (99)

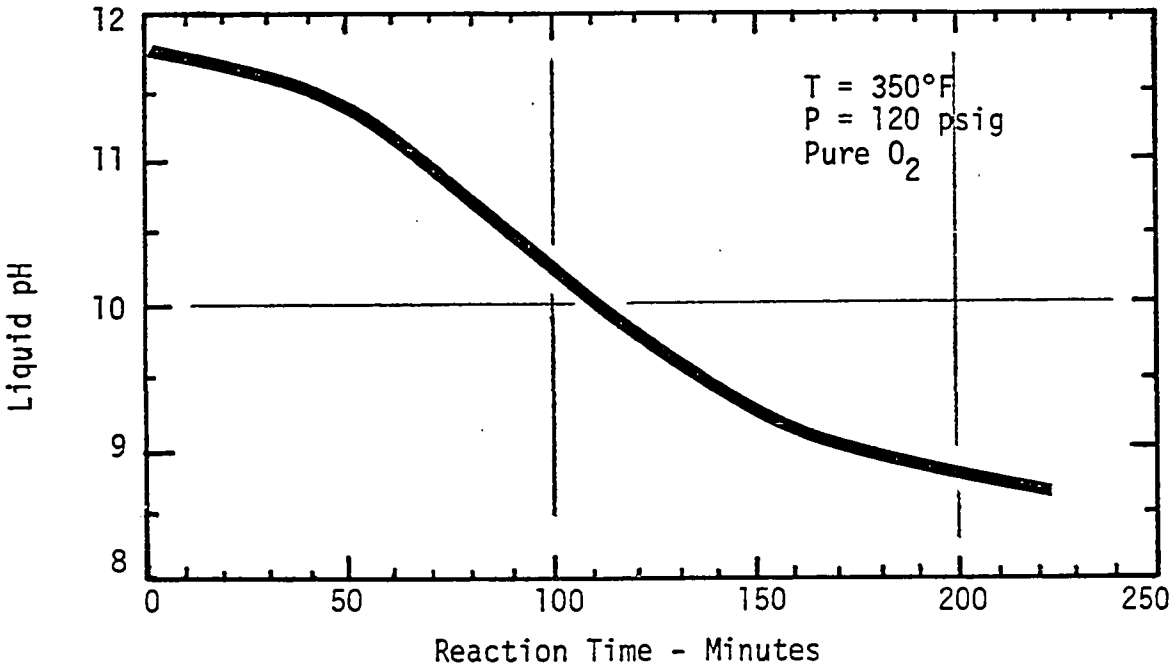


FIGURE 11. BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN IN A KRAFT DIGESTER (99)

liquid pH. Oxidation of dissolved lignin also may have lowered the liquid pH. A material balance indicated that not all the sodium sulfide could be accounted for by sodium sulfide, thiosulfate, and sulfate at intermediate stages of the oxidation process, indicating the formation of other sulfur constituents. With an oxygen consumption of approximately double that required for stoichiometric conversion of sodium sulfide to sodium thiosulfate, the process proved to be prohibitively expensive at an oxygen cost of 20 dollars per ton.

b. Kringstad and McKean

Kringstad and McKean (100) recently made a study of oxidizing sodium sulfide and mercaptide in black liquor at the end of a Kraft cook in the presence of pulp. Their results indicated that the sodium sulfide concentration in black liquor could be reduced by 90 percent, and sodium mercaptide by 99 percent by oxygen addition to a Kraft digester at the end of a cook, but that twice the stoichiometric amount of oxygen was required. An additional finding was that no sodium polysulfide or sodium sulfite could be detected in the black liquor during the oxidation period, indicating that it might be possible to reduce or eliminate potential problems associated with "reversion" to sodium sulfide. No measurements for sodium sulfate were made during the tests.

The process did not affect the pulp strength or yield, but did make the pulp easier to beat and also reduced its brightness. Oxygen addition to a digester at the end of a Kraft cook provided an effective means for oxidation of sodium sulfide and mercaptide, and could minimize potential problems associated with reversion. Of particular importance was that the relatively long retention time of about 20 minutes at a high temperature of approximately 350°F could result in the possible oxidation of substantial amounts

of sodium thiosulfate to sodium sulfate, and the oxidation of lignin. The nonselective oxidation process could then require consumption of successive quantities of oxygen in providing for effective oxidation of the sodium sulfide and sodium mercaptide, thus making the process economically unattractive. Results regarding potential degradation of pulp quality remained inconclusive, and no studies were made of potential digester corrosion resulting from introducing oxygen into a high temperature-high pressure digester.

3. Weak Liquor Oxidation

A second possibility for stabilization of the sodium sulfide and mercaptide with oxygen was oxidation of the weak black liquor. The technique would alleviate potential adverse effects on pulp quality or digester corrosion, and the lower operating temperatures might result in less oxygen consumption per unit amount of sodium sulfide oxidized. The liquid would probably not be of sufficient solids concentration to cause potential mass transfer problems. However, it might not be able to avoid the problems normally associated with the reversion to sodium sulfide of oxidized weak black liquor. Four studies have been made of weak black liquor oxidation with pure oxygen.

a. Kosaya Study

Kosaya (101) described the first reported use of molecular oxygen for weak black liquor oxidation at the Kehra pulp mill in the Soviet Union in 1956. The system was originally installed to reduce the hydrogen sulfide emissions from multiple effect evaporation to improve the water quality. The major objective was to reduce the associated odor level of evaporator condensate water at a Kraft pulp mill which did not employ direct contact evaporation of the black liquor with recovery furnace flue gas. The system

employed injection of oxygen into the black liquor upstream of the multiple effect evaporators through a "dosing apparatus." Results indicated that it was possible to achieve "essentially complete" oxidation of the sodium sulfide present in the black liquor from an inlet concentration of 7.5 grams per liter within "several minutes of retention time" in the pipe at a temperature of 70°C (158°F). No problems with foaming were observed, and essentially complete absorption of the oxygen added was obtained.

Results of the study indicated the oxygen consumption was approximately twelve percent greater than the amount required for stoichiometric conversion of sodium sulfide to sodium thiosulfate, as shown in Table 8. These findings

TABLE 8. OXYGEN REQUIREMENTS FOR WEAK BLACK LIQUOR OXIDATION (101).

Unit	Theoretical	Actual
$M^3O_2/MTNa_2S$[1]	315	370
$cfO_2/lb\ Na_2S$[2]	5.4	6.1
$lb\ O_2/TP$	48	58
cfO_2/gal b.l.[3]	0.28	0.33

Notes:
1. Cubic meters of oxygen (0°C, 1.0 atm) per metric ton (2,240 pounds) of Na_2S.
2. Cubic feet of oxygen (70°F, 1.0 atm) per pound of Na_2S.
3. Based on black liquor flow of 8 cubic meters per metric ton of pulp or 2,360 gallons per ton of pulp.
4. Black liquor conditions: 15% solids; 7.54 grams Na_2S/liter.

pointed to a slight increase in oxygen above the stoichiometric requirement, but that oxidation of weak black liquor with molecular oxygen was potentially attractive from an economic standpoint.

b. Freedman Study

Freedman (84) reported on the oxidation of weak black liquor with molecular oxygen in 1970, where an Ashbrook rotating cyclonic fluid contactor was used to provide contact between the oxygen and black liquor. The system employed tangential introduction of black liquor into a small diameter pipe and redirecting its flow in an axial direction to provide a centrifugal cyclonic liquid flow pattern. Oxygen was then introduced tangentially into the liquid at the point of concentric expansion into a larger diameter pipe. The vortex formed by the mixing of the fluids caused in large shearing forces which tended to cause the incoming air stream to form small bubbles, resulting in a large gas-liquid interfacial contact area. The system has been illustrated in Plate II.

Pilot studies were made using the contactor for oxidation of weak black liquors with oxygen. Results indicated that effective oxidation of sodium sulfide with oxygen could be attained with weak black liquors from both Northern hardwood and Southern pine wood species. Excessive foaming did not occur in either case because of the absence of the nitrogen diluent medium from the incoming gas stream. Essentially complete oxidation of sodium sulfide could be obtained within 15 to 60 seconds for hardwood black liquors, and approximately 60 seconds for Southern pine black liquors, indicating differences in oxidation rates with changes in wood species. Oxygen utilization efficiencies of 85 to 90 percent were obtained in both cases, making the technique favorable from an economic standpoint. The exothermic oxidation reactions also resulted in a warming of the black liquor by up to 10°C (18°F), which would decrease evaporator stream requirements.

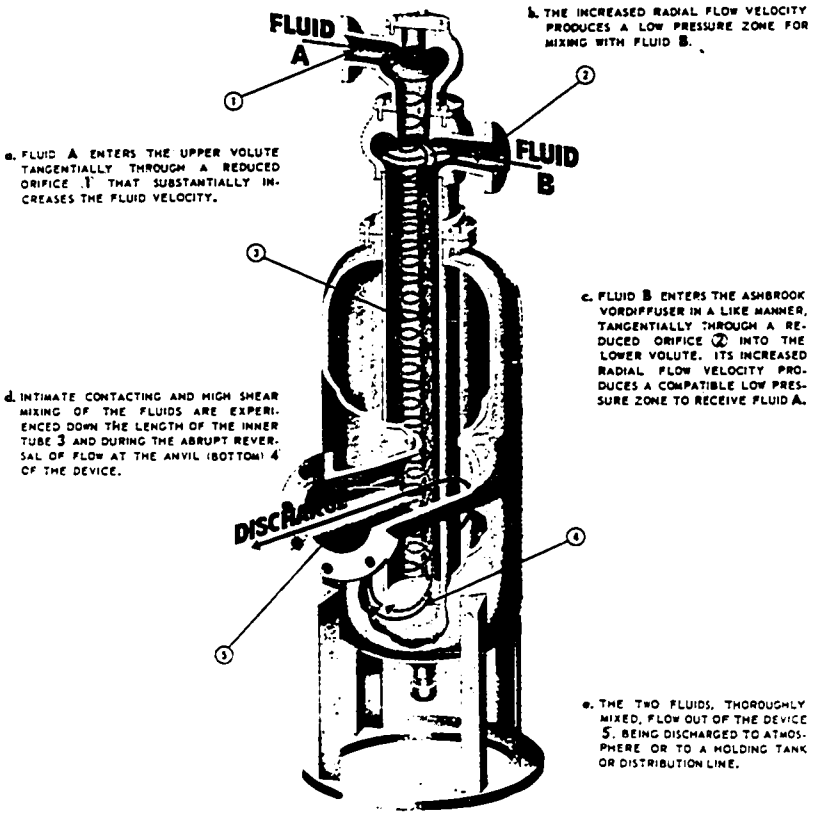


PLATE II. ROTATING FLUID CONTACTOR FOR BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN (84).

c. Miller Study

Miller (102) made an extensive study of weak black liquor oxidation with molecular oxygen, the results of which have never been formally published. The system employed a turbine mixer and sparge ring for introduction of oxygen into the black liquor in a small completely mixed tank. The black liquor then flowed at a rate of one to four gallons per minute into a 200 foot long circulating pipe loop of one inch diameter, where samples were taker periodically to measure the progress of the oxidation reactions. Results indicated that it was possible to obtain approximately 90 percent oxidation of sodium sulfide within seven to ten seconds retention time following introduction of the liquid in the pipeline reactor without excessive foaming when using the Southern pine weak black liquor. Essentially completely oxidation of the sodium sulfide could be obtained in ten to fifteen minutes, but no reaction rate constants were obtained. The major reaction product was sodium thiosulfate, but increases in sodium sulfate concentration were also observed.

d. Galeano and Amsden

Galeano and Amsden (103) reported on an extensive study of using molecular oxygen for weak black liquor oxidation at the Owens-Illinois, Inc. Kraft pulp mill in Orange, Texas, which pulped primarily Southern pine wood species. The system employed introduction of molecular oxygen into a flowing stream of black liquor in a two-step pipeline reactor with a retention time of fifteen to forty seconds, followed by a storage tank with a retention time of eight to twelve hours.

The system employed introduction of oxygen gas into a 24 inch diameter horizontal inlet pipe at a pressure of 50 pounds per square inch at a flow rate of 500 to 800 cubic feet per minute through an injector of undisclosed

configuration. The black liquor entered the inlet pipe at a flow rate of 1,000 to 1,700 gallons per minute at a sodium sulfide concentration of nine to twelve grams per liter, a solids content of 12 to 15 percent, and a temperature of 200 to 230°F. After contacting the oxygen, the black liquor then flowed through a 100 foot section of 10 inch diameter pipe, where the oxygen was absorbed and the sodium sulfide oxidized. The initial contact section provided for a liquid Reynolds numbers of 100,000 to 200,000 in highly turbulent flow. The system has been illustrated in Figure 12.

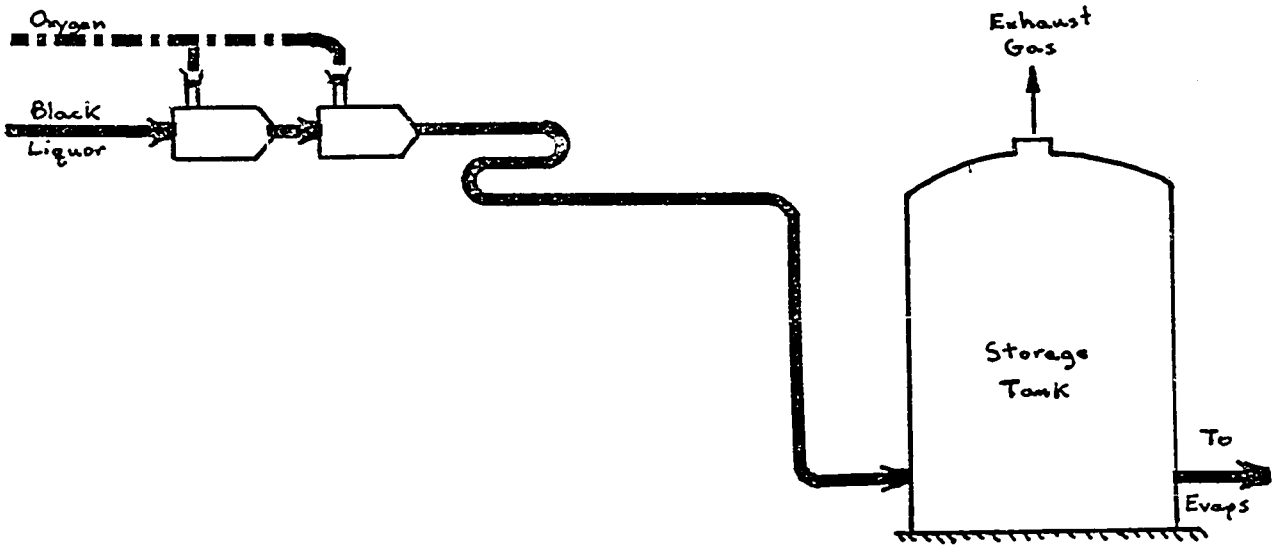
Results of their study indicated that a sodium sulfide oxidation efficiency of 85 to 98 percent (94 average) was observed without excessive foaming with an oxygen utilization efficiency of 75 to 95 percent (91 average). Approximately 90 percent (of the 94 total) of the sodium sulfide oxidation occurred within the pipeline reactor section, and there was a subsequent conversion of approximately 15 percent of the sodium thiosulfate formed to sodium sulfate, as listed in Table 9. It was not possible

TABLE 9. EFFECT OF WEAK BLACK LIQUOR OXIDATION ON LIQUID CHEMICAL COMPOSITION (103).

Location	Na_2S gms/liter	$Na_2S_2O_3$ gms/liter	Na_2SO_4 gms/liter	Total gms/liter	Account %
Reactor Inlet	4.56	0.80	0.53	5.89	100.6
Reactor Outlet	0.45	4.35	0.70	5.50	93.7
Storage Outlet	0.19	4.61	0.63	5.43	92.8

to account for all of the sulfur from the above chemical analyses alone, indicating either the formation of other products such as polysulfide, sulfite, or polythionate ions, or loss by gasification. The initial sodium sulfide oxidation reaction was found to be extremely rapid. Additional

a. Weak Black Liquor (103)



b. Strong Black Liquor (104)

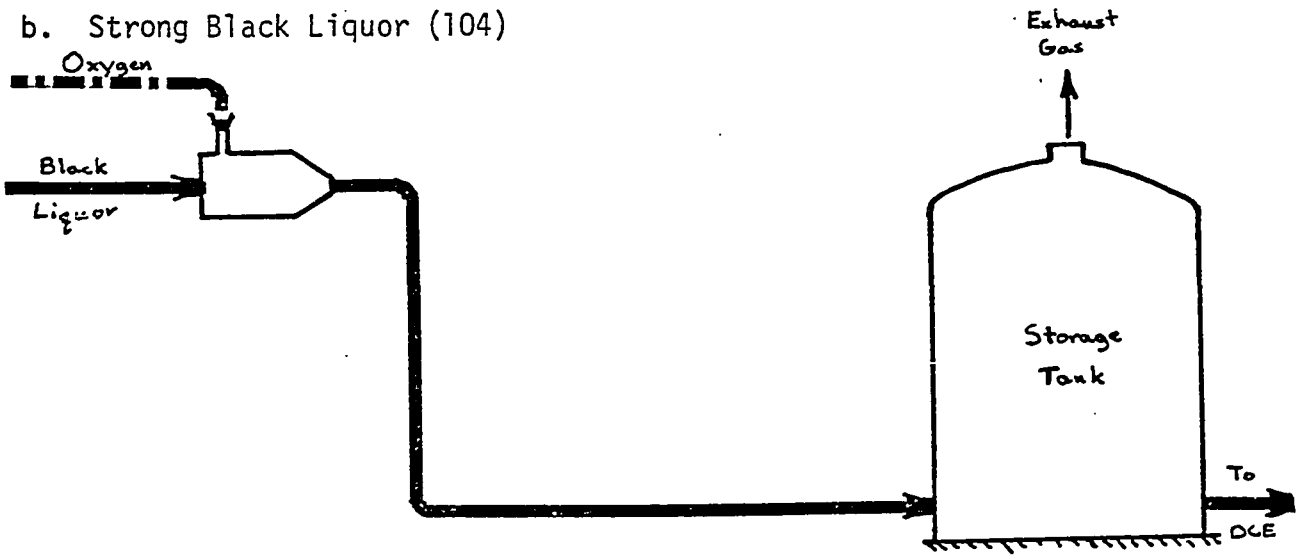


FIGURE 12. BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN AT OWENS-ILLINOIS, ORANGE, TEXAS, MILL.

changes in black liquor noted during the oxidation process were a rise of 0.1 to 3.0 pH units because of thiosulfate formation, and a temperature rise of 10 to 15°F because of heat liberated by the exothermic oxidation reactions.

Galeano and Amsden observed several benefits of weak black liquor oxidation with molecular oxygen as compared to the absence of oxidation. These observed benefits were as follows: 1) hydrogen sulfide emissions during direct contact evaporation were reduced by 95 percent and 99 percent during multiple effect evaporation; 2) sodium sulfate makeup requirements were reduced by 60 pounds per ton of pulp; 3) evaporator condensate water quality was improved; 4) tall oil yield was increased by approximately 15 percent. The effect of the weak black liquor oxidation process on sulfur gas emissions from various process sources has been listed in Table 10.

TABLE 10. EFFECT OF WEAK BLACK LIQUOR OXIDATION ON SULFUR GAS EMISSIONS FROM KRAFT MILL PROCESS SOURCES (103).

Source	Constituent	Concentration-ppm by vol		Reduction
		Unoxidized	Oxidized	%
Cyclone Evap. Exit	H_2S	191	10	95
	RSH	161	5	97
	RSR + RSSR	20	0	100
	SO_2	243	241	1
Storage Tank Vent	H_2S	553	3	99
	RSH	760	375	50
	RSR	1224	280	78
Evaporator NCG Vent[2]	H_2S	1208	4	99
	RSH	>>500	300	>50
Evaporator Condensate[3]	Sulfide	72	28	60
	BOD	863	530	38

Notes: 1. Weak liquor storage tank vent.
2. Evaporator noncondensable gases.
3. Evaporator condensate liquid (mg/liter).

The mill was located adjacent to an oxygen pipeline where the low oxygen cost of $8.50 per ton resulted in a maximum net mill operating cost of $0.05

to $0.08 per ton of pulp. Projected capital costs for similar installations were $50 to $75 per ton per day pulping capacity.

4. Strong Liquor Oxidation

Very little work to date has been devoted to to the use of molecular oxygen for strong black liquor oxidation. Galeano and Amsden also studied the use of strong black liquor oxidation with oxygen for polishing to counteract reversion to sodium sulfide from the previously oxidized weak black liquor. The system employed introduction of the oxygen into the strong black liquor in an expanded pipe section similar to that used for liquid system. The black liquor then flowed downward to take advantage of the gas bubble "holdup" phenomena associated with increased retention time in downward vertical two-phase flow and through a horizontal pipe section to a strong black liquor storage tank. The liquid Reynolds number in the pipeline reactor ranged from 10,000 to 20,000 in the liquid at 53 percent solids and 240°F temperature, with liquid retention times of 30 to 50 seconds. Initial studies indicated potential problems with black liquor cooling, lignin oxidation, and incomplete oxygen mass transfer into the black liquor, resulting in incomplete sodium sulfide oxidation. However, little reversion of the oxidized weak black liquor was observed, possibly because of the high inlet weak liquor temperatures of 200 to 230°F.

E. Refinery Spent Caustic

1. Comparison

The oxidation of sodium sulfide and mercaptide in spent caustic liquids used for sulfur removal from products in petroleum refineries was a problem similar to oxidation of sodium sulfide and mercaptide in Kraft black liquors. Both of these liquid streams were amenable to treatment by oxidation of the sulfur compounds present with either air or molecular oxygen. The presence

of phenolic materials in both types of liquids acted to catalyze the rate of the sodium sulfide oxidation. A comparison of the chemical properties of refinery spent caustic and Kraft black liquors has been presented in Table 11.

TABLE 11. COMPARISON OF TYPICAL CHEMICAL COMPOSITION RANGES FOR PETROLEUM REFINERY SPENT CAUSTIC LIQUIDS AND KRAFT PULP MILL BLACK LIQUORS.

Item	Units	Refinery (104) Spent Caustic	Black Liquors (105) Weak	Black Liquors (105) Strong
pH	-	13-14	11-13	11-13
Sulfide[1]	gm/liter	2-50	1-10	2-25
Mercaptide[1]	gm/liter	1-25	0-3	0-6
Phenol	gm/liter	2-50	50-75	150-250
Solids	% by wt.	10-25	12-20	45-55

Notes: 1. Computed as sulfur.
2. Assume lignin content of solids is 30 percent by weight (105).

2. Equipment

Smith (106) described the results of a series of tests where refinery spent caustic solutions were oxidized in three separate multiple tray cocurrent flow-type towers of sieve tray, bubble cap, and packed bed design, respectively. Optimum conditions for tower operation were found to be liquid temperatures of 250 to 265°F, pressures of 35 to 50 pounds per square inch, and air flow requirements of 1.5 to 2.0 times the amount of oxygen required for stoichiometric conversion of sodium sulfide to sodium thiosulfate. These were more severe oxidation conditions than normally required for weak or strong black liquor oxidation with air.

The differences in desired reaction products and objectives of the process may have explained the more extreme operating conditions for spent caustic oxidation as compared to black liquor oxidation. For the case of spent caustic liquids oxidation of sulfide to sulfate was desirable to minimize potential oxygen demand problems if the liquid was to be subsequently neutralized and discharged. Oxidation of phenols was desirable to reduce potential toxicity problems. With Kraft black liquor, selective oxidation of sulfide to thiosulfate without subsequent conversion to sulfate, and minimal phenolic lignin oxidation were desirable to minimize net oxygen consumption from the competing side reactions from an economic standpoint.

3. Results

Results indicated that the oxidation of sodium sulfide occurred without stripping of hydrogen sulfide in the high pH liquid but the substantial conversion to sodium sulfate occurred at liquid temperatures above 230°F (107). The overall rate of sodium sulfide oxidation was found to increase from 0.03 to 1.5 pounds of sodium sulfide per cubic foot per hour as the inlet sodium sulfide concentration increased (106)(108)(109). These values were similar to those reported by Morgan (92) for strong black liquor, where values increased from 0.2 to 1.0 pounds of sodium sulfide per cubic foot per hour as the inlet sodium sulfide concentration increased. A series of batch tests showed that the initial rate of sodium sulfide oxidation increased substantially as the liquid temperature increased from 150 to 265°F. The rate of reaction appeared to change from zero order to first order at sodium sulfide concentrations below one gram per liter.

F. Process Evaluation

Black liquor oxidation has been found to have potential benefits upon the Kraft chemical recovery system in terms of odor control, process

operation, chemical makeup, and byproduct recovery. Strong black liquor oxidation would reduce the sulfur losses only during direct contact evaporation of black liquor. Weak black liquor oxidation could reduce potential sulfur losses during both multiple effect and direct contact evaporation of black liquor, but that problems associated with "reversion" to sodium sulfide in oxidized weak black liquor would limit its effectiveness. High degree black liquor oxidation may make it feasible for existing Kraft pulp mills to meet present or proposed air pollution regulations without the necessity for undergoing the enormous expense involved with removal of direct contact evaporators with subsequent replacement by new indirect contact evaporation systems.

1. Odor Control

Black liquor oxidation has resulted in reduced sulfur gas emissions from several Kraft pulp mill sources, as follows: 1) reduced malodorous sulfur gas emissions from the recovery furnace following direct contact evaporation; 2) reduced malodorous sulfur gas emissions from evaporator noncondensable gases; 3) improved evaporator condensate water quality to minimize potential odor problems and facilitate water reuse; 4) reduced malodorous sulfur gas emissions during tall oil recovery; 5) improved ambient air quality adjacent to Kraft pulp mills.

a. Direct Contact Evaporation

The positive benefits of black liquor oxidation on direct contact evaporation have been previously reviewed by Hendrickson (1), Cooper and Rossano (2), Sarkanen (3), Blosser and Cooper (17), Murray and Rayner (18), plus Walther and Amberg (19), and have previously been summarized in Table 1. The direct contact evaporator acted to absorb sulfur dioxide and particulate matter from the recovery furnace flue gases, and under some circumstances hydrogen sulfide. Malodorous sulfur gas emissions from direct contact

evaporation were minimized by maintaining inlet black liquor pH's above 12.0 and sodium sulfide concentrations below 0.1 grams per liter (19).

b. Evaporator Noncondensable Gases

Weak black liquor oxidation was found to substantially reduce hydrogen sulfide and methyl mercaptan emissions from evaporator nondondensable gases, as reported by Douglass (110), Reid (111)(112), and Galeano (103). The emissions were found to be decreased by increasing black liquor pH and reducing inlet sodium sulfide concentration.

c. Tall Oil Vent Gases

The oxidation of weak black liquor would reduce the inlet sodium sulfide concentration to the tall oil recovery system. The amount of hydrogen sulfide liberated during acidulation of the tall oil would then be proportionately reduced. Little information was available to date regarding sulfur gas emissions from tall oil processing.

d. Evaporator Condensate Waters

The oxidation of weak black liquor also resulted in reductions of the amounts of malodorous sulfur gases liberated for subsequent absorption in the evaporator condensate waters. Two European mills employed weak black liquor oxidation primarily to control odor levels in evaporator condensate waters upon release to receiving waters, as reported by Kosaya (100) and Ghisoni (113). Shah and Stephenson (114), plus Galeano and Amsden (103) reported decreases in sulfide ion concentration in evaporator condensate waters upon installation of weak black liquor oxidation systems, along with increased liquid pH and reduced biochemical oxygen demand.

e. Ambient Air Quality

Hendrickson and Harding (72) observed that the installation of parallel strong black liquor oxidation systems substantially reduced the malodorous

sulfur gas concentrations in the ambient air in the area adjacent to the mill. The ambient odorous gas level as measured by "reducible sulfur" concentration (a general indicator of hydrogen sulfide levels) was found to be reduced by 50 to 75 percent upon the installation of black liquor oxidation facilities.

2. Process Operation

Black liquor oxidation has also influenced the operation of the Kraft chemical recovery system in addition to reducing malodorous sulfur gas emissions. Major influences noted have included the following: 1) improvement in multiple effect evaporation because of reduced scaling on heat transfer surfaces; 2) reduced corrosion rates of evaporator metal surfaces; 3) possible increases in tall oil yield; 4) reduced chemical makeup requirements for sodium sulfate and calcium oxide; 5) possible increases in green and white liquor sulfidities, with resultant effects on pulp yield and quality; 6) possible effects on black liquor heating value.

a. Evaporator Scaling

Berry (115) found that the hydrogen sulfide evolved from unoxidized weak black liquor caused the formation of an iron sulfide scale, which inhibited the rate of heat transfer in the multiple effect evaporators. The precipitation of lignin on the heat transfer surfaces could be minimized by maintaining a sufficiently high liquid pH, thus alleviating another potential source of evaporator scaling. However, any sodium sulfate formed during weak liquor oxidation became less soluble as liquid temperature increased, and could pose a potential scaling problem during the latter stages of evaporation at higher solids concentrations.

b. Evaporation Corrosion

Weak black liquor oxidation has been observed to substantially reduce the corrosion of multiple effect evaporator surfaces, particularly in the vapor shell sections. Von Essen (116) found that the corrosion of evaporator surfaces was primarily caused by the formation of iron sulfide from hydrogen sulfide in moist atmosphere on metal surfaces. The rate of corrosion was reduced by approximately 85 percent by reducing the inlet sodium sulfide concentration in black liquor to less than three grams per liter. Cyr and Harper (117) reported that the average life of multiple effect evaporator tubes was substantially increased by weak black liquor oxidation.

c. Tall Oil Yield

Weak black liquor oxidation provided a means for increasing tall oil yields for byproduct recovery by either physical or chemical mechanisms. However, foaming could be a serious problem with air oxidation of pine black liquors where large quantities of tall oil were obtained. Galeano and Amsden (103) reported that tall oil yield was increased by approximately fifteen percent during laboratory studies as the result of weak black liquor oxidation with molecular oxygen without apparent decrease in quality. Rippee (118) reported an approximate ten percent increase in tall oil yield at a Western U. S. Kraft pulp mill employing weak black liquor oxidation with air and practicing strong black liquor recycling for foam control. At a recent National Council symposium (93), black liquor oxidation was reported to result in increased tall oil yields, but at the expense of decreased quality, possibly because of oxidation of tall oil.

d. Chemical Recovery

Black liquor oxidation reduced the sulfur losses from Kraft process sources, which could result in decreased sodium sulfate and lime chemical

makeup requirements. Galeano and Amsden (103) reported that to maintain a given sulfidity level the sodium sulfate makeup rate could be reduced by 30 to 60 pounds per ton of pulp. Sodium hydroxide could then be used to provide a portion of the sodium makeup requirements. The lime makeup requirement could be reduced by two to three pounds per ton of pulp, and the total lime mud processing rate could be reduced by ten to fifteen pounds per ton of pulp produced. Specific chemical savings for maintaining particular sulfidity levels would vary between individual mills.

e. Liquor Sulfidity

Shah and Stephenson (114) observed that the installation of weak black liquor oxidation resulted in a two to five percent increase in white liquor sulfidity for given chemical makeup rates. Possible increases in pulp quality and yield could be observed during the digestion process. However, the chance for increased corrosion of the green and white liquor systems existed because of the resultant higher sodium sulfide levels. The increased sulfidity could also result in increased malodorous sulfur gas emissions from the Kraft recovery system because of the higher sulfur circulation rates.

f. Heat Recovery

The oxidation of Kraft black liquor was noted to increase the efficiency of heat transfer by reducing multiple effect evaporator scaling. Weak black liquor oxidation with air was found to increase the liquor solids concentration by one to two percent by weight because of the water evaporated, thus reducing steam and fuel purchase requirements. Freedman (84) observed that weak black liquor oxidation with pure oxygen resulted in a warming of the black liquor by 18°F, thus reducing the sensible heat requirements during multiple effect evaporation.

Several potential detrimental effects for black liquor oxidation were observed on recovery heat balances. Miller (102) observed a cooling of strong black liquor during oxidation with molecular oxygen during a series of pilot scale studies. Tomlinson and Douglas (56) noted that the endothermic heat requirements for reduction of sodium thiosulfate and sodium sulfate in the Kraft recovery furnace would result in slightly lower heat release and subsequent steam generation for use in digestion and evaporation sections. The decreased heat release could result in possible increased fuel costs. Roberson (119)(120) observed that weak black liquor oxidation with air reduced its heating value by about two percent, with resulting decreased heat release. Lindholm and Stockman (121) found that weak black liquor oxidation with molecular oxygen reduced the liquor heating value by 2.0 to 3.6 percent for sodium sulfide oxidation efficiencies of 90 and 100 percent, respectively. The loss in heating value was primarily caused by oxidation of organic matter, resulting in increased oxygen consumption and decreased heat availability.

3. Process Economics

Two recent surveys of capital and operating costs have been made for weak and strong black liquor oxidation systems employing air. Weak black liquor oxidation systems normally had higher capital costs than strong liquor systems for equivalent production because of the greater liquid volume at the lower solids concentration. Strong black liquor oxidation systems normally had higher operating costs than weak liquor systems of equivalent production because of the greater energy requirements to achieve effective oxygen mass transfer into the high viscous strong liquor.

These observations were essentially verified from calculations by Roberson (120)(121) of capital and operating costs for equivalent weak and

strong black liquor oxidation systems for a hypothetical mill situation using design criteria as follows: 1) inlet sodium sulfide concentration of 6.0 grams per liter in the weak black liquor or the equivalent strong liquor concentration; 2) a sodium sulfide oxidation efficiency of 99 percent across the system. Results of the calculations have been illustrated in Figure 13.

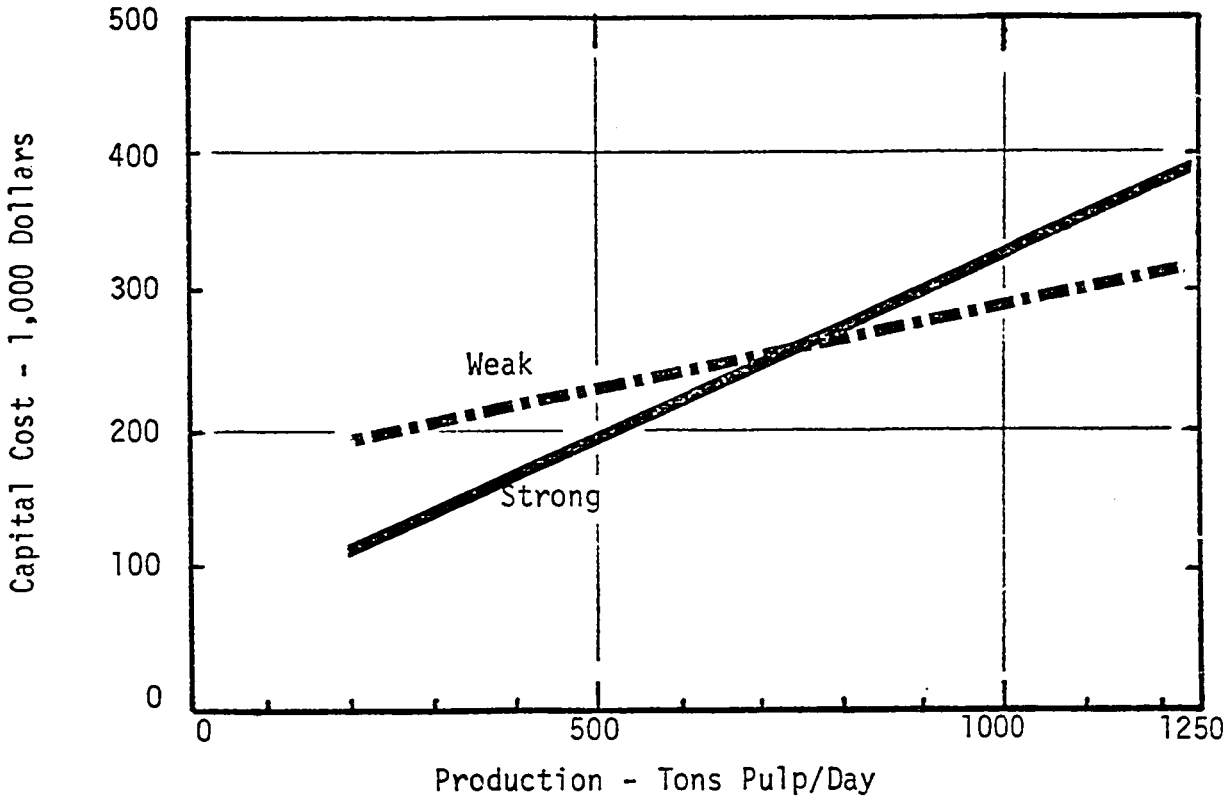
Blosser and Cooper (73) recently compiled a summary of capital and operating costs for existing weak and strong black liquor oxidation systems from data supplied by individual mills. Capital cost figures were adjusted to a base of December 1968 from reported values to correct for the effects of inflation, and have been listed in Table 12. Approximate annual operating costs for weak and strong black liquor oxidation systems employing both air and molecular oxygen, excluding any credits, have been listed in Table 13.

G. Limitations

Limitations of the previous work to date as follows. First, no detailed information was available regarding oxidation of strong black liquor with molecular oxygen, particularly in line with observed "reversion" of sodium sulfide during multiple effect evaporation (25). Second, conditions favorable to the formation of sodium sulfate and the oxidation of organic lignin were not investigated in terms of potential increased oxygen consumption. Third, the effects of liquid temperature and pH upon the respective oxidation rates of sodium sulfide and mercaptide were not investigated. Fourth, no investigations were made of the relative reaction rates for sodium mercaptide in black liquor, which may have a role in sodium sulfide "reversion" phenomena.

Of particular need for further investigation in terms of potential air pollution problems were conditions favorable to essentially complete oxidation of the sodium sulfide and sodium mercaptide in black liquor. Fifth,

a. Capital Costs (119)



b. Operating Costs (119)

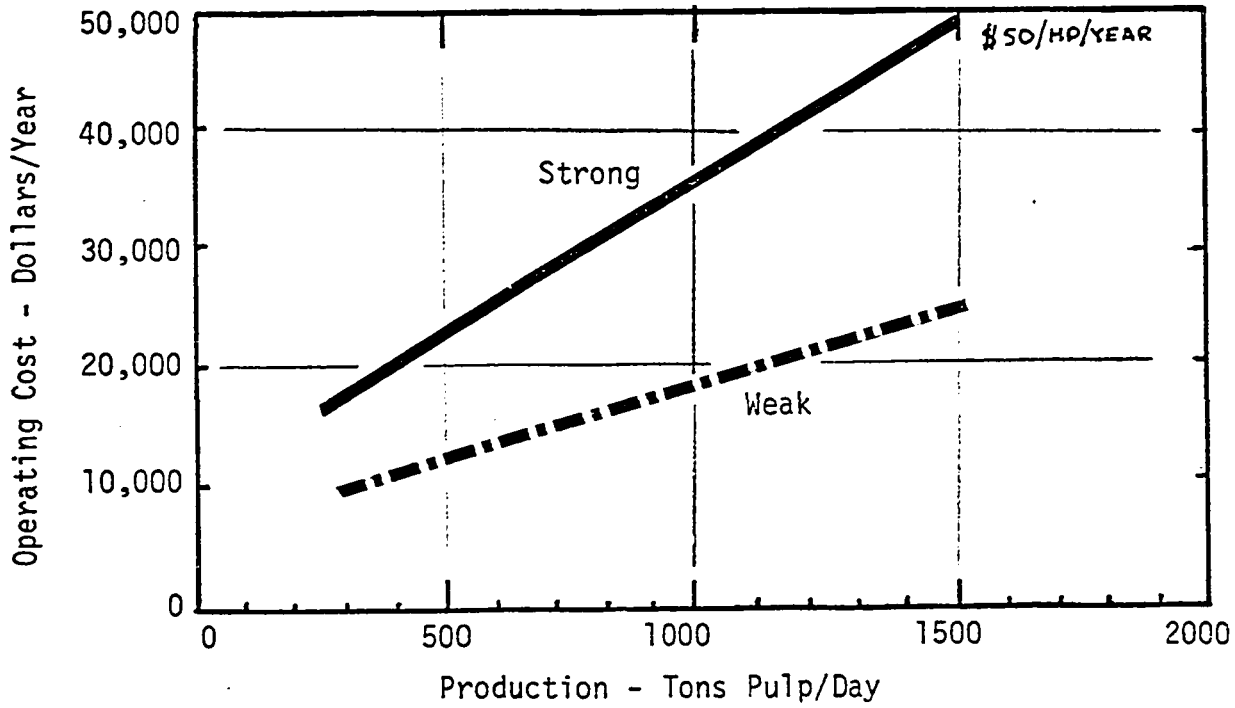


FIGURE 13. CAPITAL AND OPERATING COSTS FOR WEAK AND STRONG BLACK LIQUOR OXIDATION SYSTEMS WITH AIR

TABLE 12. ESTIMATED CAPITAL COSTS FOR BLACK LIQUOR OXIDATION SYSTEMS.

Unit Description		Installation Cost - $/Ton Pulp/Day		
Location	Type	Reported	Adjusted	Reference
Weak	Packed Tower	200-450	400-600	73
	Multiple Tray	350-800	400-800	73
	Agitated Sparger	300-330	300-350	73
	Molecular Oxygen[1]	50-75	10-100	102[2]
	Rotating Fluid	50-100	50-150	84
Strong	Unagitated Sparging	115-650	275-700	73
	Agitated Sparger	400-600	400-600	73[2]
	Plug Flow Reactor[2]	5-25	5-50	94
	Molecular Oxygen	50-75	10-100	102[2]

Notes: 1. Adjusted to base of December 1968.
2. Estimated by author.

TABLE 13. APPROXIMATE ANNUAL OPERATING COSTS FOR BLACK LIQUOR OXIDATION SYSTEMS.

Type	Operating Cost[3] $/TPD/Year	Reference
Weak-Air	5-40	73
Strong-Air	10-50	73
Oxygen	15-350	102[2]

Notes: 1. TPD = Tons of pulp per day capacity.
2. Also estimated by author.
3. Does not include any cost credits.

conditions favorable to reducing the sodium sulfide concentration in black liquor to very low concentrations have not been fully investigated. Sixth, the first-order reaction rate model proposed was only an approximation of the actual sodium sulfide oxidation rates in black liquor. The oxidation process was actually a two regime sequence which depended on sodium sulfide concentration. The initial reaction rate regime occurred at higher sodium sulfide concentrations where the reaction rate was zero-order (independent of Na_2S concentration) and dependent upon the rate of oxygen mass transfer. The second regime was a first-order reaction at low sodium sulfide concentrations where the rate of the chemical oxidation reaction was the rate-limiting step. It should be determined to enable rational design criteria for full-scale installations to be developed.

Determination of the variables affecting two phase gas-liquid flow where oxygen was introduced into black liquor had a substantial effect upon resultant oxygen utilization and liquid pressure drop. Seventh, it was necessary to determine conditions favorable to the bubble (froth) regime of flow to facilitate maximum oxygen absorption. Eighth, estimates of oxygen bubble sizes were necessary to compute mass transfer coefficients. Ninth, the degree of additional head loss resulting from the occurrence of two phase gas-liquid flow was necessary to estimate additional liquid pumping requirements.

IV. THEORETICAL PRINCIPLES

The oxidation of sodium sulfide, sodium mercaptide, and other constituents in Kraft black liquor with molecular oxygen involved a complex series of physical and chemical processes. The mass transfer of oxygen into black liquor required consideration of factors affecting oxygen gas absorption into the liquid phase. An additional factor affecting oxygen mass transfer into black liquor was the existence of two phase gas-liquid flow in the plug flow pipeline reactor. The chemistry of black liquor oxidation with molecular oxygen required knowledge of the types and concentrations of the respective reactants, plus the reaction pathways and end products. It was also necessary to consider the kinetics of the black liquor oxidation reactions for determination of the respective reaction rate constants to facilitate the design of full-scale plug flow reaction systems.

A. Mass Transfer

The mass transfer of oxygen into black liquor involved consideration of both gas absorption and two phase gas-liquid flow phenomena. The major objective of the mass transfer operation was to maximize the gas-liquid interfacial contact area by minimizing the mean oxygen bubble size. It was necessary to have a contacting device which provided for efficient dispersion of oxygen gas molecules into the liquid phase by promoting a high degree of turbulence for effective mixing. Subsequent oxidation of sodium sulfide and other constituents in black liquor could not occur without the initial step of oxygen transfer into the liquid phase.

1. Oxygen Absorption

Two basic theories explaining the interaction between gases and liquids during mass transfer operations were the film theory and the penetration theory. The film theory assumed a physical model where two imaginary films existed at the gas-liquid interface, one gas and one liquid, which provided resistance to mass transfer. The penetration theory assumed that eddies of liquid were transferred from the bulk liquid to the gas-liquid interface to absorb gas molecules. The rate of mass transfer was limited by film resistance in the former case, and by the rate of surface renewal in the latter case.

a. Film Theory

The film theory had a greater significance from a practical design viewpoint, and has been used to express the rate of oxygen mass transfer into liquids. Rich (122) presented an extensive discussion of the two film theory of gas transfer into liquids across imaginary boundaries between hypothetical gas and liquid films. For the case of oxygen, the rate of mass transfer by diffusion across the boundary at steady state conditions remained constant with time, with no net accumulation of material in either film. The rate of oxygen mass transfer across either film could be represented as the product of a constant of proportionality for the given system, a measure of the gas-liquid interfacial contact area, and a term representing concentration driving force as follows:

$$\frac{dO_2}{dt} = k_6 A \left[(p_{O_2})_g - (p_{O_2})_i\right] = k_L A \left[(c_{O_2})_i - (c_{O_2})_l\right] \qquad [1]$$

dO_2/dt = Rate of oxygen mass transfer across gas-liquid boundary in pound-moles per second

t = Time in seconds

A = Total interfacial contact area in square feet

k_G = Mass transfer coefficient across the gas film in pound-moles of oxygen per square foot per atmosphere per second

k_L = Mass transfer coefficient across the liquid film in feet per second

$(p_{O_2})_g$, $(p_{O_2})_i$ = Oxygen partial pressure in the bulk gas stream and gas-liquid interface, respectively, in atmospheres

$(c_{O_2})_j$, $(c_{O_2})_l$ = Dissolved oxygen concentration at the gas-liquid interface and bulk liquid phases, respectively, in pound moles per cubic foot.

The degree of solubility of a particular liquid increased with its partial pressure above the liquid, and decreased with increasing liquid temperature. The point of saturation occurred where the rate of gas molecules leaving the liquid was equal to the rate of gas molecules entering the liquid. Henry's law could be used to represent the quantity of gas dissolved in a liquid at any given temperature and pressure for any slightly soluble gas not undergoing subsequent chemical reaction, such as dissolved oxygen in water:

$$p_{O_2} = H_{O_2} x_{O_2} \qquad [2]$$

p_{O_2} = Partial pressure of oxygen above the liquid in atmospheres

x_{O_2} = Mole fraction of oxygen in the liquid phase in moles per mole

H_{O_2} = Henry's law constant for oxygen in atmospheres per mole fraction

The Henry's law constants, liquid densities, and individual film mass transfer coefficients could then be used to calculate the overall mass transfer coefficients as follows:

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{\rho_m}{H_o\, k_G} \qquad [3]$$

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H_{o_2}}{\rho_m k_L} \qquad [4]$$

K_L = Overall mass transfer coefficient on liquid basis in feet per second

K_G = Overall mass transfer coefficient on gas basis in pound-moles oxygen per square foot per atmosphere per second

ρ_m = Moles density of liquid phase in total pound-moles per cubic foot

For gases of low solubility such as oxygen in water, the major resistance to mass transfer was in the liquid film, and equation three could then be simplified to:

$$\frac{1}{K_L} \cong \frac{1}{k_L} \quad \text{and} \quad K_L \cong k_L \qquad [5]$$

For pure oxygen essentially all the resistance would be in the liquid film. The overall mass transfer coefficients could then be used to calculate rates of mass transfer based on measurable quantities; in contrast to individual film coefficients, which required knowledge of the interfacial boundary conditions.

The rate of oxygen mass transfer into a liquid when the liquid film resistance was the rate-limiting process could be represented by the following expression:

$$\frac{dO_2}{dt} = K_L A \left[(C_{O_2})_s - (C_{O_2})_l\right] \qquad [6]$$

$(C_{O_2})_s$ = Saturation dissolved oxygen concentration in the liquid corresponding to oxygen partial pressure $(p_{O_2})_g$ in pound-moles per cubic foot

$(C_{O_2})_l$ = Actual dissolved oxygen concentration in the bulk liquid phase in pound-moles per cubic foot

The above equation was useful for evaluating the overall mass transfer coefficient (K_L) when the exact interfacial contact area (A) was known, such as for wetted wall columns. The overall volumetric mass transfer coefficient ($K_L a$) could be used when the exact surface area was not readily applicable, but the system volume was, as follows:

$$a = \frac{A}{V} \qquad [7]$$

$$\frac{dO_2}{dt} = K_L a \, V \, [(C_{O_2})_s - (C_{O_2})_l] \qquad [8]$$

a = Interfacial contact area in square feet per cubic foot or 1/feet

V = Volume of system in cubic feet

When steady state conditions did not exist, the concentration of oxygen in the liquid phase changed with time, resulting in a decreased concentration driving force. An integral expression based on equation eight could then be set up, yielding the following expressions:

$$2.303 \log \frac{(C_{O_2})_s - (C_{O_2})_t}{(C_{O_2})_s - (C_{O_2})_o} = (K_L a)(t) \qquad [9]$$

The above equation was not directly applicable to black liquor oxidation with molecular oxygen because of difficulties in defining the saturation oxygen concentration, and the fact that oxygen would probably not exist in the free state in black liquor. The result was that the logarithmic term tended to zero, and it became impossible to determine the term ($K_L a$).

b. Penetration Theory

The penetration theory of surface film renewal attempted to account for the nonsteady state character of gas transfer across liquid surfaces. Danckwerts (123) observed that the rate of gas transfer into a liquid could

be expressed in terms of the rate of surface renewal, which increased with the level of liquid turbulence as follows:

$$\frac{dO}{dt} = [\sqrt{D_m s}]\ a\ [(C_{O_2})_s - (C_{O_2})_L] \qquad [10]$$

where:

$$K_L = \sqrt{D_m s} = \frac{D_m}{x} \qquad [11]$$

D_m = Molecular diffusivity of oxygen in the liquid phase in square feet per second

s = Surface replacement rate in 1/seconds

x = Hypothetical liquid film thickness in feet

Kishinevski (124) reported that the overall mass transfer coefficient for liquid film-controlled cases to be a function of both "molecular" and "turbulent" gas diffusivities as follows:

$$K_L = \frac{2}{\sqrt{\pi}} \sqrt{(D_m + D_T)\ s} \qquad [12]$$

D_m = Molecular diffusivity of oxygen in the liquid phase in square feet per second

D_T = Turbulent diffusivity of oxygen in the liquid phase in square feet per second

Mass transfer of gas molecules into a liquid would be more affected by turbulent than molecular diffusion in highly turbulent liquid conditions. Therefore, liquid Reynolds number would be a possible factor of considerable importance in determining oxygen mass transfer into black liquor in a plug flow reactor.

Dobbins (125) proposed a mechanism for mass transfer of gas molecules into a liquid phase based upon surface renewal which involved a three step sequence. The three successive steps in the mass transfer were as follows: 1) transfer of gas molecules through the gas film to the liquid surface;

2) passage of gas molecules through the liquid film surface by molecular diffusion; 3) mixing of the gas molecules in the liquid by diffusion and convection. At laminar film conditions involving low liquid mixing levels, the passage of gas molecules through the film was the rate-limiting process. At turbulent conditions, the film surface became disrupted, and the rate of surface renewal of unexposed liquid became the rate-limiting process. Turbulent eddies of liquid were considered to move to the liquid surface, be exposed to the gas molecules for short finite periods, and then be replaced by other eddies. The degree of mass transfer of gas into the liquid phase depended on the number of eddies reaching the surface per unit time and the amount of material transferred to each eddy exposed. A relationship for mass transfer coefficient employing this mechanism has been postulated as follows:

$$K_L = \sqrt{D_m s} \quad \text{Coth} \left(\sqrt{\frac{sx^2}{D_m}}\right) \qquad [13]$$

At levels of high liquid turbulence, the second term tends to unity and the expression simplifies to equation 11.

c. Previous Work

Several studies were made concerning attempts to evaluate mass transfer coefficients for weak black liquor. Tomlinson (50) reported on the use of a laboratory scale packed column for determining mass transfer coefficients in weak black liquor, using changes in sodium sulfide concentration as the indicator of oxygen absorption. He found the absorption rate was a maximum at 70°C (158°F). Menzies (87) studied the oxidation of sodium sulfide with air in the liquor using a wetted wall packing strip. He found that approximately 90 percent of the resistance to mass transfer was in the liquid film.

Values for mass transfer coefficient and packing surface area requirements were determined for subsequent design of black liquor oxidation systems. Wright (53)(79) and Murray (126) made studies using wetted wall packing strips for studying black liquor oxidation. Their work indicated the mass transfer to be liquid film-controlled and that the heights of transfer units for subsequent design of full-scale systems was dependent on liquid flow rate and liquid film Reynolds number. It was observed that disproportionately large increases in tower height would be required to reduce the sodium sulfide concentration below one gram per liter. These findings pointed to sufficient retention time as essential for the oxidation of sodium sulfide at low concentrations, with mass transfer no longer the rate-limiting process.

2. Process Variables

The rate of oxygen mass transfer into black liquor increased with the overall mass transfer coefficient, the interfacial contact area, and the oxygen concentration driving force. The present study involved a system where an essentially pure gas (99.5 percent oxygen by volume) was absorbed into black liquor, followed by chemical reaction of oxygen with sodium sulfide and other constituents in the black liquor. The importance of the use of a pure gas was that as the oxygen was transferred across the liquid film and reacted, its partial pressure driving force in the gas stream did not decrease. The importance of the occurrence of the chemical reactions simultaneously with the oxygen mass transfer was that the liquid concentration driving force did not decrease during the black liquor oxidation process. The result of the two processes acting simultaneously was that a high oxygen driving force between the gas and liquid bulk phases was maintained.

a. Pure Gas

The result of using a pure gas was that the concentration driving force in the gaseous phase was maintained during the entire process of black liquor oxidation with molecular oxygen by maximizing the saturation dissolved oxygen concentration in the black liquor. The relatively constant gaseous phase driving force with molecular oxygen was in marked contrast to that of air, where the inlet oxygen concentration of approximately 20 percent by volume was being continually depleted by selective diffusion as the gas bubbled passed through the liquid. The only factors which would tend to decrease the oxygen partial pressure in the gas stream would be evaporation of water from the liquid, and the stripping of any odorous gases present. The evaporation of water from black liquor with subsequent dilution of the oxygen was particularly a potential problem with strong black liquor oxidation with molecular oxygen where relatively inefficient mass transfer into the highly viscous liquid could be expected.

Additional benefits of using an essentially pure gas for black liquor oxidation were as follows. First, the interfacial gas-liquid contact area per unit amount of oxygen present would increase because of the decrease in bubble size as oxygen molecules diffused across the gas-liquid boundary. The rate of mass transfer would tend to increase as the reaction proceeded, and there would be no theoretical lower limit to oxygen bubble size. Second, the pure gas would virtually eliminate gas film resistance to mass transfer because there would be essentially no change in oxygen concentration in the gas film. Third, the absence of an inert gas reduced the tendency for diffusion of water molecules across the liquid film into the gaseous phase, thus reducing the amount of evaporation with resultant liquor cooling. Fourth,

the absence of the inert diluent medium (nitrogen) would reduce the tendency for foaming in the black liquor.

b. Chemical Reaction

The occurrence of chemical reactions in the black liquor tended to minimize the actual dissolved oxygen concentration in the black liquor by preventing its accumulation in the liquid as free oxygen. The result was to maintain a maximum oxygen concentration driving force into the black liquor. An additional result of the chemical reactions was that oxygen mass transfer may not be the rate-limiting process of the black liquor oxidation process, particularly at the lower reactant concentrations. It was also doubtful that oxygen would exist in the free state in black liquor because of the high concentrations of reducing materials present, exerting an oxygen demand.

c. Gas Solubility

Liquid temperature and total gas pressure also affected the concentration driving force of oxygen into black liquor. The solubility of oxygen decreased with increasing temperature because of increasing activity of the molecules. The result was that the saturation oxygen concentration was reduced with increasing temperature, thus decreasing the effective oxygen concentration driving force. The problem could be especially severe for strong black liquor at high liquid temperatures of 220 to 240°F. One method of counteracting the potential detrimental effects of increasing liquid temperature was to increase the total pressure of the inlet gas stream to compensate for the effects of temperature.

d. Mass Transfer Coefficients

The overall mass transfer coefficients for weak and strong black liquor were physical constants dependent in large part on solids concentrations and

other physical characteristics of individual black liquors. Direct determination of these constants could be made difficult because of the necessity for determining oxygen transfer by indirect measurement of sodium sulfide, and possible absorption of oxygen by lignin materials. Difficulties in determining mass transfer-limiting from chemical reaction-limiting phases of the oxidation reactions would make exact determination of these constants very difficult, plus problems in working with the high temperature, highly viscous, caustic, nontransparent liquid material.

e. Interfacial Contact Area

An additional variable was to maximize the amount of gas-liquid interfacial contact area between the oxygen and the black liquor. It was necessary to have an efficient contacting device to probide for a dispersion of oxygen bubbles of minimum diameter into the black liquor to maximize the gas-liquid interfacial contact area. The use of a pure gas meant that there was no theoretical lower limit to the gas bubble size until the oxygen was completely consumed. The solids content of the black liquor affected the gas-liquid interfacial contact area because liquid viscosity and surface tension were proportional to the liquor solids concentration. The result was that at the higher solids concentrations associated with strong black liquor the allowable gas bubble size in the liquid became greater, the interfacial contact area was then reduced, and the rate of oxygen mass transfer decreased.

f. Turbulence and Mixing

Effective turbulence and mixing were necessary to promote rapid breakup of the gas stream into small bubbles for efficient oxygen mass transfer into black liquor. Maintenance of high liquid Reynolds numbers in the turbulent region were necessary for rapid mixing, which were favored by high liquid velocities, large pipe diameters, and low fluid viscosities. Reynolds number

involved consideration of both mass transfer coefficient and interfacial contact area, plus two phase gas-liquid flow.

B. Two Phase Flow

When oxygen was introduced into black liquor in a plug flow reactor, the conventional laws of fluid mechanics no longer applied because of the occurrence of two phase gas-liquid flow. The effect of the two phase flow was to affect the flow configuration and ultimate rate of oxygen mass transfer, increase the net retention time by a phenomenon known as "holdup" caused by occurrence of void spaces, and increase the fluid resistance to flow. It was desirable to maintain the liquid in the bubble or froth regime of two phase flow to maximize the rate of oxygen mass transfer into black liquor. Bubble (froth) flow occurred at conditions of high liquid and low gas flow rates under highly turbulent conditions where a large number of small gas bubbles were dispersed in the liquid medium. DeGance and Atherton (127) prepared an extensive review of all major aspects of two phase gas-liquid flow phenomena.

1. Flow Configurations

The two phase gas-liquid flow configuration was of particular importance for oxidation of black liquor with molecular oxygen in a plug flow reactor because it determined the amount of gas-liquid interfacial contact area available for oxygen mass transfer into the black liquor. Variables which had a particular influence on the resultant two phase flow configuration were the injector configuration, the direction of liquid flow, the pipe diameter, the gas flow rate, the liquid Reynolds number, and the liquid solids concentration. The different types of horizontal two phase flow configurations between gases and liquids in pipes were classified by Baker

(128) as follows: 1) froth flow; 2) bubble flow; 3) plug flow; 4) slug flow; 5) stratified flow; 6) wavy flow; 7) annular flow; 8) spray flow. Alves (129) described the patterns for vertical two phase flow as follows: 1) froth flow; 2) bubble flow; 3) plug flow; 4) wavy flow; 5) annular flow; 6) spray flow. The different configurations for horizontal two-phase flow have been illustrated in Figure 14 from data developed for oil-gas mixtures.

a. Homogeneous Flow

Thw two major classifications of two phase gas-liquid flow were homogeneous and nonhomogeneous configurations. The three basically homogeneous configurations were froth flow, bubble flow, and spray flow. The froth and bubble flow configurations were particularly desirable in terms of facilitating oxygen mass transfer into black liquor. The froth flow configuration consisted of a highly turbulent, relatively uniform dispersion of extremely small gas bubbles in the form of a froth. The bubble flow configuration consisted of a dispersion of discrete gas bubbles of varying sizes with either uniform or nonuniform distribution in the liquid. The dividing line between the two was a matter of arbitrary definition, as the main differences between the two were the relative bubble sizes and degrees of liquid turbulence. Both flow regimes were characterized by high liquid Reynolds numbers, relatively low gas flow rates, and small diameter gas bubbles. The spray flow regime was characterized by conditions of extremely high gas flow rates and liquid flow rates sufficiently low for a dispersion of fine droplets to be formed. The spray flow configuration would not normally be encountered during black liquor oxidation with molecular oxygen.

b. Nonhomogeneous Flow

The nonhomogeneous flow regimes were less desirable in terms of oxygen mass transfer into black liquor because they provided for considerably less

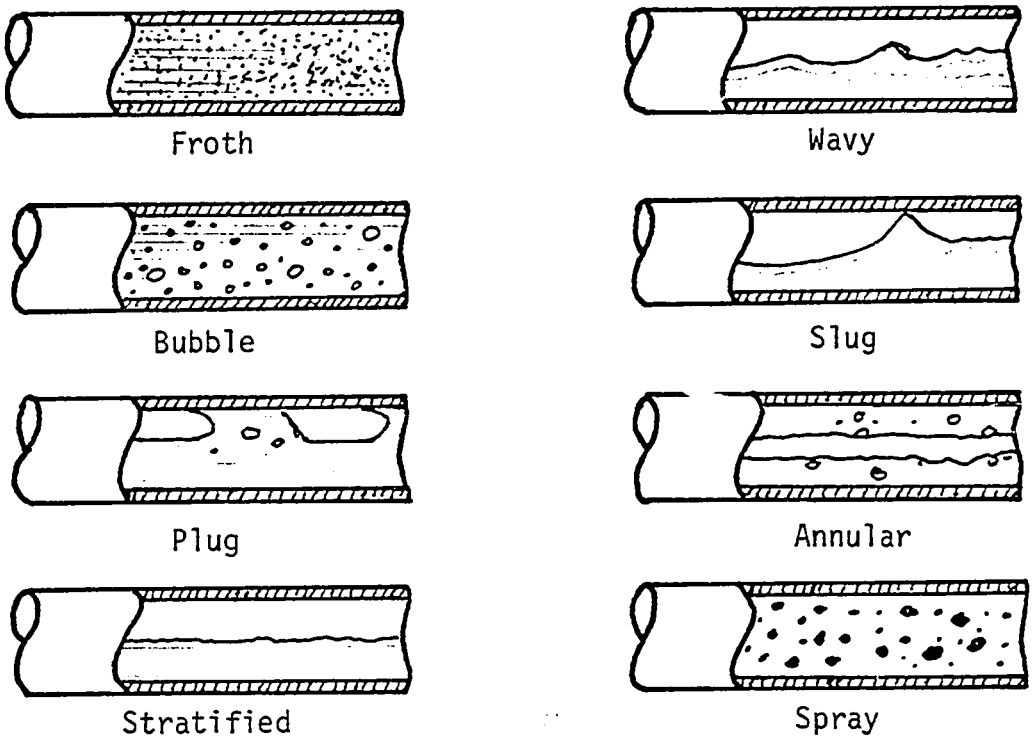


FIGURE 14. COCURRENT TWO PHASE GAS-LIQUID FLOW CONFIGURATIONS IN HORIZONTAL PIPES (128).

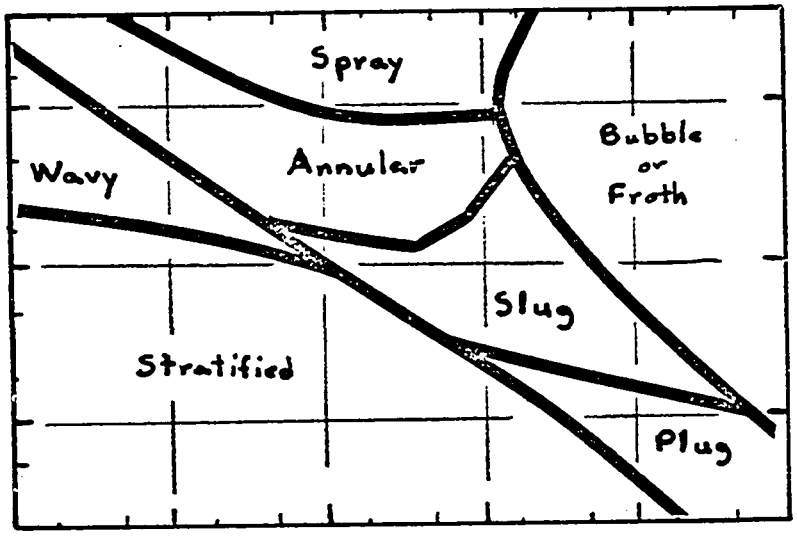


FIGURE 15. COCURRENT TWO PHASE GAS-LIQUID FLOW REGIMES IN HORIZONTAL PIPES (128).

gas-liquid interfacial contact area than froth or bubble flow. Particularly to be avoided were stratified, wavy, and slug flow, which provided two separate gas and liquid layers with little contact area. The condition would be favored at low liquid flow rates in large diameter pipes. Annular flow would occur at extremely high gas flow rates relative to the liquid flow rate, with the liquid then being forced to the outsides of the pipe in an annular ring. It would be a likely occurrence during oxidation of strong black liquor with high sodium sulfide concentrations.

Baker (128) characterized the flow configurations in terms of the superficial gas and liquid mass flow velocities, plus a density parameter (Λ) and a liquid surface tension and viscosity parameter (Ψ), as illustrated in Figure 15. The respective parameters were defined as follows:

$$\Lambda = \left[\left(\frac{\rho_G}{0.075}\right)\left(\frac{62.3}{\rho_L}\right)\right]^{1/2} \qquad [14]$$

$$\Psi = \frac{73}{\sigma}\left[\mu_L \left(\frac{62.3}{\rho_L}\right)\right]^{1/3} \qquad [15]$$

Λ = Gas and liquid density parameter

Ψ = Liquid viscosity and density parameter

ρ_G = Density of gas stream in pounds per cubic foot

ρ_L = Density of liquid stream in pounds per cubic foot

μ_L = Liquid viscosity in centipoise

M_H = Gaseous superficial mass velocity in pounds per square foot per hour

M_L = Liquid superficial mass velocity in pounds per square foot per hour

σ = Surface tension of liquid in dynes per centimeter

The chart could then be used for estimation of the two phase flow regime from the respective gas and liquid flow rates, plus the respective densities, viscosities and surface tension.

2. Flow Effects

a. Pressure Drop

The resistance to flow was found to substantially increase when a gas was added to a liquid flowing in a pipe. The major reasons for the increased pressure drop were that the effective cross-sectional area available to the flow of either phase was reduced by the presence of the other, and that additional energy was then required to move the liquid through the pipe (128). Numerous correlations have been developed to describe the increase in pressure drop during different two phase flow conditions, and are examples of work by Baker (128), Alves (129), plus Lockhart and Martinelli (130). Many of these correlations related changes in pressure drop during two phase flow as compared to either gas or liquid flow alone. The problem involved with using these correlations was that they often applied to specific situations, and could not be readily extrapolated with any degree of accuracy. The effect of two phase gas-liquid flow was to require additional liquid pumping capacity to overcome the increased pressure drop in the pipe.

b. Retention Time

An additional effect of two phase gas-liquid flow was to increase the resultant retention time of the gas-liquid mixture as compared to either the gas or liquid flow alone by a phenomenon known as "holdup" (131). It was particularly significant for vertical downward flow, where the gas bubbles tended to rise even though the liquid was flowing in the opposite direction. The effect would be of considerable importance in attempting to dissolve oxygen into the highly viscous strong black liquor.

c. Reynolds Number

Two recent studies pointed to the influence of Reynolds number on mass transfer coefficient, as summarized by Cichy and Russell (132) in a review of design parameters for plug flow reactors. Banerjee (133) observed that over a range in liquid Reynolds numbers from 2,000 to 10,000 the liquid film mass transfer coefficient varied as follows:

$$k_L = 2.93 \times 10^{-3} \sqrt{D_L} \, (N_{Re_L})^{0.993} \qquad [16]$$

where:

$$N_{Re_L} = \frac{D_p U_L \rho_L}{\mu_2} \qquad [17]$$

D_L = Diffusivity of the gas in the liquid in square centimeters per second

N_{Re_L} = Liquid Reynolds number (dimensionless)

D_p = Pipe diameter in feet

U_L = Liquid velocity in feet per second

k_L = Liquid film mass transfer coefficient in centimeters per second

Lamont and Scott (134) found that over a range in liquid Reynolds numbers from 2,000 to 30,000 when absorbing carbon dioxide into sodium hydroxide, that the liquid film mass transfer coefficient obeyed the following expression:

$$k_L = 3.00 \times 10^{-2} \, (N_{Re_L})^{0.491} \qquad [18]$$

k_L = Liquid film mass transfer coefficient in centimeters per minute

The above expressions were not necessarily applicable to black liquor oxidation with molecular oxygen in a plug flow reactor, but they indicated the importance of liquid Reynolds number on oxygen transfer into the liquid phase.

Sittel (135) observed that conditions of completely turbulent flow existed for liquid Reynolds numbers greater than 40,000, in pulse test studies of sodium chloride dispersion into water in a glass pipe system.

d. Froth Flow

Heuss, King, and Wilke (136) made an extensive study of gas transfer of ammonia and air into water during froth or bubble two phase flow in a plug flow reactor. Variables studied included bubble sizes, liquid film mass transfer coefficients, and lengths of transfer units in the transparent tube. The air-water system was essentially liquid film-limited because approximately 98 percent of the resistance to mass transfer was in the liquid film. The mean bubble diameter for ammonia into water was found to decrease from two to 0.2 millimeters as the mean gas-liquid velocity increased from ten to fifty feet per second. They also found that the rate of oxygen was ten to one hundred times the values predicted from molecular diffusion alone. These findings indicated that turbulent diffusion would be the primary mechanism for oxygen mass transfer into black liquor in a plug flow reactor during turbulent liquid flow.

C. Reaction Chemistry

The objective of black liquor oxidation was the conversion of sodium sulfide and mercaptide to stabilized end products to prevent their release as odorous gases. Variations in chemical composition could affect the amounts of oxygen necessary to achieve effective oxidation of the sodium sulfide and mercaptide, plus the rates at which the oxidation reactions occurred. The oxidation of the inorganic and organic sulfur compounds involved a complex sequence of chemical reactions with several possible reaction products. The presence of other constituents in the black liquor, such as phenolic lignins, increased the possibility for competing side reactions with an additional

oxygen demand. An additional problem was that sodium sulfide and sodium mercaptide became less soluble in black liquor with decreasing pH, resulting in greater potential for release of hydrogen sulfide and methyl mercaptan.

1. Chemical Composition

The oxidation of sodium sulfide and sodium mercaptide in black liquor was made extremely complicated because of its complex and variable composition. The wide variations in composition between individual black liquors occurred because of individual differences in chemical makeup requirements, cooking conditions, and wood species. Arhippainen and Jungerstam (137) listed approximate ranges for chemical composition of weak black liquors, as presented in Table 14.

The major inorganic sulfur compounds present in black liquor were sodium sulfide, polysulfide, thiosulfate, sulfite and sulfate. Sodium polysulfide consisted of elemental sulfur atoms joined to sulfide ions in mixed ionic-covalent bonding arrangements. It existed in several forms, including disulfide, trisulfide, tetrasulfide, pentasulfide, and octasulfide ions, which were favored in alkaline media. The sulfur could also exist in a variety of polythionate forms, which were favored in acidic media. Organic sulfur compounds which could be present included sodium mercaptides, dialkyl sulfides, and dialkyl disulfides. Major organic compounds present in black liquor included lignins, hemicelluloses, organic acids, plus alcohols and esters. Some of these compounds could exert an additional oxygen demand during the black liquor oxidation process.

2. Air Pollution

The main objectives of black liquor oxidation were the conversion of sodium sulfide and sodium mercaptide to prevent their subsequent release as hydrogen sulfide and methyl mercaptan during multiple effect evaporation, tall oil recovery, and direct contact evaporation of black liquor.

TABLE 14. CHEMICAL COMPOSITION OF WEAK BLACK LIQUOR (137).

Classification	Material	Concentration[2] grams/liter	Proportion % by weight
Inorganic	Na_2S	1-20	1-15
	Na_2S	0-5	0-3
	$Na_2S_2O_3$	0-10	0-7
	Na_2SO_3	0-1	0-1
	Na_2SO_4	0-10	0-7
	NaOH	1-15	1-10
	Na_2CO_3	10-50	5-30
	Total Inorganic	-----	30-60
	pH	11-13	-----
Organic	Lignin	50-100	30-50
	Cellulose	0-0.1	0-0.1
	Sugar	0-0.3	0-0.2
	Polysaccharides	0.1-2	0.1-1
	Resin Acids	1-10	1-7
	Organic Acids	10-25	7-15
	Other Organic	10-15	20-30
	Total Organic	-----	40-70

Notes: 1. Listed in pH units.
2. Based on 15 percent solids in weak black liquor.

a. Multiple Effect Evaporation

The major potential source of release of odorous gases during multiple effect evaporation was the thermal decomposition of sodium sulfide and sodium mercaptide as follows:

$$Na_2S + 2H_2O \rightleftharpoons 2NaOH + H_2S \quad [19]$$

$$NaSCH_3 + H_2O \rightleftharpoons NaOH + CH_3SH \quad [20]$$

The degree of emission of reduced sulfur gases increased with respective inlet sulfide and mercaptide concentrations, plus the degree of liquid heating and agitation, and decreased with increasing black liquor pH. Malodorous sulfur gas emissions could be minimized by maintenance of high black liquor pH and oxidation of the weak black liquor upstream of the multiple effect evaporators, or by scrubbing and incineration of the offgases.

b. Tall Oil Recovery

Tall oil was normally recovered from black liquor by flotation following acidulation with sulfuric acid. The acidulation step resulted in release of hydrogen sulfide and methyl mercaptan from black liquor remaining in the tall oil as follows:

$$Na_2S + H_2SO_4 \rightleftharpoons Na_2SO_4 + H_2S \quad [21]$$

$$2NaSCH_3 + H_2SO_4 \rightleftharpoons Na_2SO_4 + 2CH_3SH \quad [22]$$

The release of hydrogen sulfide and methyl mercaptan increased with increasing inlet concentrations of sulfide and mercaptide ions, the amount of acid added, and the degree of liquid agitation. The primary means for reducing malodorous sulfur gas emissions from tall oil recovery were oxidation of the weak black liquor to prevent release, and alkaline scrubbing of the flue gas stream following release.

c. Direct Contact Evaporation

Hydrogen sulfide and methyl mercaptan could be released during direct contact evaporation of black liquor by the acidification of sodium sulfide and sodium mercaptide by contact with carbon dioxide, sulfur dioxide, or sulfur trioxide from the recovery furnace flue gases:

$$Na_2S + CO_2 + H_2O \rightleftharpoons Na_2CO_3 + H_2S \quad [23]$$

$$Na_2S + SO_2 + H_2O \rightleftharpoons Na_2SO_3 + H_2S \quad [24]$$

$$Na_2S + SO_3 + H_2O \rightleftharpoons Na_2SO_4 + H_2S \quad [25]$$

$$2NaSCH_3 + CO_2 + H_2O \rightleftharpoons Na_2CO_3 + CH_3SH \quad [26]$$

$$2NaSCH_3 + SO_2 + H_2O \rightleftharpoons Na_2SO_3 + CH_3SH \quad [27]$$

$$2NaSCH_3 + SO_3 + H_2O \rightleftharpoons Na_2SO_4 + CH_3SH \quad [28]$$

Major variables affecting the release of malodorous sulfur gas emissions during direct contact evaporation included inlet sodium sulfide and mercaptide concentrations in the black liquor, black liquor pH and alkalinity, the degree of gas-liquid contact, the types and concentrations of acidic constituents in the furnace exit gas, and the inlet temperatures of the respective strong black liquor and flue gas streams. The main techniques for minimizing malodorous sulfur gas emissions during direct contact evaporation were by oxidation of the weak and/or strong black liquor, and by maintenance of high black liquor pH.

3. Inorganic Sulfur

a. Overall Reactions

The primary objective of black liquor oxidation was the selective oxidation of sodium sulfide to sodium thiosulfate. The reaction proceeded

through the formation of a polysulfide ion intermediate (represented as $S_2^{=}$) as follows:

Overall: $2Na_2S + 2O_2 + H_2O \rightleftharpoons Na_2S_2O_3 + 2NaOH$ [29]

Detailed: $2Na_2S + 1/2O_2 + H_2O \rightleftharpoons Na_2S_2 + 2NaOH$ [30]

$Na_2S_2 + 3/2\ O_2 \rightleftharpoons Na_2S_2O_3$ [31]

It was noted that one mole of oxygen was required to oxidize one mole of sodium sulfide to sodium thiosulfate, with the liberation of one mole of sodium hydroxide.

The sodium thiosulfate formed could undergo subsequent oxidation to sodium sulfate through the formation of sodium sulfite as a reaction intermediate as follows:

Overall: $Na_2S_2O_3 + 2O_2 + 2NaOH \rightleftharpoons 2Na_2SO_4 + H_2O$ [32]

Detailed: $Na_2S_2O_3 + O_2 + 2NaOH \rightleftharpoons 2Na_2SO_3 + H_2O$ [33]

$2Na_2SO_3 + O_2 \rightleftharpoons 2Na_2SO_4$ [34]

One mole of oxygen was required for conversion of one mole of sodium thiosulfate to sodium sulfate, with the resultant consumption of one mole of sodium hydroxide. The oxidation of sodium sulfide to sodium sulfate essentially doubled the oxygen consumption requirement, an economic detriment to the process. The formation of sodium sulfate also resulted in consumption of sodium hydroxide, with the potential for drop in liquid pH and possible lignin precipitation. Liquid pH was a potential variable in determining the overall rate of sodium sulfide oxidation.

Murray (138) indicated the potential importance of sodium polysulfide as a reaction intermediate during black liquor oxidation. Ricca (97) observed that sodium sulfite reacted rapidly in alkaline solutions with either sodium polysulfide or elemental sulfur as follows:

$$Na_2SO_3 + Na_2S_2 \rightleftharpoons Na_2S_2O_3 + Na_2S \quad [35]$$

$$Na_2SO_3 + S \rightleftharpoons Na_2S_2O_3 \quad [36]$$

The above reactions indicated that the simultaneous accumulation of sodium polysulfide and sodium sulfite in black liquor was highly improbable. The presence of large quantities of sodium polysulfide in black liquor would inhibit the potential for formation of sodium sulfate, but would enhance the possible regeneration of sodium sulfide. Menzies (87) reported that the sodium polysulfide concentration during black liquor oxidation reaction reached a maximum at approximately 50 percent sodium sulfide oxidation efficiency, and decreased at higher efficiencies. Sodium polysulfide would be a significant reaction product during conditions of oxygen starvation (incomplete sulfide oxidation) or inadequate energy (low liquid temperatures).

The oxidation of sodium sulfide to sodium thiosulfate and its subsequent conversion to sodium were exothermic in nature, as determined by Ziegelmeyer and Feischl (139).

TABLE 15. HEATS OF REACTION FOR OXIDATION OF SODIUM SALTS (139).

Reactant	Product	Heat of Reaction kcal/gm-mole Na_2S
Na_2S	$Na_2S_2O_3$	+215
$Na_2S_2O_3$	Na_2SO_4	+220

These findings pointed to a possible warming of the liquid phase from oxidation of sodium salts and other materials during black liquor oxidation with molecular oxygen.

b. Reaction Mechanisms

Murray (138) found that the oxidation of sodium sulfide proceeded through a polysulfide intermediate. At temperatures above 160°F, the formation of sodium thiosulfate was favored, but at temperatures below 160°F, the formation of elemental sulfur was the main end product, as shown in the following sequence:

Polysulfide Formation:

$$16Na_2S + 7O_2 + 14H_2O \rightleftharpoons 2Na_2S_8 + 28NaOH \quad [37]$$

At Temperatures above 160°F:

$$2Na_2S_8 + 9O_2 + 12NaOH \rightleftharpoons 8Na_2S_2O_3 + 6H_2O \quad [38]$$

At Temperatures below 160°F:

$$2Na_2S_8 + O_2 + 2H_2O \rightleftharpoons 2S_8 + 4NaOH \quad [39]$$

The formation of incomplete reaction products, sodium polysulfide and elemental sulfur, were favored at tower temperatures with less energy in the system.

From a series of similar studies, Douglass (140) proposed a similar but more complicated mechanism for the formation of several different polysulfide and polythionate ion intermediates for oxidation of sodium sulfide to sodium thiosulfate. The formation of sodium sulfide was favored at temperatures greater than 60°C (140°F), with a hydrosulfide ion initiator.

Hydrosulfide Formation:

$$Na_2S + H_2O \rightleftharpoons NaHS + NaOH \quad [40]$$

Polysulfide Formation:

$$4NaHS + O_2 \rightleftharpoons 2NaHS_2 + 2NaOH \quad [41]$$

$$4NaHS_2 + O_2 \rightleftharpoons 2NaHS_4 + 2NaOH \quad [42]$$

$$4NaHS_4 + O_2 \rightleftharpoons 2NaHS_8 + 2NaOH \quad [43]$$

Temperatures below 60°C

$$2NaHS_8 + O_2 \rightleftharpoons 2S_8 + 2NaOH \quad [44]$$

Temperatures above 60°C:

$$NaHS_2 + NaOH \rightleftharpoons NaHS + NaHSO \quad [45]$$

$$NaHS_3 + NaOH \rightleftharpoons NaHS_2 + NaHSO \quad [46]$$

$$NaHS_4 + NaOH \rightleftharpoons NaHS_3 + NaHSO \quad [47]$$

The thionate (HSO^-) reaction intermediate could then form sodium thiosulfate through the following sequence of reactions:

$$2NaHSO \rightleftharpoons NaHSO_2 + NaHS \quad [48]$$

$$NaHSO_2 + NaHSO \rightleftharpoons NaHSO_3 + NaHS \quad [49]$$

or:

$$Na_2SO_2 + Na_2SO \rightleftharpoons Na_2SO_3 + Na_2S \quad [50]$$

$$Na_2SO_3 + Na_2S_2 \rightleftharpoons Na_2S_2O_3 + Na_2S \quad [51]$$

Two recent studies involved the oxidation of sulfide ion at low concentrations, where the primary reactive species was the hydrosulfide (HS^-) ion. Cline and Richards (141) proposed the following mechanism for oxidation of sodium hydrosulfide in sea water at pH 7.5 and a liquid temperature of 10°C (50°F):

$$2HS^- + O_2 \rightleftharpoons 2S + 2OH^- \quad [52]$$

$$2HS^- + 2O_2 \rightleftharpoons S_2O_3^= + H_2O \quad [53]$$

$$2HS^= + 3O_2 \rightleftharpoons 2SO_3^= + 2H^+ \quad [54]$$

$$2HS^- + 4O_2 \rightleftharpoons 2SO_4^= + 2H^+ \quad [55]$$

They noted a preponderance of sulfate ion formation in sea water with a slight drop in liquid pH, where their results were not necessarily applicable to black liquor oxidation.

Avrahami and Golding (142) observed that sulfite ion was an important reaction intermediate for oxidation of sodium sulfide in dilute alkaline solutions, and was formed as follows:

$$S^{=} + 3/2\ O_2 \rightleftharpoons SO_3^{=} \quad [56]$$

$$HS^{-} + 3/2\ O_2 \rightleftharpoons HSO_3^{-} \rightleftharpoons H^{+} + SO_3^{=} \quad [57]$$

The sulfite ion intermediate could then react rapidly with either hydrosulfide ion or elemental sulfur as follows:

$$HS^{-} + 2SO_3^{=} + O_2 \rightleftharpoons 2S_2O_3 + 2OH^{-} \quad [58]$$

$$S + SO_3^{=} \rightleftharpoons S_2O_3^{=}$$

The thiosulfate ion could then undergo reaction to form sulfate ion as follows:

$$S_2O_3^{=} + 1/2\ O_2 \rightleftharpoons SO_4^{=} + S \quad [59]$$

$$S_2O_3^{=} + OH^{-} \rightleftharpoons SO_4^{=} + HS^{-} \quad [60]$$

The rate-limiting step appeared to be oxidation of the thiosulfate ion in solution, which could explain its tendency to accumulate in black liquor. However, little mention of polysulfide ion was made in the above treatment, and the results were primarily applicable to sulfide ion concentrations below 0.1 grams per liter.

4. Organic Sulfur

Murray (143) found that both methyl mercaptan and dimethyl disulfide were oxidized by molecular oxygen in aqueous alkaline solutions, but that dimethyl sulfide was resistant to conversion. Alferova and Titova (78) observed that sodium mercaptide was oxidized to dimethyl disulfide as follows:

$$4NaSCH_3 + O_2 + 2H_2O \rightleftharpoons 2CH_3SSCH_3 + 4NaOH \quad [61]$$

Murray and Rayner (144), and Ricca (97) found that sodium mercaptide was oxidized more slowly than sodium sulfide in black liquor. Harkness and Murray (145) found that the rate of sodium mercaptide oxidation in alkaline solutions was considerably enhanced by the presence of trace metal catalysts such as copper or iron, with dimethyl disulfide and hydrogen peroxide being the principal reaction products. Recent work by Murray (143) as well as

McKean, Hrutfiord, and Sarkanen (146)(147) indicated that both the oxidation and alkaline hydrolysis of dimethyl sulfide were negligible in magnitude.

Murray and Rayner (144) found that dimethyl disulfide would undergo alkaline hydrolysis to form sodium methyl sulfenate and sodium mercaptide as follows:

$$CH_3SSCH_3 + 2NaOH \rightleftharpoons NaSOCH_3 + NaSCH_3 + H_2O$$

The sodium methyl sulfenate can then undergo either oxidation to form sodium methyl sulfonate, or thermal decomposition to regenerate sodium mercaptide as follows:

$$NaSOCH_3 + O_2 \rightleftharpoons NaSO_3CH_3 \qquad [62]$$

$$3NaSOCH_3 \rightleftharpoons NaSO_3CH_3 + 2NaSCH_3 \qquad [63]$$

The extent of dimethyl disulfide oxidation was negligible at room temperatures but became a relatively rapid reaction at 100°C (212°F).

5. Reversion Phenomena

Reversion, or regeneration of sodium sulfide upon storage of oxidized black liquor has been observed by Murray (148), Martin (95), Padfield (90), and Christie (149). Murray (148) observed that the amount of reversion of sodium sulfide increased with increasing storage time, decreasing oxidation time, and decreasing black liquor temperature, as illustrated in Figure 16. Possible explanations for reversion were as follows: 1) alkaline decomposition of elemental sulfur formed by low temperature oxidation; 2) reaction between sodium polysulfide and sodium sulfite in the black liquor; 3) thermal decomposition of sodium mercaptide; 4) alkaline hydrolysis of sodium mercaptide. The effect of reversion was to counteract the influence of black liquor oxidation. The reactions have been illustrated as follows, where the inorganic reactions were probably predominant:

Elemental Sulfur (138)(150):

$$16Na_2S + 7O_2 + 14H_2O \rightleftharpoons 2Na_2S_8 + 28NaOH \quad [64]$$

$$2Na_2S_8 + O_2 + 2H_2O \rightleftharpoons 2S_8 + 4NaOH \quad [65]$$

$$4S + NaOH \rightleftharpoons 2Na_2S + Na_2S_2O_3 + 3H_2O \quad [66]$$

Sodium Polysulfide (87):

$$Na_2S_2 + Na_2SO_3 \rightleftharpoons Na_2S_2O_3 + Na_2S \quad [67]$$

Sodium Mercaptide (150):

$$2NaSCH_3 \rightleftharpoons CH_3SCH_3 + Na_2S \quad [68]$$

$$2NaSCH_3 + S \rightleftharpoons CH_3SSCH_3 + Na_2S \quad [69]$$

Dimethyl Disulfide (3):

$$CH_3SSCH_3 + 2NaOH \rightleftharpoons NaSOCH_3 + NaSCH_3 + H_2O \quad [70]$$

$$NaSOCH_3 \rightleftharpoons NaSO_3CH + 2NaSCH_3 \quad [71]$$

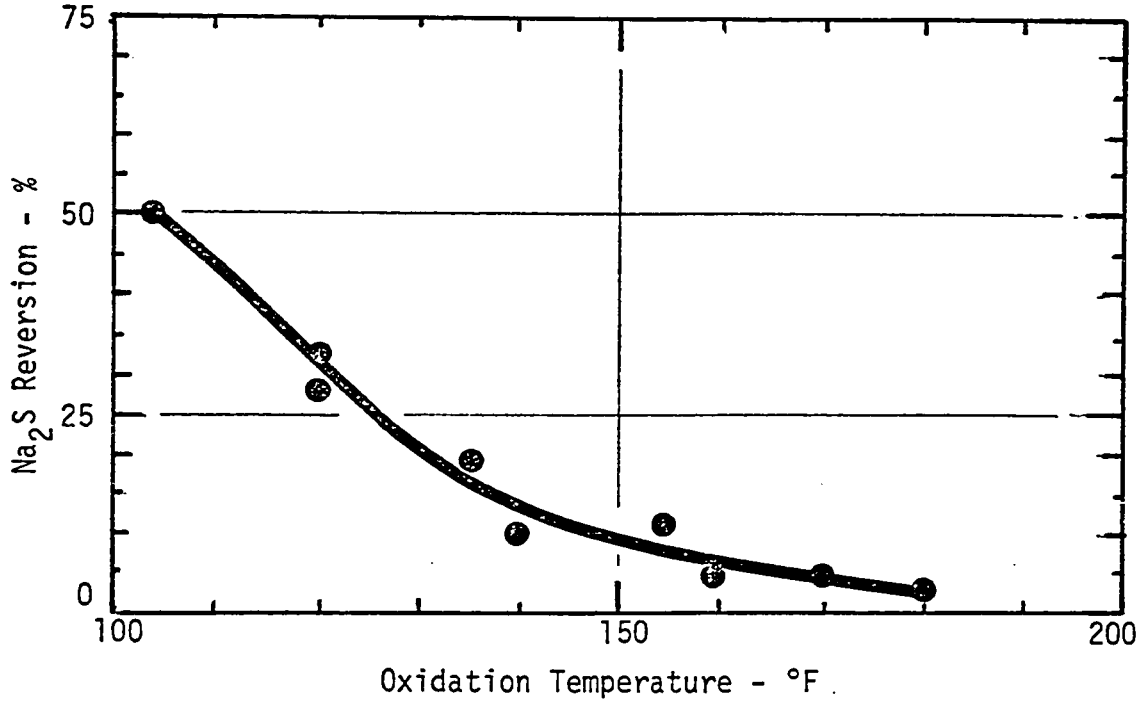
6. Organic Catalysis

The phenolic lignin present in the black liquor was important during black liquor oxidation because it catalyzed the oxidation of sodium sulfide and also because it could exert an additional oxygen demand.

a. Catalysis

Ricca (97), Sakhuja and Basu (98), Enkvist and Ekman (151), plus Bialkowsky and DeHaas (51) all observed that the rate of sodium sulfide oxidation in black liquor was substantially increased by the presence of organic, phenolic-like, catalytic materials such as lignin. Ziegelmeyer and Feischl (139) found that the presence of organic materials in the black liquor was found to increase the rate of sodium sulfide oxidation by 10 to 30 times as compared to alkaline solutions of sodium sulfide alone. Lindberg and Nordstrom (152) observed that the lignin monomers reacted to form quinone-type resonance structures by oxygen addition to the aromatic ring. They acted in

a. Effect of Oxidation Temperature (149)



b. Effect of Storage Time (90)

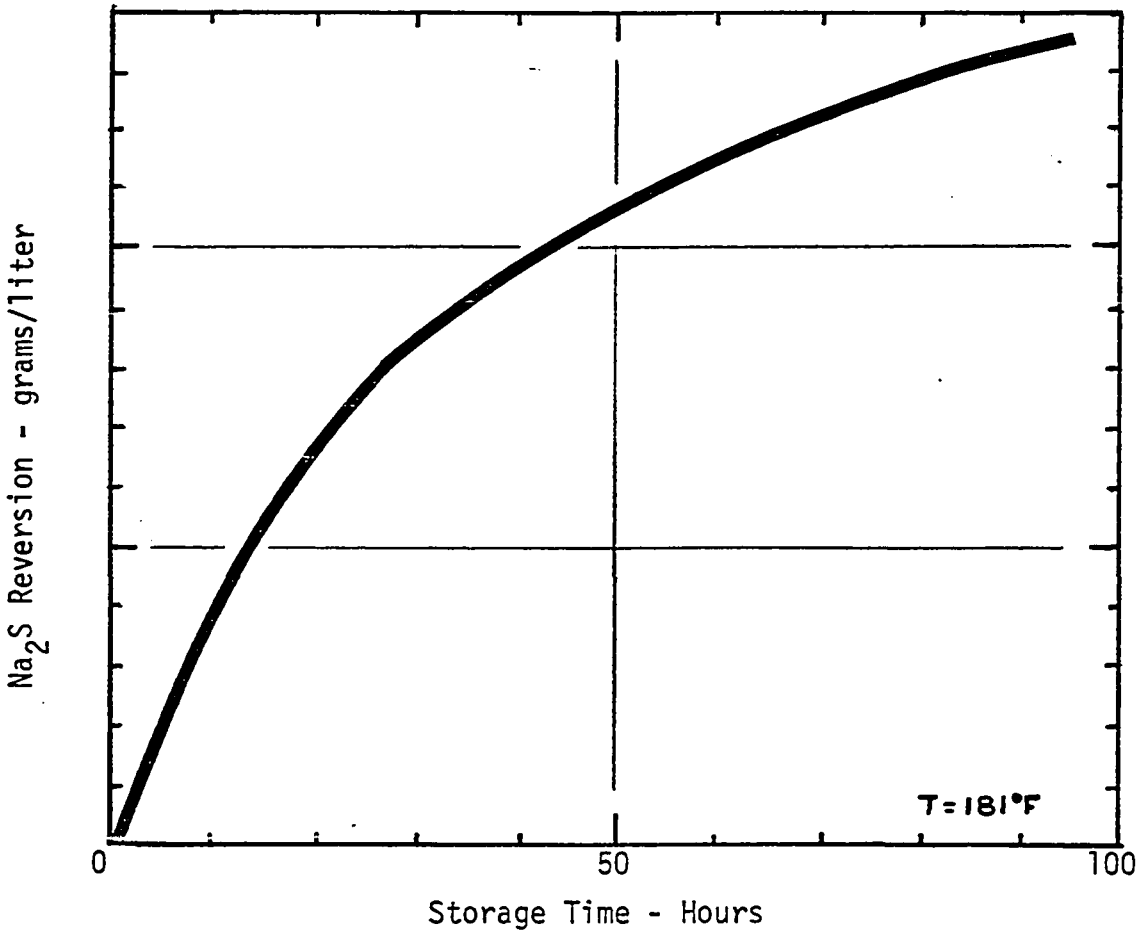
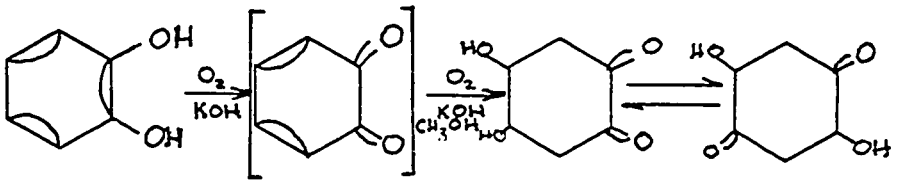


FIGURE 16. SODIUM SULFIDE REVERSION IN BLACK LIQUOR

effect with the sulfide ions acting in turn to protect the lignin molecules from oxidation. The mechanism of oxidation of catechol in alkaline solutions was shown as follows:



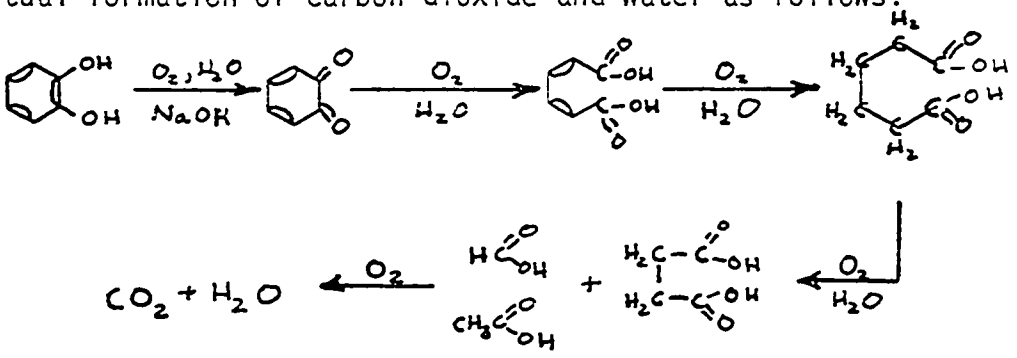
[72]

The relative catalytic effect was probably a function of wood species, where the effect was proportional to the ease by which the aromatic ring structure could be attacked. Hardwoods would probably have a greater catalytic effect than softwoods because their ring structures normally contained more electronegative groups, thus contributing to the instability of the ring. Additional factors affecting catalysis were pH and temperature. Increasing the liquid pH would probably increase the degree of ionization of the phenolic hydroxyl groups on the ring, thus increasing its electronegativity and decreasing its stability. Increasing the liquid temperature would increase the rate of oxygen addition to the phenolic ring structures, but would probably result in oxidation of some of the organic material present. The effect of lignin catalysis was shown in Figure 16.

b. Oxidation

Sarkanen and Ludwig (153) recently published an extensive review of the chemistry of lignin, including a chapter on lignin oxidation reactions. The significance of lignin oxidation was that it provided an additional source of exothermic reactions for heating black liquor. However, there was a slight loss in liquor heating value for steam generation in the recovery furnace, and the oxidation of lignin was a potential competing side reaction which might require increased oxygen consumption, particularly

at elevated temperatures. Klein (154) observed that the breakdown of phenolic catechol proceeded through a muconic acid ring-breaking intermediate, with eventual formation of carbon dioxide and water as follows:

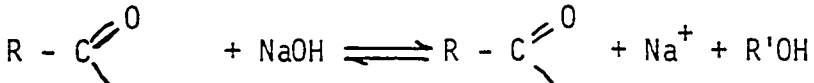


[73]

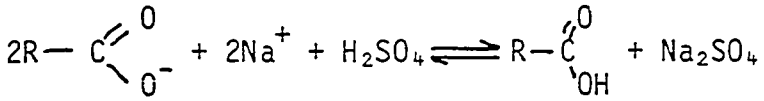
Phenolic lignin oxidation would probably follow a similar pathway.

7. Tall Oil Recovery

Black liquor oxidation has been reported to result in a slight increase in tall oil yield for mills pulping substantial quantities of pine wood species, thus providing an economic return. The major portion of the tall oil was found to be composed of fatty and resin acids, with additional quantities of esters and other extractive materials also present (155). One possible reason for increased tall oil yield was because of physical flotation and subsequent separation by entrainment of foam in the air stream. A second possible reason was possible saponification of organic esters present in the tall oil as follows:



[74]



[75]

An additional possibility was oxidation of the high molecular weight organic acid by contact with oxygen. Recent reports of increased yields along with decreased quality of tall oil during strong black liquor oxidation provided supportive evidence of possible oxidation (93).

D. Reaction Kinetics

The kinetics of black liquor oxidation involved complex sequences of chemical reactions where inorganic sulfur, organic sulfur, and organic compounds all reacted simultaneously with molecular oxygen at varying rates. Determination of the rate of sodium sulfide oxidation was of primary concern, with the oxidation rate for sodium mercaptide also of interest. Determining the respective oxidation rates was complicated because the reaction sequences involved more than one reaction rate regime, intermediate reaction products could be formed, and competing side reactions could take place, such as oxidation of sodium thiosulfate and phenolic lignins. It was necessary to determine to respective concentration profiles for sodium and other constituents in the plug flow reactor as functions of time. Primary emphasis was placed on the respective rates of disappearance of sodium sulfide and mercaptide during oxidation. This information was the basis for calculation of the respective reaction rate constants necessary for the design of full-scale plug flow reaction systems for oxidation of black liquor with molecular oxygen.

1. Rate Expressions

Several factors and simplifying assumptions were used for defining the reaction kinetics of the plug flow reactor used for black liquor oxidation with molecular oxygen. These conditions have been listed as follows: 1) steady state conditions in terms of concentration profile with respect to distances and liquid retention times for specific locations for the plug

flow reactor; 2) heterogeneous concentration profile in terms of distances at different points corresponding to varying liquid retention times; 3) liquid density was assumed to be essentially constant throughout the reactor, so that space time (τ) and retention time (t) were essentially the same for constant liquid flow rates (156); 4) diffusion was entirely in an axial direction, with no radial diffusion across the boundaries of the reactor, as described by Wehner and Wilhelm (157).

a. General Expressions

Levenspiel (158) presented an extensive discussion of the rate equations involved in the kinetics of chemical reactions. The general terminology employed for concentration (C), fractional conversion of reactant (X), and fractional volume change (E) were defined as follows:

Reactant Concentration: $C = N/V$ or $C = m/V$ [76]

Fractional Conversion: $X = 1 - C_t/C_o$ [77]

Volume Change: $E = 1/V_o\ (V_t - V_o)$ [78]

where: C = Reactant concentration in moles per unit volume or mass per unit volume

N = Number of moles of reactant in gram-moles or pound-moles

m = Amount of reactant in grams or pounds

V = Volume of system in gallons, cubic feet, or liters

X = Fraction of reactant converted to product(s)

E = Fractional change in volume during reaction period

C_o = Initial concentration of reactant at time zero

C_t = Concentration of reactant at time t

V_o = Initial volume of system at time zero (as in V)

V_t = Volume of system at time t (as in V)

The simplifying assumption was made that any change in volume for the liquid phase was negligible. Space time was then equal to retention time, there was no net change in system volume, and the volume change (E) was equal to zero.

The expression describing the rate of disappearance of a reactant with time was defined as follows:

$$-r = \frac{dC}{dt} = kC^n \qquad [79]$$

r = Rate of reaction of reactant in moles per unit volume per unit time

k = Reaction rate constant (variable units)

C = Reactant concentration in moles per unit volume

n = Order of the reaction

For plug flow reactors, the rate of reaction (r) varied with distance and retention time, in contrast to completely mixed reactors. The fractional conversion (X) was substituted for the concentration (C), and the time (t) required to achieve a given degree of conversion was found by integration as follows:

$$C_t/C_o = 1 - X \text{ and } dX = \frac{dC}{C_o} \qquad [80]$$

$$t = \frac{V}{L} = \int_o^t dt = \int_{C_o}^{C_o} \frac{dC}{kC^n} = C_o \int_o^{X_t} \frac{dX}{kC^n} = C_o \int_o^{X_t} \frac{dX}{(-r)} \qquad [81]$$

X_t = Fractional conversion of reactant to time t

L = Liquid flow rate through reactor in volume per unit time

V = Reactor volume in volumetric units

The liquid retention time in the plug flow reactor required to achieve a given degree of conversion of reactant could be calculated from equation 80, provided that the reaction rate constant and reaction order were known. Reactions involved in black liquor oxidation phenomena could be either zero order, first order, or second order in nature.

b. Zero Order Reactions

Zero order reactions were characterized by a constant rate of change in concentration with time when plotted on a linear scale. The rate of the reaction was essentially independent of reactant concentration for zero order reactions. The initial phase of sodium sulfide oxidation in black liquor at relatively high concentrations was a zero order reaction which was primarily limited by the rate of oxygen mass transfer into the liquid phase. Zero order reactions could be represented mathematically by the following equations:

Reactant Concentration: (n = o)

$$-r = \frac{dC}{dt} = kC^n = kC^\circ = k \qquad [82]$$

$$C_t - C_o = Kt \text{ or } k = \frac{C_t - C_o}{t} \qquad [83]$$

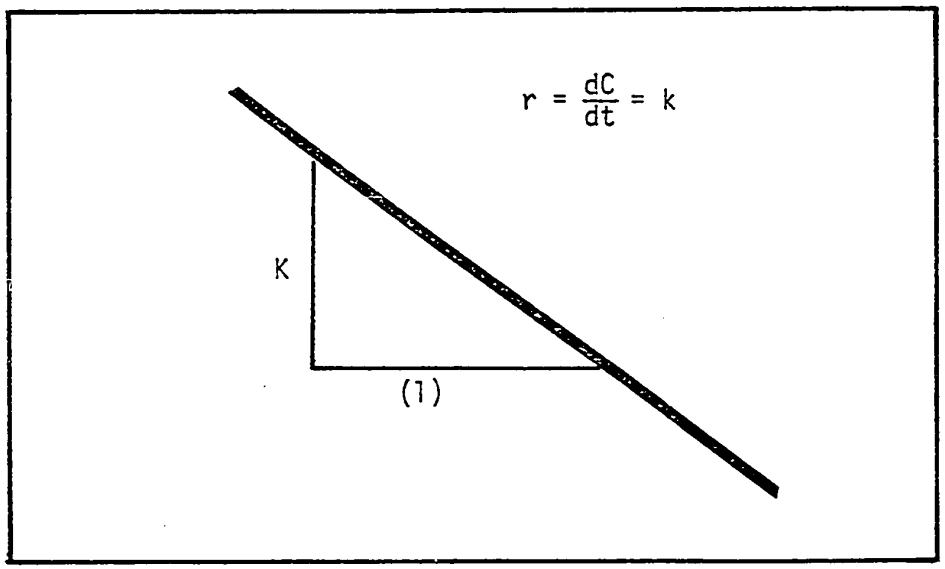
Fractional Conversion:

$$t = \int_{C_o}^{C_t} \frac{dC}{kC^n} = \int_{C_o}^{C_t} \frac{dC}{k} = \frac{C_o}{k} \int_{o}^{X_t} dX \qquad [84]$$

$$t = \frac{C_o}{k} X_t \text{ or } X_t = \frac{k}{C_o} t \qquad [85]$$

The reaction rate constant (k) for a zero order reaction could be determined as the slope of linear plot of reactant concentration or fractional conversion as functions of reaction time as shown in Figure 17.

a. Reactant Concentrations



b. Fractional Conversion

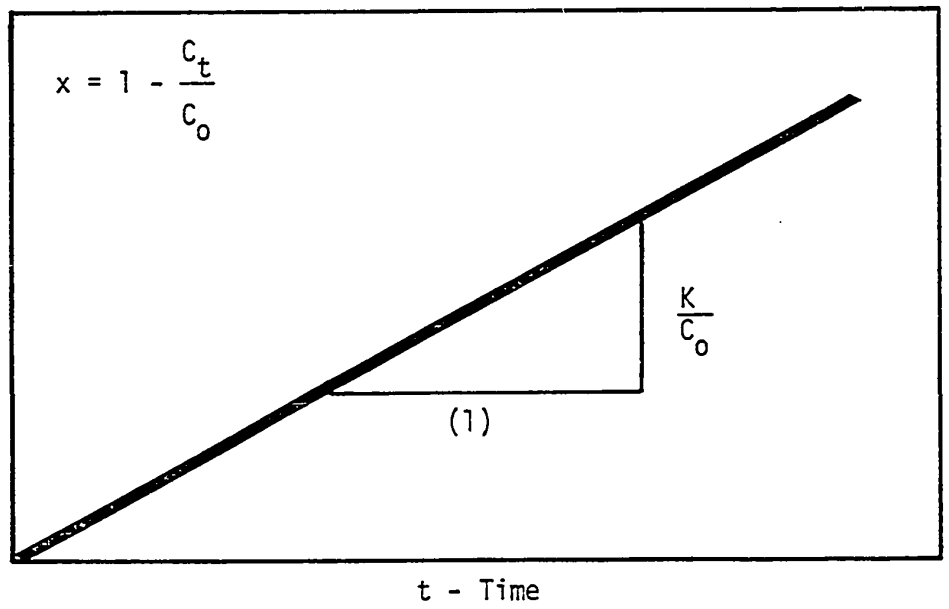


FIGURE 17. GRAPHICAL DETERMINATION OF RATE CONSTANTS FOR ZERO ORDER REACTIONS

c. First Order Reactions

First order reactions were monomolecular reactions where the rate of change in concentration was proportional to the concentration of the reacting species. The rate of reaction of sodium sulfide at relatively low concentrations was a first order reaction which was primarily limited by the rate of chemical oxidation reaction. First order reactions could be represented mathematically as follows:

Reactant Concentration: (n = 1) A $\rightarrow$ Products

$$-r = \frac{dC}{dt} = kC^n = kC' = kC \qquad [86]$$

$$\frac{dC}{dt} = kC \text{ and } \int_{C_o}^{C_t} \frac{dC}{C} = kt \qquad [87]$$

$$\ln \frac{C_t}{C_o} = 2.303 \log \frac{C_t}{C_o} = kt \qquad [88]$$

Fractional Conversion:

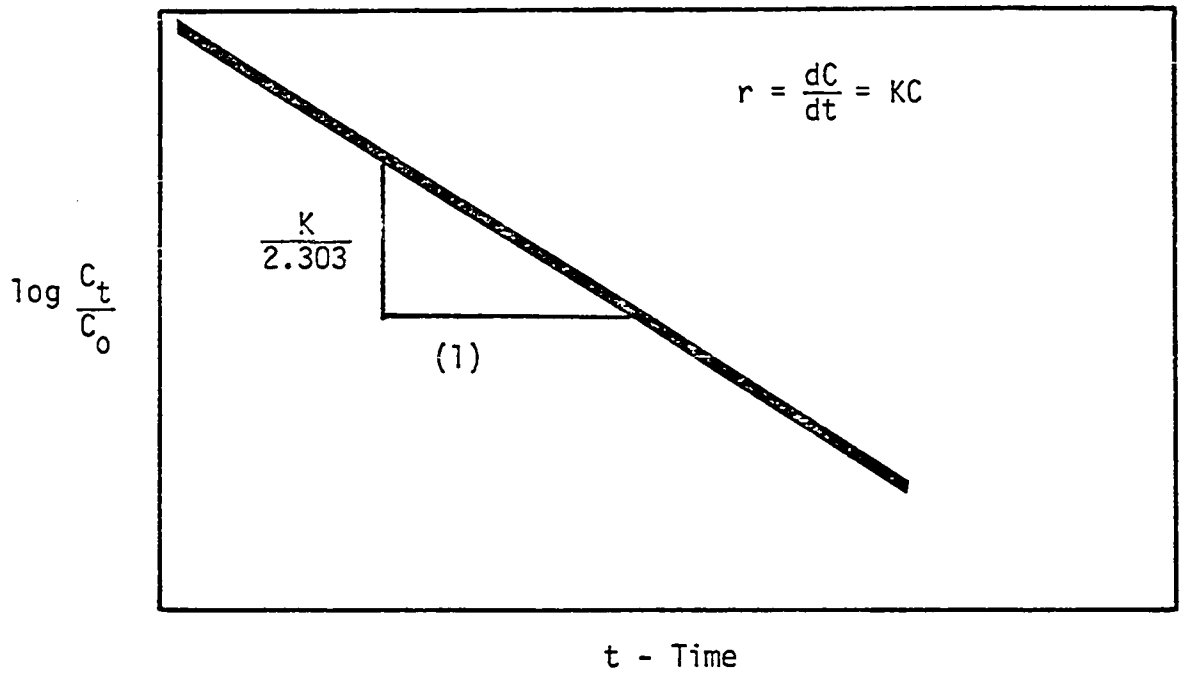
$$dC = C_o\, dX \text{ and } C = C_o\,(1 - X) \qquad [89]$$

$$t = \int_{C_o}^{C_o} \frac{dC}{kC^n} = \int_{C_o}^{C_t} \frac{dC}{kC} = \int_{o}^{X_t} \frac{C_o dX}{kC_o(1-X)} = \frac{1}{k}\int_{o}^{X_t} \frac{dX}{(1-X)} \qquad [90]$$

$$\ln (1 - X) = 2.303 \log (1 - X) = kt \qquad [91]$$

The reaction rate constant (k) for a zero order reaction could then be determined from semilogarithmic plots of reactant concentration ratio (C_t/C_o) or (1 - X) as functions of reaction time, as illustrated in Figure 18.

a. Reactant Concentrations



b. Fractional Conversions

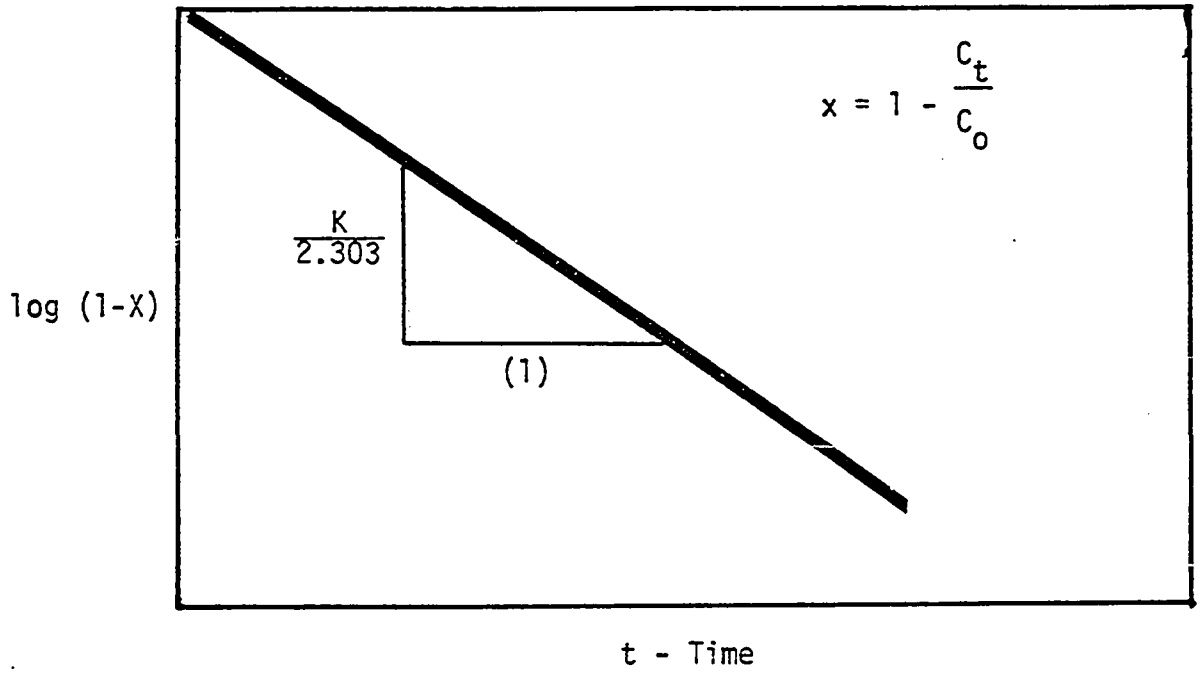


FIGURE 18. GRAPHICAL DETERMINATION OF RATE CONSTANTS FOR FIRST ORDER REACTIONS

d. Second Order Reactions

Second order reactions were bimolecular reactions where the rate of change in reactant or product concentration was proportional to the concentrations of two different species. Possible examples of second order reactions were the formation of sodium sulfate, and the reversion to sodium sulfide by reaction of sodium polysulfide and sodium sulfite. Second order reactions where the two reactant concentrations were equal could be represented mathematically as follows:

Reactant Concentration: (n = 2) $A + B \longrightarrow$ Products

$$-r = \frac{dC}{dt} = kC^n = kC^2 \qquad [92]$$

$$\int_{C_o}^{C_t} \frac{dC}{C^2} = kt \text{ and } \frac{1}{C_t} - \frac{1}{C_o} = kt \qquad [93]$$

Fractional Conversion:

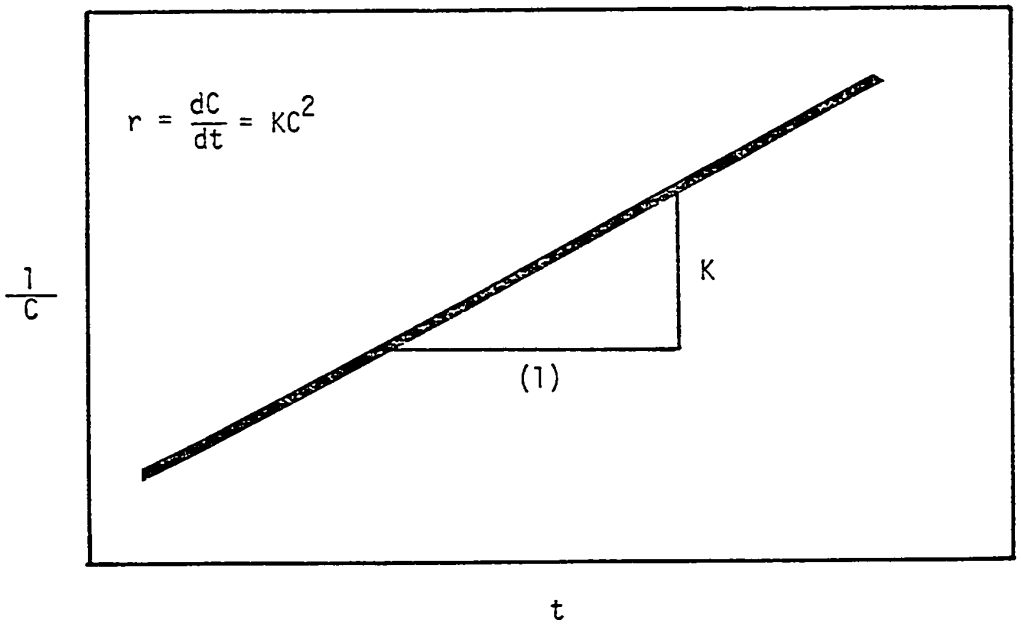
$$dC = C_o dX \text{ and } C = C_o (1 - X) \qquad [89]$$

$$\frac{dC}{dt} = k\, C_o\, (1 - X)^2 \qquad [94]$$

$$\frac{1}{C_t} - \frac{1}{C_o} = \frac{1}{C_o} \frac{X}{1 - X} = kt \qquad [95]$$

The reaction rate constant (k) could then be determined by linear plots of the reciprocal of reactant concentration (1/C) or fractional conversion ratio (X/1 - X) as functions of reaction time, as illustrated in Figure 19. If the reactant concentrations (C_A) and (C_B) were unequal it was then necessary to make a semilogarithmic plot of the ratio of reactant

a. Reactant Concentrations



b. Fractional Conversion

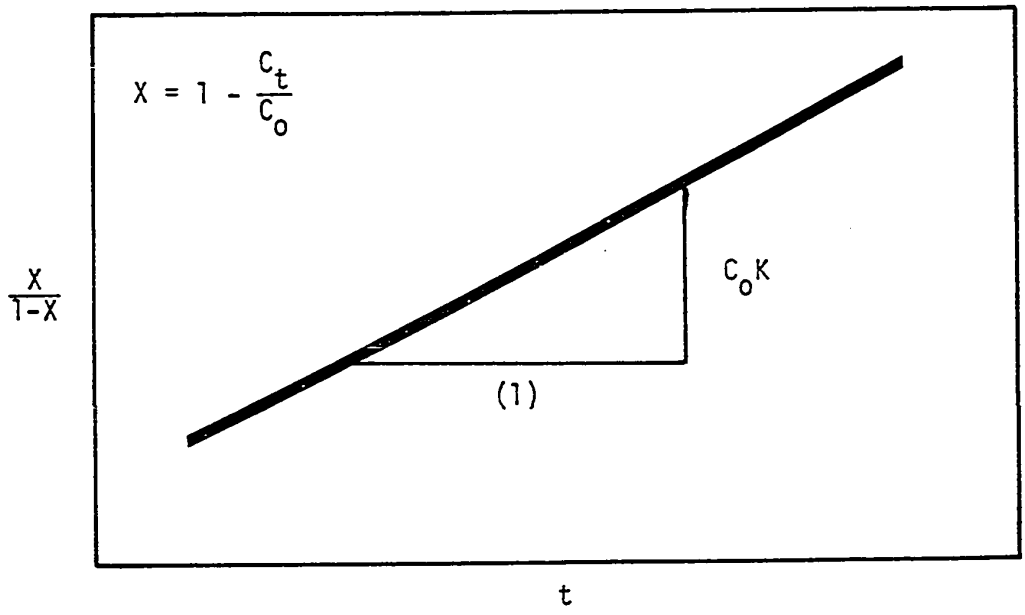


FIGURE 19. GRAPHICAL DETERMINATION OF RATE CONSTANTS FOR SECOND ORDER REACTIONS

concentrations (C_A/C_B) as a function of reaction time, as described by Levenspiel (158).

e. Temperature Dependence

The rates of chemical reactions have been observed to increase dramatically with increasing temperature where a temperature increase of 10°C would tend to double the reaction rates. Arrhenius' law (158) postulated the effect of temperature on reaction rate constant to be as follows:

$$k_T = k_o \, e^{-E_a/RT} \qquad [96]$$

k_T = Reaction rate constant at temperature T

k_o = Reaction rate constant at base temperature

E_a = Energy of activation in gram-calories per gram-mole.

R = Universal gas constant (1.98 calories per gram-mole-°K)

T = Absolute temperature in °K

A semilogarithmic plot of reaction rate constant (k) as a function of the reciprocal of temperature provided a means for determining the energy of activation (E) from the slope of the plot represented by (E/R). However, for reactions where chemical reaction was not rate-limiting, such as zero order reactions where mass transfer was limiting, the variation of reaction rate constant with temperature would not necessarily follow Arrhenius' relationship.

f. Reactant Half-Life

An alternative method for expressing the rates of chemical reactions instead of reaction rate constants was the use of half-lifes for reactants. Levenspiel (158) defined the half-life for a reactant as the time required for its concentration to be reduced to 50 percent of its original value, with a generalized definition as follows:

$$t_{1/2} = \frac{2^{n-1} - 1}{k\,(n-1)}\, C_o^{1-n} \qquad [97]$$

$t_{1/2}$ = Reactant half-life in seconds

k = Reaction rate constant in variable units

n = Order of the reaction

C_o = Initial reactant concentration in grams per liter.

For first-order irreversible reactions, the above expression was simplified to the following:

$$t_{1/2} = \frac{0.693}{k} \qquad [98]$$

The above expression was particularly suitable for expressing the rate of disappearance of sodium sulfide and mercaptide at low concentrations where the rate of the chemical reaction became limiting.

2. Design Equation

a. Material Balance

The concentration of chemical reactant in a steady state plug flow reactor would change with distance along a pipe, but remain constant with time at any given point. Levenspiel (158), plus Galeano and Amsden (103), derived the mass balance for a component "s" in the differential volume dV of the plug flow reactor flowing in time t illustrated in Figure 20 as follows:

$\text{Input}_s = \text{Output}_s + \text{Disappearance by Reaction}_s$

$$L(C_s)_o\, dt = L[(C_s)_o + dC_s]\, dt + (-r_s)dVdt \qquad [99]$$

L = Liquid flow rate in gallons per minute

C_{s_o} = Inlet concentration of "s" in pound-moles per gallon

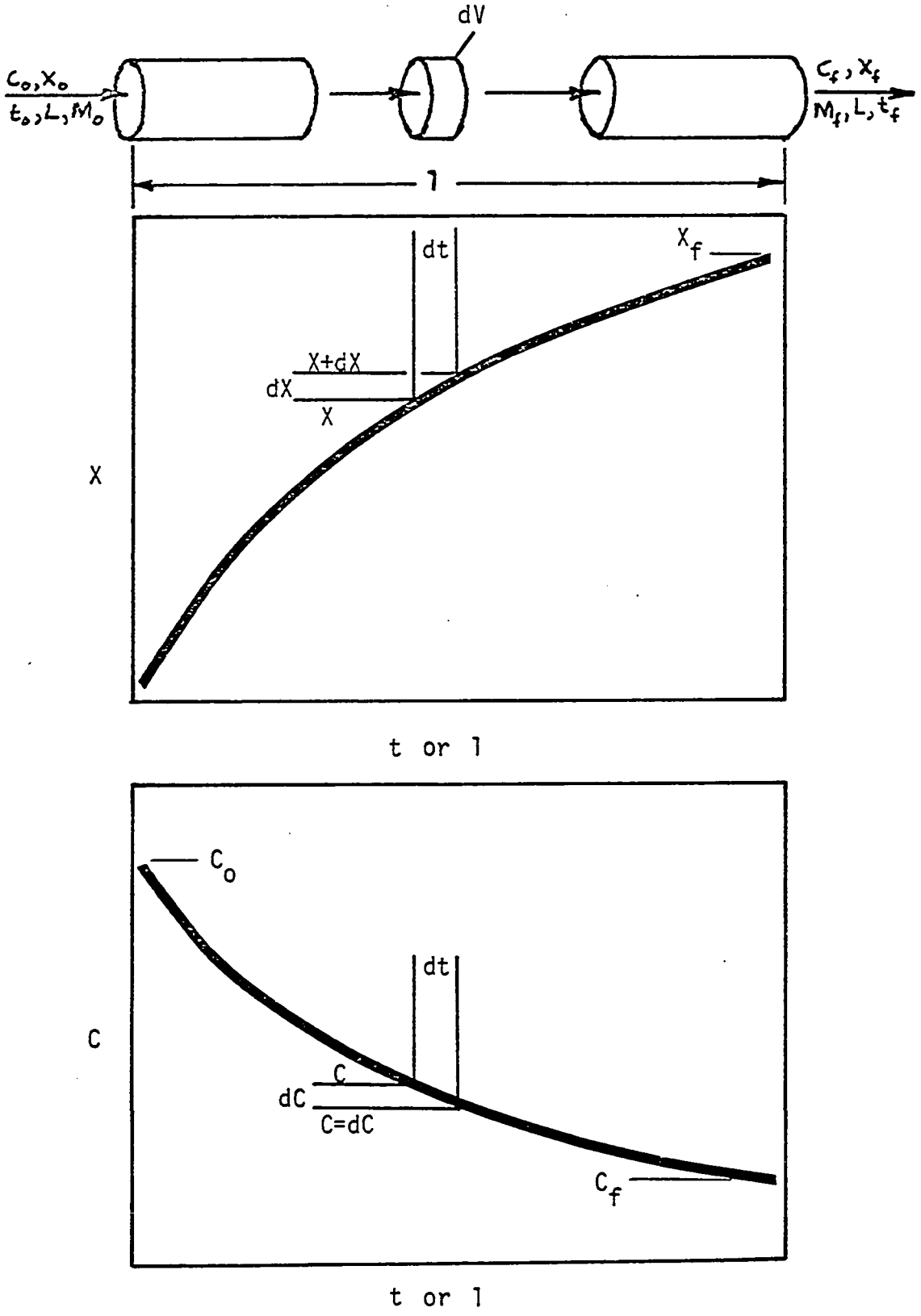


FIGURE 20. MASS BALANCE ACROSS A PLUG FLOW REACTOR

dC_s = Change in concentration of "s" across element dV in pound-moles per gallon

X_s = Fractional conversion of reactant "s."

r_s = Rate of disappearance of "s" in pound-moles per gallon per minute

t = Time in minutes

V = Volume in gallons

dV = Differential element of volume in gallons

By previous substitutions:

$$(C_{s_o})t\ dC_s = (C_s)_o(1-dX_s) \qquad [100]$$

$$dV = Ldt$$

$$-r_s = k(C_s)^n$$

$$L(C_{s_o})dt = L(C_{s_o})(1-X_s)dt + (-r_s)dVdt \qquad [101]$$

$$L(C_s)_o\ dX_s = (-r_s)dV = -(r_s)Ldt \qquad [102]$$

$$t = \int_o^t dt = (C_s)_o \int_o^{X_t} \frac{dX_s}{-r_s} = (C_s)_o \int_o^{X_t} \frac{dX_s}{K(C_s)^n} \qquad [103]$$

b. Retention Time

From the previous simplifying assumptions of constant reactor volume and no radial diffusion through the reactor boundaries, the above equation yields the following expressions for retention time required to achieve a given degree of conversion of reactant "s":

$$\text{Zero Order:}\quad t = \frac{(C_s)_o}{k_o}\ X_s = \frac{(C_s)_t - (C_s)_o}{k_o} \qquad [104]$$

First Order (Irreversible):

$$t = \frac{1}{k_1} \ln \frac{1}{1-X_s} = \frac{2.303}{k_1} \ln \frac{(C_s)_t}{(C_s)_o} \qquad [105]$$

Second Order (Irreversible, Equal Reactant Concentrations):

$$t = \frac{1}{k_2(C_s)_o} \frac{X_s}{1-X_s} = \frac{1}{k_2} \left[\frac{1}{C_t} - \frac{1}{C_o}\right] \qquad [106]$$

When a reaction proceeded through more than one reaction rate regime, the total retention time requirements (t_r) could be estimated as the summation of the individual retention times (t_i):

$$t_r = \sum_i t_i = t_1 + t_2 + \cdots + t_n \qquad [107]$$

The oxidation of sodium sulfide in black liquor proceeded in two successive reaction rate sequences of consecutive zero and first order reactions, where the total retention time was:

$$t_r = \sum_i t_i = t_{n=o} + t_{n=1} = \frac{(C_s)_1 - (C_s)_o}{k_o} + \frac{2.303}{k} \ln \frac{(C_s)_2}{(C_s)_1} \qquad [108]$$

c. Mathematical Model

Galeano and Amsden (103) proposed a mathematical model for describing the oxidation of sodium sulfide in weak black liquor with molecular oxygen in a plug flow reactor to facilitate the subsequent full-scale systems. Their reaction model employed the following simplifying assumptions: 1) first order reaction in sodium sulfide; 2) steady state conditions for liquid and gas flow rates, and sodium sulfide concentrations; 3) constant volume for the plug flow reactor; 4) no radial diffusion across the boundaries of the

confined reactor (157). From the mass balance listed in equation 99 the following expression could be written:

$$U_L A_p (C_{Na_2S})_i \, dt = UA_p \, [(C_{Na_2S}) + dC_{Na_2S}] \, dt + K(C_{Na\ S}) A_p dl dt \qquad [109]$$

U_L = Liquid velocity in feet per second

A_p = Cross-sectional area of pipe in square feet

l = Pipe length in feet

C_{Na_2S} = Sodium sulfide concentration in pound-moles per cubic foot

t = Reaction time in seconds

From the simplifying assumptions, the above equation was reduced to:

$$-UdC_{Na_2S} = k(C_{Na_2S}) \, dl \qquad [110]$$

Boundary conditions for the reactor were specified as follows:

Inlet: $A + l = 0$, $t = 0$: $C_{Na_2S} = (C_{Na_2S})_i = C_i$

Outlet: $A + l = 1$, $t = t$: $C_{Na_2S} = (C_{Na_2S})_o = C_o$

$$dl = U_L dt$$

By rearrangement and substitution of variables, equation 109 was integrated to:

$$\int_{C_i}^{C_o} \frac{dC_{Na\ S}}{C_{Na\ S}} = \frac{k}{U} \int_o^L dL = k \int_o^t dt \qquad [111]$$

$$\log \frac{C_o}{C_I} = - \frac{k}{2.303} t \qquad [112]$$

A value for the constant (k) was estimated from previous studies, and values calculated for sodium sulfide concentration ratio (C_o/C_i) as a measure of oxidation efficiency were compared to those observed in passage through 100 feet of tubular reactor, as listed in Table 16.

TABLE 16. COMPARISON OF OBSERVED AND CALCULATED VALUES FOR SODIUM SULFIDE CONCENTRATION RATIO IN A PLUG FLOW REACTOR (103).

Retention Time sec.	Inlet Na S gm/liter	Na_2S Concentration Ratio - C_o/C_i Observed	Predicted	Observed / Predicted
15.5	10.3	0.11	0.17	0.65
15.5	10.8	0.18	0.17	1.06
16.2	10.3	0.12	0.15	0.80
17.5	10.9	0.14	0.14	1.00
20.0	9.7	0.07	0.10	0.07
21.0	9.9	0.12	0.09	1.34
25.5	12.6	0.04	0.05	0.80
27.5	11.6	0.02	0.04	0.50
Average				0.85

Reactor Conditions: T = 200°F, S = 14% by weight, l = 100 feet

Results indicated that the observed values for sodium sulfide concentration ratio were lower than those predicted from the model by an average of about fifteen percent, so that oxidation efficiencies observed in the plug flow reactor section were greater than predicted. However, when the values for reaction rate constant (k) were extrapolated to the storage tank for extended retention times, the observed reductions in sodium sulfide concentrations were less than predicted. These findings pointed to the existing of more than one reaction rate regime governing the oxidation of sodium sulfide. The possibility for substantial error existed by overestimating oxidation efficiencies when assuming that the oxidation reaction was entirely first order in nature.

3. Previous Investigations

Early work by Bergstrom and Trobeck (49) indicated that the absorption of oxygen into black liquor occurred in more than one rate sequence. They found that sodium sulfide was initially oxidized before other constituents in the black liquor began exerting an oxygen demand. Wright (53) observed that the oxidation of sodium sulfide in black liquor proceeded in two distinct phases of oxygen absorption into black liquor followed by reaction with the sodium sulfide. Wright also observed that the rates of oxidation for both sodium sulfide and sodium mercaptide were accelerated by the presence of organic materials present in black liquor as compared to alkaline solutions of these salts alone.

a. Rate Expressions

Murray (148) was perhaps the first to extensively characterize the reaction rate regimes of sodium sulfide oxidation in black liquor by means of studies in a stirred tank reactor, using air as the source of oxygen. The rate of oxygen mass transfer into black liquor limited the rate of sodium sulfide oxidation at concentrations greater than approximately two grams per liter, while chemical reaction was rate-limiting at sodium sulfide concentrations below one gram per liter. The following semiempirical expression was used to account for the two-step nature of sodium sulfide oxidation in black liquor in completely-mixed stirred tank reactors:

$$\frac{d\,(C_{Na\,S})}{dt} = k\,[bP_{O_2} + C_{Na_2S}] \qquad [113]$$

Mass Transfer — Chemical Reaction

$$kt = 2.303 \log [bP_{O_2} + C_{Na_2S}] \qquad [114]$$

C_{Na_2S} = Sodium sulfide concentration in grams per liter

P_{O_2} = Oxygen partial pressure in atmospheres

b = Rate constant for oxygen absorption in grams Na_2S per liter per atmosphere

k = Overall reaction rate constant in reciprocal hours

t = Reaction time in hours

The term (bP_{O_2}) was predominant when oxygen mass transfer was rate-limiting while the second term was predominant when the chemical reaction of sodium sulfide was rate-limiting.

Ricca (97) used the previous relationship in equation 111 developed by Murray to determine the reaction rate constants for oxidation of sodium sulfide in black liquor with molecular oxygen. The rate of oxygen absorption into black liquor as represented by the term "bP_{O_2}" was substantially greater with molecular oxygen than atmospheric oxygen. However, the test results were directly applicable only to stirred tank reactors because the effects of turbulent diffusion in plug flow reactors would not be observed. Therefore, it was possible to substantially overestimate the retention time requirements to achieve a given degree of sodium sulfide oxidation during the mass transfer-limiting reaction rate regime in attempting to extrapolate the results of kinetics studies from completely mixed batch stirred tank reactors to continuous plug flow reactors (102).

Morgan and Murray (159) developed a somewhat more sophisticated semi-empirical expression to describe the oxidation of sodium sulfide in strong black liquor for stirred tank reactors as follows:

$$\frac{d\,(C_{Na_2S})}{dt} = \frac{k_1 k_2\, P_{O_2}\, (C_{Na_2S})}{k_1\, H_{O_2} + K\ (C_{Na_2S})} \qquad [115]$$

H_{O_2} = Henry's law constant for oxygen in atmospheres per mole fraction O_2

k_1 = Rate constant for Na_2S oxidation in oxygen mass transfer-limiting phase in mole fraction O_2-grams Na_2S per liter per atmosphere per hour

k_2 = Rate constant for Na_2S oxidation in chemical reaction limiting phase in reciprocal hours

P_{O_2} = Oxygen partial pressure in atmospheres

The zero order term in sodium sulfide was oxygen mass transfer-limited, and was predominant at sodium sulfide concentrations above one gram per liter:

$$k_2 (C_{Na_2S}) >> k_1 H_{O_2}$$

$$\frac{d (C_{Na_2S})}{dt} = k_1 P_{O_2} \qquad [116]$$

At sodium sulfide concentrations below one gram per liter, the first order reaction dependent on sodium sulfide concentration was rate-limiting:

$$k_1 H_{O_2} >> k_2 (C_{Na_2S})$$

$$\frac{d (C_{Na_2S})}{dt} = \frac{k_2 P_{O_2}}{H} (C_{Na_2S}) \qquad [117]$$

Morgan and Murray also observed that the rate of sodium sulfide oxidation increased with air flow rate and inlet sodium sulfide concentration, but decreased with retention time and black liquor height in the completely mixed tank (160). Harkness and Murray (145) developed an equation similar to equation 115 to describe the oxidation of sodium mercaptide in stirred tank reactors.

b. Aqueous Solutions

The oxidation of sulfide ion in aqueous solutions provided a useful comparison to black liquor. Cline and Richards (140) previously postulated

that the oxidation of extremely dilute concentrations of sodium sulfide in marine waters was a second order reaction with hydrosulfide (HS^-) ion the reactive species and substantial proportions of bisulfite (HSO_3^-) ion were formed, along with the virtual absence of elemental sulfur formation. Chen and Morris (161) made an extensive laboratory study of the oxidation of sodium sulfide with air in alkaline aqueous solutions using a batch stirred tank reactor and a Warburg oxygen absorption apparatus. They found that the rate of sodium sulfide oxidation increased with dissolved oxygen concentration, inlet sodium sulfide concentration, upon addition of organic phenolic or metallic catalysts, and in general with liquid pH. The rate of oxidation was found to decrease with increasing sodium thiosulfate concentration and the addition of inhibitors such as EDTA.

They observed that the reaction of bisulfite ion with elemental sulfur to form thiosulfate ion was favored as liquid pH increased, in agreement with work by Ricca (97) for black liquor. They postulated an empirical rate expression for the oxidation of sulfide ion with atmospheric oxygen for the pH range from 7.5 to 12.5 and sodium sulfide concentrations from 0.05 to 1.2 grams per liter.

$$\frac{d\,(C_s)}{dt} = k_A\,(C_s)(C_{O_2})\{1 + k_B\,[(C_s)/(O_2)]^{0.5}\} \qquad [118]$$

k_A, k_B = Specific rate parameters

C_s = Sulfide ion concentration in gram-moles per liter

C_{O_2} = Dissolved oxygen concentration in gram-moles per liter

The above equation would not be directly applicable to black liquor because dissolved oxygen would not normally exist in the free state in black liquor. The relation would be pertinent for the chemical reaction-limiting phase at low sodium sulfide concentrations.

c. Process Variables

Several factors might affect the rate of sodium sulfide oxidation with molecular oxygen in black liquor. Factors affecting the rate of absorption of oxygen into black liquor have been described in the previous section on mass transfer. Factors which could affect the rate of oxidation of sodium sulfide into black liquor included inlet sodium sulfide concentration, liquid pH, liquid temperature, oxygen partial pressure, and the type of wood species being pulped.

Morgan and Murray (160) previously observed that the rate of sodium sulfide oxidation in strong black liquor in an air sparged, completely mixed reactor increased with inlet sodium sulfide concentration in a logarithmic manner. The probable reason was the increasing influence of the oxygen mass transfer rate limiting step at increasing inlet concentrations. Murray (148) observed that the rate of sodium sulfide oxidation decreased upon addition of sodium thiosulfate, possibly because of decreased concentration driving force.

Alferova and Titova (78) observed that the initial rate of sodium sulfide oxidation in black liquor increased substantially in going from pH 12.2 to 12.8. Possible reasons were removal of sodium thiosulfate product by oxidation to sulfate to increase concentration driving force or increase in the catalytic effect of phenolic lignin by increased ionization of the acidic hydroxyl groups. Blosser and Cooper (73) observed that oxidation rates for hardwoods tended to be more rapid than for softwoods, possibly because of

greater catalytic effect on the initial sulfide oxidation reaction. Avrahami and Golding (142) found that the initial rate of sodium sulfide oxidation in alkaline solutions increased with liquid temperature, liquid pH, and oxygen partial pressure in the gas stream, in tests run for a batch reactor.

Murray (148) observed that the rate of sodium sulfide oxidation in black liquor was two to three times as fast as atmospheric oxygen in a stirred tank reactor. The maximum rate of sodium sulfide oxidation was found to occur at approximately 160°F (70°C), as shown in Figure 21.

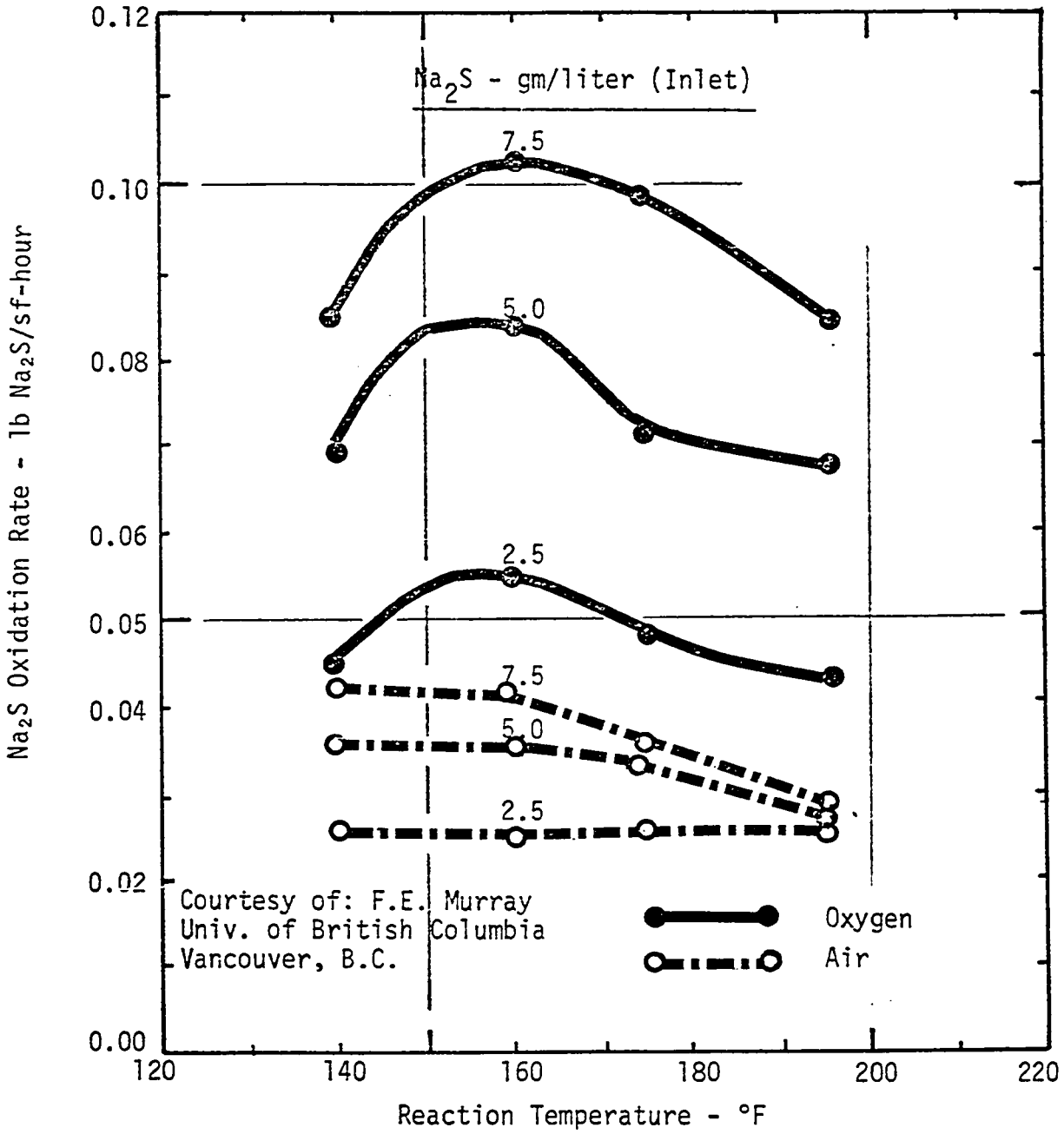


FIGURE 21. EFFECT OF TEMPERATURE ON Na_2S OXIDATION RATE WITH AIR AND OXYGEN IN WEAK BLACK LIQUOR (148).

V. EXPERIMENTAL APPROACH

A. Study Plan

The approach used for the present investigation of black liquor oxidation with molecular oxygen in a plug flow reactor was primarily experimental in nature. The four major stages of the experimental work were preliminary laboratory studies, mass transfer studies, pilot plant construction, and pilot plant operation. Results of these experiments were to be used to develop design criteria for subsequent construction of full scale systems, and to make projections of economic feasibility for use of the technique at Kraft pulp mills.

1. Preliminary Laboratory Studies

The initial phase of the study involved investigations of the rate of oxygen absorption into black liquor, and the rate of oxidation of sodium sulfide and sodium mercaptide in black liquor. The initial study of oxygen absorption was made in a variable volume, constant pressure, batch system to provide information regarding the effect of retention time on changes in the rate of oxygen absorption into black liquor. Additional information regarding the kinetics of oxygen absorption into black liquor was provided by means of a variable pressure, constant volume, batch system similar to the one previously described. The rate of oxidation of sodium sulfide and sodium mercaptide in black liquor with molecular oxygen was investigated in a completely mixed batch reaction. The purposes were to provide information on storage tank requirements for high degree oxidation and to provide a comparison to results obtained in the plug flow reactor. An additional reason was to provide familiarity with analytical techniques for sodium sulfide and mercaptide in black liquor.

2. Mass Transfer Studies

The second major phase of the research project was to determine conditions favorable to effective mass transfer of gaseous oxygen into the liquid phase in a plug flow reactor configuration. The investigation involved considerations of both gas absorption into liquids and two phase gas-liquid flow. The approach taken was to study the dispersion patterns of oxygen into water in a transparent Acrylic plastic pipe by visual observations and high speed photography studies. Water was chosen because of its transparency and availability, as it was virtually impossible to see gas bubble dispersions in the highly colored black liquor. Two phase gas-liquid flow configurations and, if applicable, oxygen gas bubble sizes were to be observed in terms of gas and liquid flow rates, tube diameters, and the method of oxygen introduction. Two phase flow configurations and oxygen bubble diameters could then be correlated to comparable conditions of liquid Reynolds number and other parameters with black liquor in plug flow reactors to facilitate the subsequent design of the oxygen introduction system in the pilot scale reaction system.

3. Pilot Plant Construction

The third step in the research was the construction of the pilot scale reactor for black liquor oxidation with molecular oxygen. Test results from the mass transfer studies were used for the design of the plug flow reactor section of the pilot scale reaction system. Results from the batch oxidation studies were used to provide information regarding the retention time requirements for storage tank facilities to achieve high degrees of oxidation of sodium sulfide and sodium mercaptide. Equipment was then obtained and the pilot plant was then constructed so that the necessary experiments could be performed. Equipment requiring special fabrication, such as storage tanks, heat exchangers, and support racks, was then constructed in modular form to

facilitate ease of assembly and disassembly. Periodic modifications in the pilot plant were made as the studies progressed for different experiments.

4. Pilot Scale Studies

A number of studies were made following construction of the pilot scale reactor on both weak and strong black liquor. The first set of experiments were preliminary in nature, and were made to determine the general reaction pattern of oxidation for sodium sulfide and sodium mercaptide in both weak and strong black liquor, along with their reaction products. These tests also facilitated making any modifications in the pilot scale reactor design or arrangement, and also to develop familiarity with analytical techniques. Subsequent tests were then made for weak liquor relating to both mass transfer and chemistry-related phenomena. Tests on strong black liquor were then made in terms of both inlet sodium sulfide concentration and contactor configuration. Special studies were also to be made regarding sulfate formation, oxygen utilization efficiency, lignin oxidation, and tall oil recovery.

a. Weak Black Liquor

The tests with weak black liquor provided the major portion of the experimental work of the present research because of the potential applicability and the ease of analyses. Initial studies of weak black liquor oxidation with molecular oxygen involved determination of pressure drops during two phase gas-liquid flow, and the efficiency of oxygen absorption as functions of liquid and gas flow rates in the pilot scale reactor. The efficiency of oxygen mass transfer into weak black liquor was studied by noting the respective initial rates of sodium sulfide oxidation upon making changes in the following variables: 1) liquid Reynolds number; 2) total oxygen pressure; 3) oxygen partial pressure; 4) liquid temperature. The effect of chemistry-related phenomena on the relative rates of sodium sulfide oxidation was observed by noting

changes in the following variables: 1) liquid temperature; 2) liquid pH; 3) sodium thiosulfate concentration; 4) liquid retention time.

b. Strong Black Liquor

The oxidation of strong black liquor with molecular oxygen in a plug flow reactor was also a matter of considerable interest during the research project. Major problems with strong black liquor oxidation were difficulties in obtaining effective oxygen mass transfer and performing accurate analyses in the highly concentrated and viscous liquid. Studies were made of strong black liquor oxidation at two different ranges of inlet sodium sulfide concentration: 1) high inlet sodium sulfide concentrations expected during full scale use of strong black liquor oxidation alone; 2) low inlet sodium sulfide concentrations expected with strong liquor polishing to counteract reversion of sodium sulfide from oxidized weak black liquor in a two stage system. Studies were also to be made of the effect of certain changes in the method of oxygen introduction to black liquor with three different contactor configurations.

c. Special Studies

Several special studies were made regarding black liquor oxidation with molecular oxygen which related to either chemistry or economics. The studies relating to chemistry were as follows: 1) characterization of the reaction products of the oxidation of sodium sulfide, in particular sodium polysulfide, sodium thiosulfate, sodium sulfite, and sodium sulfate; 2) determination of the effect of extended storage times on the reversion of sodium sulfide; 3) making a total sulfur balance to determine the extent of analytical errors. Studies of chemical phenomena which also had economic implications were as follows: 1) variables affecting the formation of sodium sulfate; 2) the degree of lignin oxidation in both weak and strong black liquor; 3) the efficiency of oxygen utilization during both weak and strong black liquor

oxidation; 4) the effect of black liquor oxidation on tall oil recovery.

B. Test Equipment

There were several different sets of equipment to be used during the experimental studies of oxygen absorption into black liquor. The first system was a laboratory setup to measure the absorption of oxygen into solutions of black liquor. The second system was used to make studies of the respective rates of sodium sulfide and sodium mercaptide oxidation in black liquor on a batch basis. The third system was a transparent plastic pipe through which oxygen was introduced into water in a cocurrent flow arrangement. It was used for studies of the respective two phase gas-liquid flow configurations and, where applicable, to determine oxygen bubble sizes in the liquid to facilitate the subsequent design of the plug flow reactor. The fourth system was the pilot plant in which the oxidation of sodium sulfide in black liquor was to be carried out. It employed a two-stage reaction system in which the initial oxygen absorption took place in the plug flow tubular reactor section and the subsequent final oxygen conversion occurred in a storage tank with extended retention time.

1. Oxygen Absorption System

a. Purpose

The effect of reaction time on the rate of oxygen absorption into black liquor was determined by means of studies using two different types of batch reactors. The information obtained provided information regarding changes in the rate of oxygen absorption as indicators of the kinetics of black liquor oxidation in different rate regimes.

b. Equipment

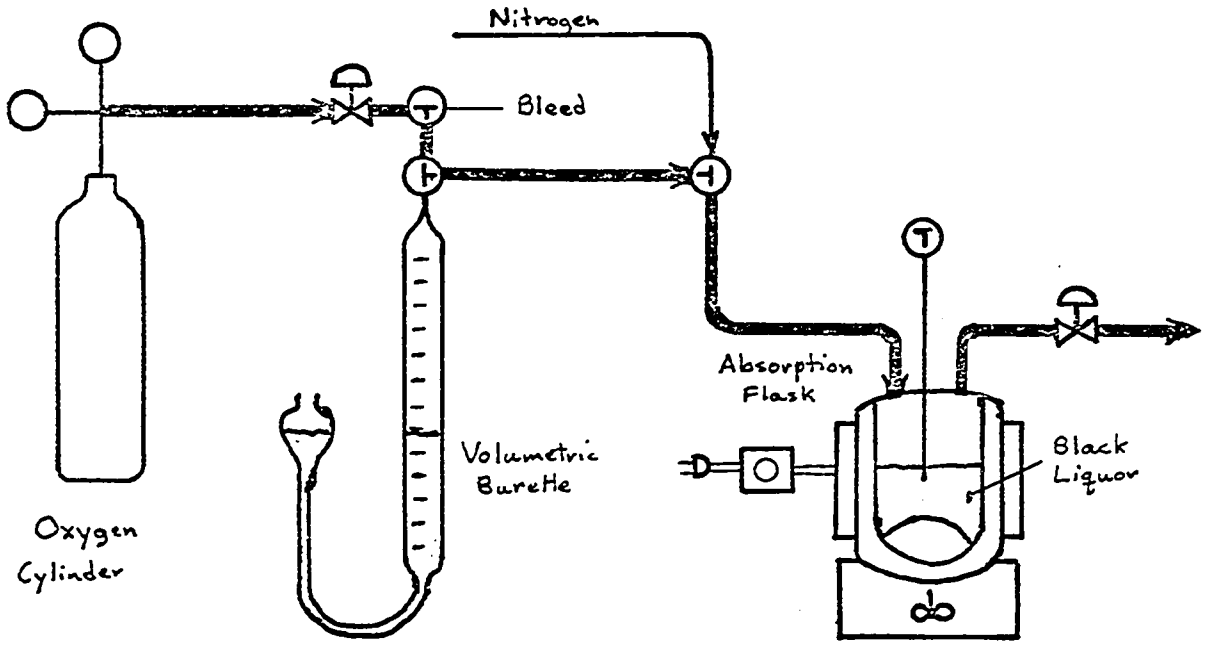
The absorption of oxygen into black liquor was carried out in two different types of batch reactors. One system was a variable volume, constant

pressure, batch reactor where the oxygen absorption was carried out in a sealed, straight-sided, round bottom, 200 milliliter absorption flask. The flask could be heated over the range from 25 to 100°C by means of an externally-located electrical heating mantle. The liquid in the flask was kept well-stirred by means of an internally located magnetic stirring bar, whose rotational speed was varied by means of an externally located rheostat control. The oxygen was fed from a pressurized cylinder of the pure gas into a graduated gas burette containing a colored liquid for level control, and then to the absorption flask. A similar system employing a constant volume, variable pressure device for oxygen absorption into black liquor was also employed. Both systems have been illustrated in Figure 22.

b. Procedure

For the constant pressure, variable volume system, the oxygen was withdrawn from a pressurized cylinder of the high purity gas (99.5 percent) through a 250 milliliter graduated gas burette containing a colored liquid against which the gas was hydrostatically balanced at essentially atmospheric pressure. Following evacuation and purging of its contents with oxygen, 100 milliliters of black liquor was added to the flask, and oxygen fed from the gas burette to the absorption flask. The amount of oxygen absorbed into the black liquor the volume of gas displaced by the colored fluid in the gas burette as a function of time by volume readings at regular intervals during a four hour period. A similar procedure was followed with the constant volume, variable pressure system except that one liter of black liquor was used as the sample, and the indicator of oxygen consumption was the reduction in total oxygen pressure in the autoclave with time. The effect of reaction time on the changes in oxygen absorption rate as possible indicators of different reaction regimes was noted from variations in the rate of oxygen consumed by the black liquor per unit

a. Constant Pressure System



b. Constant Volume System

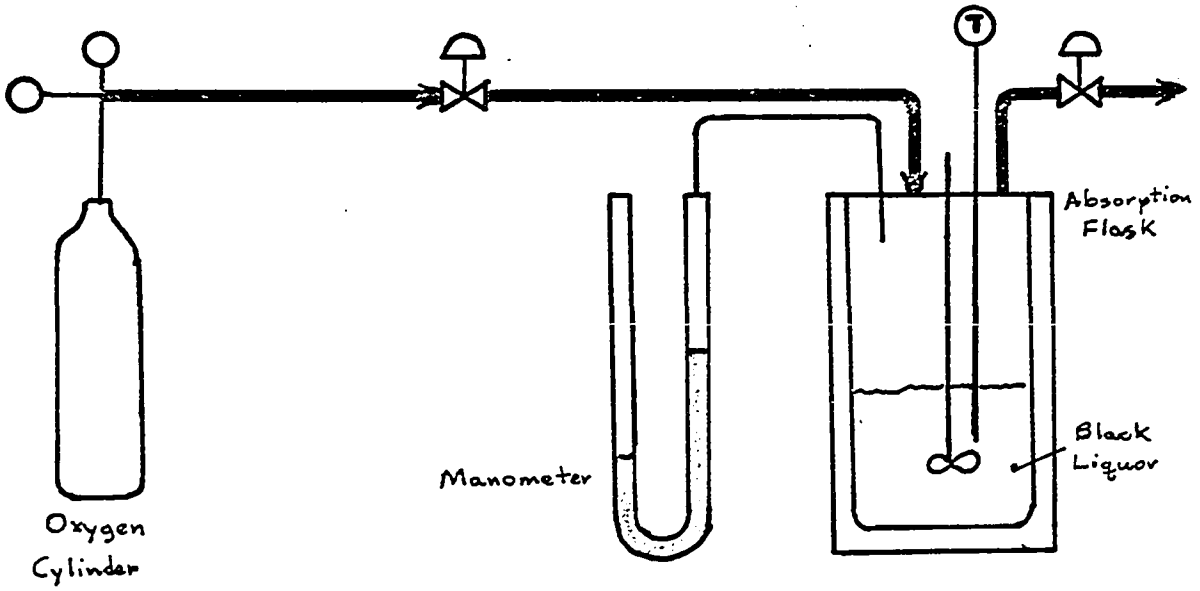


FIGURE 22. BATCH SYSTEMS FOR MEASURING OXYGEN ABSORPTION INTO WEAK BLACK LIQUOR.

time.

2. Batch Oxidation System

a. Purpose

The effect of retention time on the respective oxidation rates of sodium sulfide and sodium mercaptide in black liquor with molecular oxygen was studied by a series of tests in a batch oxidation reactor. The purposes of the tests were to provide background data on the respective oxidation rates of sodium sulfide and sodium mercaptide in black liquor. The information obtained would be used to provide design information regarding liquor storage tank retention time requirements necessary for achieving high degrees of sodium sulfide oxidation at concentrations below 0.1 grams per liter. An additional reason was to provide comparative Kinetics data regarding respective oxidation rates of sodium sulfide and sodium mercaptide in black liquor with molecular oxygen between batch, completely mixed reactors and plug flow reactors.

b. System

The system used for black liquor oxidation employed a 250 milliliter tall form cylindrical reaction bottle for batch oxidation of the liquid phase with a continuous flow gaseous phase. Weak black liquor from the inlet line to the multiple effect evaporators was collected in a two liter glass bottle with a side tap and completely filled and stoppered to inhibit air oxidation. A sample of known volume of black liquor was displaced from the collection bottle through the side tap by displacement with nitrogen, and placed in the reaction bottle. Oxygen gas was introduced at a metered constant rate into the black liquor through a cylindrical porous fritted gas dispersion tube located near the bottom of the reaction bottle. The excess foam generated was removed by a suction tube located immediately above the liquid surface and the unabsorbed oxygen removed through the exhaust vent at the top of the reaction bottle, as

shown in Figure 23.

c. Procedure

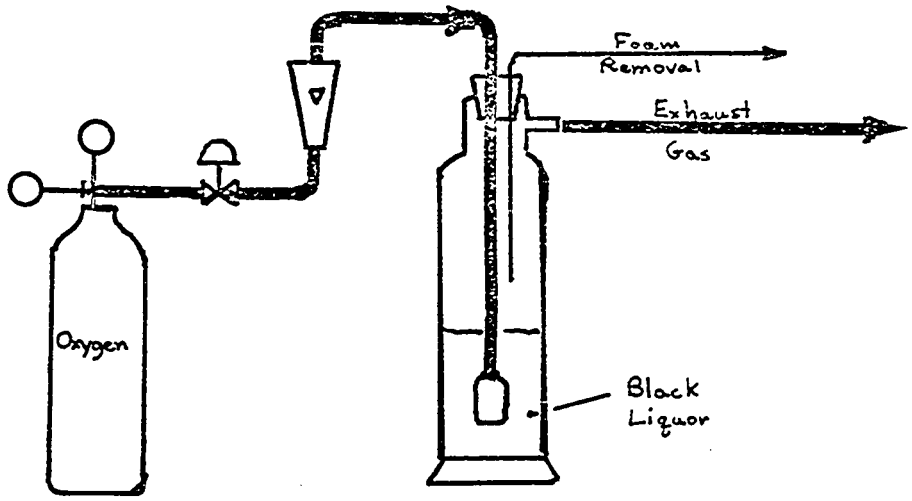
The procedure used in performing the batch oxidation studies involved placing successive 100 milliliter samples of weak black liquor into the reaction bottle. The reaction bottle was maintained at a constant elevated temperature by placing in a constant temperature bath. The oxygen gas was then fed into the black liquor at a constant rate of approximately three liters per minute for given time intervals ranging from one to twenty minutes. The samples were analyzed for sodium sulfide and sodium mercaptide at the beginning and end of each test to determine the extent of oxidation as a function of reaction time. Results could then be compared to those obtained with the plug flow reactor system.

3. Mass Transfer Studies

a. Purpose

It was necessary to simulate the conditions favorable to maximum rate of oxygen mass transfer into a transparent liquid in cocurrent two phase gas-liquid flow to facilitate the subsequent design of a plug flow reactor for black liquor oxidation. One major concern was to determine the gas and liquid flow conditions for particular tube diameters favorable to either froth or bubble regimes of two phase gas-liquid flow. A second concern was to establish the respective gas and liquid flow conditions favorable to minimum oxygen bubble size to facilitate maximum gas-liquid interfacial contact area. Attempts were to be made to correlate two phase flow regimes and oxygen bubble sizes in terms of liquid Reynolds numbers, gas flow rates per unit cross-sectional areas, pipe diameters, and method of oxygen introduction into the liquid phase. Water was used in place of black liquor because it was not possible to make visual observations of two phase gas-liquid flow patterns in the dark nontransparent

a. Oxidation



b. Collection

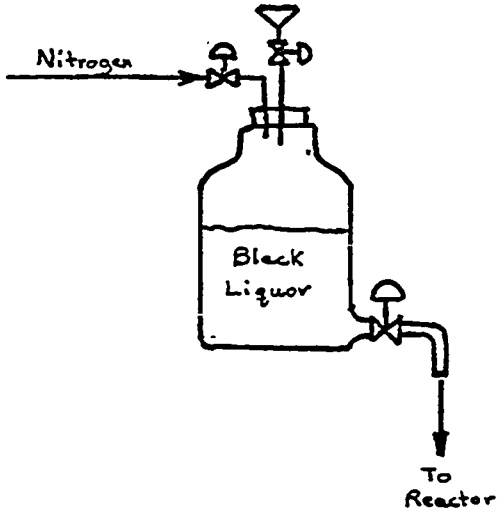


FIGURE 23. BATCH REACTOR FOR BLACK LIQUOR OXIDATION.

liquid.

b. System

The system used to simulate the plug flow reactor used for oxygen absorption into black liquor employed a transparent pipe section where the respective two phase gas-liquid flow and oxygen absorption could be observed. Oxygen gas was introduced from a pressurized cylinder into the liquid through an axial cylindrical porous glass dispersion tube located at the upstream end of the transparent plastic tube. Hot or cold water was introduced to the system upstream of the point of oxygen introduction, where the gas-liquid mixture flowed cocurrently through the transparent tube section and drained into the sink. Transparent six foot sections of acrylic plastic pipe of 3/8 inch, 1/2 inch, 3/4 inch, and one inch inside diameters were used in the studies, where different flow conditions were obtained by subsequent variations in respective oxygen and water flow rate. The system has been illustrated in Figure 24.

c. Procedure

The experimental procedure involved taking a series of visual observations and high speed photographs of flow configurations at particular gas and liquid flow rates at different tube diameters. Photographs of the respective bubble sizes in the transparent pipe were taken at a distance approximately 18 inches downstream of the point of oxygen introduction along the transparent tube with the aid of a strobe light and a black background. Oxygen bubble size could be estimated from the photographs at particular conditions by placing a reference dimension within the photographic field, subject to limitations imposed by corners and film resolution limits at high liquid velocities. Two phase gas-liquid flow configurations and oxygen bubble sizes for bubble or froth flow regimes could then be ascertained by observations from the photographs.

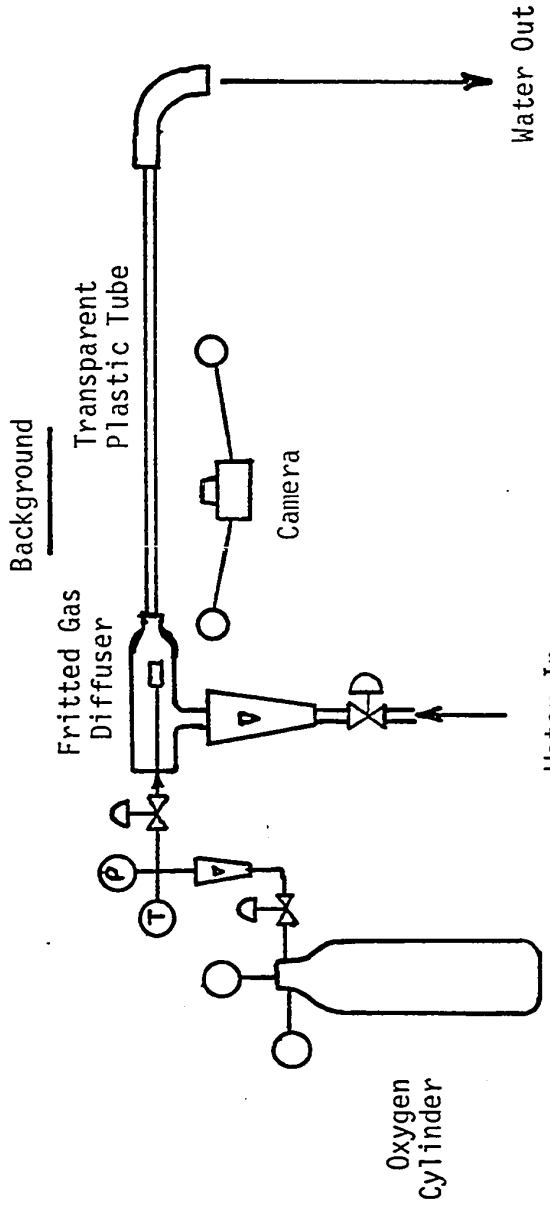


FIGURE 24. TRANSPARENT PIPE SYSTEM FOR OXYGEN-WATER STUDIES

4. Pilot Scale Reactor

a. Purpose

The pilot scale reactor was designed to perform the studies where weak or strong black liquor was oxidized with molecular oxygen. The system was designed to simulate Kraft pulp mill operating conditions on a small scale, where the results could be extrapolated to the subsequent design of full scale installations. Studies were to be made to determine the respective reaction rate constants for the oxidation of sodium sulfide and sodium mercaptide in weak and strong black liquor, plus chemistry studies of reaction products and competing side reactions as functions of reaction time.

b. Overall System

The pilot scale reaction system used for oxidation of weak or strong black liquor with molecular oxygen employed a two stage system. The first stage was a plug flow pipeline reactor for oxygen mass transfer into the liquid phase. It was followed in series by a black liquor storage tank to provide sufficient retention time for the chemical reactions to occur. The initial plug flow reactor section was designed to provide for effective oxygen mass transfer into the black liquor, where the oxidation reactions would subsequently be carried to completion in the completely mixed storage tank section. Black liquor was drawn from either the weak liquor line immediately upstream of the multiple effect evaporators at approximately 17 percent solids and 180°F, or from the strong liquor line at the downstream end of the multiple effect evaporators upstream of the storage tank at 50 percent solids and 225°F. Following the oxidation tests, the black liquor could either be discharged to the mill sewer system, or be returned to the chemical recovery system by pumping into the strong black liquor storage tank. A schematic flow diagram of the pilot plant for oxidation of black liquor with molecular

oxygen has been illustrated in Figure 25.

c. Inlet Section

The inlet section of the pilot scale reactor consisted of the systems for introducing weak or strong black liquor as well as oxygen gas to the plug flow reaction system. Provisions were also made to modify the conditions of the incoming black liquor in terms of temperature, solids concentration, or by chemical addition. The oxygen gas inlet system consisted of taking the gas from pressurized cylinders and passing it through a rotameter for volumetric flow measurements, valves for controlling the gas flow rates, plus temperature and pressure gauges to measure inlet gas flow conditions, as shown in Plate III and Figure 26. It was particularly important to locate a valve on the oxygen inlet line immediately upstream of the point of introduction to the liquid to minimize the possibility of black liquor leakage into the oxygen rotameter. The oxygen was introduced to the black liquor through an axially located cylindrical fritted porous glass dispersion tube, where the tube was held in place by a compression fitting to minimize the possibility of leakage.

Black liquor was withdrawn from adjacent weak or strong liquor lines and allowed to flow into the pilot scale reactor by gravity flow. Black liquor flow rates above four gallons per minute for weak liquor and two gallons per minute for strong liquor required the use of a stainless steel centrifugal pump. The pump was mounted on top of a 55 gallon barrel which served as a storage tank, as shown in Plate IV. The pump could be connected to or disconnected from the inlet system by a series of pipe unions, as shown in Plate V. Chemicals such as sodium hydroxide, hydrochloric acid, or sodium thiosulfate could be added to the black liquor through the pump suction line by means of piping from the reagent storage bottle through a rotometer and associated valving. The black liquor could also be passed through a multiple pass heat

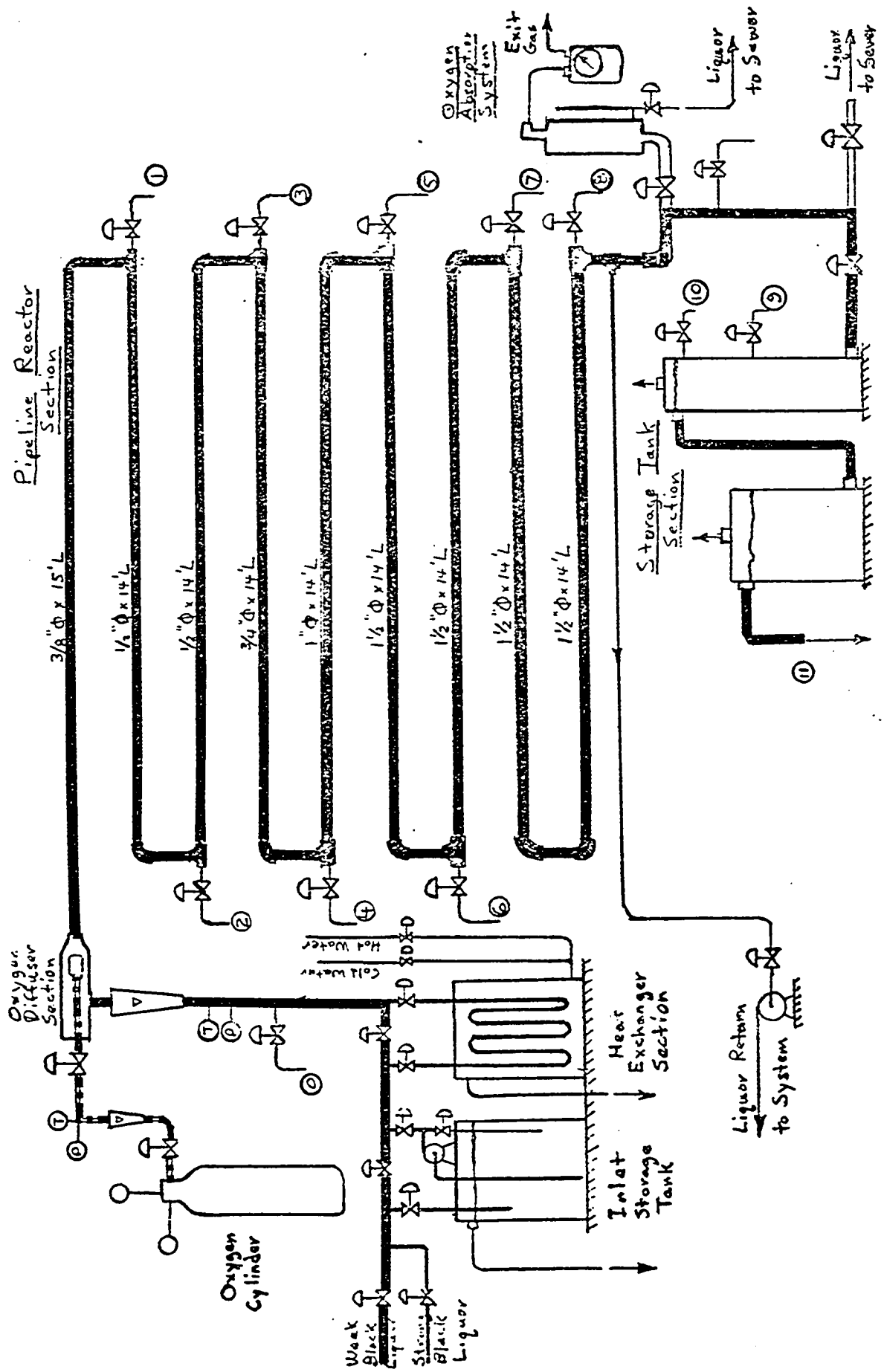


FIGURE 25. PILOT SCALE PLUG FLOW REACTOR FOR BLACK LIQUOR OXIDATION.

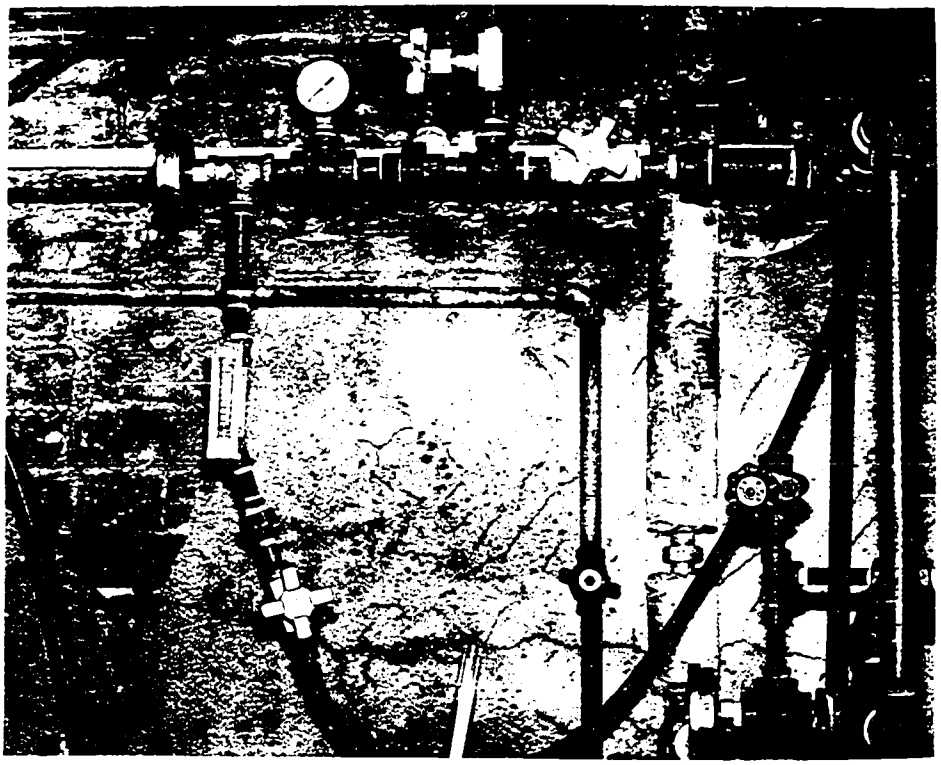


PLATE III. OXYGEN GAS FLOW INLET SYSTEM.

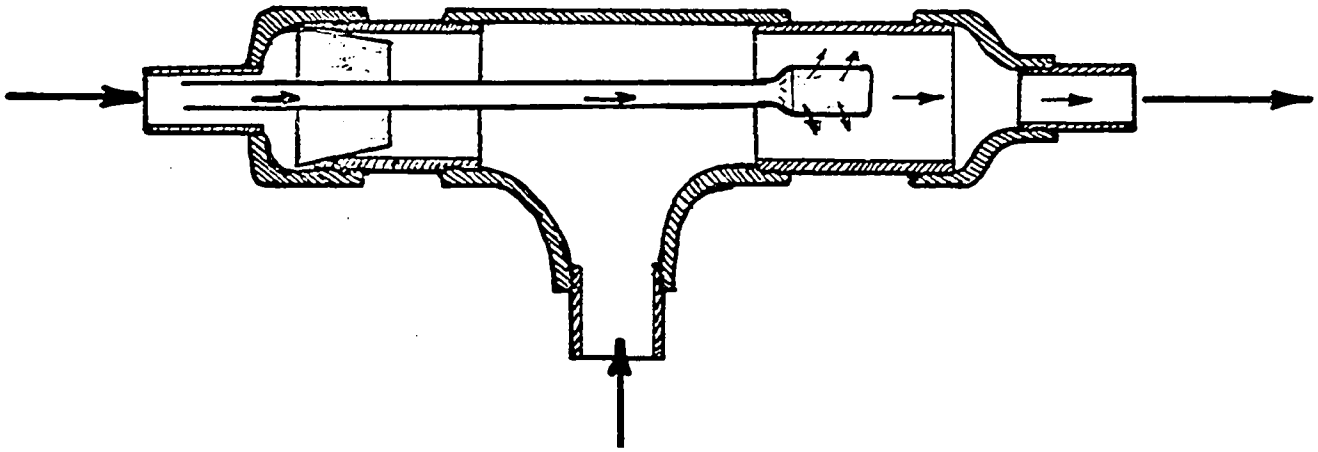


FIGURE 26. DETAILS OF OXYGEN INJECTION SYSTEM.

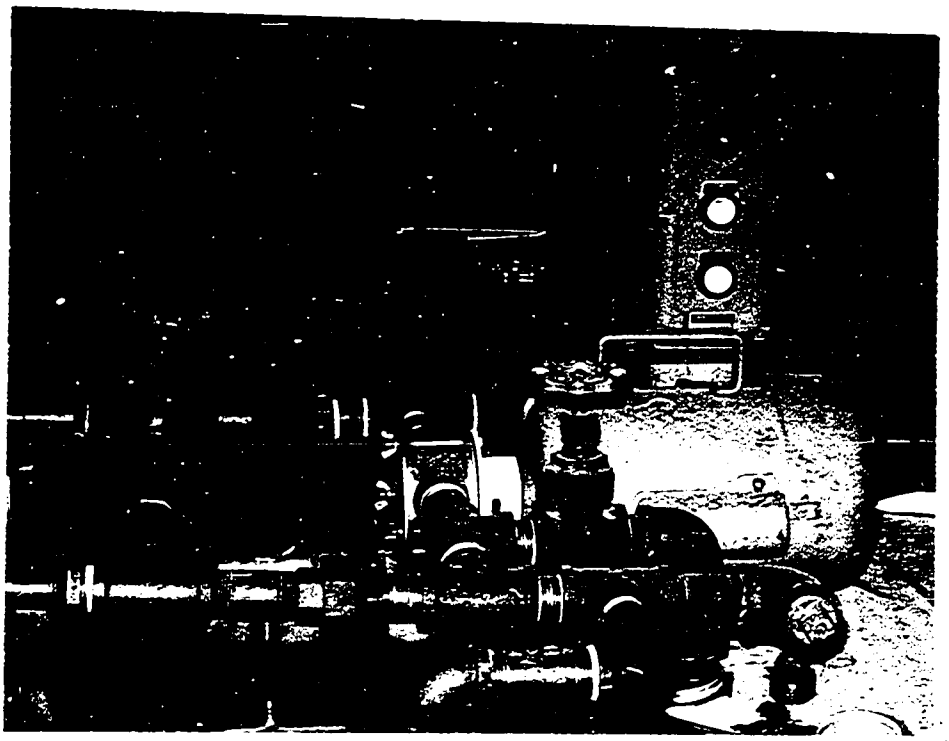


PLATE IV. PIPING FOR BLACK LIQUOR PUMP.

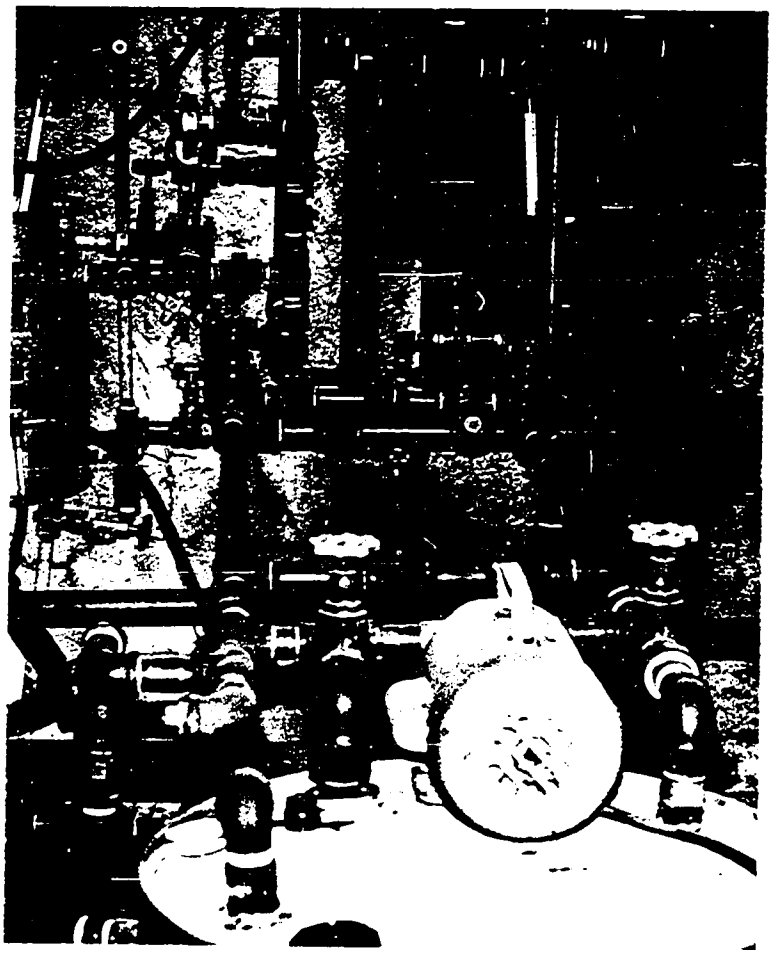


PLATE V. INLET PIPING FOR PLUG FLOW REACTOR.

exchanger employing 16 consequtive 30 inch passes of one inch pipe mounted in an open top 55 gallon barrel, as shown in Plate VI. Heating or cooling was provided by addition of hot or cold water to the barrel in which the pyses were housed. Black liquor flow rate was controlled by a series of steel gate valves, and the flow rate measured by a glass rotameter with a stainless steel float. All piping and fittings in the system were of mild steel construction. Sampling valves existed to facilitate taking of black liquor samples.

d. Plug Flow Reactor

The plug flow reactor consisted of the oxygen dispersion section, the telescopic pipeline section, and provisions for taking liquid samples. Oxygen was introduced to the black liquor through a coarse grade (40 to 60 micron pore size) cylindrical porous glass dispersion tube axially mounted in a 1 1/4 inch nominal diameter tee section, where the black liquor was introduced immediately upstream in a radial direction. For weak black liquor where oxygen mass transfer problems were minimal, the oxygen-black liquor mixture then flowed cocurrently in horizontal flow into a fifteen foot section of 3/8 or 1/2 nominal diameter pipe. The black liquor then flowed through a horizontal series of telescopically increasing diameters of 1/2, 3/4, and 1 1/2 inches, respectively, where each fourteen foot pipe section was connected by a double elbow union pipe section as shown in Plate VII. It was necessary to restrict the lengths of the pipe passes because of the restraints imposed by the room size and the necessity for not interfering with mill operating personnel. The black liquor then flowed to the storage tank section following the last pipe section of the plug flow reactor.

It was necessary to modify the system for injecting oxygen into strong black liquor because of the difficulties involved in achieving effective oxygen transfer into the highly viscous liquid. The modified system employed a

PLATE VI. DETAILS OF MULTIPLE PASS HEAT EXCHANGER.

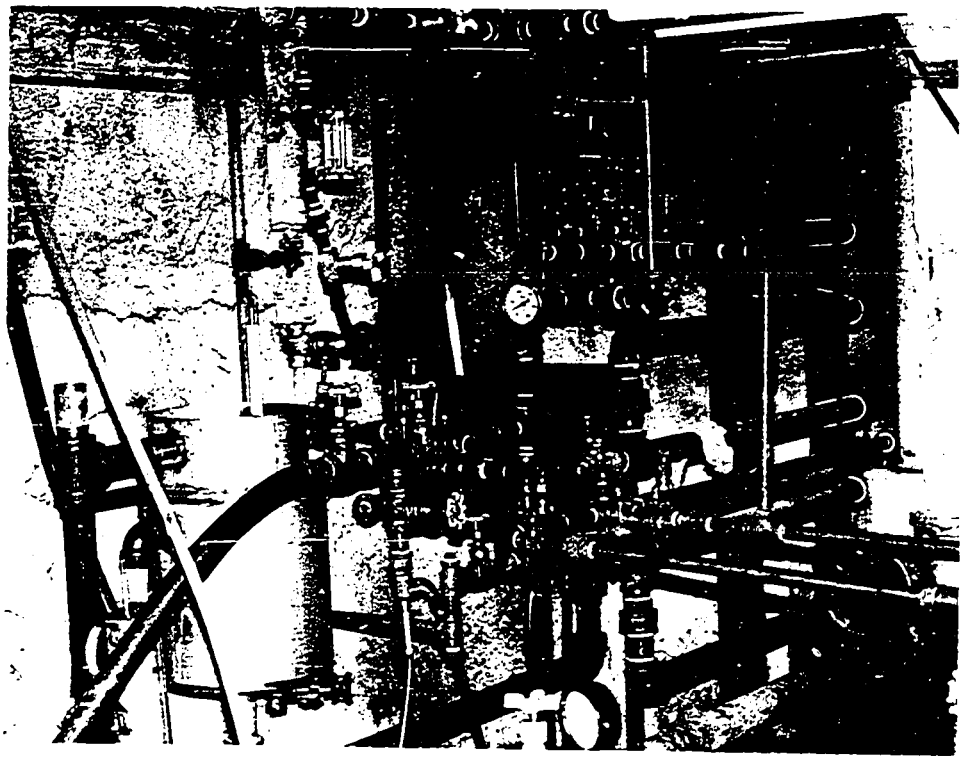


PLATE VII. SIDE VIEW OF PLUG FLOW REACTOR INLET.

series of expansion chambers following introduction of the oxygen to gas-liquid interfacial contact area, turbulence and mixing, and additional retention time. The device employed a series of 2 1/2 inch pipe sections connected by 1/2 inches short pipe nipples to promote turbulence. The contact was mounted in a vertical downflow configuration to facilitate gas bubble "holdup" with additional retention time. Oxygen was introduced either through the fritted glass diffuser upstream of the contactor or through a series of four nozzles located on the inlet of the first expansion section. Following the downflow expansion section, the liquid then flowed upward through a two inch vertical flow section to provide additional retention time. The system has been illustrated in Figure 27.

e. Storage Tank

The high efficiency oxidation of sodium sulfide and mercaptide in black liquor required liquid retention times between five and sixty minutes for the reactions to proceed to completion. Major operating variables were liquid retention time and liquor height in the storage tank section. The system used employed two storage tanks which could be operated in either a series or parallel arrangement, as illustrated in Figure 28. The black liquor flowed from the plug flow reactor, where a side stop line allowed the volumetric flow rate to be determined by collection of measured liquid volumes during observed time intervals. The black liquor then flowed to the tall storage tank where any unabsorbed oxygen and the black liquor flowed cocurrently upward through the narrow cylindrical tank. A tube projecting into the black liquor with holes on the underside provided for additional dispersion of any unabsorbed oxygen. The black liquor could then flow to a 55 gallon barrel storage tank where the liquid was introduced through the bottom and flowed out through a side tap at

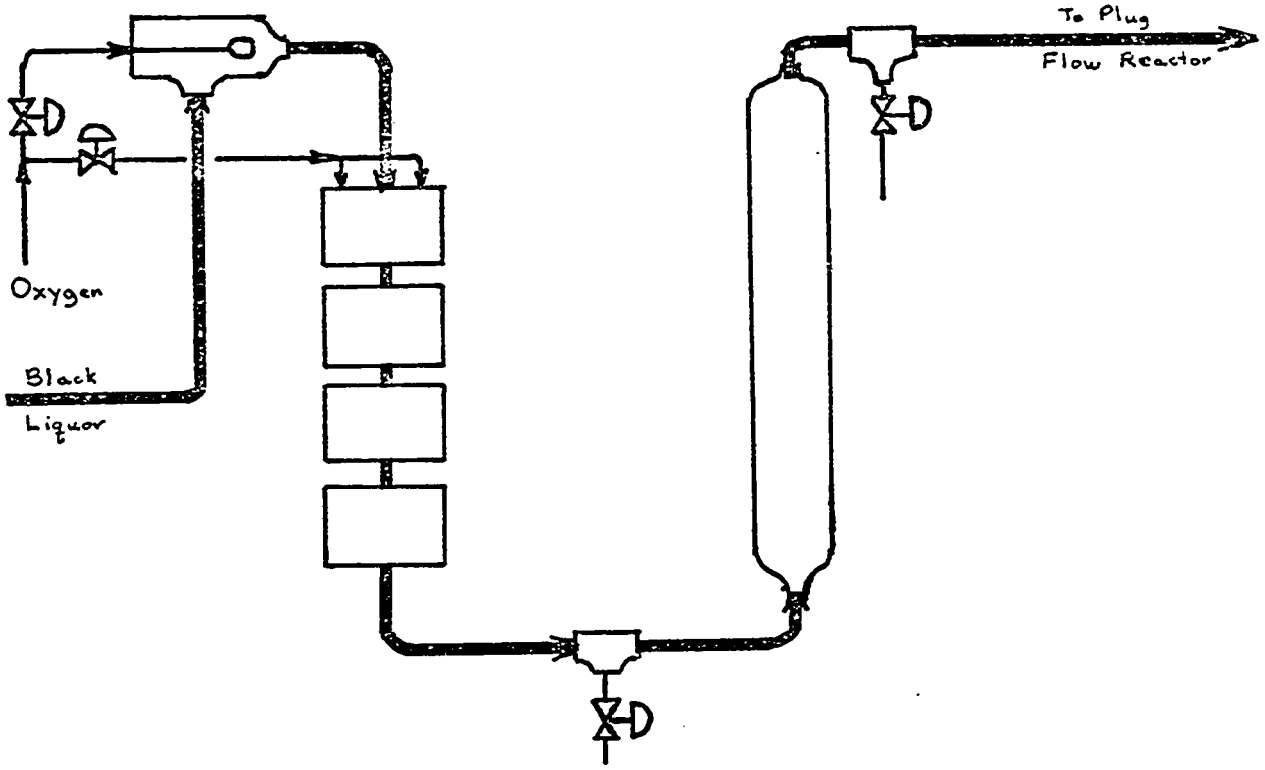


FIGURE 27. VERTICAL DOWNFLOW CONTACTOR FOR STRONG BLACK LIQUOR OXIDATION WITH OXYGEN.

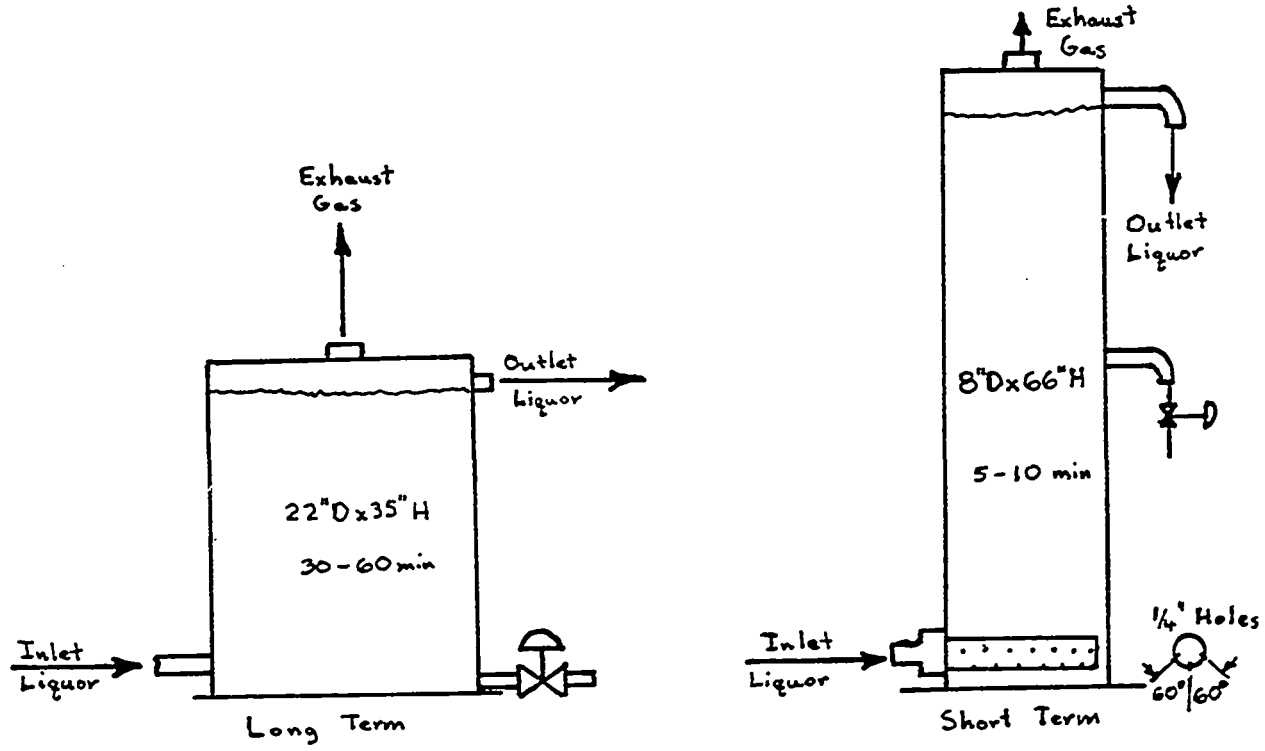


FIGURE 28. STORAGE TANKS FOR PILOT SCALE REACTOR.

top. The black liquor could then flow either to the mill sewer or be pumped into the strong black liquor storage tank. The downstream end of the reactor has been shown in Plates VIII and IX.

f. Procedure

The procedure for operating the pilot plant involved the three stages of setting the respective operating conditions, taking the liquid samples, and making the necessary chemical analyses. The first step involved setting up the equipment and setting the respective oxygen and black liquor flow rates for a particular set of operating conditions, as shown in Plate X. The system was allowed to operate at constant conditions for ten to fifteen minutes to establish equilibrium. Samples of black liquor were then taken from the valves located at the downstream end of each horizontal pipe section to facilitate determination of progress of the oxidation reactions at different liquid retention times. Samples were collected in preheated narrow neck glass stoppered reagent (BOD) collection bottles by filling completely with liquid and closing tightly to inhibit the possibility of air oxidation as shown in Plate XI. Sample bottles were then taken to the laboratory to facilitate subsequent chemical analyses.

C. Analytical Techniques

The principal analyses of interest during black liquor oxidation included sodium sulfide, sodium polysulfide, sodium thiosulfate, sodium sulfite, and sodium sulfate, plus sodium mercaptide and total sulfur, liquor heating valve, and tall oil content. Also of importance were measurement of gas and liquid flow rates entering the pilot scale reactor.

1. Sodium Sulfide

Sodium sulfide was analyzed in black liquor by means of potentiometric

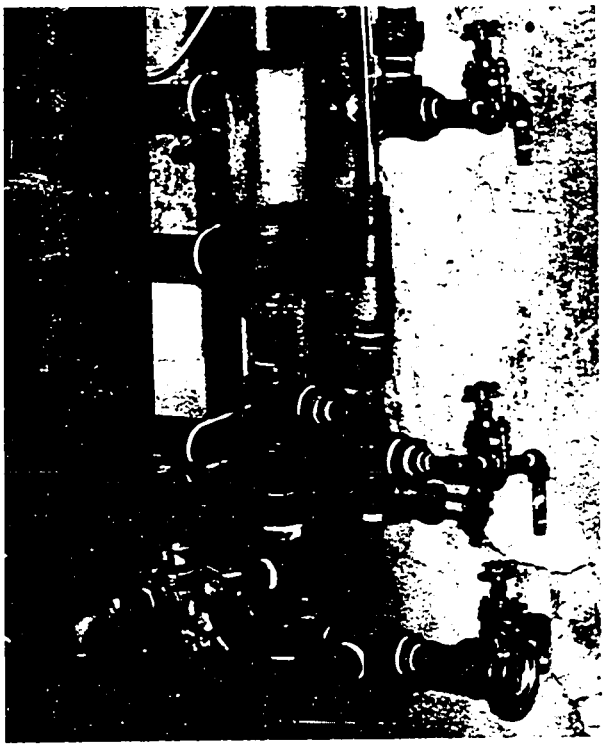


PLATE VIII. EXIT PIPING OF PLUG FLOW REACTOR.

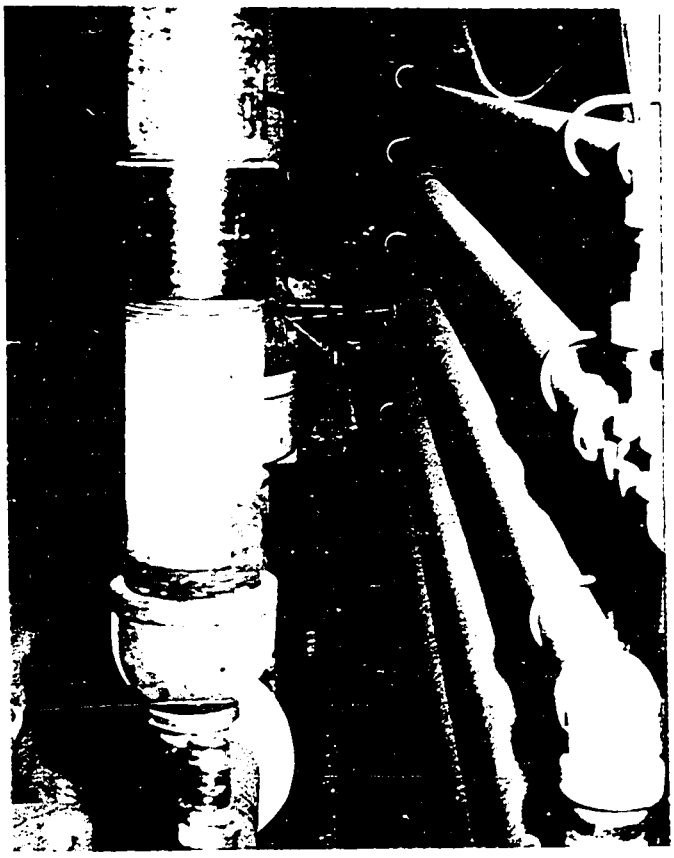


PLATE IX. VIEW FROM EXIT SIDE OF PLUG FLOW REACTOR.

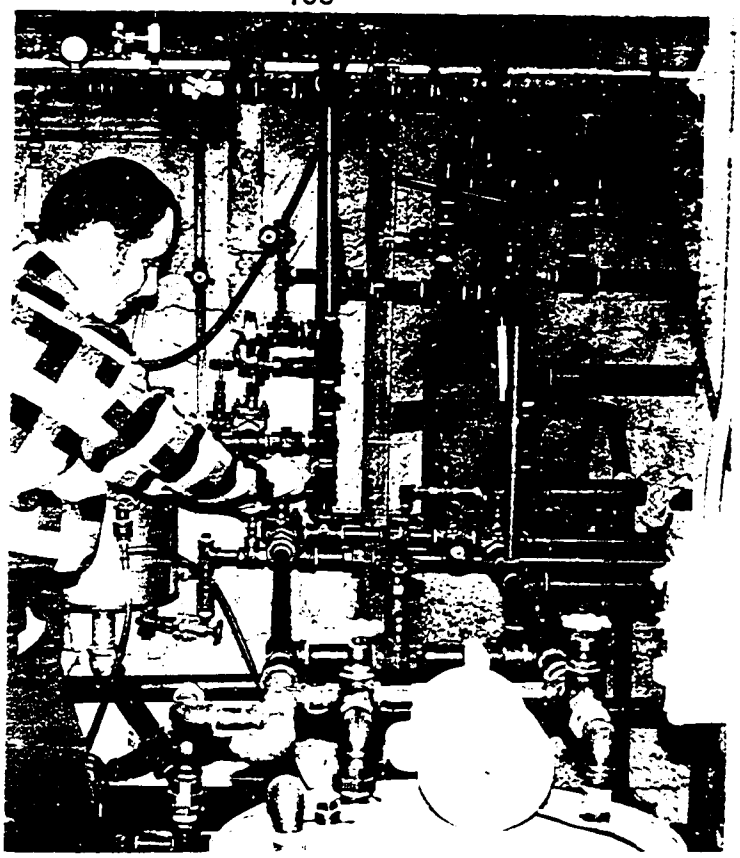


PLATE X. SETTING LIQUID FLOW RATE DURING TEST.

PLATE XI. COLLECTING BLACK LIQUOR SAMPLES DURING TEST.

titration with silver nitrate, using the method developed by Borlew and Pascoe (162). The basis for the method was that there was a change in the electrochemical potential of an alkaline solution containing sodium sulfide when silver nitrate was added because of the precipitation of silver sulfide as follows:

$$Na_2S + 2AgNO_3 \rightleftharpoons 2NaNO_3 + Ag_2S \qquad (119)$$

Small volumes of five milliliters for weak black liquor and two milliliters for strong black liquor were added to the alkaline solution of sodium hydroxide to minimize potential lignin interference while providing a sufficient amount of material for analysis. Small amounts of ammonium hydroxide were added to retard potential silver oxide formation, and gelatin was added to prevent deposition of silver sulfide on the electrode tip (163).

The sodium hydroxide was placed in a covered, stirred beaker and purged with nitrogen to inhibit possible oxidation of sulfide ion. Measured quantities of black liquor, ammonium hydroxide, and gelatin were added to the stirred beaker. The electrodes used were silver-silver sulfide and glass colomel reference types connected to the millivolt scale of a pH meter. Initial millivolt readings were taken and the change in millivolts noted as successive small increments of silver nitrate were added. The end point for the titration was taken as the bottom of the sharp drop in potential where the millivolt readings began to remain nearly the same as more silver nitrate was added (162)(164). End points were normally minus 150 to 175 millivolts for weak liquor, and minus 300 to 400 for strong liquor.

Problems associated with the method were sometimes sluggish response at high concentrations, inconsistent readings at low concentrations, possible lignin interference, and reduction of silver ion to silver metal by polysulfide ions and phenolic groups (165). The presence of lignin and other

constituents in the black liquor tended to make the end points unclear, so that careful titration techniques were necessary. Very small increments of silver nitrate were added at low concentrations so that the end points could be observed. Polysulfide ion could also interfere with the sulfide in a positive manner, which could only be eliminated by acidification and subsequent collection of the offgas in caustic solution, at which time occlusion of sulfide in the lignin became a problem. To minimize potential electrode coating, the samples were run from most dilute to most concentration to assure electrode response.

2. Sodium Mercaptide

Tamele and Ryland (166)(167)(168) found that sodium mercaptide concentration in alkaline solution could be determined simultaneously with sodium sulfide by means of potentiometric titration with silver nitrate as follows:

$$NaSCH_3 + AgNO_3 \rightleftharpoons NaNO_3 + AgSCH_3 \qquad (120)$$

The mercaptide end point was found to follow the sulfide end point so that the two could be differentiated. The procedure was the same as for the sodium sulfide analysis except that following the first end point silver nitrate was added until a second end point was observed in a manner similar to the first in the region of minus 75 to 125 millivolts. The technique was also found to be useful for simultaneous analysis of sulfide and mercaptide concentrations in alkaline solutions by Felicetta, Peniston, and McCarthy (169).

Potential problems with the method were that the mercaptide end point was often very difficult to detect because of the presence of lignins, polysulfides, and other materials, particularly at high sodium sulfide concentrations. Sodium mercaptide could react with elemental sulfur to form sodium sulfide, and any drop in liquid pH would cause loss as methyl mercaptan, either before or during the analysis.

A modification to the method provided for minimization of potential interferences and more selective differentiation between sodium sulfide and sodium mercaptide. It employed acidification of an alkaline solution of black liquor with hydrochloric acid to convert sodium sulfide and mercaptide to hydrogen sulfide and methyl mercaptan, respectively. The gases were then stripped from the liquid in the enclosed flask by purging with nitrogen. The gas stream then passed through an impinger containing a solution of cadmium sulfate and boric acid to selectively absorb hydrogen sulfide in a manner similar to methods used in flue gas sampling (170)(171). The methyl mercaptan was then absorbed in a second impinger containing sodium hydroxide, which was then titrated with silver nitrate as previously described. The apparatus used has been shown in Figure 29.

4. Sodium Thiosulfate

Sodium thiosulfate was determined by potentiometric determination with mercuric chloride in a neutral solution, using methods developed by Bilberg (174) and Danielson (175), employing the following reaction:

$$HgCl_2 + 2Na_2S_2O_3 \rightleftharpoons Na_2Hg(S_2O_3)_2 + 2NaCl \qquad (122)$$

Samples of black liquor were first treated with a solution of zinc chloride and sodium carbonate to precipitate the sodium sulfide and the lignin materials. The samples were then filtered to remove the precipitates, formaldehyde added to consume any sulfite ion present, and then neutralized to pH 7.5 with acetic acid prior to analyses.

The analyses were performed in a specially designed titration beaker with a side arm, and a mercury seal in the bottom of the beaker sufficient to completely cover the opening to the side arm, as shown in Figure 30. A known volume of sample was placed atop the mercury in the main portion of the beaker, into which a calomel double junction reference electrode was immersed. A

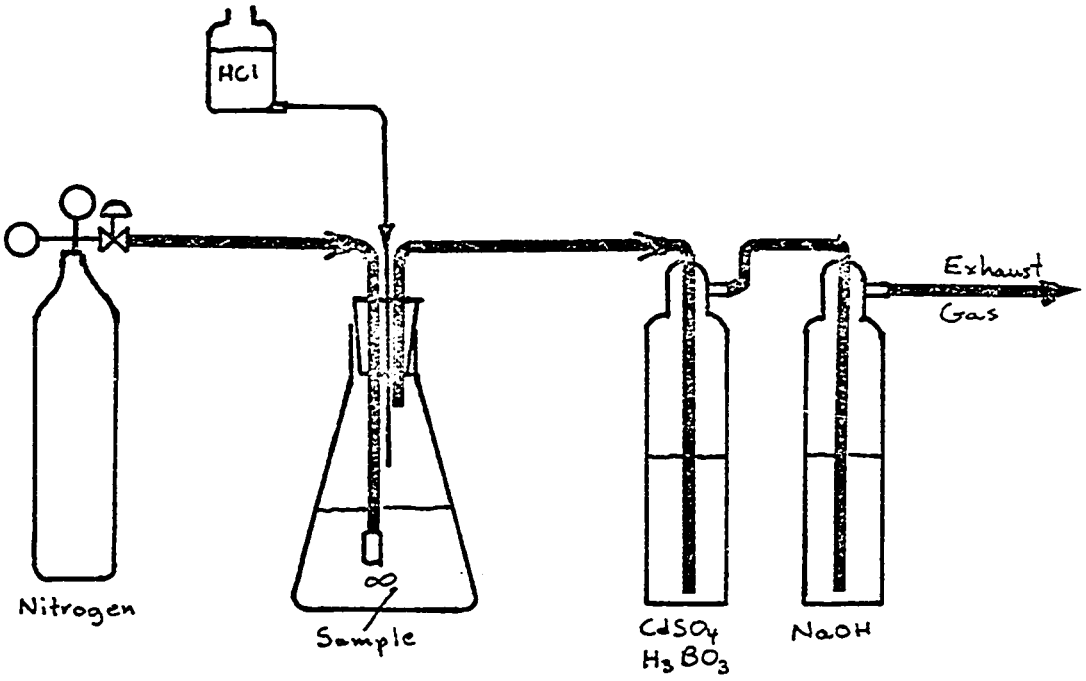


FIGURE 29. LABORATORY APPARATUS FOR $NaSCH_3$ DETERMINATION.

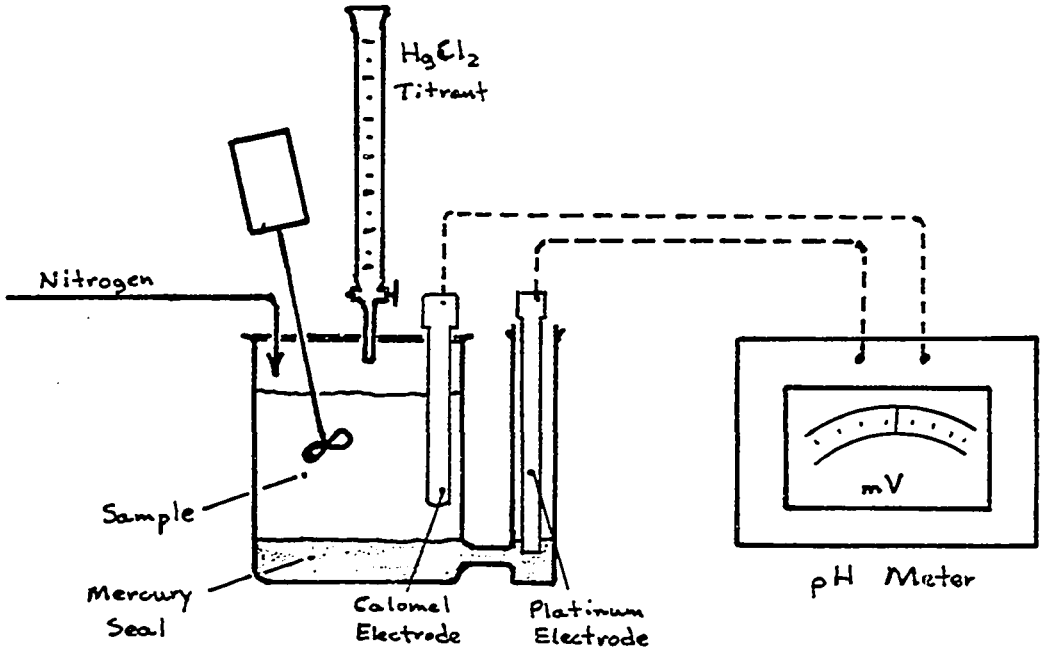


FIGURE 30. LABORATORY APPARATUS FOR $Na_2S_2O_3$ DETERMINATION.

platinum electrode was immersed in the mercury at the bottom of the side arm so that there was no direct contact with the solution. The circuit was completed by connecting both electrodes to a pH meter set to a negative millivolt scale. The titration beaker was kept covered and purged with nitrogen to inhibit air oxidation, and agitated by an immersion mixer through the top of the beaker. Increments of mercuric chloride solution were added to the solution and the change in electrochemical potential noted until a sudden sharp change was noted. The titration end point was considered to be the point of inflection corresponding to the maximum rate of change of potential, and was normally between plus and minus fifty millivolts.

The mercuric chloride titration method provided a rapid and reproducible method for determination of sodium thiosulfate concentrations in Kraft black liquor. The method was subject to potential interference from sulfite ion, which could be eliminated by formaldehyde addition. The presence of any unprecipitated sodium sulfide would be indicated by potential readings of greater than minus 250 millivolts, requiring the addition of more zinc chloride. The test for sodium thiosulfate with mercuric chloride was relative time-consuming as it required pretreatment of the samples. An additional problem was that mercuric chloride could form more than one complex form in addition to $Hg(S_2O_3)_2^{-2}$, including $Hg(S_2O_3)_3^{-4}$, and $Hg(S_2O_3)_4^{-6}$, particularly at elevated sodium thiosulfate concentrations, which could affect titration response. The sharpness of the end point was somewhat dependent on pH, as alkaline solutions caused the precipitation of mercuric hydroxide and acidic solutions caused the mercuric thiosulfate complex to be unstable.

5. Sodium Sulfite

Sodium sulfite was determined by means of a different starch-iodine titration in a two step sequence, with successive titrations for sulfite plus

thiosulfate, and thiosulfate alone by means of the following reactions (176):

$$2Na_2S_2O_3 + I_2 \rightleftharpoons Na_2S_4O_6 + 2NaI \quad (123)$$

$$Na_2SO_3 + I_2 + H_2O \rightleftharpoons Na_2SO_4 + 2NaI + 2H^+ + 2e^- \quad (124)$$

Sodium sulfide and lignin were first removed from black liquor samples by precipitation with zinc chloride and sodium carbonate, followed by filtration. The super-natant liquid was then divided into two aliquots of equal volume for subsequent iodometric analyses. Formaldehyde was first added to one of the aliquots to selectively consume the sodium sulfite, and acetic acid then added to both to provide the acidic conditions necessary to perform the iodometric titrations. Both aliquots were then titrated with standardized iodine solution to a blue starch end point, and the difference in titrant volumes used to provide an index of sodium sulfite concentration.

The iodometric titration method was nonspecific and suffered from potential interferences caused by polysulfides and organic materials in the black liquor. The use of two titrations perhaps minimized these problems, but also resulted in taking the small difference between two large numbers. An additional problem was that the amount of sodium sulfite to be expected in black liquor would probably be extremely low if sodium polysulfide was present in any appreciable quantities. The method was an approximation at best.

6. Sodium Sulfate

Sodium sulfate was analyzed by means of a turbidometric analysis of barium sulfate formed by precipitation with barium chloride as follows (177):

$$Na_2SO_4 + BaCl_2 \rightleftharpoons BaSO_4 + 2NaCl \quad (125)$$

Sodium sulfide was first precipitated from the black liquor by addition of zinc chloride, and the solution acidified to pH 4.0 to precipitate the lignin by addition of hydrochloric acid, where both were subsequently removed by filtration. The supernatant solution was then heated and refiltered to assure

complete removal of any organic material present. The resulting solutions were diluted to the appropriate concentration range of zero to fifty milligrams per liter for subsequent optical analyses. They were then adjusted to the appropriate liquid pH, salinity, and viscosity by addition of specific amounts of hydrochloric acid, sodium chloride, and glycerine, respectively. The percent transmittance of the diluted samples were then determined at 420 millimicrons wavelength on a spectrophotometer and compared to values observed for standard sodium sulfate solutions at known concentrations.

The turbidometric method was employed after initial tests with the gravimetric sulfate trials were unsuccessful because of difficulties in burning the filter paper after precipitation, the possible presence of ash materials in the paper, and the excessive time required to perform analyses. The turbidometric method was subject to wide variations in readings with any differences in operating procedure, was subject to possible interferences from any other materials which might form a precipitate with barium chloride, and was not always reproducible. The large dilutions required also could lead to a lack of sensitivity for the method.

7. Total Sulfur

The method used for determination of total sulfur in black liquor employed high temperature of the sulfur present to form sulfur dioxide (178). The sulfur dioxide generated was then passed through a solution of potassium iodate-iodide, where the end point was determined from a blue starch indicator in a commercially available photometric titrator. The sample of black liquor was first evaporated to dryness to determine the solids concentration, and a small portion of the solids then placed in a special tared crucible. Magnesium oxide and iron filings were then added to provide proper temperature and combustion conditions, and the crucible placed in a heated induction furnace. Oxygen was

then passed through the crucible to burn off the sulfur as sulfur dioxide, at 1500°F, which was then automatically titrated with potassium iodate to provide an index of total sulfur concentration of the black liquor solids. The method was rapid and relatively simple, but loss of volatile sulfur compounds during sample storage or evaporation would cause low results to be obtained. A correction also had to be made to provide for the sulfur trioxide formed during the combustion process of about ten percent by weight.

8. Liquor pH

Determination of the pH of black liquor was made difficult because of its high temperature, viscosity, and alkalinity. It was first necessary to standardize the pH meter at pH 7.0 and 10.0 by means of standard solutions. Black liquor samples were collected separately from those used for chemical analyses in preheated small glass bottles, which were then sealed and cooled to room temperature by being placed in a water bath. The pH of weak black liquor was then determined by direct immersion of the electrodes into the bottles and recording the readings. The pH of strong black liquor was determined by first diluting the samples by a ratio of one-to-three and then recording the readings for the diluted liquid to overcome potential clogging of electrode tips in the highly viscous liquid.

9. Lignin Content

The lignin content of black liquor was determined by means of gravimetric analyses of the material collected from acidification of the black liquor. A known volume of black liquor was initially treated with hydrochloric acid to reduce the liquid to pH 4.0. The liquid was subsequently stripped with nitrogen to remove the hydrogen sulfide and volatile organic sulfur gases, and the lignin was then separated by filtration onto a tared filter paper. The lignin was then washed with several washes of cold and hot distilled water to remove

soluble inorganic compounds, with methanol to remove organic constituents, with sulfuric acid, and then distilled water. The filters were then dried overnight and weighed to provide an approximation of the lignin content of black liquor. The method would need to be refined to make more exact determination of the highly variable material, as described by Bagby (179).

10. Tall Oil

The amount of tall oil present in black liquor was estimated by means of solvent extraction from the liquid. The initial step involved oxidation of sodium sulfide by addition of small amounts of hydrogen peroxide to the black liquor. Lignin was then precipitated by addition of sodium carbonate and zinc chloride to the black liquor, and then separated by filtration. The lignin was then washed with water and methanol to remove any tall oil materials. The washings and the supernatant were then extracted with petroleum ether to remove the tall oil materials, and the other evaporated at room temperature to yield a tall oil residue. The method was similar to that described by Saltsman and Kuiken (180), and would yield only approximate results. An additional problem was that the wood furnish employed at the mill during the study contained very little tall oil materials.

11. Heat of Combustion

The heat of combustion of black liquor was determined by placing a known amount of liquid in a calorimeter, adding benzoic acid, and firing in a pressurized atmosphere of pure oxygen (181). The amount of heat liberated by the combustion was measured by a thermometer balance between the bomb and the cooling jacket. The heat of combustion was computed by the degree of warming of the water in the jacket. The method provided for a total heat of combustion and was directly applicable only for black liquor samples of 50 percent or greater able to support their own combustion.

VI. RESULTS AND DISCUSSION

A. Overall Test Program

A series of tests were made to determine the suitability of using molecular oxygen for black liquor oxidation in a plug flow reactor. Initial studies in the laboratory involved measuring the rate of absorption of oxygen into black liquor and the rate of oxidation of sodium sulfide and mercaptide in a batch reactor. These studies provided useful information regarding the kinetics of the oxidation reactions in terms of retention time requirements for storage tank facilities. Mass transfer studies were made by visual observation and high speed photography to determine the operating conditions favoring minimal oxygen bubble size in the bubble or froth regimes of two phase flow. Results of these studies were used to facilitate the subsequent design of the plug flow reactor system used for contacting molecular oxygen with black liquor. Additional preliminary studies involved the increases in liquid pressure drop during two phase gas-liquid flow, and the efficiency of oxygen absorption into black liquor in the plug flow reactor.

Major emphasis during the study involved a series of experiments with a pilot scale plug flow reactor to determine the feasibility of using molecular oxygen for oxidation of weak and strong black liquor. Pilot scale studies of weak black liquor oxidation with molecular oxygen involved changes in liquid Reynolds number, oxygen total and partial pressure, liquid temperature, liquid pH, sodium thiosulfate addition, and liquid retention time. Pilot scale studies of strong black liquor oxidation involved respective high and low inlet sodium sulfide concentrations, changes in contactor configuration, and liquid Reynolds number. Special studies were made regarding the efficiency

of oxygen utilization during black liquor oxidation, formation of sodium sulfide, oxidation of lignin, and tall oil recovery.

B. Laboratory Studies

1. Oxygen Absorption

Laboratory studies were made of the rate of oxygen absorption into black liquor in batch reactors, with liquid temperature and sample acidification the two major variables. Both constant pressure variable volume- and constant volume-variable pressure batch absorption reactors were used for the oxygen uptake studies.

a. Sample Acidification

The effect of acidification of the black liquor on the resulting rate of oxygen uptake was determined from oxygen absorption kinetics studies on successive unmodified and acidified 100 milliliter samples of weak black liquor at essentially room temperature. One of the samples was acidified with five milliliters of concentrated sulfuric acid to convert sodium sulfide and sodium mercaptide to their respective acidic gases, hydrogen sulfide and methyl mercaptan, for subsequent evolution by stripping with nitrogen, and the black liquor then recausticized to the original pH by addition of sodium hydroxide. The volume of oxygen absorbed for each black liquor sample was then measured as a function of time in the constant pressure-variable volume batch absorption reactor at essentially atmospheric pressure.

The absorption of oxygen into black liquor took place in two major reaction rate regimes separated by a transition region. From previous work by Bergstrom and Trobeck (49), the initial reaction oxygen uptake regime was probably the oxidation of sodium sulfide, and the final region the oxidation of organic materials such as lignin. These findings were verified by comparing the respective rates of oxygen uptake for black liquor samples for

unmodified and acidified samples of black liquor. Results indicated that the amount of oxygen absorbed into the unmodified black liquor sample during the reaction period was substantially higher than for the acidified sample. The oxygen uptake rate was found to be much greater particularly during the initial hour of absorption time, probably because of the oxygen uptake resulting from oxidation of sodium sulfide. Acidification of the black liquor indicated that other materials in the black liquor also exerted on oxygen demand, of which oxidation of phenolic lignin and oxidation of sodium thiosulfate to sodium sulfate were two possibilities. The effect of sample acidification on oxygen absorption has been illustrated in Figure 31.

b. Liquid Temperature

The effect of liquid temperature on the rate of oxygen absorption into black liquor was observed by running successive 100 milliliter samples of unmodified weak black liquor at temperatures of 25 and 80°C, respectively. The liquid temperature of 80°C (176°F) corresponded to operating conditions which would be expected for full-scale installations at Kraft pulp mills. The rate of oxygen into black liquor was measured in the constant pressure-variable volume batch reactor by the rate of oxygen depletion in the calibrated volumetric gas burette.

The pattern of oxygen absorption at the elevated temperatures followed the same general pattern as observed at room temperature with three major exceptions. First, the initial period of rapid oxygen absorption occurred within 30 minutes at 80°C as compared to 60 minutes for 25°C. Second, the initial region of oxygen absorption occurred in two distinct steps at the high temperature, as compared to a more gradual change at the lower liquid temperature. The initial period of relatively rapid oxygen uptake occurred during the first 30 minutes, which was probably the region of sodium sulfide

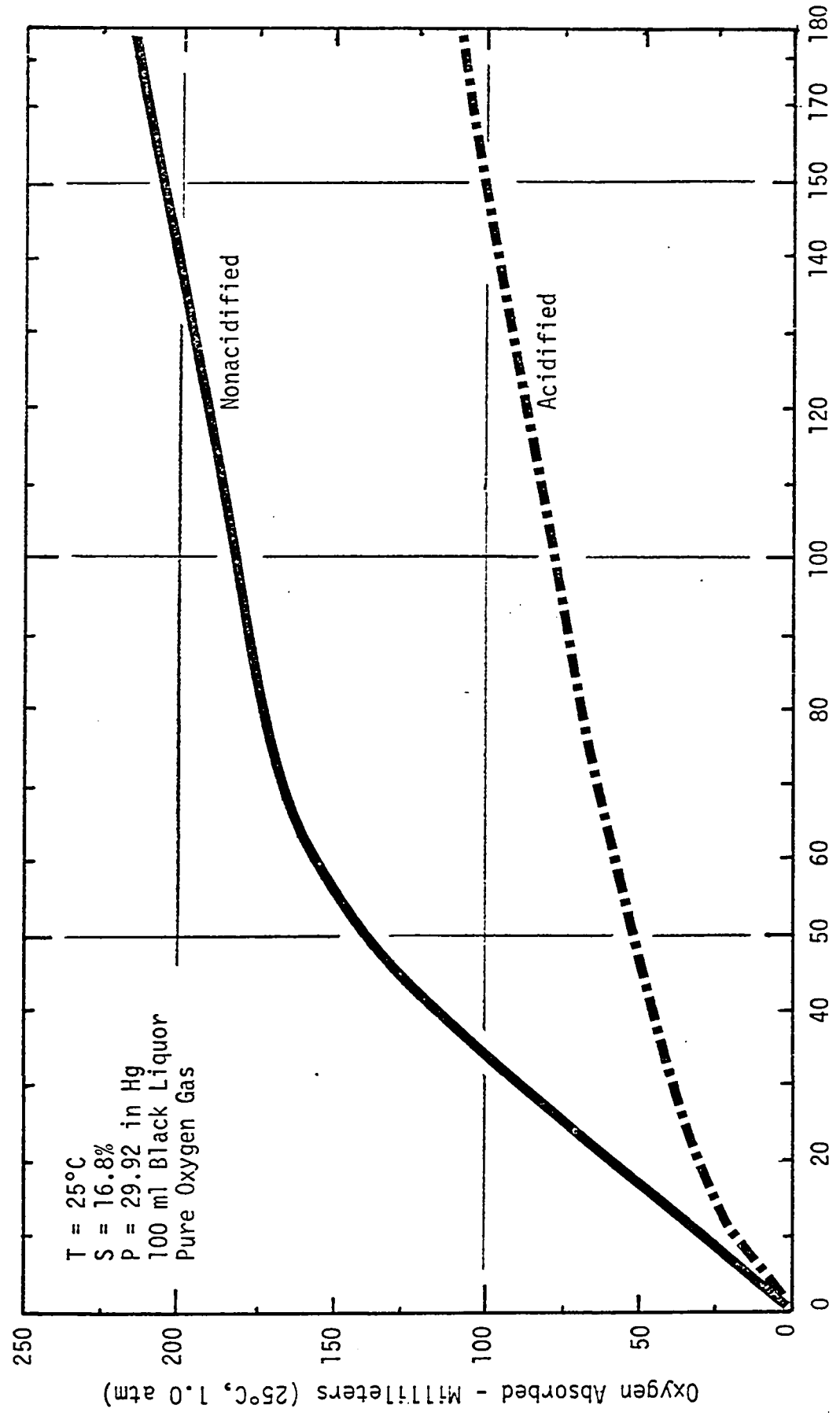


FIGURE 31. EFFECT OF SAMPLE ACIDIFICATION ON OXYGEN ABSORPTION INTO WEAK BLACK LIQUOR

oxidation, actually occurred in two distinct regimes of oxygen absorption. The initial oxygen uptake rate was very rapid during the first four minutes, and was followed by a somewhat slower absorption rate for approximately 30 minutes. The absorption of oxygen at room temperature was more gradual and occurred during the first hour of absorption. These findings indicated that the oxidation of sodium sulfide in black liquor probably occurred in two successive reaction rate-limiting sequences.

The third major difference between oxygen absorption rates was that the transition period of approximately 50 to 70 minutes was somewhat more complicated at 80°C than at 25°C because it displayed subregions of varying oxygen absorption rates. These varying uptake rates possibly corresponded to the oxidation of sodium thiosulfate, sodium polysulfide, and other constituents in the black liquor. The oxygen uptake rates during the final region after about two hours of absorption, was essentially the same at both 25 and 80°C. It was probably the region of oxidation of organic materials such as phenolic lignin. The effect of reaction temperature on the rate of oxygen absorption into weak black liquor has been listed in Table 17. It was also observed that there was a warming of the black liquor during the initial reaction period of one to two °C at room temperature (25°C) and three to five °C at 80°C.

c. Pressure Variation

Additional studies of the kinetics of oxygen absorption into black liquor were made using an agitated, batch, constant volume-variable pressure autoclave. The basis for determining the rate of oxygen absorption was the change in total gas pressure with time as the oxygen was consumed by reaction with materials in the black liquor. A sample of 500 milliliters of black liquor was placed in the two liter autoclave, the system evacuated, and purged with

purified oxygen gas. Readings of total oxygen pressure were then taken at periodic time intervals to determine the rate of oxygen absorption into the weak black liquor at 27°C.

The absorption of oxygen into black liquor was found to occur in more than one rate sequence, as shown in Figure 32. The oxidation of sodium sulfide probably occurred during the first hour of reaction, where the oxygen absorption rate during this period occurred in two distinct stages. The initial step occurred during the first five minutes, and was characterized by rapid oxygen absorption. The second step occurred between five and sixty minutes of reaction time, and was much slower than the initial rate, as listed in Table 18. The rate of oxygen absorption into black liquor was observed to be substantially higher in the variable pressure reactor than the variable volume batch reactor. A possible reason was that the increased pressure provided a greater gaseous phase driving force to facilitate oxygen absorption. Additional oxygen absorption into black liquor took place during the four hour reaction period, but at variable rates which were greater than those observed during the latter stages of tests with the variable volume batch reactor.

2. Batch Oxidation

The respective oxidation rates for sodium sulfide and sodium mercaptide in weak black liquor with molecular oxygen were observed in a laboratory-scale batch reactor. Tests were made where successive 100 milliliter volumes of unoxidized weak black liquor were placed in the completely mixed batch reactor, which was heated to a constant temperature of 71°C (160°F). Oxygen gas was then introduced to the black liquor through a porous fritted glass cylinder located near the bottom of the batch reactor at a constant flow rate of 240 milliliters per minute. Samples were oxidized for given periods

TABLE 17. EFFECT OF LIQUID TEMPERATURE ON RATE OF OXYGEN ABSORPTION INTO BLACK LIQUOR

Liquid Temperature °C	Units	Oxygen Uptake Rate		
		Initial Region		Final Region
		First	Second	
25	$\frac{\text{cf Oxygen}^1}{\text{gal b.l.-hour}^2}$	0.255	0.170	0.035
80		0.401	0.188	0.035
25	$\frac{\text{lb-mole } O_2}{\text{cf b.l.-hour}}$	0.00495	0.00330	0.00068
80		0.00781	0.00372	0.00068

Notes: 1. Oxygen conditions referred to 70°F, 29.92 in. Hg as standard conditions.

2. Black liquor is abbreviated as "b.l."

TABLE 18. OXYGEN ABSORPTION RATES INTO WEAK BLACK LIQUOR IN A VARIABLE PRESSURE BATCH REACTOR.

Quantity	Oxygen Absorption Rate	
	Initial	Secondary
$\frac{\text{cf Oxygen}}{\text{gal b.l.-hour}}$	2.005	0.206
$\frac{\text{lb Oxygen}}{\text{gal b.l.-hour}}$	0.1605	0.0165
$\frac{\text{lb-mole } O_2}{\text{cf c.l.-hour}}$	0.0376	0.00387

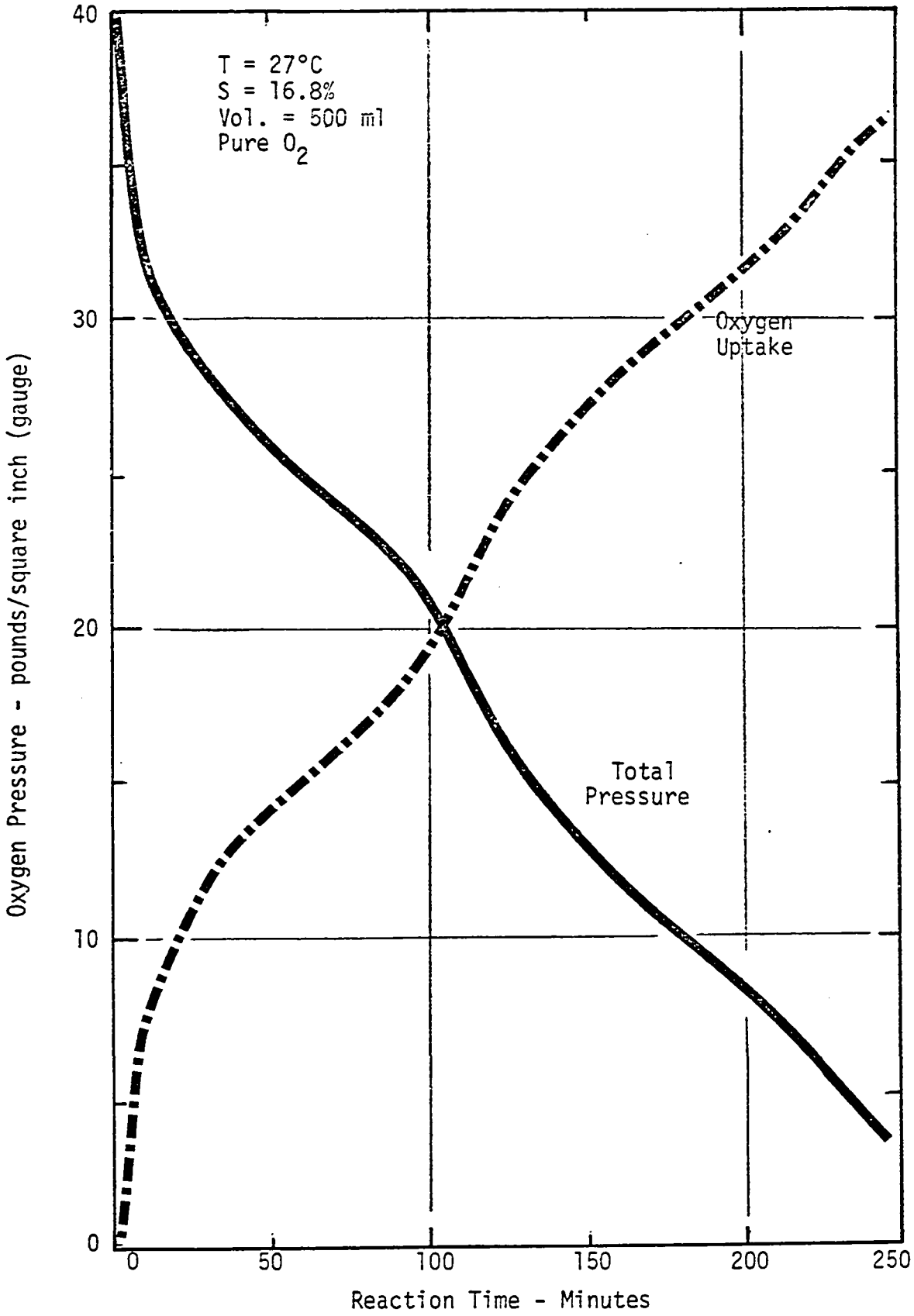


FIGURE 32. OXYGEN ABSORPTION INTO WEAK BLACK LIQUOR IN A VARIABLE PRESSURE BATCH REACTOR

of time ranging from 30 seconds to 18 minutes. The sodium sulfide and mercaptide concentrations were measured for the unoxidized weak black liquor and at the end of each test. A considerable amount of foam was generated at the liquid surface by passage of oxygen gas through the weak black liquor. The problem was alleviated by locating a suction spout above the liquid surface which was connected to a water aspirator.

a. Sodium Sulfide

The oxidation of sodium sulfide in weak black liquor proceeded in more than one rate regime during the test period, as illustrated in Figure 33. An initial rapid decrease in sodium sulfide concentration during the first two to four minutes of reaction time was followed by a transition period and a relative slow oxidation rate at concentrations below 0.25 grams per liter. The initial reaction for rapid sodium sulfide oxidation in the first 30 seconds appeared to be zero order in sodium sulfide. The relatively slow secondary oxidation reaction at low sodium sulfide concentrations became predominant after five minutes of reaction time, and approximated a first order reaction in terms of sodium sulfide concentration. Reaction rate constants observed for sodium sulfide and mercaptide during the batch oxidation study with molecular oxygen have been listed in Table 19.

Results of the study indicated consecutive rapid and slow reactions for sodium sulfide oxidation, pointing to the potential use of a two-stage reactor system. A liquor retention time of approximately 20 minutes would be required to achieve a sodium sulfide oxidation efficiency of 99 percent for the test conditions studied.

b. Sodium Mercaptide

The rate of sodium mercaptide oxidation was considerably slower than sodium sulfide, as the presence of high concentrations of sodium sulfide

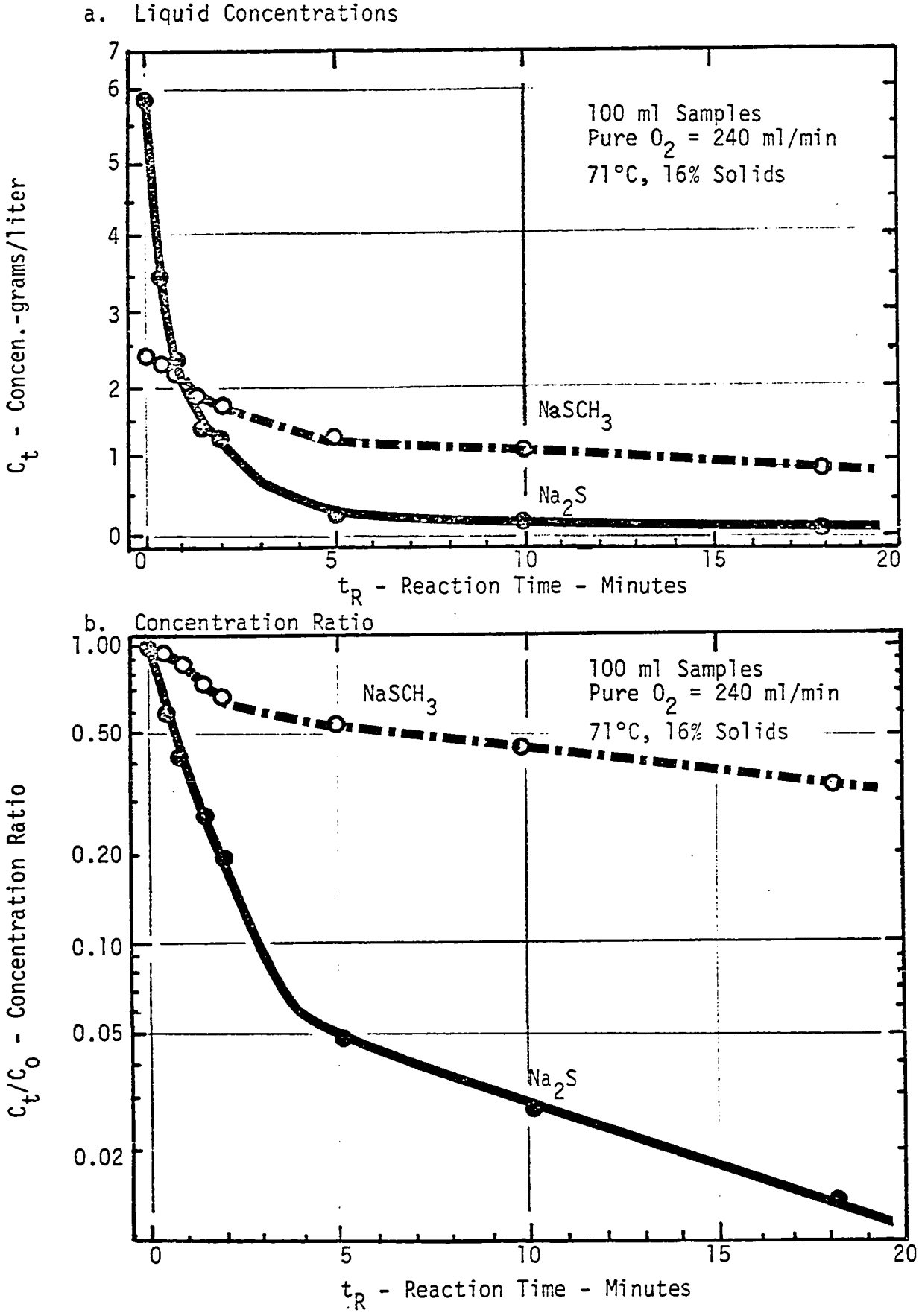


FIGURE 33. BATCH OXIDATION OF Na_2S AND $NaSCH_3$ IN WEAK BLACK LIQUOR

TABLE 19. OXIDATION RATES FOR SODIUM SULFIDE AND MERCAPTIDE IN A BATCH REACTOR.

Constant	Units	Sodium Sulfide Order	Sodium Sulfide k	Sodium Mercaptide Order	Sodium Mercaptide k
Primary	$\frac{\text{grams}}{\text{liter b.l.-sec}}$	0	-0.0817	0-1	-0.00565 (Est.)
Secondary	1/sec	1	-0.00148	1	-0.00077

appeared to inhibit the reaction. The oxidation of sodium mercaptide proceeded in two different reaction rate regimes, as shown in Figure 33. The initial reaction during the first five minutes was variable between a zero and first order reaction, and was estimated as zero order during the initial two minutes of reaction time for comparative purposes. The secondary oxidation of sodium mercaptide in black liquor appeared to be a first order reaction, which was considerably slower than the corresponding secondary sodium sulfide oxidation rate. A liquid retention time of 20 minutes would result in only a 65 to 70 percent conversion of sodium mercaptide.

3. Significance

The laboratory studies provided useful information regarding the kinetics of sodium sulfide and mercaptide oxidation in weak black liquor. The oxidation of sodium sulfide appeared to take place in successive sequences of a zero order reaction at high concentrations followed by a first order reaction at low concentrations. The oxidation of sodium mercaptide was inhibited by the presence of sodium sulfide, and also appeared to take place in a two-step sequence. The initial reaction varied between a zero and first order reaction while the secondary reaction was first order in nature. Materials in the black liquor other than sodium sulfide and mercaptide also exerted an oxygen demand, which resulted in oxygen absorption into black liquor

for extended periods. Sodium sulfide could be effectively oxidized within 20 to 30 minutes with molecular oxygen, but not sodium mercaptide.

The initial rates of oxygen absorption into weak black liquor with the batch reactors were substantially less than for the plug flow reactor, and that there was a substantial difference between the types of batch reactors, as shown in Table 20.

TABLE 20. EFFECT OF REACTOR CONFIGURATION ON INITIAL OXYGEN ABSORPTION RATE INTO WEAK BLACK LIOUOR.

Reactor Configuration	Absorption Rate lb-mole O_2/cf b.l.-hour
Constant Pressure-Variable Volume	0.005
Constant Volume-Variable Pressure	0.038
Batch Oxidation Reactor	0.018[1]
Plug Flow Reactor[2]	0.482[1]

Notes: 1. Oxygen absorption rate computed from sodium sulfide oxidation by assuming the following reaction:

$$2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$$

2. Continuous pilot scale plug flow reactor.

The oxygen mass transfer rate was much greater in the plug flow reactor than for any of the batch reactors, probably because of the effects of additional liquid turbulence in the pipe. It was necessary to interpret the results of the batch kinetics studies of oxygen absorption into black liquor with considerable caution in the subsequent extrapolation to the design of full-scale continuous flow systems.

C. Preliminary Field Studies

1. Two Phase Flow

a. System

A series of tests were made to determine the effects of liquid and gaseous flow parameters and pipe diameter on the mean bubble size produced when oxygen was added in cocurrent horizontal flow to a stream of water passing through a transparent plastic pipe. The approximate bubble diameters and respective two phase gas-liquid flow regimes were estimated by means of both visual observations and high speed photography studies. It was necessary to use transparent water for the tests because of difficulties in observing any bubble development in the highly colored black liquor. The oxygen was injected into the water by means of a porous fritted glass cylinder located axially to the direction of liquid flow. The oxygen-water mixture then flowed through a length of transparent Acrylic plastic tube with subsequent discharge to the sink through a hose.

The procedure involved installation of the plastic tube of proper diameter in place, setting the respective oxygen and water flow rates, plus making the necessary observations and taking the pictures of the particular flow conditions in the horizontal pipe. Transparent pipes of 3/8, 1/2, 3/4, and one inch inside diameters were employed, with water flow rates from two to ten gallons per minute, and the oxygen flow rates from 0.5 to 2.5 cubic feet per minute. Camera shots were taken at a distance of approximately six inches from the surface of the pipe with a shutter exposure of 1/250th second and a strobe flash setting of 1/1000th of a second.

b. Flow Configurations

Visual observations indicated that it was necessary for the liquid Reynolds number to be 40,000 or greater to produce a minimum oxygen bubble

size, regardless of gas flow rate or pipe diameter. At liquid Reynolds numbers of 40,000 or above, a relatively uniform (radially and axially) dispersion of extremely fine bubbles was produced which was characteristic of the froth regime of two phase gas-liquid flow. At lower Reynolds numbers between 40,000 and 20,000 to 25,000, discrete larger bubbles were produced which were characteristic of the bubble regime of two phase flow. These two homogeneous two phase gas-liquid flow regimes were conducive to providing for a maximum gas-liquid interfacial contact area and a high rate of oxygen mass transfer into the liquid phase.

The nonhomogeneous two phase gas-liquid flow regimes characteristic of less efficient oxygen mass transfer into the liquid phase became predominant when the liquid Reynolds number was less than approximately 20,000 to 25,000. At liquid Reynolds numbers between 10,000 to 15,000 and 20,000 to 25,000 the annular regime of two phase flow became predominant. At liquid Reynolds numbers below approximately 10,000 the plug, slug, wavy, and stratified regimes of two phase gas-liquid flow became predominant. The above boundaries for flow regimes with liquid Reynolds numbers were approximate, as each of these actually involved a transition zone dependent on respective liquid and gas flow rates, pipe diameters, and fluid characteristics. A summary of the effect of liquid Reynolds number on the oxygen-water system over a range in pipe diameters from 3/8 to one inch has been presented in Table 21.

The observation that a liquid Reynolds number of 40,000 was necessary for rapid oxygen bubble dispersion into water in the froth flow regime could not be verified from other literature sources. The finding was in exact agreement with studies by Sittel (135) where completely developed turbulent flow existed at liquid Reynolds numbers greater than 40,000 for the sodium chloride-water system.

TABLE 21. EFFECT OF LIQUID REYNOLDS NUMBER ON HORIZONTAL TWO PHASE GAS-LIQUID FLOW REGIME FOR THE OXYGEN-WATER SYSTEM.

Liquid Reynolds Number	Two Phase Flow Regime
40,000 or Above	Froth Flow
20-25,000 - 40,000	Bubble Flow
10-15,000 - 20-25,000	Annular Flow
5,000 - 10-15,000	Plug, Slug, Wavy Flow
5,000 or Less	Stratified Flow

Illustrations of actual two phase gas-liquid flow configurations have been presented by means of the following four photographs. Plate X provided an illustration of fully developed froth flow where the oxygen bubbles appeared as a series of rapidly flowing fine streaks. It was necessary to estimate bubble size by measurements in a radial direction only to avoid the horizontal distortions caused by the rapid liquid velocities. The froth flow condition was particularly favorable to high gas-liquid interfacial contact areas and rapid oxygen mass transfer into the liquid phase. Plate XI illustrated the bubble regime of two phase flow with relatively large discrete oxygen bubbles passing through the tube, where some agglomeration of bubbles was noted. Plate XIV illustrated the development of the annular configuration of two phase flow with a central stream of gas surrounded by liquid. There was minimal bubble development and a relatively small interfacial contact area. Plate XV illustrated the development of two-layered stratified two phase flow with a relatively inefficient degree of gas-liquid contact which would not be conducive to effective oxygen mass transfer into the liquid.

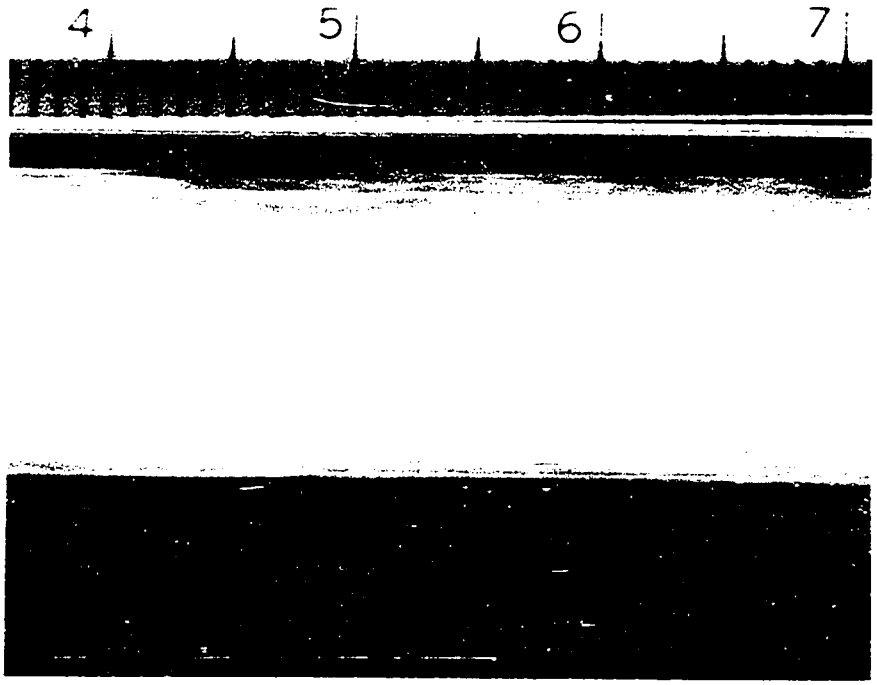


PLATE XII. FROTH REGIME OF TWO PHASE GAS-LIQUID FLOW.

PLATE XIII. BUBBLE REGIME OF TWO PHASE GAS-LIQUID FLOW.

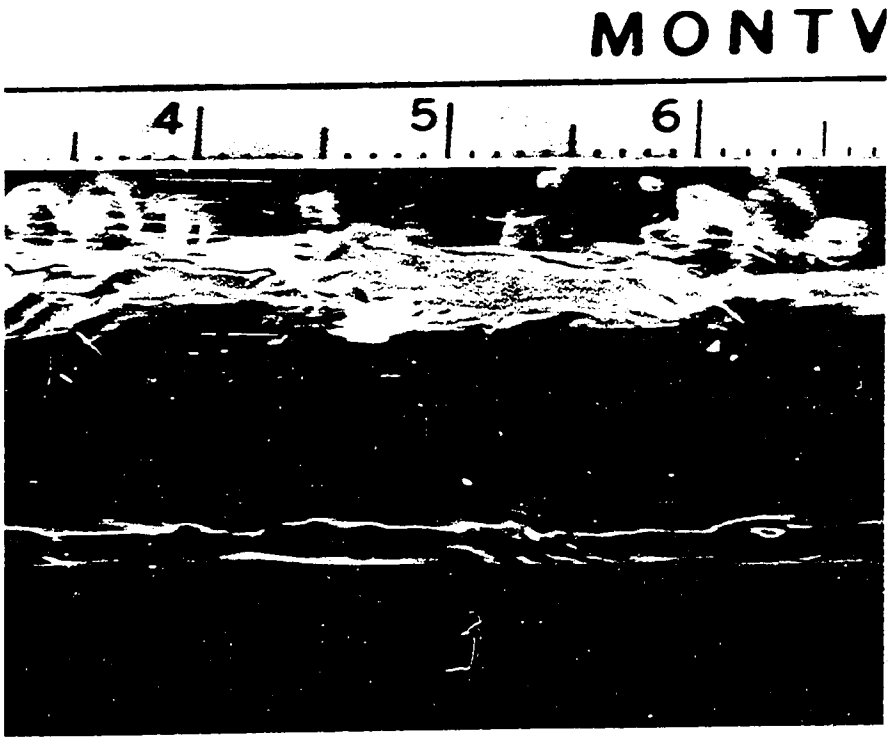


PLATE XIV. ANNULAR REGIME OF TWO PHASE GAS-LIQUID FLOW.

PLATE XV. STRATIFIED REGIME OF TWO PHASE GAS-LIQUID FLOW.

c. Bubble Diameter

High speed photography studies indicated that oxygen bubble diameters of 0.1 millimeter or less in water were produced at liquid Reynolds numbers of 40,000 or greater, which appeared to be relatively independent of both pipe diameter and gas flow rate. At lower liquid Reynolds numbers, the arithmetic mean oxygen bubble diameter appeared to increase with decreasing liquid Reynolds number, decreasing superficial gas velocity, and increasing pipe diameter. The effect of liquid Reynolds number on arithmetic mean bubble diameter for the oxygen-water system has been illustrated in Figure 34. The relationship between mean oxygen bubble diameter and liquid Reynolds number over a range from 20,000 to 40,000 for a given pipe diameter and superficial gas velocity was approximated by the following empirical equation:

$$d_b = C(N_{Re_L})^n \qquad [126]$$

d_b = Oxygen arithmetic maan bubble diameter in millimeters

C = Constant of proportionality for a given system in millimeters

N_{Re_L} = Liquid Reynolds number

n = Exponential value for a particular system

where: For 3/8 Inch Diamtter Tube: $n = -1.5$

For 1/2 Inch Diameter Tube: $n = -1.2$

Individual calibrations would have to be made for particular systems in order to obtain exact values for "C" and "n."

The range between minimum and maximum oxygen bubble size observed for a particular pipe diameter and superficial oxygen gas velocity appeared to increase as liquid Reynolds number decreased. Results for one particular set

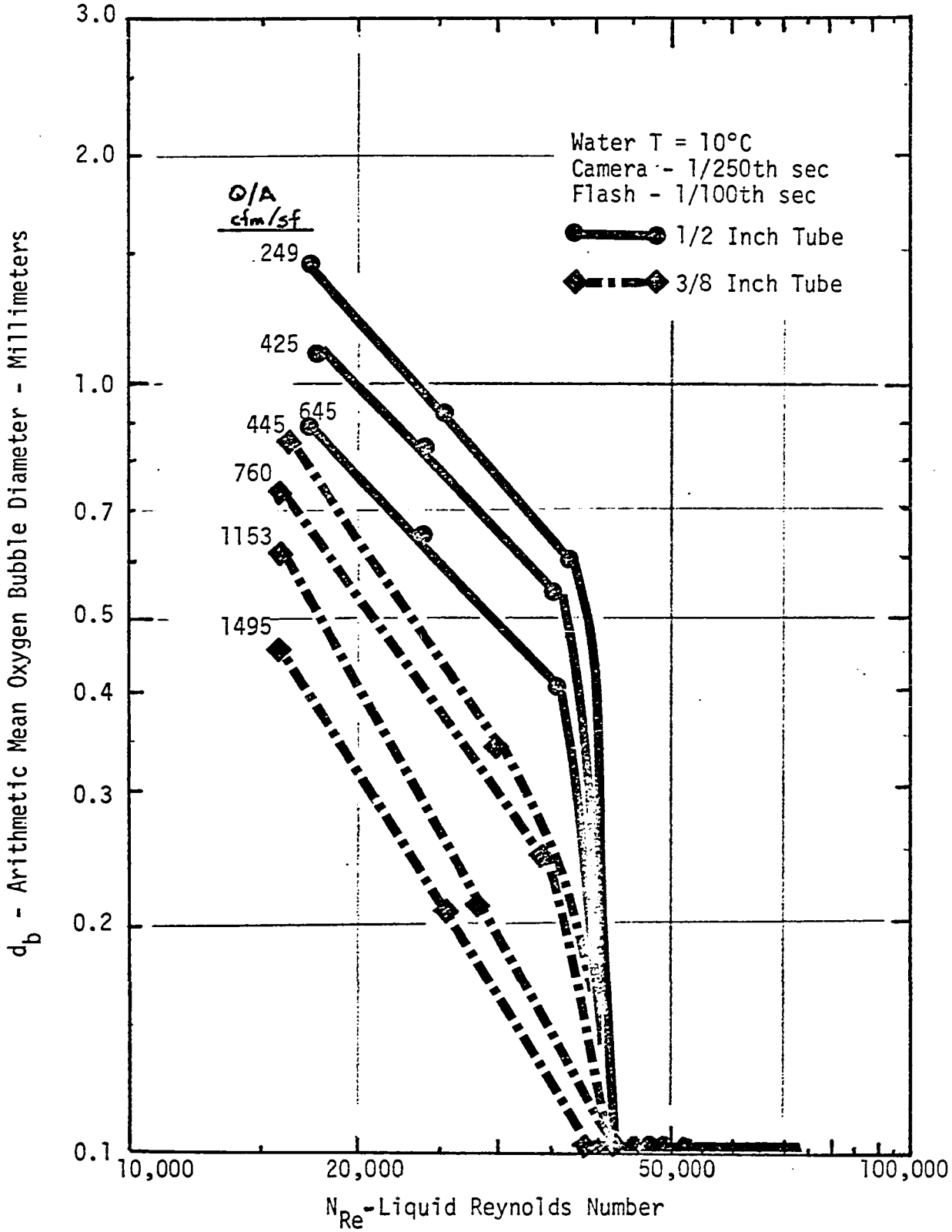


FIGURE 34. EFFECT OF LIQUID REYNOLDS NUMBER ON OXYGEN BUBBLE DIAMETER IN WATER

of operating conditions have been listed in Table 22. The lower limit for resolution was bubbles of approximately 0.1 millimeters in diameter. Efforts were made to count bubbles in the center of the pipe to minimize any possible effects of curvature in magnification. Additional results have been listed in the Appendix.

The probable reason for the increasing tendency for variability in bubble diameters at lower liquid Reynolds numbers was that there was less turbulence and shearing of bubbles formed. As a result the bubbles formed tended to become larger by agglomeration and tended to produce the annular regime of two phase flow from the center jet of the oxygen dispersion device because there was less turbulence to produce gas-liquid mixing. At very low liquid Reynolds numbers, large pockets of gas tended to form plugs or slugs with virtually no bubble formation. The effect appeared to be diminished with decreasing pipe diameter and accentuated with increasing pipe diameter.

It was not possible to find literature sources listing values for bubble diameters with the oxygen-water system in cocurrent horizontal two phase gas-liquid flow. Heuss, King, and Wilke (136) made an extensive study of ammonia (highly soluble) and air (relatively insoluble) bubble dispersion into water in the froth regime of two phase gas-liquid flow. No specific values for air bubble diameters were reported for the air-water system, but values for ammonia bubble diameter were found to be in the range of 0.2 to five millimeters over a range in liquid Reynolds numbers from 70,000 to 100,000. The oxygen bubble diameters reported by Heuss were somewhat larger than those reported by James and Silberman (182) for the ammonia-water system, with values ranging from 0.2 to 0.8 millimeters at liquid Reynolds numbers above 200,000. All of the above values for the ammonia-water system were in

TABLE 22. EFFECT OF LIQUID REYNOLDS NUMBER ON OXYGEN BUBBLE DIAMETERS IN WATER.

a. Means:

Liquid Reynolds Number	Mean Bubble Diameter - Millimeters				
	Arith Mean	Areal Mean	Volum. Mean	Median Diameter	Most Frequent
17,000	0.9	1.0	1.3	1.0	0.6
23,200	0.6	0.5	0.5	0.7	0.6
35,000	0.4	0.2	0.1*	0.5	0.3
44,000	0.1*	0.10*	0.1*	0.1*	0.1*

* Or less

b. Variabilities

Liquid Reynolds Number	Maximum Diameter	Minimum Diameter	Variability of Diameter	Dia. where 95% Gtr.	Dia. where 5% Gtr.
17,000	1.8	0.2	1.6	0.2	1.7
23,200	1.4	0.1	1.3	0.2	1.2
35,000	0.9	<0.1	>0.8	<0.1	0.8
44,000	0.5	<0.1	>0.4	<0.1	0.2

Operating Conditions:

$$Q_{O_2}/A_p = 745 \text{ cfm O /sq. ft.}$$

$$Dp = 1/2 \text{ Inch}$$

the same range in oxygen bubble diameters of 0.1 to 2.0 millimeters, with values between 0.1 and 0.2 millimeters for liquid Reynolds numbers of 40,000 or greater.

It was not possible during the above experiments to make an accurate determination of the effects of increased liquid viscosity and surface tension on the resultant oxygen bubble diameters during two phase gas-liquid flow. Attempts to increase liquid viscosity by adding an organic cellulose viscosity aid material resulted in excessive liquid foaming and the inability to observe individual bubbles. Attempts to increase liquid density caused the liquid to become excessively murky in terms of making photographic studies of oxygen bubble size.

It was postulated that bubble diameters of oxygen introduced into the black liquor were initially larger than those in water for equivalent flow conditions because of the greater gas-liquid surface tension. The effect would be particularly pronounced for strong black liquor, where the tendency of bubbles to grow and agglomerate would be such as to favor the occurrence of annular and stratified configurations of two phase gas-liquid flow. For weak black liquor, the bubbles would decrease rapidly in size because of the relatively high rate of oxygen absorption in comparison to water. However, strong black liquor would not necessarily display the same tendency because of its lower oxygen absorption rate.

d. Importance

From the above information, it was possible to predict that it would be possible to perform oxidation of weak black liquor in a horizontal plug flow reactor because liquid Reynolds numbers of 40,000 or greater could be easily attained in full-scale systems. In extrapolating the results from the oxygen-water system, the mean oxygen bubble diameters in the froth flow regime

would probably be 0.1 millimeters or less. The interfacial gas-liquid contact area at the point of introduction at liquid Reynolds numbers of 40,000 or greater would then be at least 4,500 square feet per cubic foot of oxygen added. However, it would probably be very difficult to achieve a liquid Reynolds number of 40,000 with strong black liquor because of its high viscosity. It would then be difficult to achieve effective oxygen mass transfer into strong black liquor in a plug flow reactor.

2. Fluid Resistance

An additional aspect of two phase gas-liquid flow was that there was a substantial increase in the hydraulic resistance to flow in a pipe as compared to either the gas or liquid flow alone. It was no longer possible to apply the conventional laws of fluid mechanics to calculation of pressure drops through pipe sections, and the resulting pressure drops for the black liquor-oxygen system would have to be determined experimentally.

a. Procedure

A series of pilot scale experiments were subsequently conducted where oxygen from cylinders was introduced to the black liquor through a fritted glass dispersion cylinder located axially to the liquid flow, where both subsequently flowed cocurrently through the pilot scale plug flow reactor. Pressure differentials were measured by means of pressure gauges located upstream of the point of oxygen introduction, and at the downstream end of the reactor, where the actual pressure differentials were calculated from the two respective pressure gauge readings. Initial efforts to measure pressure differential directly using a mercury manometer were unsuccessful because of black liquor filling the manometer lines. Tests were made for oxygen using both water and weak black liquor as the liquid medium.

b. Results

Results of the studies indicated substantially increased resistance to flow when oxygen was introduced to the flowing liquid as compared to the liquid flowing alone because of the occurrence of two-phase gas-liquid flow. The degree of resistance to flow was found to increase with increasing oxygen gas flow rate per unit cross-sectional area of pipe, and decreasing pipe diameter for constant gas and liquid flow rates. The pressure differential across the reactor increased with increasing oxygen and black liquor flow rates, as shown in Figure 35. Most of the increased pressure drop occurred immediately downstream of the point of introducing oxygen before it could be absorbed into the black liquor. The pressure drop across the reactor also increased as inlet pipe diameter decreased, as shown in Figure 36. The increased pressure drop across the one-half inch inlet pipe was substantially greater than the larger pipes because the reduction in volume available for liquid flow caused by the presence of oxygen was relatively more important.

An additional consideration affecting the increase in pressure drop across a plug flow reactor during two phase gas-liquid flow as compared to either gas or liquid flow alone was the two phase flow configuration involved. Previous work by Baker (128) indicated that the resultant pressure drop across a pipe during two phase gas-liquid flow varied with the flow regime. The effects of superficial gas (Q/A) and liquid (L/A) superficial velocities, volumetric loading rates on the ratio of reactor pressure drop during two phase flow to liquid flow above ($\Delta P_{TP}/\Delta P_{BL}$) have been illustrated in Figure 37 for a one-half inch diameter pipe. The pressure differential ratio was found to increase with liquid volumetric loading rate to a maximum of 1,500 gallons per square foot per minute, and then decreased for higher

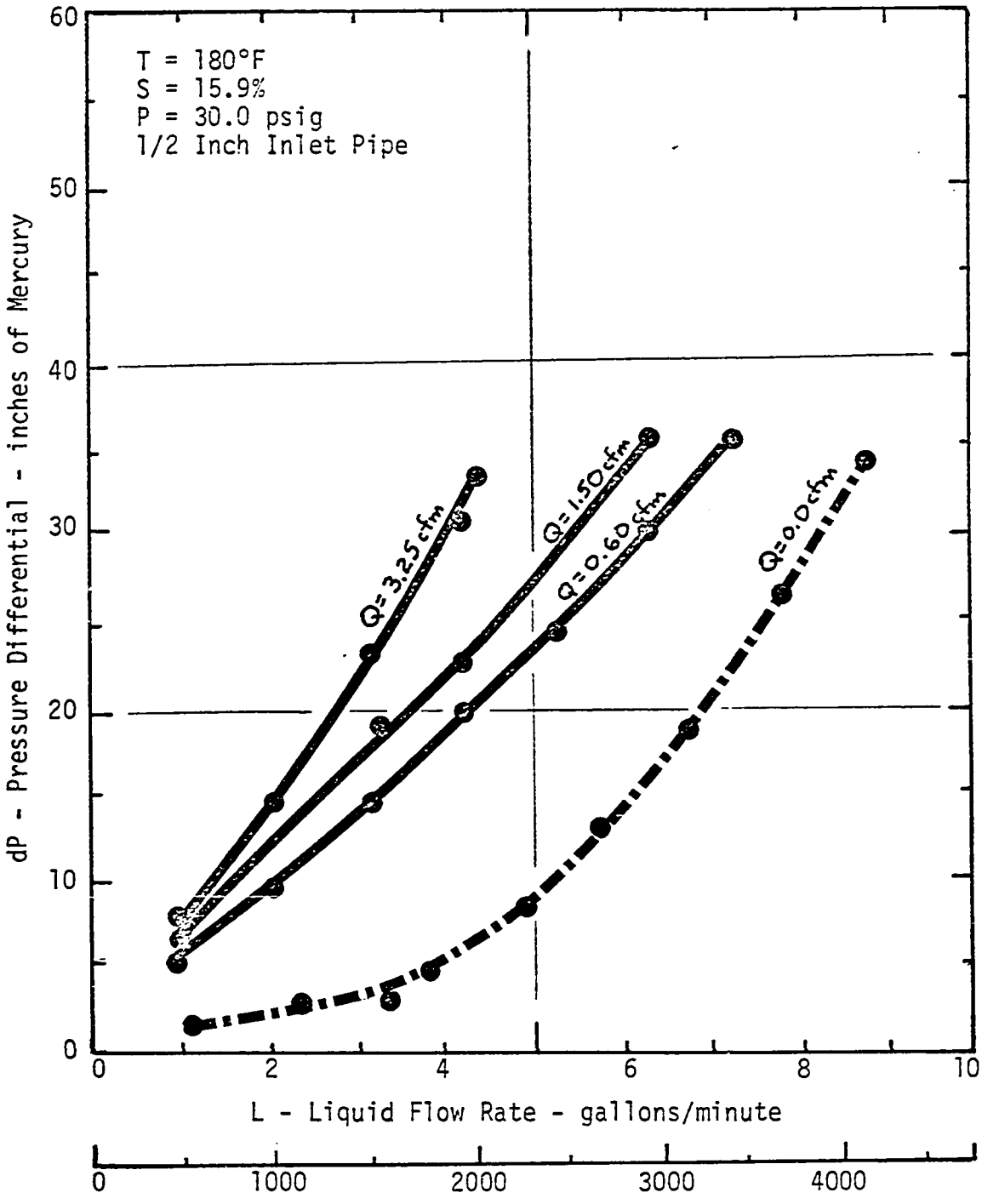


FIGURE 35. EFFECT OF OXYGEN FLOW RATE ON PRESSURE DIFFERENTIAL ACROSS PLUG FLOW REACTOR

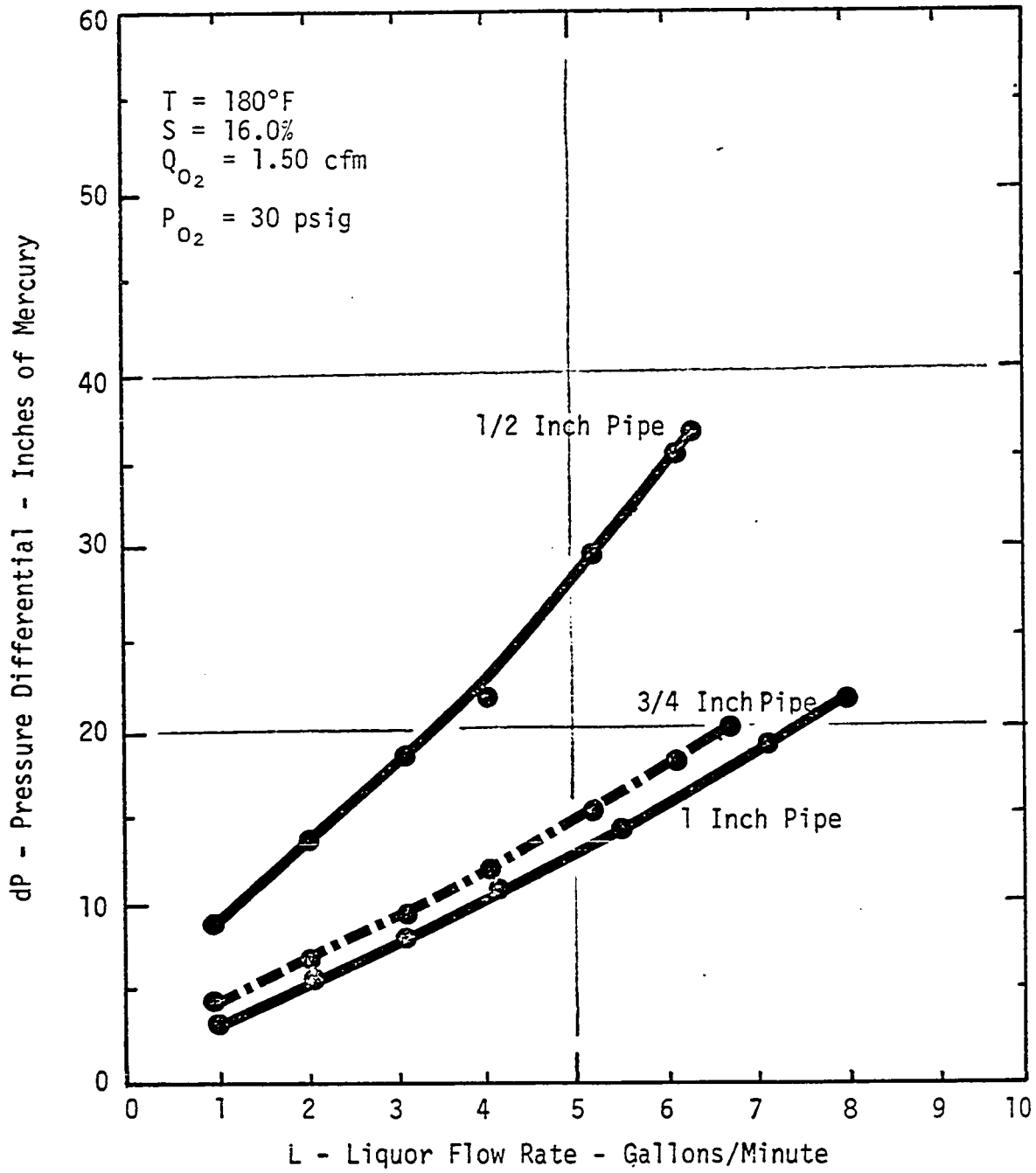


FIGURE 36. EFFECT OF INLET PIPE DIAMETER ON PRESSURE DIFFERENTIAL ACROSS PLUG FLOW REACTOR

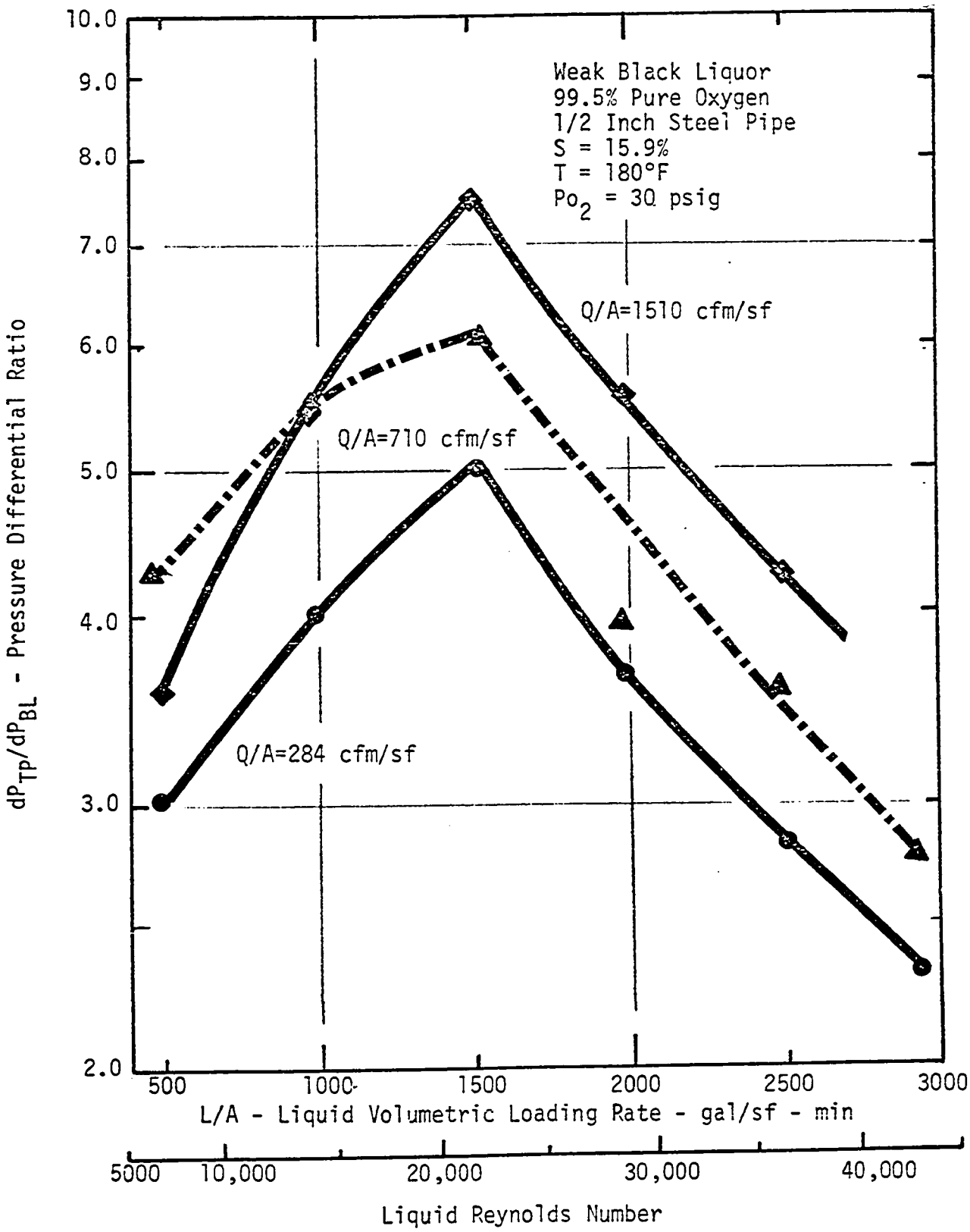


FIGURE 37. PRESSURE DIFFERENTIAL RATIO INCREASE DURING TWO PHASE GAS-LIQUID FLOW

loading rates. The maximum value was probably the transition between the annular and bubble regimes of two phase flow, as it corresponded to a liquid Reynolds number of 22,000. For one inch pipe, there was a continued decrease in pressure differential ratio with increasing liquid flow rate. Separate studies in the transparent pipe at equivalent gas and liquid flow rates indicated that stratified, plug, or slug flow configurations were predominant with one inch pipe for these conditions.

An additional result of the study was that the pressure differential across the plug flow reactor was found to be ten to 25 percent higher for weak black liquor than water for equivalent gas and liquid flow rates of any given diameter pipe. A probable reason was that liquid viscosity and surface tension affected pressure drop during two phase flow. This fact would be useful in any subsequent model studies for extrapolating pressure differentials to the design of full-scale systems.

c. Importance

The importance of the above findings was that substantial increases in pressure drop could be expected across a pipe when oxygen was added to black liquor. The increased pressure drop would be two to seven times that of the liquid flowing alone for the bubble or froth regimes of two phase gas-liquid flow. It may then become necessary to install additional liquid pumping capacity if molecular oxygen is used for black liquor oxidation in a plug flow reactor located in the piping of an existing system.

3. Oxygen Absorption

It was desired to determine the efficiency of oxygen absorption into weak black liquor in pipes of varying diameters, plus liquid and gas flow rates. The results were to be used as a design aid for modification of the

the pilot plant, to verify findings from previous studies of two phase gas-liquid flow, and for subsequent economic analyses where oxygen utilization efficiency was an important factor.

a. System

The amount of oxygen absorbed by the black liquor was measured as the difference between the amount injected and the amount of oxygen released at the downstream end of the reactor. The experimental apparatus was the pilot scale plug flow reactor, where the oxygen was introduced to the black liquor through a fritted glass dispersion cylinder located axially to the direction of liquid flow. The oxygen and black liquor then passed co-currently through a series of pipes of gradually increasing diameter, where the diameter of the inlet pipe could be changed to vary liquid Reynolds number. The inlet oxygen flow rate was measured by means of a calibrated rotameter upstream of the point of introduction to the black liquor. The flow rate of the unabsorbed oxygen at the downstream end of the reactor was measured by means of a dry gas meter connected to the exhaust of a deaeration chamber where the oxygen was separated from the black liquor. It was noted that some of the oxygen bubbles remained in the liquid phase and were not released in the deaeration chamber. The method for measurement of outlet oxygen flow rate was operable as long as the downstream end of the reactor was under positive pressure.

b. Results

Results of the study indicated that liquid Reynolds number, pipe diameter, and oxygen feed ratio (actual/theoretical) all affected the efficiency of oxygen absorption. The amount of oxygen absorption into weak black liquor appeared to be independent of inlet pipe diameter for a given oxygen

flow rate when the liquid Reynolds number exceeded 40,000, as shown in Figure 38. The oxygen flow rate during these tests was maintained at 0.60 cubic feet per minute throughout the series of tests. The absorption efficiency of oxygen into weak black liquor was 100 percent for all tests performed where the inlet pipe section was 3/8 inch diameter by 15 feet long. Absorption efficiency for the 1/2 inch diameter by 15 foot long inlet pipe dropped off rapidly for liquid Reynolds numbers below 36,000, probably because of increasing oxygen bubble diameter. Intermediate values for oxygen absorption efficiency with the pipe employing a 3/8 inch diameter by 12 inch long inlet section followed by a 1/2 inch by 14 foot extension section. The above findings pointed to the importance of the effect of inlet pipe diameter immediately downstream of the point of oxygen introduction into black liquor.

Further studies were devoted to the effect of oxygen feed ratio and inlet pipe diameter on the efficiency of oxygen absorption. The theoretical oxygen requirement for stoichiometric conversion of sodium sulfide to sodium thiosulfate was calculated by assuming an Na_2S concentration of 3.5 grams per liter, based on previous measurements. Results of the studies indicated a reduction in oxygen absorption efficiencies at oxygen feed ratios greater than 1.5 for 3/8 and 1/2 inch pipes. The results also indicated that materials in the black liquor other than sodium sulfide may also have been consuming oxygen. Absorption efficiencies for the 3/4 and one inch pipes were much lower than for the smaller diameter pipes, probably because of less efficient gas-liquid contact.

c. Importance

Results of the oxygen absorption studies tended to verify the results of the previous studies regarding two phase gas-liquid flow. Essentially

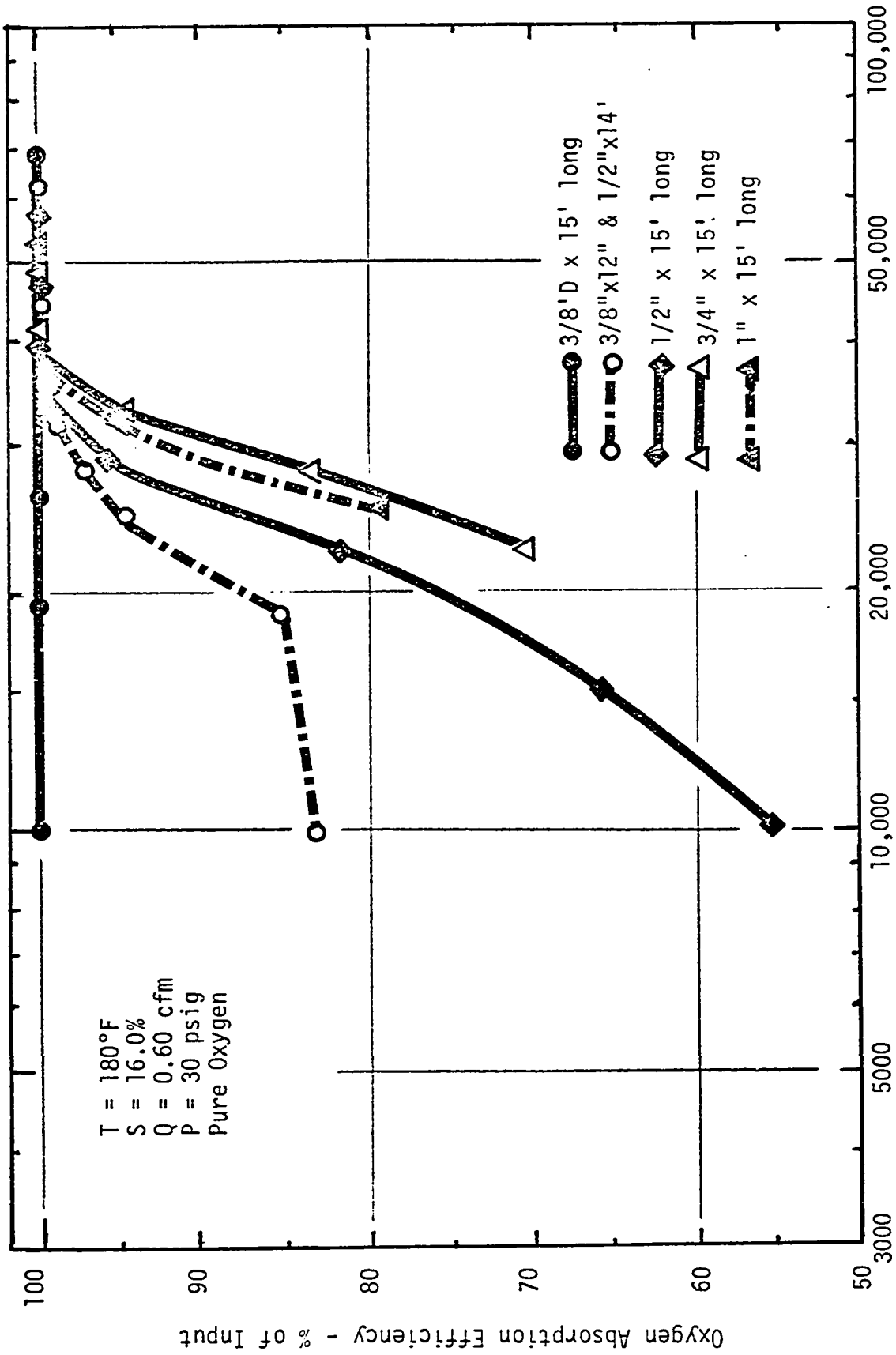


FIGURE 38. EFFECT OF LIQUID REYNOLDS NUMBER AND INLET PIPE DIAMETER ON OXYGEN ABSORPTION EFFICIENCY INTO WEAK BLACK LIQUOR

complete oxygen absorption was obtained for liquid Reynolds numbers greater than 40,000 with weak lack liquor. The oxygen absorption efficiency generally increased with decreasing pipe diameter, which would also involve greater liquid pressure drops and resultant pumping costs. It also appeared that oxygen absorption efficiencies of 90 percent or greater were possible with the plug flow reactor, making weak black liquor oxidation with molecular oxygen potentially attractive from an economic standpoint.

4. Reynolds Number

Reynolds number of the liquid stream appeared to be an important parameter affecting the efficiency of oxygen dispersion into black liquor. It affected the degree of turbulence and mixing, the ultimate size of oxygen gas bubbles formed upon injection, the degree of gas-liquid contact, and ultimately the rate of oxygen absorption. Previous experiments indicated that the Reynolds number must be at least 40,000 in the inlet pipe section of the experimental apparatus for effective transfer of oxygen gas molecules into the liquid phase. A complicating factor in interpretation of liquid Reynolds number data was the occurrence of two phase gas-liquid flow when oxygen was introduced to the pipeline reactor.

a. Pilot Scale System

A series of calculations were made regarding the effect of liquid flow rate and inside pipe diameter on liquid Reynolds numbers. For the experimental pipeline reactor system, liquid Reynolds numbers were computed for both weak and strong black liquor at typical operating temperatures and solids contents, based on no oxygen flow in the pipes. Results shown in Figure 39 indicated that Reynolds numbers for weak black liquor exceeded 40,000 for the 3/8 and 1/2 inch pipes at flow rates of greater than about six gallons per minute. Higher liquid flow rates of eight gallons per

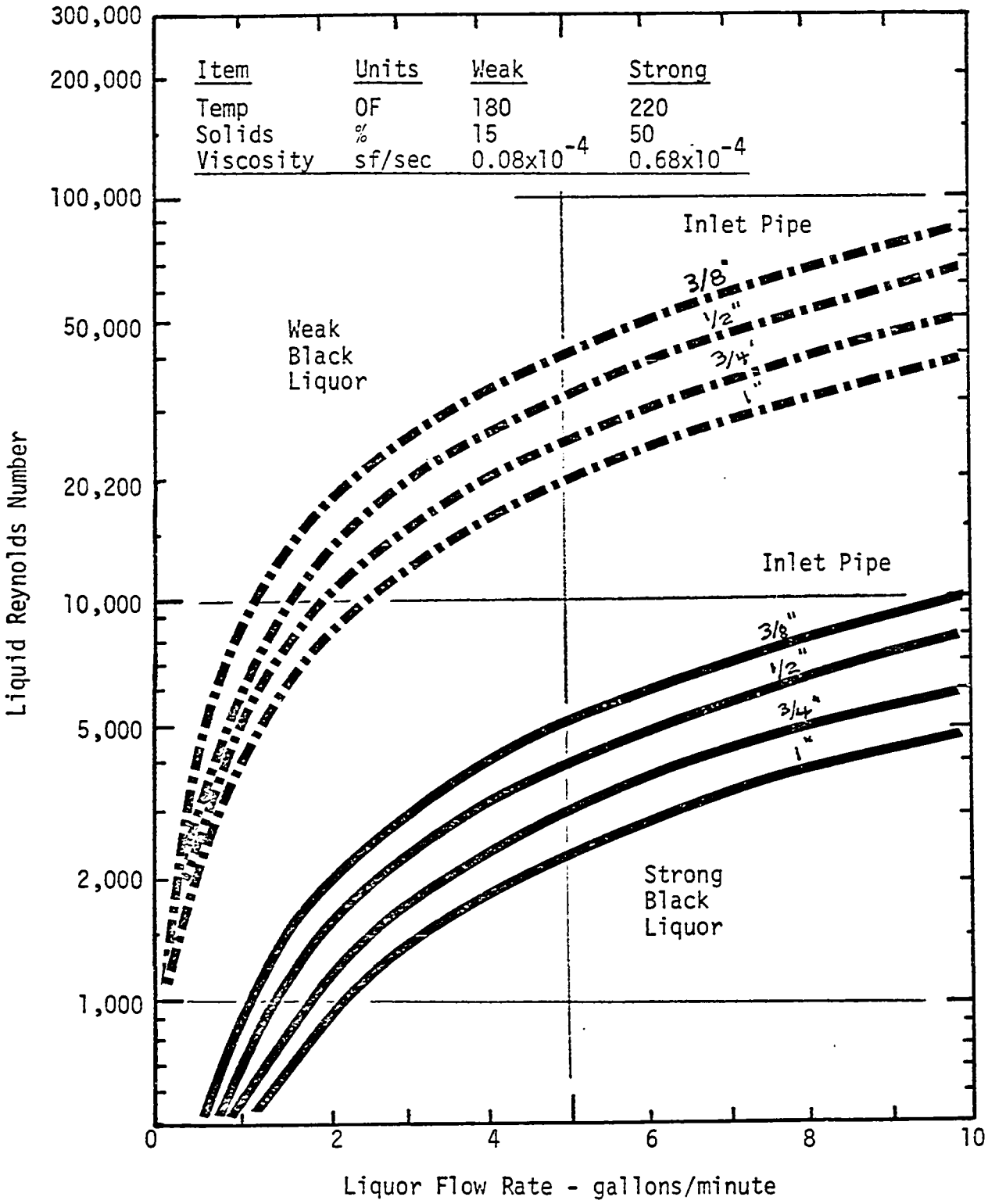


FIGURE 39. LIQUID REYNOLDS NUMBERS FOR BLACK LIQUOR IN THE PILOT SCALE PLUG FLOW REACTOR

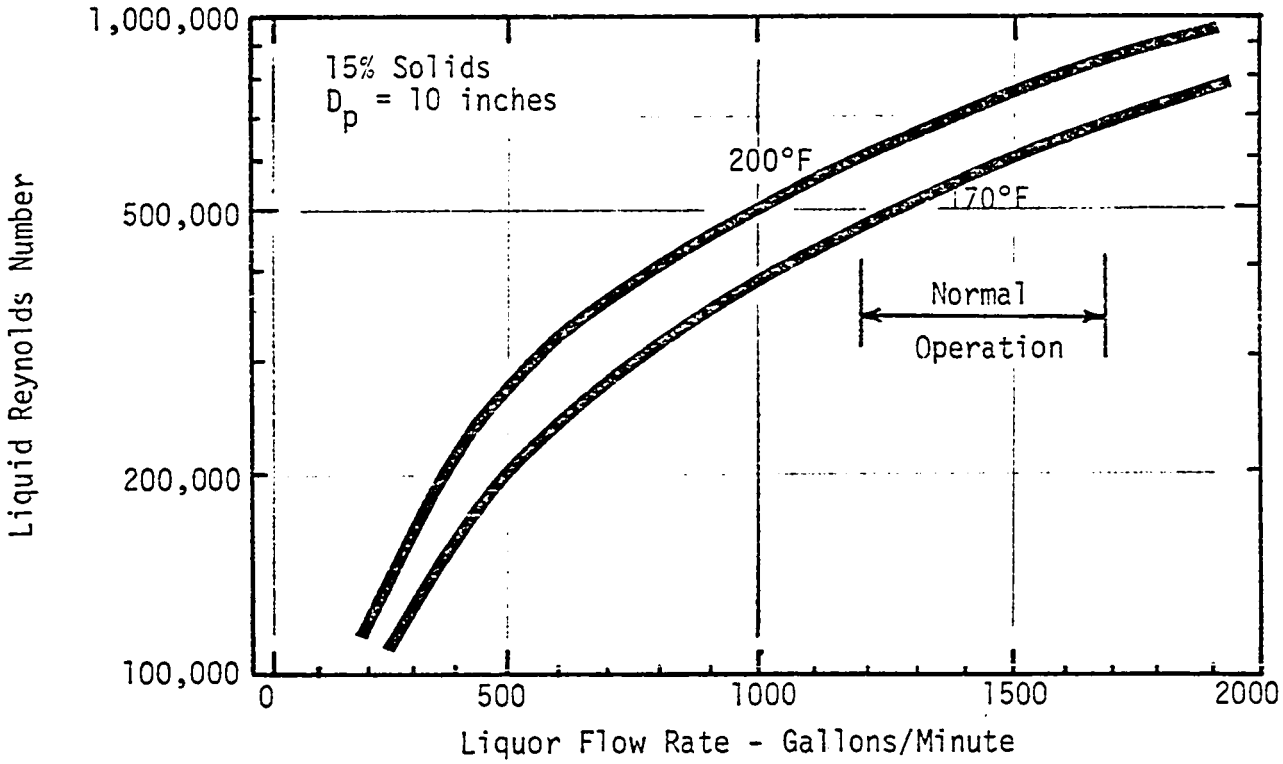
minute or more were necessary for the 3/4 and one inch pipes to achieve a liquid Reynolds number of greater than 40,000. However, for strong black liquor it did not appear that the liquid Reynolds number could become high enough to provide for effective oxygen transfer into the liquid phase. The primary reason for the low liquid Reynolds numbers was that increasing the solids content from 15 to 50 percent by weight resulted in increasing the black liquor viscosity by a factor of eight.

b. Full Scale Systems

Calculations were made of the liquid Reynolds numbers for the weak and strong black liquor oxidation pipeline reaction systems employing molecular oxygen at the Owens-Illinois, Inc., Kraft pulp mill at Orange, Texas (103). Results shown in Figure 40 indicated liquid Reynolds numbers of 300,000 to 900,000 for the system during periods of normal operation with the weak black liquor oxidation system at liquor flow rates from 500 to 1,700 gallons per minute at temperatures of approximately 200°F. Liquid Reynolds numbers for the weak black liquor oxidation system were well in excess of the minimum value of 40,000 reported from previous experiments, and indicated a highly turbulent situation for contacting oxygen with black liquor. Liquid Reynolds numbers of 20,000 to 30,000 were calculated for the strong black liquor oxidation system, with considerably less liquid turbulence to provide for oxygen mass transfer. However, the liquid-oxygen flow was in a vertical downward direction to provide for additional gas bubble retention time and alleviate the stratified flow configuration in a horizontal direction at low liquid Reynolds numbers.

An additional factor was that the liquid Reynolds number for black liquor increased with temperature, particularly for the strong black liquor because

a. Weak Black Liquor



b. Strong Black Liquor

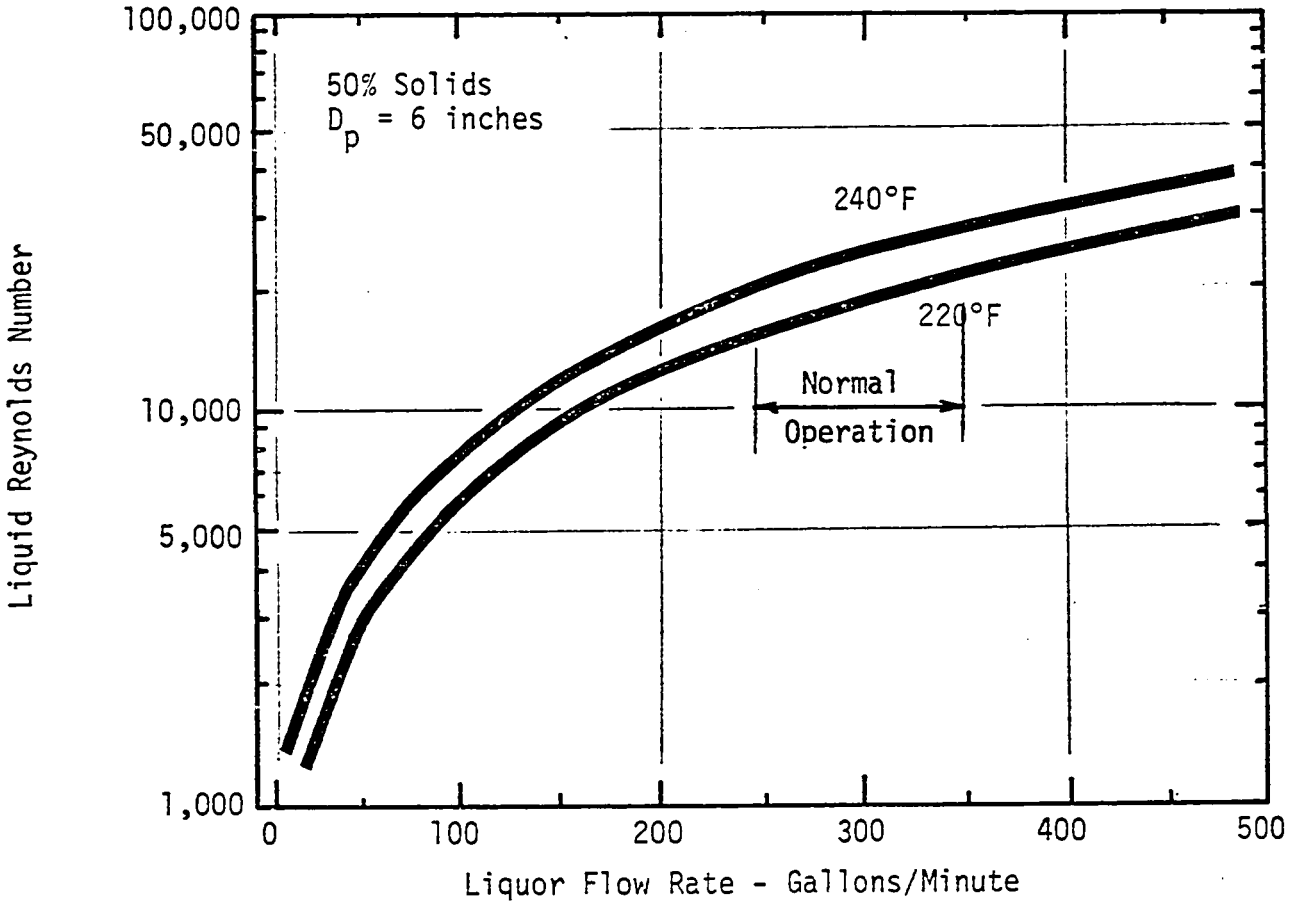


FIGURE 40. EFFECT OF LIQUOR FLOW RATE ON REYNOLDS NUMBER FOR OWENS-ILLINOIS SYSTEM

of reduction in liquid viscosity. One way to increase the potential rate of oxygen mass transfer into the liquid phase would be to heat the strong black liquor stream prior to injecting oxygen. However, it would then be necessary to raise the inlet oxygen pressure to offset the corresponding decrease in gas solubility with increased temperature. The possibility of increased oxygen consumption caused by corresponding increases in the rates of competing side reactions would also limit the potential suitability of heating strong black liquor to reduce its viscosity.

D. Weak Black Liquor Studies

A series of experiments were made to determine the rate of oxidation of sodium sulfide and sodium mercaptide in weak black liquor. Oxygen was introduced into a section of 3/8 inch diameter pipe through a porous fritted glass dispersion cylinder into a cocurrently flowing stream of weak black liquor. The progress of the oxidation reaction was determined by taking samples of black liquor at several different points along the pipeline reactor which represented increasing retention times. Chemical analyses for sodium sulfide and sodium mercaptide concentrations were then made in each black liquor sample. The kinetics of the oxidation reactions was then derived from the rate of disappearance of sodium sulfide and sodium mercaptide. Additional chemical analyses were made for other constituents as required for specific tests, including polysulfide, thiosulfate, sulfite, and sulfate ions, plus liquid pH.

Pilot scale investigations were conducted regarding the effects of several variables on the chemistry and kinetics of the oxidation of sodium sulfide and sodium mercaptide and other reactions in the weak black liquor. Physical parameters investigated included the following: 1) liquid Reynolds

number; 2) oxygen total pressure; 3) oxygen partial pressure; 4) liquid temperature. Chemical parameters investigated included the following: 1) liquid ph; 2) sodium thiosulfate concentration; 3) liquid retention time; 4) oxygen ratio. The effect of these variables upon the relative rates and the end products of the oxidation reactions were then determined with the results obtained from each of the respective experiments.

Primary consideration was given to determination of the effects of the above variables upon the respective reaction rate for oxidation of sodium sulfide and sodium mercaptide in weak black liquor with molecular oxygen. It was also desired to determine the respective oxidation rates of sodium polysulfide and sodium thiosulfate, plus the rate of formation of sodium sulfate and the rate of reversion to sodium sulfide. The above information regarding reaction rates would be useful for the subsequent design of full-scale installations in terms of retention time requirements, and for predicting the additional oxygen consumption by potentially competing side reactions.

1. Reaction Kinetics

a. Sodium Sulfide

The oxidation of sodium sulfide in weak black liquor was found to proceed in two distinct phases separated by a transition region. The initial conversion of sodium sulfide occurred within the first three to ten seconds of reaction, and accounted for approximately 90 to 95 percent of the total amount of sodium sulfide oxidized. The primary initial reaction appeared to be a rapid, essentially zero-order reaction which was relatively independent of sodium sulfide concentration at levels greater than 0.25 to 0.50 grams per liter. The initial rapid zero-order oxidation of sodium sulfide was primarily limited by factors affecting the rate of oxygen mass

transfer into the weak black liquor, but also chemical factors such as relative lignin catalysis and reaction end product concentrations.

The intermediate or transition region of sodium sulfide oxidation or weak black liquor was observed in terms of the period of variably decreasing reaction rate. It occurred following the initial oxidation step of three to ten seconds to approximately 60 to 120 seconds of reaction time at sodium sulfide concentrations between 0.10 and 0.50 grams per liter. The variable reaction rates during the transition period was determined by a combination of factors affecting both the initial and final reaction periods.

The final secondary region of sodium sulfide oxidation occurred at relatively low sodium sulfide concentrations below 0.10 to 0.25 grams per liter at reaction periods greater than 60 to 120 seconds. The oxidation of sodium sulfide at these low concentrations was found to approximate a relatively slow first-order reaction in terms of sodium sulfide concentration. The reaction rate at low concentrations was also affected by the liquid temperature, the amount of reaction end product, and the amount of oxygen initially added.

Reaction rate constants for the primary initial zero order and secondary first order reactions were determined graphically from experimental data by means of equations described in a previous section as follows:

a. Primary Zero Order Reaction:

$$r_1 = \frac{dC}{dt} = k_1 \qquad [82]$$

$$X_t = \frac{k_1}{C_o} t \qquad [85]$$

b. Secondary First Order Reaction:

$$r_2 = \frac{dC}{dt} = k_2 C \qquad [86]$$

$$2.303 \log \frac{C_t}{C_o} = k_2 t \qquad [88]$$

$$t_{1/2} = \frac{0.693}{k_2} \qquad [98]$$

Values for these constants were found to vary as listed in Table 23.

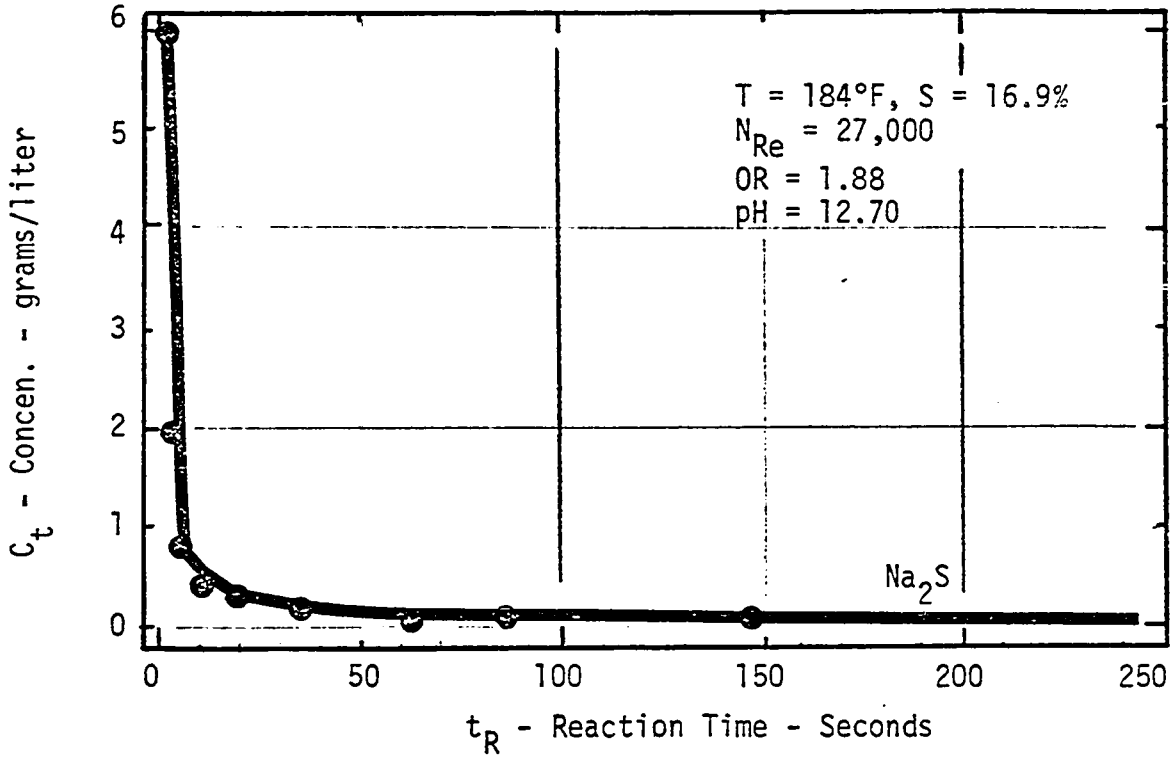
TABLE 23. OXIDATION RATES FOR SODIUM SULFIDE IN WEAK BLACK LIQUOR.

Constant	Order	Units	Mean	Maximum	Minimum
Primary k_1	0	$\frac{\text{gm } Na_2S}{\text{liter b.l.-sec}}$	-1.150	-1.483	-0.432
	0	$\frac{\text{lb } Na_2S}{\text{gal b.l.-hour}}$	-34.50	-44.50	-12.82
Secondary (k_2)	1	$\frac{1}{\text{seconds}}$	-0.00305	-0.00770	-0.00055
	1	$\frac{1}{\text{minutes}}$	-0.183	-0.462	-0.033
($t_{1/2}$)	1	seconds	326	1260	90

Notes: 1. Values for k_2 are calculated to base "e" logarithms.
2. Minus sign signifies concentration decrease for zero and first order reactions.

Reasons for variations in the above constants were to be discussed in subsequent chapters. A graphical presentation of the effect of reaction time on the respective concentrations of sodium sulfide and sodium mercaptide for a typical run have been presented in Figure 41, using both linear and semi-logarithmic plots.

a. Linear Plotting



b. Semilogarithmic Plotting

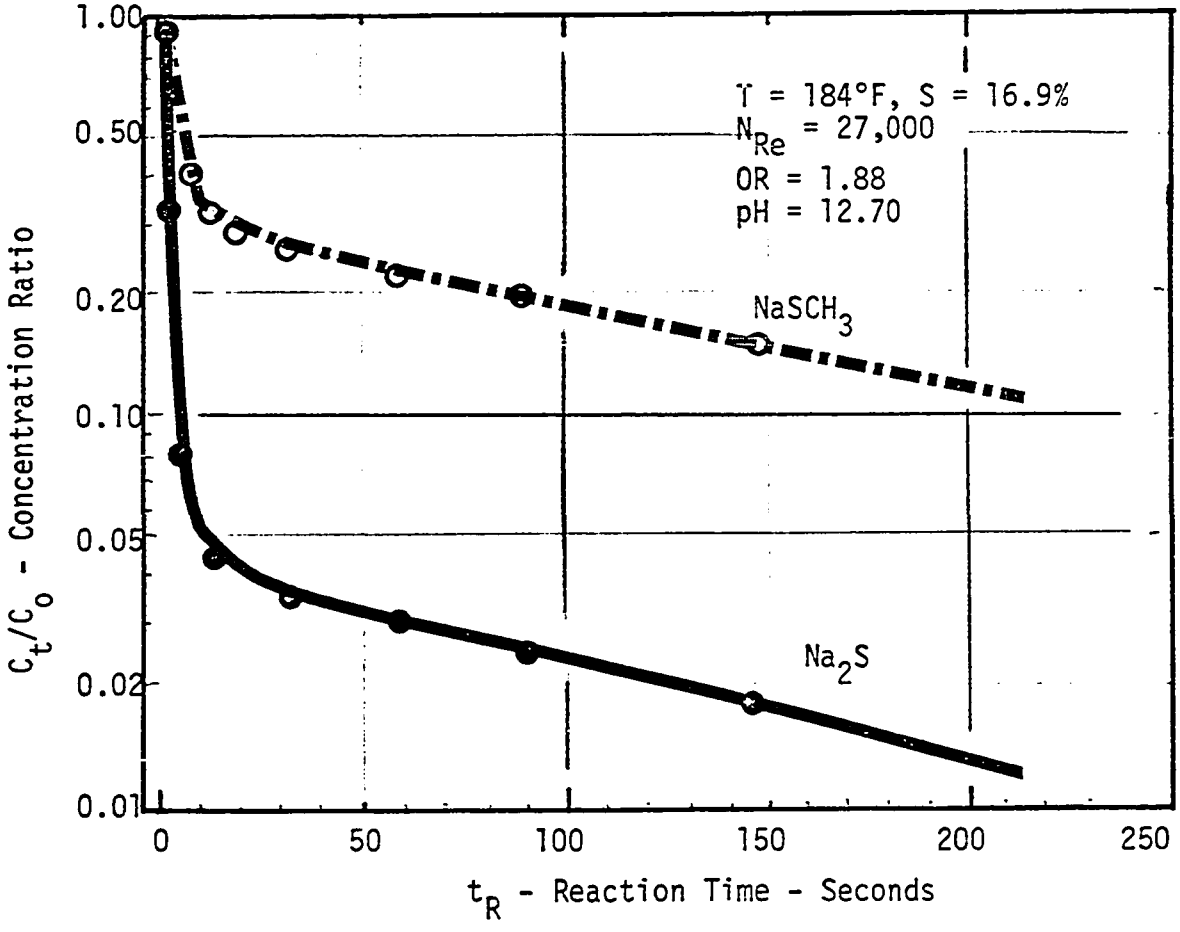


FIGURE 41. Na_2S and $NaSCH_3$ OXIDATION IN WEAK LIQUOR.

The findings of consecutive zero and first-order reactions for sodium sulfide oxidation in black liquor were in agreement with formulae previously described by Murray (138). Successive rate-limiting steps were oxygen mass transfer at high concentrations and chemical reaction rate at low sodium sulfide concentrations, though no specific values were presented for the respective rate constants. Galeano and Amsden (103) reported on a simplified reaction rate model which assumed the entire oxidation of sodium sulfide followed a first-order reaction. Their values of the constant ranged from 0.135 to 0.165 reciprocal seconds and were much higher than those observed during the study for the secondary rate constant (k_2). The reason for the difference was that their constant was for the overall reaction and did not account for the fact that the reaction occurred in successive zero and first-order reactions. The possibility for substantial errors could result by underestimating the necessary retention time requirements during storage to achieve high degrees of sodium sulfide oxidation.

Avrahami and Golding (142) presented values for reaction rate constants for the oxidation of sodium sulfide at low concentrations in alkaline solutions. They found that the oxidation of sodium sulfide (or hydrosulfide) followed consecutive steps of a relatively rapid initial reaction followed by a slow, essentially first-order reaction. Values for the secondary rate constant k_2 varied from 0.002 to 0.010 reciprocal minutes with a half-life of 150 minutes, with an activation energy of 8,000 gram-calories per gram-mole observed. Test conditions were a temperature of 45°C (113°F) and pure oxygen gas at initial sodium sulfide concentrations of approximately 0.008 grams per liter. The above values for secondary rate constant and half-life indicated a much slower reaction than comparable values observed in weak

black liquor, which could be explained by the much higher concentrations present, the higher temperatures, possible lignin catalysis and other differences in the test conditions.

b. Sodium Mercaptide

Sodium mercaptide oxidation in weak black liquor was found to follow a pattern similar to sodium sulfide. Principal differences were that the reaction was inhibited by the presence of sodium sulfide and that the initial oxidation rates tended to be slower than for sulfide. When sufficient oxygen was added to the weak black liquor, the initial oxidation rate of sodium mercaptide was relatively rapid and approached being a zero-order reaction.

When insufficient amounts of oxygen were added, an initial log period was followed in succession by a rapid initial reaction, a transition period, and a secondary slow reaction at low sodium mercaptide concentrations with increasing retention times. The initial lag period normally occurred during the initial five to ten seconds of rapid sodium sulfide oxidation, and was noted by minimal changes in sodium mercaptide concentration. The period from five to thirty seconds of reaction time corresponded to a relatively rapid oxidation of from 50 to 80 percent of the sodium mercaptide present, where the rapid reaction approached being zero-order in nature. An additional ten to twenty percent of the sodium mercaptide was oxidized during the transition period from 30 to 60 seconds, which was characterized by a gradually decreasing reaction rate. The oxidation of sodium mercaptide approached a slow first-order reaction at concentrations below 0.2 to 0.3 grams per liter at approximately the same level as noted with sodium sulfide. An additional facet of the reaction was that the dimethyl disulfide formed during oxidation of sodium mercaptide could be reabsorbed into the black liquor during storage, and subsequently undergo alkaline hydrolysis to reform sodium mercaptide.

Reaction rate constants noted for the oxidation of sodium mercaptide generally followed the pattern of successive zero and first-order reactions of sodium sulfide, except that values observed were generally lower, as shown in Table 24.

TABLE 24. OXIDATION RATES FOR SODIUM MERCAPTIDE IN WEAK BLACK LIQUOR

Constant	Order	Units	Mean	Maximum	Minimum
k_3	0-Var	$\frac{\text{gm Na SCH}}{\text{liter b.l.-sec}}$	-0.110	-0.271	-0.013
	0-Var	$\frac{\text{lb NaSCH}}{\text{gal b.l.-hour}}$	-3.30	-8.13	-0.39
k_4	1	1/seconds	-0.00222	-0.00854	-0.00032
	1	1/minutes	-0.133	-0.512	-0.019
$t_{1/2}$	1	seconds	611	2160	81

Notes: 1. Values for k_4 are calculated to base "e" logarithms.

2. Minus sign corresponds to concentration decrease in zero and first-order reactions.

Values for reaction rate constants appeared to be affected by oxygen ratio, temperature, and pH.

Values for rate constants regarding sodium mercaptide oxidation with oxygen were not reported in the literature. Harkness and Murray (145) found that the oxidation of methyl mercaptan in alkaline solutions appeared to proceed in two different reaction rate sequences where dimethyl disulfide and hydrogen peroxide were the primary reaction products. The initial reaction at high concentrations was dependent on oxygen pressure above the liquid, while the secondary reaction was a first-order reaction in mercaptan concentration in

the liquid and also oxygen pressure. The mechanisms reported by the study were the same as reported in the literature, but no comparative values for rate constants were possible.

c. Sodium Polysulfide

The concentration of sodium polysulfide in black liquor appeared to be inversely related to the concentration of sodium sulfite in weak black liquor. Sodium polysulfide concentrations varied between 0.05 and 0.5 grams per liter in weak black liquor. Sodium polysulfide levels approximated a steady state condition in weak black liquor, particularly when sodium sulfite concentrations were extremely low. Increases in sodium polysulfide concentration were normally observed during the initial reaction period of three to thirty seconds, probably because of its accumulation as a reaction intermediate in the conversion of sodium sulfide to sodium thiosulfate. Sodium polysulfide levels in weak black liquor either increased or decreased after ten to fifteen minutes of reaction time, possibly because of reversion to sodium sulfide. It was not possible to obtain sufficient data to postulate possible reaction rate constants and mechanisms because of the number of different forms of sodium polysulfide which could exist, the extreme complexity of the reactions involved, and difficulties in making accurate analysis. Slight increases in sodium polysulfide concentration during oxidation of weak black liquor with oxygen were also reported by Ricca (97).

d. Sodium Sulfite

Sodium sulfite concentrations in weak black liquor were found to be extremely low during most tests, and appeared to be inversely proportional to sodium polysulfide levels. The probable reason was the occurrence reaction of sodium polysulfide and sodium sulfite to form sodium sulfide and sodium thiosulfate as follows:

$$Na_2S_2 + Na_2SO_3 \longrightarrow Na_2S + Na_2S_2O_3 \qquad [35]$$

The occurrence of the above rapid reaction would tend to inhibit the simultaneous accumulation of sodium sulfite and sodium polysulfide in black liquor. An additional consequence of the above reaction would be to inhibit the oxidation of sodium thiosulfate through the sulfite ion intermediate to form sodium sulfate. The sodium polysulfide and sodium sulfite would be considered as intermediate products in the oxidation of sodium sulfide to sodium thiosulfate to sodium sulfate, respectively. A previous study by Ricca (97) pointed to the virtual absence of sodium sulfite in detectable quantities because of its rapid reactions to form other constituents.

e. Sodium Thiosulfate

Sodium thiosulfate was observed to be the primary end product of the oxidation of sodium sulfide in weak black liquor. Changes in sodium thiosulfate concentration appeared to follow a three step sequence in terms of reaction time, as shown in Figure 42. The initial step involved a rapid increase in sodium thiosulfate concentration which closely paralleled the initial rapid decrease in sodium sulfide concentration, and was essentially a zero order reaction. The initial rate of sodium thiosulfate increase was primarily determined by factors affecting the initial rate of sodium sulfide oxidation, particularly in terms of liquid temperature and pH.

The second stage of the sodium thiosulfate concentration involved the transition from a rapidly increasing concentration during the initial five to ten seconds of reaction to a relatively slow decrease in concentration. It normally occurred during the period of ten to sixty seconds reaction time, and was the region where the sodium thiosulfate concentrations reached a maximum value of between two and three times the initial concentration.

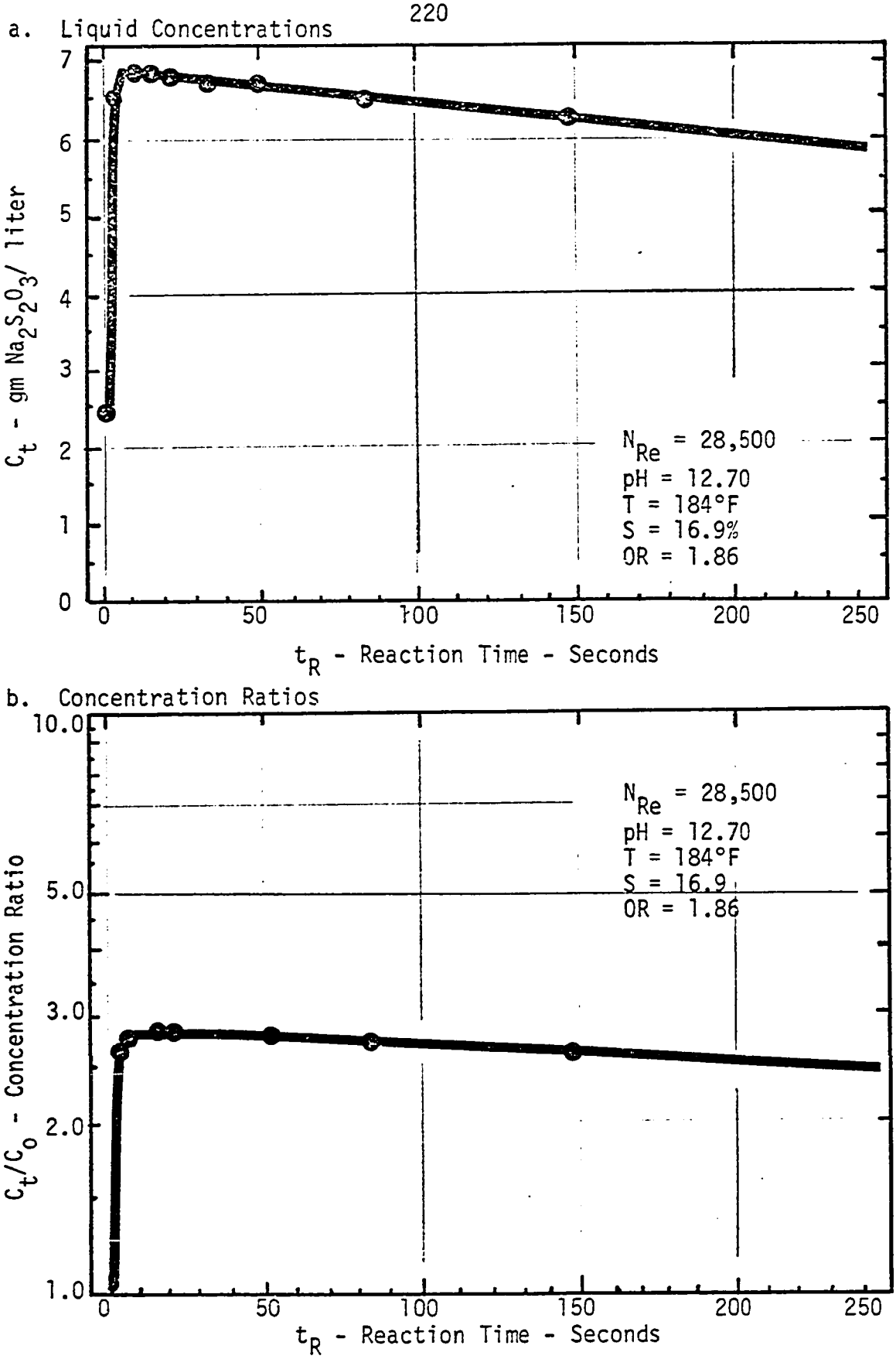


FIGURE 42. $Na_2S_2O_3$ CONCENTRATIONS IN WEAK LIQUOR.

The final region of sodium thiosulfate concentration change became predominant after approximately 60 to 120 seconds of reaction time. The region was characterized by a relatively slow decrease in sodium thiosulfate concentration with increasing reaction time which appeared to be first-order in terms of sodium thiosulfate concentration. The decrease in sodium thiosulfate concentration with time was probably caused by its oxidation to sodium sulfite by a slow reaction with oxygen as follows:

$$Na_2S_2O_3 + 2NaOH + O_2 \rightleftharpoons 2Na_2SO_3 + 2H_2O \qquad [33]$$

The above reaction was relatively slow and was probably the rate-limiting step in the process, which would explain the accumulation of sodium thiosulfate as a primary reaction product. The sodium sulfite formed could then undergo subsequent reaction with either oxygen to form sodium sulfate, or regenerate sodium sulfide and thiosulfate as follows:

$$2Na_2SO_3 + O_2 \rightleftharpoons Na_2SO_4 \qquad [34]$$

$$Na_2SO_3 + Na_2S_2 \rightleftharpoons Na_2S_2O_3 + Na_2S$$

The rate of sodium thiosulfate oxidation was found to increase with both liquid temperature and pH, placing it in agreement with kinetic theory and the above reaction sequence.

Rate constants for the successive reactions of zero order increase and first order decrease in sodium thiosulfate concentration with time have been listed in Table 25. Reaction rate constants during the initial reaction period with sodium thiosulfate (k_5) averaged slightly lower than for sodium sulfide (k_1). These findings indicated that approximately ten percent of the thiosulfate initially present was oxidized during the initial period, possibly to sodium sulfate. The rate constant for sodium thiosulfate oxidation (k_6)

in the final phase was substantially less than the equivalent rate constant for sodium sulfate oxidation in the same period.

TABLE 25. REACTION RATES FOR SODIUM THIOSULFATE IN WEAK BLACK LIQUOR.

Constant	Order	Units	Mean	Maximum	Minimum
k_5	0	$\frac{gm\ Na_2S_2O_3}{liter\ b.l.-sec}$	+1.148	+1.340	+0.427
	0	$\frac{lb\ Na_2S_2O_3}{gal\ b.l.-hour}$	+31.42	+40.20	+12.82
k_6	1	1/seconds	-0.00021	-0.00042	-0.00006
	1	1/minutes	-0.0123	-0.0254	-0.0037
$t_{1/2}$	1	seconds	3,300	11,500	1,650

Notes: 1. Values for k_6 are calculated to base "e" logarithms.

2. Minus sign corresponds to concentration decrease in first-order reactions.

Little information has been reported to date regarding changes in sodium thiosulfate concentration in black liquor with reaction time, except that it was the primary product of sodium sulfide oxidation. Avrahami and Golding (142) observed that after an initial period of concentration increase during oxidation of sodium sulfide in alkaline solutions, the sodium thiosulfate concentration decreased with time. The decrease in sodium thiosulfate concentration with time approximated a first-order reaction whose rate was much slower than the equivalent rate of sodium sulfide oxidation, where the primary reaction product was sodium sulfate. Pryor (150) also observed the decomposition of sodium thiosulfate to be a first-order reaction, and reported similar values for the rate constants. The oxidation of sodium thiosulfate

was the slowest reaction in the system, which would explain its accumulation during oxidation of sodium sulfide with oxygen. Specific values for rate constants could not be determined from the study, but values for thiosulfate half-life were larger than with black liquor, probably because of the lower temperatures and concentrations, and differences in the systems studied. Basic trends regarding sodium thiosulfate oxidation were the same for both weak black liquor and dilute alkaline solutions.

f. Sodium Sulfate

The formation of sodium sulfate in weak black liquor was found to occur in a three step sequence, as illustrated in Figure 43. The major portion of the sodium sulfate formed was generated during the initial reaction period of five to fifteen seconds, and probably resulted from the oxidation of the sodium thiosulfate initially present. When insufficient quantities of oxygen were added to the weak black liquor, the formation of sodium sulfate was inhibited by the presence of sodium sulfide, and an initial lag period resulted similar to that observed for sodium mercaptide. The initial formation rate for sodium sulfate appeared to approximate a zero order reaction, and was affected both by liquid temperature and pH.

The transition period between ten and 60 to 120 seconds was characterized by a variable decrease in the rate of sodium sulfate formation reaction from the rapid zero order reaction to the slower final reaction. The third region of the sodium sulfate formation was characterized by a relatively slow increase in sodium sulfate concentration which appeared to approximate a second order reaction, as illustrated in Figure 43. The rate of sodium sulfate formation in the final region appeared to be slower than the rate of sodium thiosulfate disappearance. These findings indicated that products other than sodium sulfate were being formed by oxidation of sodium thiosulfate in weak black liquor.

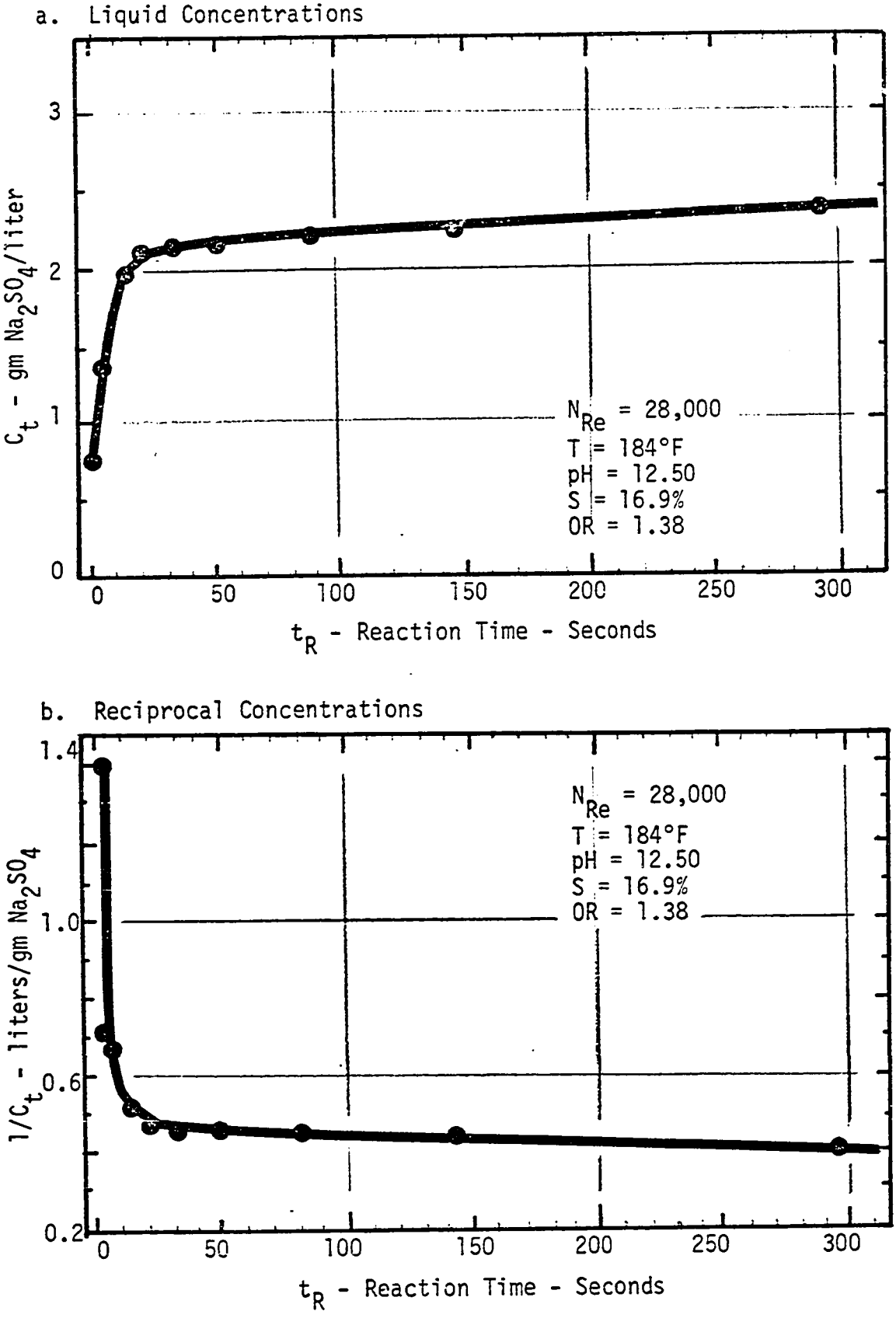


FIGURE 43. Na_2SO_4 FORMATION IN WEAK BLACK LIQUOR.

Reaction rate constants for the formation of sodium sulfate during the primary initial zero order and secondary final second order regimes have been listed in Table 26.

TABLE 26. REACTION RATES FOR SODIUM SULFATE FORMATION IN WEAK BLACK LIQUOR.

Constant	Order	Units	Mean	Maximum	Minimum
k_7	0	$\frac{gm\ Na_2SO_4}{liter\ b.l.\text{-}sec}$	+0.119	+0.290	+0.010
	0	$\frac{lb\ Na_2SO_4}{gal\ b.l.\text{-}hour}$	+3.57	+8.70	+0.30
k_8	2	$\frac{liter\ b.l.}{gm\ Na_2SO_4\text{-}sec}$	-0.0007	-0.00013	-0.00001
	2	$\frac{gallon\ b.l.}{lb\ Na\ SO\ -hour}$	-28.7	-55.4	-4.2

Note: 1. Minus sign corresponds to concentration increase in second order reaction.

Temperature and pH of the black liquor both appeared to have an important effect on the rate of the above reactions, in agreement with both kinetic theory and black liquor oxidation chemistry. The formation of sodium sulfate was of potential importance in providing an additional source of oxygen consumption which might have an economic impact on the prospective use of molecular oxygen for black liquor oxidation.

Little available information has appeared in the literature regarding sodium sulfate formation in black liquor. Miller (102) reported increases in sodium sulfate concentration in weak black liquor of one to two grams per liter during oxidation with molecular oxygen. Galeano and Amsden (103) reported increases of two to three grams per liter during extended periods

of reaction time. A rate constant was calculated from their values for concentration increases with estimated retention times during storage by assuming a second order reaction. These calculations showed a rate constant value approximately equivalent to the lower limit of values observed for second order reaction rate constant during the studies. It was not possible to make an accurate comparison because of the differences in reaction conditions and incomplete test data.

2. Process Variables

Considerable variability in the respective reaction rates and rate constants was noted for the oxidation of sodium sulfide and sodium mercaptide in weak liquor, along with changes in sodium thiosulfate concentration and sodium sulfate formation. The respective reaction rates and rate constants appeared to be functions of reaction time with successive regimes of a primary initial rapid reaction, a transition period, and a secondary, relatively slow reaction. The reaction rates for each of the compounds were also determined by their inlet concentrations, the amounts of oxygen added, the nature and extent of the chemical reactions taking place, the reactor configuration, and by specific process variables.

Process variables which were found to have particular influence on the weak black liquor oxidation reactions included the following: 1) liquid Reynolds number; 2) solids concentration of the weak black liquor; 3) oxygen inlet or static pressure; 4) oxygen partial pressure of the inlet gas stream; 5) oxygen ratio, or ratio of oxygen added to that required for stoichiometric conversion of sodium sulfide to sodium thiosulfate; 6) inlet liquid temperature; 7) inlet liquid pH; 8) inlet sodium thiosulfate concentration. An additional variable of potential importance was the wood species being pulped,

but this parameter could not be varied at the mill where tests were being conducted.

In running a series of tests by making changes in a particular parameter, attempts were made to hold other variables constant to the maximum extent possible. Maintaining constant operating conditions during and particularly between successive tests was made difficult by frequent changes in mill operating conditions. Running an entire sequence of tests at one time was perhaps the best way to compensate for the problem of changes in process operating conditions.

a. Physical Parameters

(1) Effect of Liquid Reynolds Number

Results from previous experiments indicated that liquid Reynolds number was a particularly important parameter in determining the effectiveness of oxygen mass transfer into a liquid stream in a plug flow reactor. The effect of maintaining large liquid Reynolds numbers in the weak black liquor was to promote a high degree of gas-liquid interfacial contact area by favoring the following conditions: 1) the bubble or froth regimes of two phase gas-liquid flow necessary for maximum contact area; 2) a minimum oxygen bubble diameter in the liquid stream consistent with a maximum gas-liquid contact area; 3) a high degree of turbulence to promote rapid renewal of the liquid film surface adjacent to the bubbles.

Studies were conducted regarding the effect of liquid Reynolds number on the respective oxidation rates of sodium suliide and sodium mercaptide in weak black liquor in terms of retention time. Results indicated that the primary oxidation rates (zero order) for sodium sulfide (k_1) and sodium mercaptide (k_3) during the initial reaction period five to ten seconds increased substantially with increasing Reynolds number of the inlet reactor

section, as listed in Table 27. An additional effect of increasing the liquid Reynolds number of the weak black liquor was that the overall oxidation efficiency for sodium sulfide and sodium mercaptide across the plug flow reactor system (point 0 to 8) was considerably increased, as shown in Table 28.

Results of the studies regarding the effects of liquid Reynolds number on oxidation of sodium sulfide and sodium mercaptide in a plug flow reactor verified the findings of the previous studies on oxygen mass transfer into water in a transparent pipe. The primary initial oxidation rate constants for sodium sulfide were particularly affected by liquid Reynolds number because the rapid zero order-type reactions at relatively high concentrations would be particularly affected by the rate of oxygen mass transfer into weak black liquor. Though no specific tests were made, the secondary reaction rate constants defining the first order oxidation reactions were primarily limited by factors affecting the chemical reactions. These constants were not appreciably affected by the mass transfer-related liquid Reynolds number. The above findings underlined the necessity for maintaining the liquid Reynolds number above 40,000 when oxygen was introduced to weak black liquor in a plug flow reactor. No studies have been reported to date have involved determining the effect of liquid Reynolds number on sodium sulfide oxidation rate. Previous discussions of the system used by Galeano and Amsden (103) indicated liquid Reynolds numbers of 300,000 or greater, well above the 40,000 minimum value.

(2) Effect of Liquor Solids Concentration

Increasing in black liquor solids concentrations would tend to increase its viscosity, thus reducing its liquid Reynolds number for equivalent volumetric flow rates. The result would be increased resistance to oxygen

TABLE 27. EFFECT OF LIQUID REYNOLDS NUMBER ON PRIMARY Na_2S AND $NaSCH_3$ OXIDATION RATES IN WEAK BLACK LIQUOR.

Reynolds Number N_{Re_L}	Primary Oxidation Rate	
	Na_2S $(-r_1=k_1)$ gm Na_2S/liter b.l.-sec	$NaSCH_3$ $(-r_3=k_3)$ gm $NaSCH_3$/liter b.l.-sec
11,500	-0.102	-0.012
19,500	-0.427	-0.027
25,000	-0.716	-0.071
30,000	-1.057	-0.133
38,000	-1.482	-0.193

Notes: 1. Minus sign corresponds to concentration decrease in zero order reactions.

2. Reaction conditions: pH = 12.6-12.7; T = 184°F, S = 18.4% by wt.

TABLE 28. EFFECT OF LIQUID REYNOLDS NUMBER ON OVERALL Na_2S AND $NaSCH_3$ OXIDATION EFFICIENCIES IN WEAK BLACK LIQUOR.

Reynolds Number N_{Re_L}	Retention Time seconds	Oxidation Efficiency - %	
		Na_2S	$NaSCH_3$
11,500	345	73.2	15.0
19,500	202	92.9	60.0
25,000	160	95.4	62.5
30,000	130	97.9	93.0
38,000	130	98.3	95.0

Notes: 1. Oxidation Efficiency: $OE = (1 - C_8/C_o) \times 100$.

2. Operating Conditions: pH = 12.6-12.7; T = 184°F; S - 18.4% by wt.

3. Inlet Concentrations: C_{Na_2S} = 5.38 gm/liter; C_{NaSCH_3} = 1.35 gm/liter.

mass transfer into the liquid phase, and a decrease in the rate of oxidation for sodium sulfide and sodium mercaptide. The effect would be particularly pronounced during the initial reaction phase within the first five to ten seconds where oxygen mass transfer into weak black liquor was an important parameter. The expected result of increased liquor solids concentration was a reduction in the primary initial rate constant for sodium sulfide oxidation.

No specific tests were made where weak black liquor solids concentration was varied to determine its effect upon the rate of sodium sulfide oxidation. However, results of three tests were observed under similar conditions of liquid temperature, pH, and Reynolds number where variations in liquor solids concentrations were observed. Results indicated a reduction in the primary initial reaction rate constant for sodium sulfide oxidation with increasing solids concentration, as listed in Table 29.

TABLE 29. EFFECT OF SOLIDS CONCENTRATION ON PRIMARY Na_2S OXIDATION RATE IN WEAK BLACK LIQUOR.

Solids Concentration % by wt.	Primary Rate ($r_1=k_1$) gm Na_2S/liter b.l.-sec
16.9	-1.490
17.3	-1.280
18.4	-1.057

Note: 1. Operating Conditions: pH = 12.6-12.8; T = 184°F
N_{R_e} = 30,000-32,000

Maximum oxygen mass transfer rates were favored injecting the oxygen into weak black liquor at point of minimum solids concentrations to facilitate minimum retention time requirements to achieve given sodium sulfide oxidation

efficiency levels. Oxidation of weak black liquor from Kamyr continuous digesters employing internal washing or where strong black liquor was recycled to control foaming in existing air oxidation systems could result in substantially greater retention time requirements when using molecular oxygen in plug flow reactors because of the resultant higher inlet solids concentrations. Specific tests would have to be made at individual mills to determine exact values for reaction rate constants of sodium sulfide oxidation in weak black liquor in terms of solids concentrations and other parameters. No specific values have been reported in the literature regarding the effect of weak black liquor solids concentration on initial sodium sulfide oxidation rate.

(3) Effect of Oxygen Inlet Pressure

Increasing the static pressure of a gas above a liquid would tend to increase its solubility in that liquid because of the greater net driving force across the boundary, as previously described by Henry's law. Therefore, increasing the inlet pressure of the oxygen introduced into the black liquor would tend to increase its solubility in the liquid phase and counteract the tendency towards reduced solubility of gases at increasing temperatures. The result of increasing the oxygen total pressure of the inlet gas stream would be to produce a slight increase in the rate of sodium sulfide oxidation in the initial reaction phase because of the increased gaseous pressure driving force and gas solubility in the weak black liquor.

A series of tests were made where a stream of essentially pure (99.5 percent by volume) oxygen was introduced at constant mass flow rate into a stream of weak black liquor at constant flow rate. The inlet pressure of the oxygen was varied from 30 to 60 psig in successive tests, and its effect observed on the rate of sodium sulfide oxidation as a function of

reaction time. Results indicated a slight increase in the primary initial reaction rate constant for sodium sulfide oxidation, as listed in Table 30.

TABLE 30. EFFECT OF OXYGEN PRESSURE ON PRIMARY Na_2S OXIDATION RATE.

Oxygen Inlet Pressure psig	Primary Rate ($r_1=k_1$) gm Na_2S/liter b.l.-sec
30	-1.260
40	-1.306
50	-1.335
60	-1.367

Operating Conditions: 1. T = 184°F, S = 17.0%
N_{R_e} = 28,000-30,000
pH = 12.8-12.9
2. Oxygen = 99.5% Purity

The rate constants (k_1) listed in the previous table were in actuality the product of a constant term and a term expressing pressure variation, but there was insufficient data to establish an exact relationship. The increase in overall sodium sulfide oxidation rate approximated a linear relationship over the range studied, indicating agreement with Henry's law regarding increased gas solubilities at increasing pressures.

The importance of the above findings was that increasing the oxygen inlet pressure provided a means for counteracting the tendency for decreasing gas solubility with increasing liquid temperature. The technique was potentially suitable for systems used to oxidize weak black liquor from Kamyr continuous digesters employing internal pulp washing, where the liquid

temperature was often between 200 and 220°F. The drawback of increased inlet oxygen pressure for high temperature liquids was that it could require additional compressor capacity and increased operating costs for additional electric power.

(4) Oxygen Partial Pressure

It was desirable to maintain a relatively pure stream of oxygen gas being introduced to weak black liquor in a plug flow reactor for several reasons. A pure gas would have the greatest partial pressure driving force into the liquid phase, in accordance with Henry's law. A high partial pressure driving force would result in a maximum gas solubility and optimum primary initial oxidation rate for sodium sulfide and sodium mercaptide. Maintaining a minimum gas-to-liquid volumetric flow ratio provided for a maximum tendendency for the plug flow reactor to be in the bubble or froth regimes of two phase gas-liquid flow to maintain a maximum gas-liquid interfacial contact area. Minimizing the amount of nonreactive constituents of the incoming gas stream minimized the tendency for liquid cooling by evaporation of water, with potential resultant pumping problems, greater atmospheric emissions, and possible increased evaporator steam requirements. The potential for foaming of weak black liquor was minimized by the use of a pure oxygen gas stream.

A series of tests were made where an oxygen gas stream of constant flow rate was introduced to weak black liquor in the plug flow reactor. The oxygen partial pressure was varied in successive runs by addition of nitrogen gas at known flow rates to the oxygen stream upstream of the point of introduction to the black liquor. The effect of oxygen partial pressure on the respective rates of sodium sulfide and sodium mercaptide oxidation were then determined as functions of retention time. Results of these studies indicated

that decreased oxygen partial pressure caused a slight decrease in the primary initial rate constant for sodium sulfide oxidation, probably because of reduced gas solubility at the lower oxygen partial pressure driving force. There was no observed effect on the secondary oxidation rate constant for sodium sulfide in the weak black liquor, as shown in Table 31.

TABLE 31. EFFECT OF OXYGEN PARTIAL PRESSURE ON Na_2S and $NaSCH_3$ OXIDATION RATES IN WEAK BLACK LIQUOR.

	Sodium Sulfide		Sodium Mercaptide	
Oxygen Partial Pressure % of Total	$r_1=k_1$ gm Na_2S liter-sec	$k_2{}^2$ 1/seconds	$r_3=k_3$ gm $NaSCH_3$ liter-sec	$k_4{}^2$ 1/seconds
99.5	-1.262	-0.00161	-0.156	-0.00212
90.2	-1.247	-0.00161	-0.174	-0.00120
79.7	-1.172	-0.00161	-0.182	-0.00120

Notes: 1. Operating Conditions: N_{R_e} = 29,000-30,000; P_T = 30.0 psig
T = 184°F; S = 18.1% by wt.
2. Secondary rate constants are computed to basic "e" logarithms.

Somewhat contrary trends in the reaction rate constants were observed for conversion of sodium mercaptide, as observed from the above table. The primary oxidation rate constant for sodium mercaptide appeared to increase with decreasing oxygen partial pressure of incoming gas stream. A possible reason for the increased removal rate was from stripping of either methyl mercaptan in equilibrium with the sodium mercaptide or dimethyl disulfide as a reaction product to increase the concentration driving force. A decrease in the secondary rate constant was observed between the essentially pure oxygen gas and the lower purity oxygen gas streams. A possible reason for the decrease was reabsorption of methyl mercaptan or dimethyl disulfide (with

alkaline hydrolysis) previously evolved. The stripping of methyl mercaptan or dimethyl disulfide from the black liquor would constitute an increased potential for sulfur gas emissions at the vent in the oxidation system.

Specific results for the effect of oxygen partial pressure in the gas stream on sodium sulfide oxidation in black liquor have not appeared in the literature. Avrahami and Golding (142) reported that the rate of sodium sulfide oxidation in dilute alkaline solutions was approximately eight times greater with pure oxygen than for air as the feed gas. They also reported that the half-life for sodium sulfide in alkaline solutions decreased with increasing partial pressure of the gas stream. Basic trends of increased oxidation rate and efficiency for sodium sulfide were in agreement with findings reported during the study.

The primary reason for conducting tests for variable oxygen partial pressures in the incoming gas stream was to test for the possible use of molecular sieve absorption-generated oxygen at a lowerpurity (90 to 95 percent) than cryogenic oxygen. The molecular sieve oxygen could be obtained at lower cost for equivalent production rates than cryogenic oxygen with small systems of less than 100 tons per day capacity. For approximately 90 percent purity oxygen, a minimal decrease in primary sodium sulfide oxidation rate constant was noted, along with slightly increased potential for stripping of malodorous organic sulfur gases. The major problem observed with the lower purity oxygen streams was the dramatic increase in foaming potential for weak black liquor (not pine), particularly for the 80 percent purity oxygen. An oxygen gas purity of 90 percent would be the probable lower limit with molecular sieve absorption systems to minimize foaming problems, although the potential existed for increasing tall oil yields flotation.

b. Chemical Parameters

(1) Effect of Oxygen Ratio

It was important to add a sufficient quantity of oxygen to provide for oxidation of sodium sulfide to sodium thiosulfate and sodium mercaptide for dimethyl disulfide. However, addition of excessive quantities of oxygen would result in increased operating costs because of inefficient utilization and possible increased oxygen consumption. For purposes of the present study, the oxygen ratio was defined as the ratio of the amount of oxygen actually added (OA) to that theoretically required for stoichiometric conversion of sodium sulfide to sodium thiosulfate and sodium mercaptide to dimethyl disulfide ($\overline{OT}$).

$$OR = \frac{OA}{\overline{OT}} \qquad [127]$$

The oxygen utilization efficiency was calculated as the amount of oxygen consmmed (OC) in the above reactions plus conversion of sodium thiosulfate to sodium sulfate in relation to the amount added (OA).

$$OU = \frac{OC}{\overline{OU}} \times 100 = \% \qquad [128]$$

It was not possible to measure directly the amount of oxygen consumed in oxidation of lignin and other organic constituents in weak black liquor.

A series of tests were run where the oxygen ratio was successively changed by a series of increases in the oxygen flow rate with respect to the weak black liquor flow rate. Oxygen ratio influenced both the overall efficiencies and respective oxidation rates for both sodium sulfide and sodium mercaptide in weak black liquor, plus the efficiency of oxygen utilization in the plug flow reactor system (points 0 to 8). The effect of oxygen ratio

on the change in sodium sulfide concentration as a function of reaction time has been presented in Figure 44.

The overall sodium sulfide oxidation efficiency was found to increase to a maximum at an oxygen ratio of 1.25, and then gradually decrease with increasing oxygen ratio, as illustrated in Figure 45. The overall oxidation efficiency tended to increase up to the maximum value as sufficient oxygen was added to provide for oxidation of sodium sulfide plus other oxygen-consuming reactions. A possible reason for the slight decrease in the oxidation efficiency with increasing oxygen ratio during the relatively short retention time in the plug flow reactor was decreased oxygen mass transfer efficiency. This decrease may have been caused by the tendency towards larger bubble sizes and disturbances in the bubble or froth regimes of two phase gas-liquid flow at increased gas flow rates. It was noted that the highest overall oxidation efficiency occurred at oxygen ratios between 1.0 and 1.4, with a maximum at approximately 1.25.

Results shown in Figure 46 indicated that the oxygen utilization efficiency during weak black liquor oxidation with molecular oxygen decreased as the oxygen ratio was increased above unity, closely agreeing with expected results. Increasing the oxygen ratio from 1.0 to 1.4 resulted in decreasing the oxygen utilization of the process in terms of sodium sulfide oxidation to enhance its economic attractiveness. An important factor affecting oxygen utilization efficiency was the relative selectivity of sodium sulfide oxidation during the reaction process. Results indicated that the relative proportion of oxygen used for oxidation of sodium sulfide decreased with increasing oxygen ratio, as listed in Table 32.

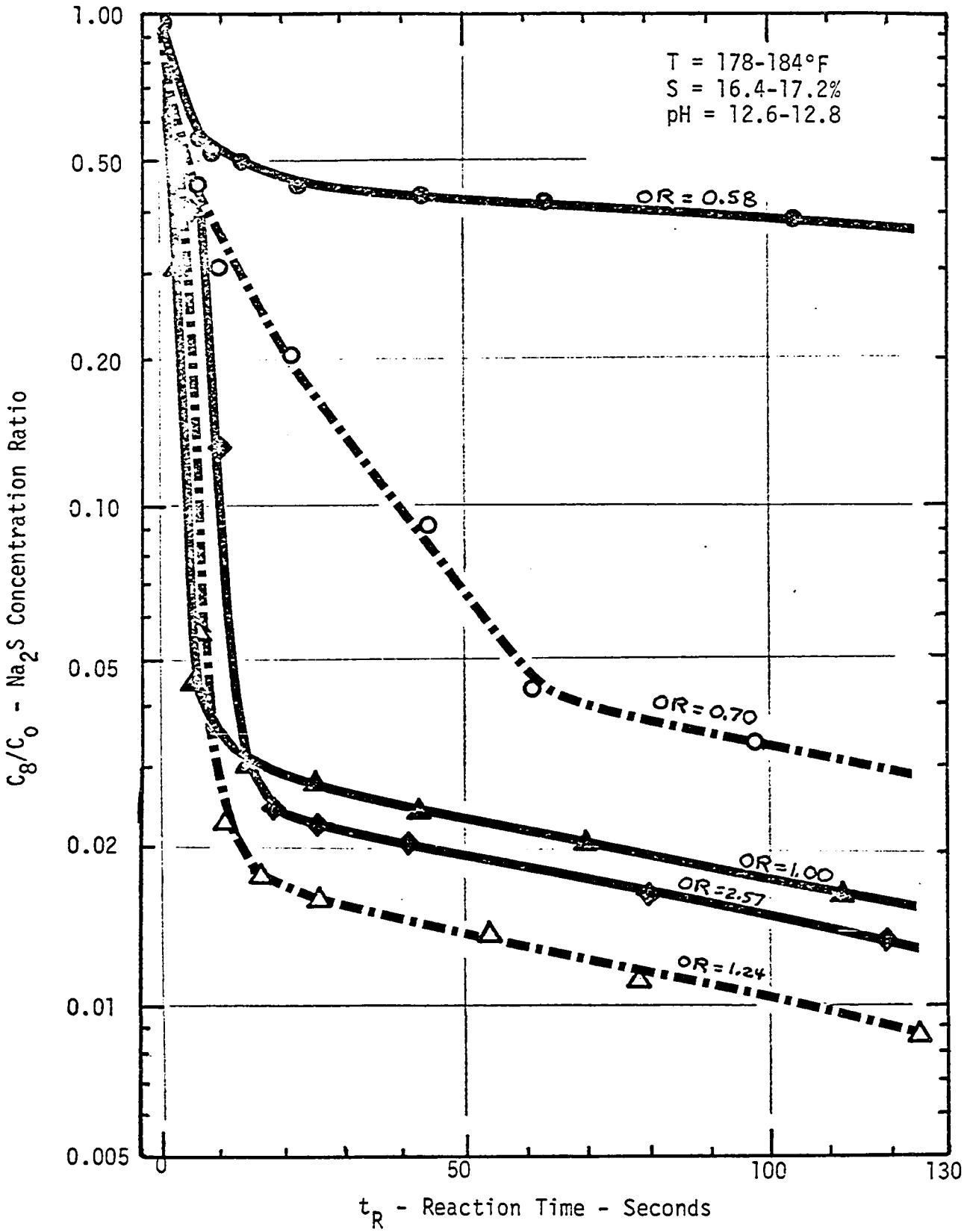


FIGURE 44. EFFECT OF OXYGEN RATIO ON SODIUM SULFIDE OXIDATION IN WEAK BLACK LIQUOR

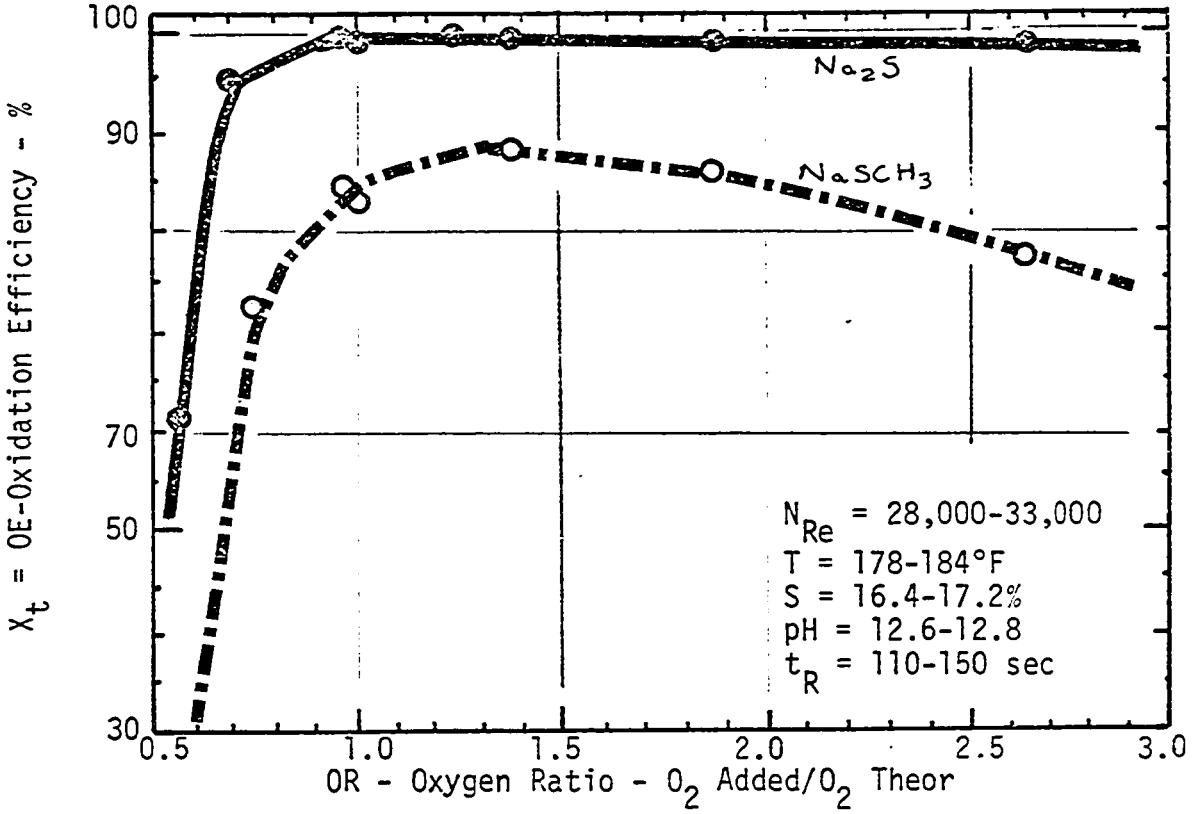


FIGURE 45. EFFECT OF OXYGEN RATIO ON Na_2S and N_aSCH_3 OXIDATION EFFICIENCY IN WEAK BLACK LIQUOR

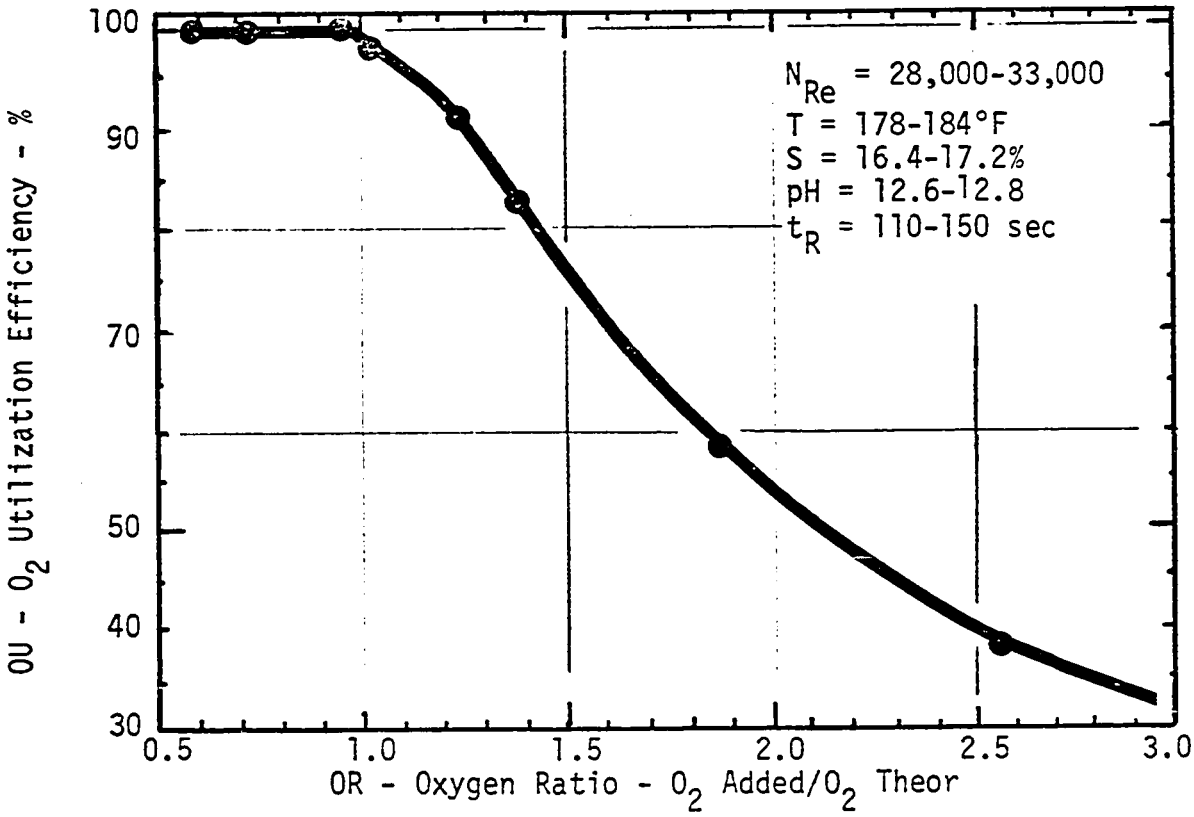


FIGURE 46. EFFECT OF OXYGEN RATIO ON UTILIZATION EFFICIENCY IN WEAK BLACK LIQUOR

TABLE 32. EFFECT OF OXYGEN RATIO ON OXYGEN CONSUMPTION IN WEAK BLACK LIQUOR.

Constituent	Amount O_2 Reacted/Amount O_2 Added x 100 %		
	OR = 1.00	OR = 1.38	OR = 1.86
Na_2S	86.5	68.8	50.0
$NaSCH_3$	6.0	3.6	2.8
Na_2SO_4	7.5	10.2	9.7
Other	0.0	10.5	19.5
Exhaust	0.0	6.9	18.0
Total	100.0	100.0	100.0

It was noted that increasing the oxygen ratio beyond a certain point (1.2 to 1.4) would probably not result in greater sodium sulfide oxidation efficiencies, but would lead to increased oxidation of constituents such as phenolic lignin, and also result in wasting of oxygen added as exhaust gas. The optimum value for oxygen ratio would have to be determined by experiments for each individual mill.

An additional effect of oxygen ratio was to influence the primary rate constant (k_1) for sodium sulfide oxidation during the initial reaction period, as shown in Figure 47. The primary constant was found to increase with oxygen ratio up to a maximum at 1.25 (corresponding to maximum sodium sulfide oxidation efficiency), and then to decrease with increasing oxygen ratios. The reduced values at low oxygen ratios below 1.25 probably represented conditions of oxygen starvation. The progressive decrease in value for the primary constant at increasing values for oxygen ratio above 1.25 probably occurred because of decreases in oxygen mass transfer at elevated gas-to-liquid flow ratios because of the increased tendency for annular two

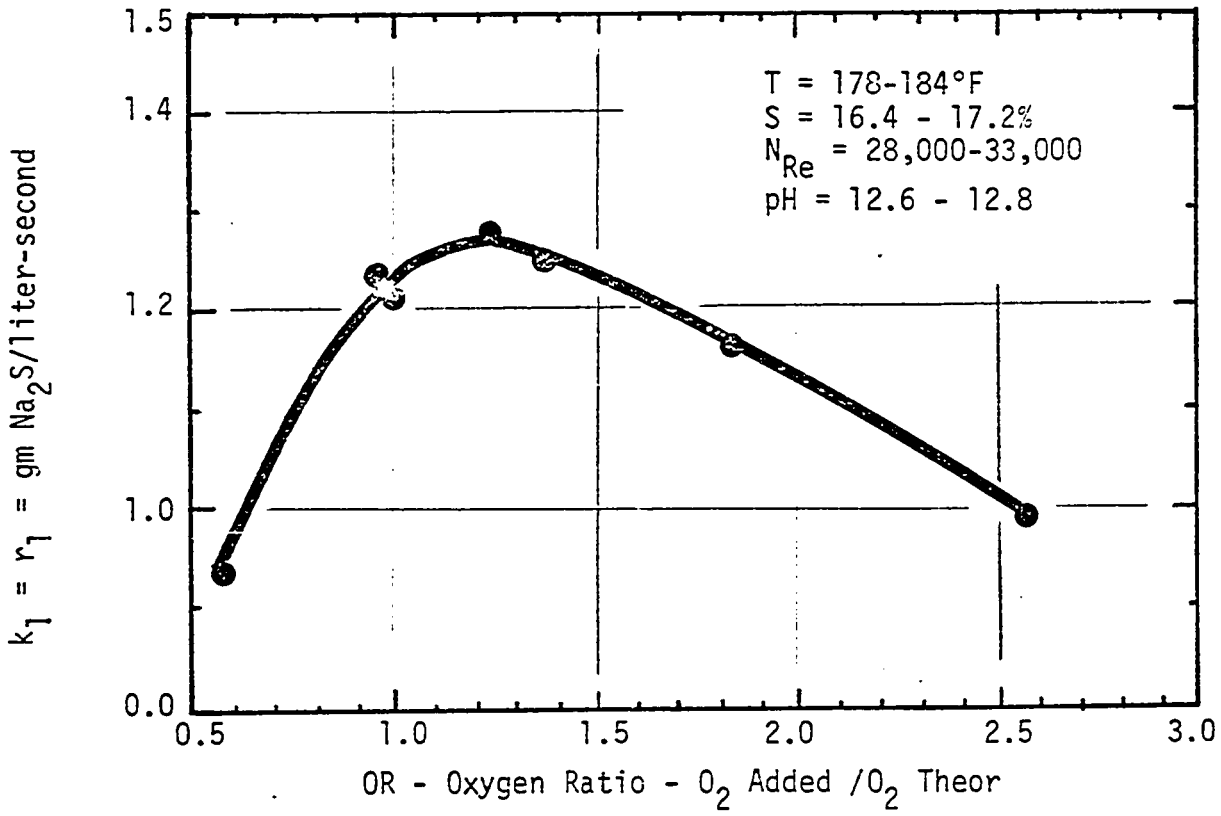


FIGURE 47. EFFECT OF OXYGEN RATIO ON PRIMARY Na_2S OXIDATION RATE IN WEAK BLACK LIQUOR

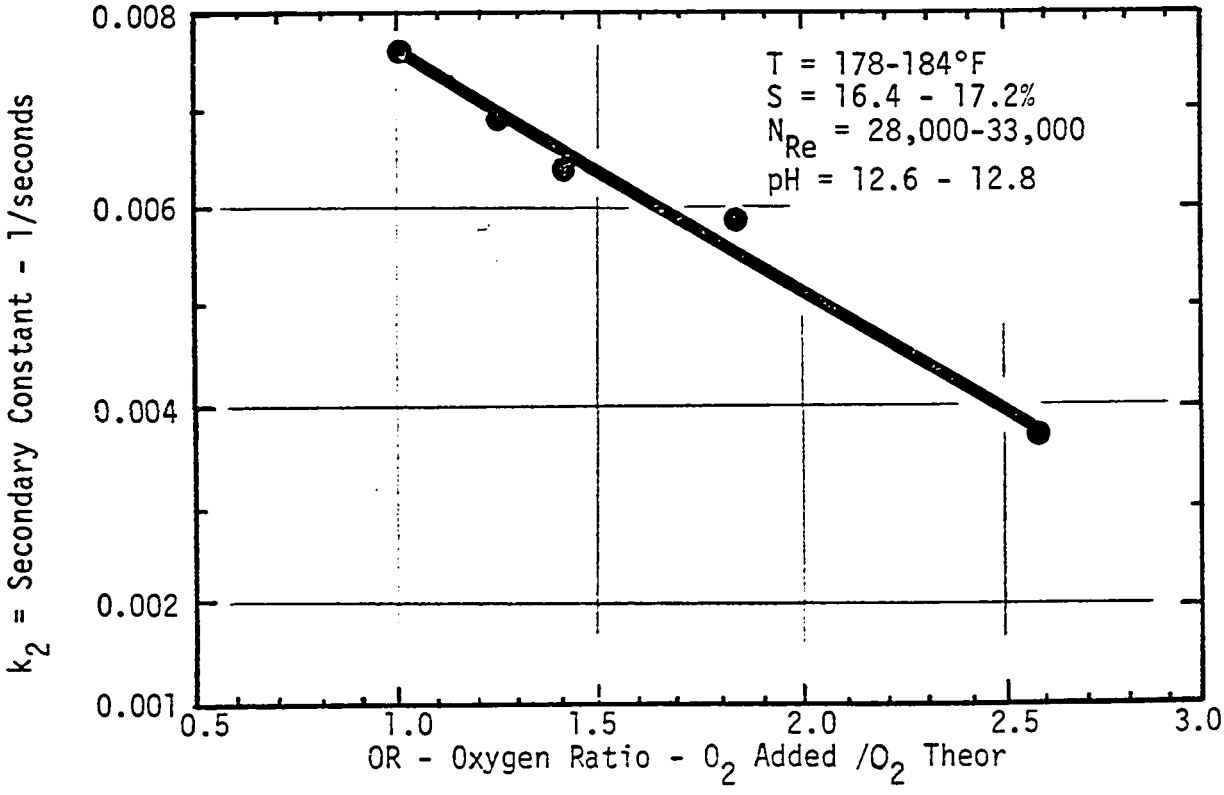


FIGURE 48. EFFECT OF OXYGEN RATIO ON SECONDARY Na_2S OXIDATION RATE IN WEAK BLACK LIQUOR

phase gas-liquid flow to occur, with a resultant decrease in interfacial contact area between oxygen and black liquor. These findings underlined the effect of oxygen mass transfer into weak black liquor on the primary zero order reaction rate constant for sodium sulfide oxidation during the initial reaction period. An additional possibility was that increased oxygen ratios increased the tendency for sodium thiosulfate oxidation to sodium sulfite, with the possible reaction of sulfite with polysulfide to regenerate sodium sulfide.

The secondary reaction rate constant for sodium sulfide oxidation (k_2) displayed a pattern of decreasing values for the constant with increasing oxygen ratios greater than unity, as illustrated in Figure 48. These findings indicated the constant was not necessarily dependent only upon sodium sulfide concentration in the first order reaction, as the oxygen levels in black liquor appeared to also play a role. Possible reasons for the reduction were possible increases in sodium sulfide regeneration by reversion from sodium sulfite and polysulfide, different reaction intermediates, or less effective oxygen mass transfer into black liquor so that it would also bec me limiting in terms of the reaction. The most likely reason was that the value for secondary rate constant (k_2) was an overall value expressing the reaction rate of sodium sulfide, and in actuality expressed the difference in reaction rates between the disappearance and the formation of sodium sulfide. As the amount of excess oxygen in black liquor increased, the chance for oxidation of sodium thiosulfate to sodium sulfite increased. The resultant potential for reaction of sodium sulfite with sodium polysulfide was increased, with sodium sulfide as an end product. For oxygen ratios of less than unity, decreases in the value for the secondary constant (k_2) were

observed. These findings pointed to formation of reaction end products such as sodium polysulfides and polythionates instead of sodium thiosulfate in the oxygen-starvation atmosphere.

No comparable values were obtainable regarding the effect of oxygen ratio on sodium sulfide oxidation in the literature. Galeano and Amsden (103) reported that oxygen utilization efficiency decreased with increased oxygen ratios with a system employing oxygen for black liquor oxidation. Blosser and Cooper (73) reported that sodium sulfide oxidation efficiency increased with the amount of air added per unit amount of sodium sulfide present in completely mixed systems.

The significance of oxygen ratio was that it was important to add an amount of oxygen sufficient for oxidation of the sodium sulfide and sodium mercaptide present. Addition of excessive quantities of oxygen produced a slight reduction in overall oxidation efficiencies and oxidation rates for sodium sulfide and sodium mercaptide, led to added oxygen consumption by competing side reactions, and made the process less attractive from an economic standpoint. For the system studied, optimum oxidation rates and overall oxidation efficiencies for sodium sulfide and mercaptide were observed for oxygen ratios between 1.0 and 1.4, with maximum values observed for an oxygen ratio of 1.25.

(2) Effect of Liquid Temperature

Liquid temperature would affect the rate of oxygen mass transfer into the liquid phase and the rate of chemical reactions occurring in weak black liquor. Predictions from theory indicated reduced rates of oxygen mass transfer and increased rates for chemical reactions in the weak black liquor with increasing temperatures. In addition, temperature might be expected to affect upon the chemistry of the oxidation reactions by influencing the

end products formed. Changes in liquid temperature would tend to influence not only the oxidation of sodium sulfide and methyl mercaptan, but the oxidation of sodium thiosulfate, the formation of sodium sulfate, and reactions involving other constituents such as phenolic lignin.

A series of tests were made where oxygen at constant flow rate was introduced to a stream of weak black liquor at an essentially constant flow rate. The temperature of the weak black liquor was modified upstream of the point of introducing oxygen by passage through a heat exchanger over a temperature range from 140 to 203°F in successive tests. Results of the studies indicated that liquid temperature played an important role in determining the respective oxidation rates for oxidation of sodium sulfide, sodium mercaptide, and sodium thiosulfate, and the formation of sodium sulfate. Liquid temperature also appeared to affect the end products formed in the oxidation of sodium sulfide, and the total sulfur balance of the weak liquor as a function of reaction time.

Liquid temperature affected both the primary (k_1) and secondary (k_2) reaction rate constants for oxidation of sodium sulfide in weak black liquor, as shown in Figure 49. For the primary rate constant for the initial reaction rate period of three to five seconds, its value was found to decrease with increasing temperature above 155°F. The possible reason for the decrease was that the effective rate of oxygen mass transfer into the black liquor was reduced at increasing temperatures because of decreasing gas solubility, with resultant lower oxygen partial pressure driving force into the liquid phase. It was also possible that the relative catalytic effect of phenolic lignin on the oxidation of sodium sulfide was reduced because of its increasing tendency for oxidation with increasing temperatures. Possible reasons for the decrease

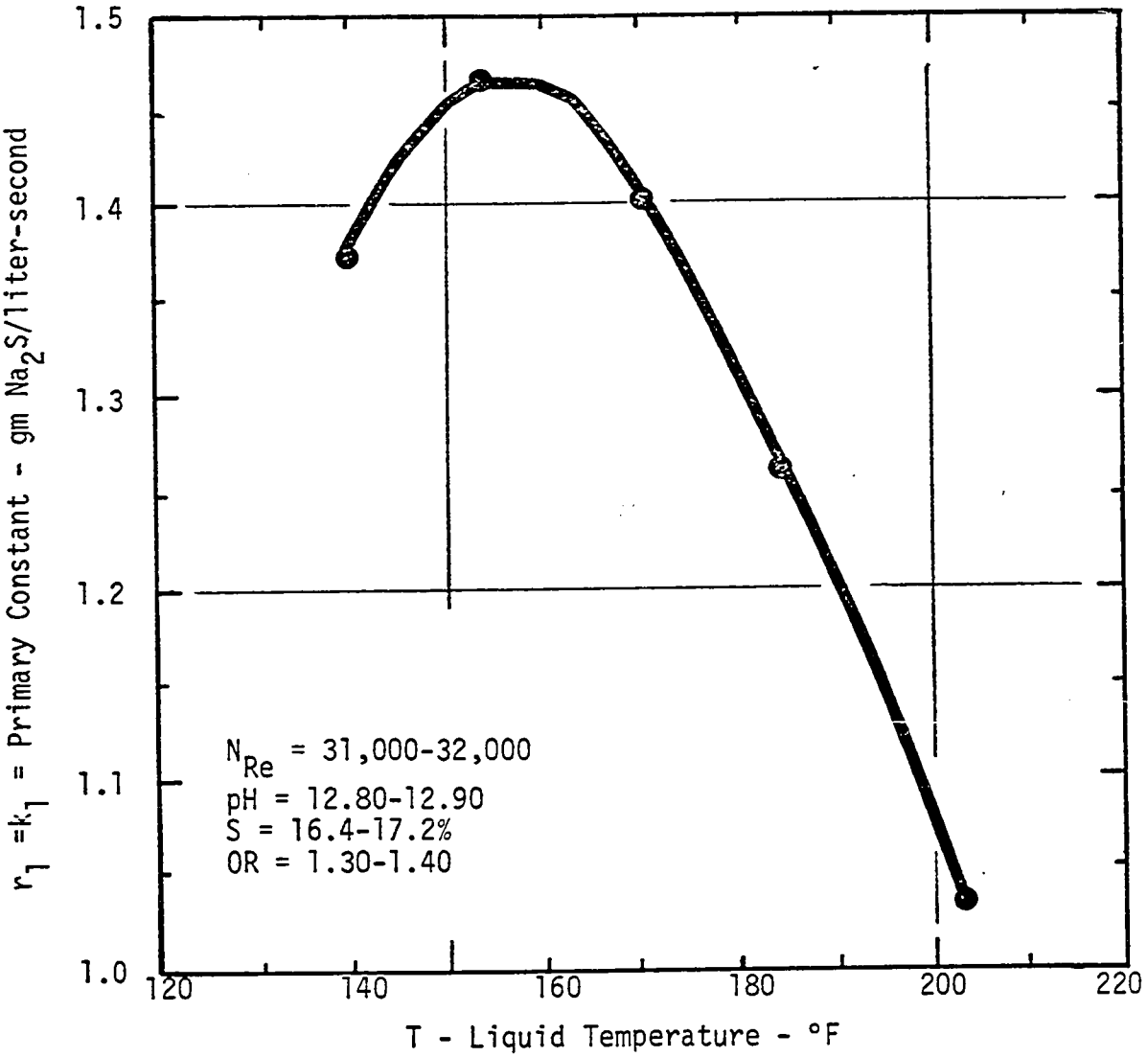


FIGURE 49. EFFECT OF TEMPERATURE ON PRIMARY Na_2S OXIDATION RATE IN WEAK BLACK LIQUOR

in initial reaction rate at temperatures below 155°F were decreased oxygen mass transfer because of increased liquor viscosities, changes in reaction end products at lower temperatures, and decreased catalytic activity by the lignin.

The secondary rate constant for sodium sulfide oxidation (k_2) at low concentrations appeared to increase with temperature above 155°F, as illustrated in Figures 50 and 51. The increase in the reaction rate constant for the first order chemical oxidation of sodium sulfide at low concentrations with increasing temperature was in agreement with the kinetic theory. However, an increase was noted in the secondary rate constant for sodium sulfide oxidation as the temperature was reduced from 155 to 140°F. The probable reason was that the primary end product of the oxidation of sodium sulfide was no longer sodium thiosulfate, which was verified by subsequent chemical analyses for sodium thiosulfate. The primary end products were probably intermediates such as one or more forms of either or both sodium polysulfide or polythionate, or elemental sulfur.

Liquid temperature did not appear to have a definitive impact upon the primary oxidation rate constant (k_3) for sodium mercaptide in weak black liquor, which was probably related to the rate of oxygen mass transfer, plus other factors. The secondary reaction rate constant (k_4) for sodium mercaptide appeared to increase with temperature up to a maximum value at 184°F, in agreement with kinetic theory. A decrease in the secondary constant was noted with an increase in liquid temperature from 184 to 203°F. One possible explanation was that there was increased competition for the available oxygen caused by the icnreased secondary rate of sodium sulfide oxidation and particularly an increase in the oxygen demand caused by the oxidation of phenolic lignin present in relatively high concentrations.

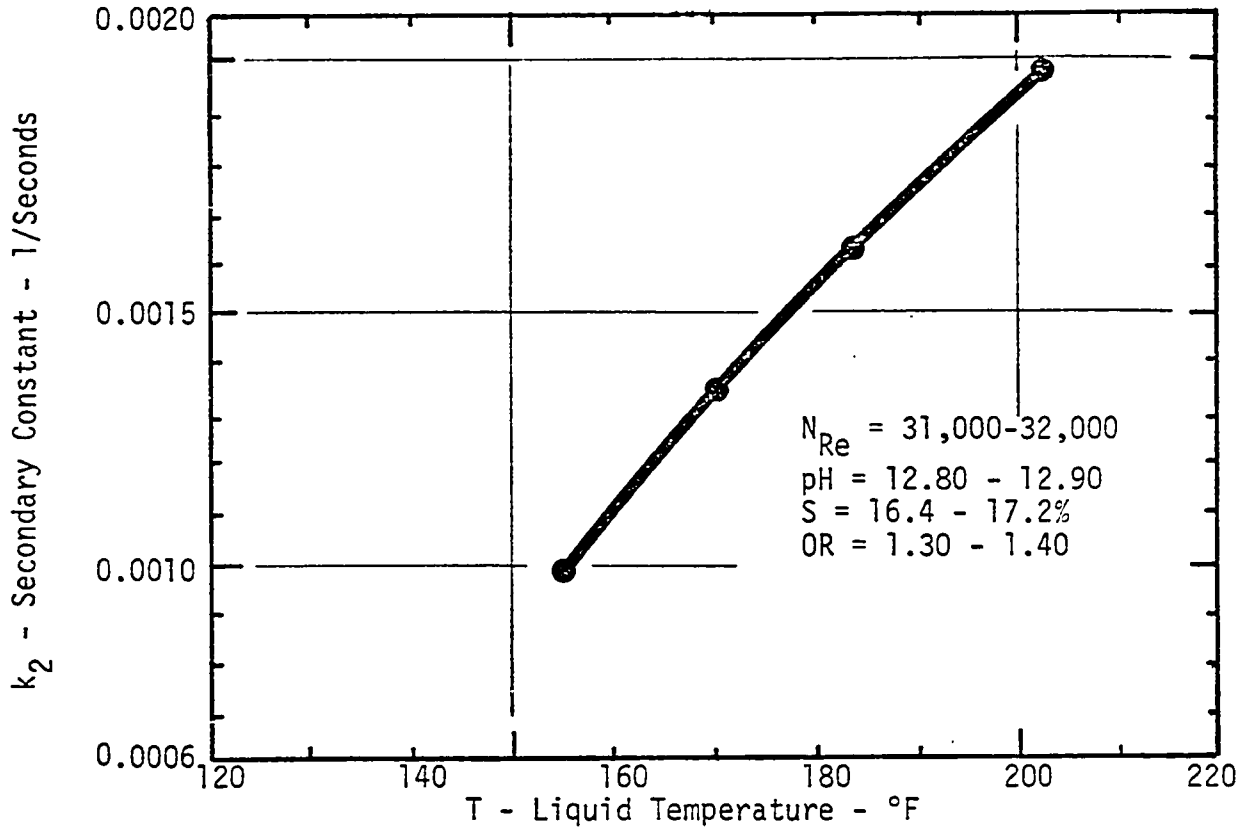


FIGURE 50. EFFECT OF TEMPERATURE ON SECONDARY Na_2S OXIDATION RATE IN WEAK BLACK LIQUOR

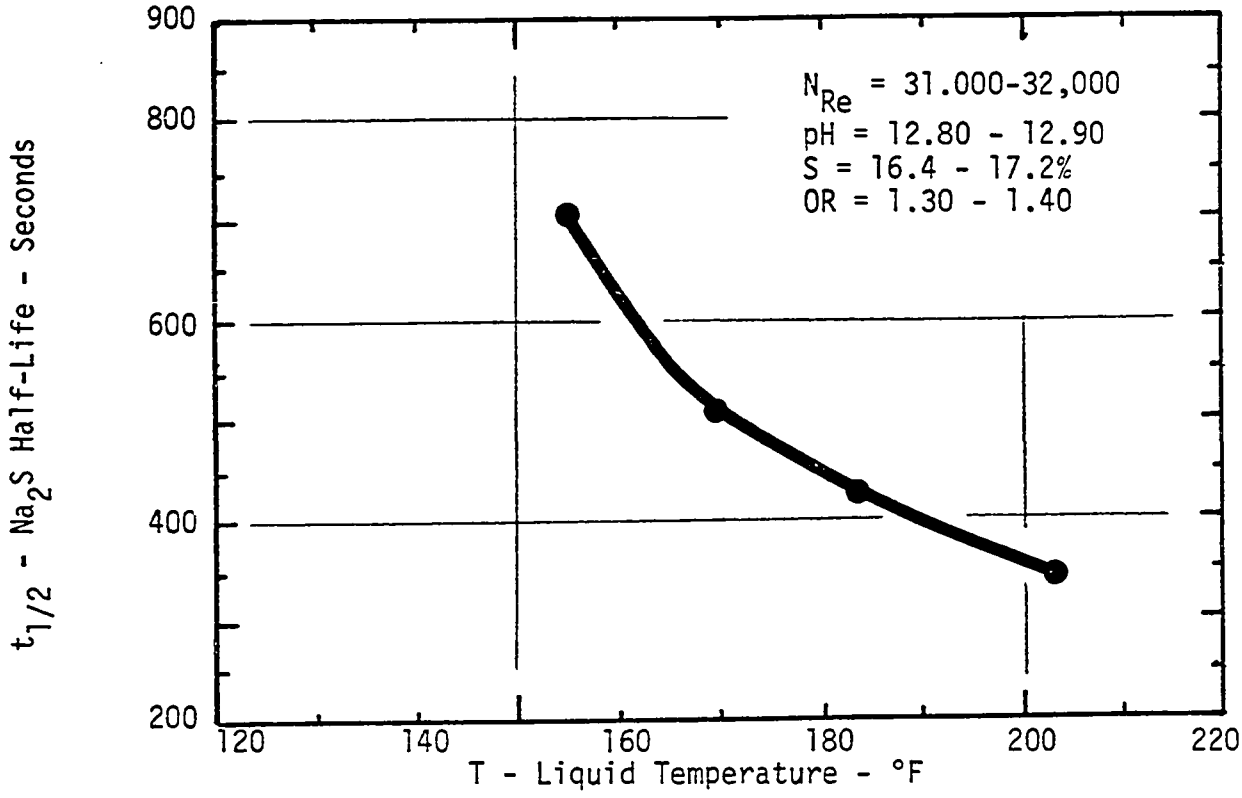


FIGURE 51. EFFECT OF TEMPERATURE ON SECONDARY Na_2S HALF-LIFE IN WEAK BLACK LIQUOR

The effect of liquid temperature on the respective oxidation rate constants for sodium mercaptide has been presented in Table 35.

TABLE 33. EFFECT OF TEMPERATURE ON SODIUM MERCAPTIDE OXIDATION RATES.

Liquid Temperature °F	Primary Rate ($r_1=k_1$) gm $NaSCH_3$/liter-sec	Secondary Rate (k_2) 1/Seconds
203	-0.142	-0.00048
184	-0.156	-0.00212
170	-0.040	-0.00148
155	-0.169	-0.00104
140	-0.153	-0.00051

Note: Values for k_2 are computed to base "e" logarithms.

TABLE 34. EFFECT OF TEMPERATURE ON Na_2S AND $NaSCH_3$ OXIDATION EFFICIENCIES IN WEAK BLACK LIQUOR.

Liquid Temperature °F	Concentration Ratio - C_{10}/C_0 Sodium Sulfide	Sodium Mercaptide
203	99.1	82.5
184	99.4	90.0
170	98.4	75.5
155	99.1	82.5
140	98.8	85.5

Liquid temperature appeared to have a slight effect on the overall oxidation efficiencies for both sodium sulfide and sodium mercaptide. The overall oxidation efficiencies reflected a composite of both primary and

secondary rates of oxidation, and represented the differences in concentration between points zero and ten following the tall storage tank. The overall oxidation efficiency appeared to approach a maximum value for both sodium sulfide and mercaptide at a liquid temperature of 184°F, as shown in Table 34.

Liquid temperatures appeared to affect the primary and secondary rate constants for sodium thiosulfate in accordance with both reaction kinetics and kinetic theory. The initial reaction rate constant was primarily dependent on the rate of sodium sulfide oxidation because it was the primary reaction product. The secondary reaction rate constant (k_6) for oxidation of sodium thiosulfate was found to increase with temperature over the entire range from 140 to 203°F, placing its increased with temperature in agreement with kinetic theory, as listed in Table 35.

TABLE 35. EFFECT OF TEMPERATURE ON $Na_2S_2O_3$ REACTION RATES IN WEAK BLACK LIQUOR.

Liquid Temperature °F	Na_2S k_1 gm Na_2S/liter-sec	$Na_2S_2O_3$ k_5 gm $Na_2S_2O_3$/liter-sec	$Na_2S_2O_3$ k_6^2 1/seconds
203	-1.032	+1.035	-0.00036
184	-1.260	+1.060	-0.00027
170	-1.400	+1.040	-0.00019
155	-1.430	+1.340	-0.00013
140	-1.370	+1.427	-0.00012

Notes: 1. Molecular weights in reaction: $2Na_2S$ = 156; $Na_2S_2O_3$ = 158.

2. Values for k_2 are computed to base "e" logarithms.

Most of the sodium sulfide initially present in the black liquor reacted to form sodium thiosulfate. The difference in values between primary rate constants in the initial reaction phase for sodium sulfide oxidation (k_1) and sodium thiosulfate formation (k_3) was probably caused by the oxidation of thiosulfate initially present to sodium sulfate. The initial rate of sodium thiosulfate was observed to decrease substantially at temperatures below 155°F, along with the total amount formed, indicating that materials other than sodium thiosulfate were the primary reaction products. Subsequent chemical analyses indicated increases in concentrations of sodium polysulfide. Sodium polysulfide increase did not account for all of the sulfur oxidized, indicating that other materials such as polythionate ions were also being formed.

The formation of sodium sulfate in weak black liquor also appeared to be affected by liquid temperature. The primary reaction rate constant (k_7) sodium sulfate formation during the initial reaction period displayed a definite increase with increasing liquid temperature, as listed in Table 36. Values for the secondary rate constant appeared to increase with temperature from 140 to 184°F in accordance with kinetic theory. Further liquid temperature increase to 203°F resulted in a substantial decrease in the secondary reaction rate constant similar to that observed for sodium mercaptide. A possible reason was greater competition at elevated temperatures for the available oxygen because of increased oxygen demand by sodium sulfide and particularly phenolic lignin.

Changes in liquid temperature appeared to have two additional effects in the oxidation of weak black liquor. First, increasing the liquid temperature appeared to increase the total amount of sodium sulfate formation across the plug flow reactor, as listed in Table 37. The trends closely followed those

TABLE 36. EFFECT OF TEMPERATURE ON Na_2SO_4 FORMATION RATES IN WEAK BLACK LIQUOR.

Liquid Temperature °F	Primary[1] Rate (k_7) gm Na_2SO_4/liter-sec	Secondary[2] Constant (k_8) liter bl/gm Na_2SO_4-sec
203	+0.222	-0.00001
184	+0.138	-0.00013
170	+0.068	-0.00008
155	+0.086	-0.00007
140	+0.011	-0.00006

Notes: 1. Positive values for zero order reactions mean concentration increase.

2. Negative values for second order reactions mean concentration increase.

TABLE 37. EFFECT OF TEMPERATURE ON TOTAL SODIUM SULFATE FORMATION IN WEAK BLACK LIQUOR.

Liquid Temperature °F	Na_2SO_4 Formation gm Na_2SO_4/liter
203	1.50
184	1.58
170	1.31
155	1.04
140	0.56

established for the reaction rate constants for sodium sulfate formation. Second, the amount of total sulfur by chemical addition of individual constituents which could not be accounted for appeared to increase with decreasing temperature, as listed in Table 38. The decrease in the relative proportion of sodium thiosulfate noted was particularly observed, indicating formation of other reaction products.

TABLE 38. EFFECT OF TEMPERATURE ON TOTAL SULFUR BALANCE ACROSS PLUG FLOW REACTOR DURING WEAK BLACK LIQUOR OXIDATION.

Liquid Temperature °F	Total Sulfur Ratio S_{11}/S_0
203	0.867
184	0.950
170	0.735
155	0.877
140	0.516

Murray (148) observed that the overall rate of sodium sulfide oxidation with oxygen in weak black liquor in a batch reactor was a maximum at a temperature of approximately 160°F as previously illustrated in Figure 21. His findings were essentially in agreement with those reported in the present study where a maximum initial rate of sodium sulfide oxidation was observed at a temperature of 155°F. Avrahami and Golding (142) observed that the rate of sodium sulfide oxidation increased with increasing temperature in dilute alkaline solutions, and determined an activation energy of 8,000 gram-calories per gram-mole. Ricca (97) observed a maximum rate of sodium sulfide oxidation at approximately 175°F, with increased oxygen consumption and decreased

sulfide oxidation rates at higher temperatures. Little other information was available regarding the specific effects of temperature on the black liquor oxidation reactions.

The significance of liquid temperature as a process variable was that it did not appear to have a substantial impact on the overall oxidation efficiency or reaction rates of sodium sulfide oxidation, but it did have other effects. Operating at relatively low temperatures appeared to reduce the amount of excess oxygen consumption resulting from formation of sodium sulfate and probably phenolic lignin. It also probably caused the formation of intermediate reaction products other than sodium thiosulfate such as various forms of polythionate and polysulfide, which might enhance the potential for reversion to sodium sulfide during subsequent storage and evaporation of weak black liquor. Operating at relatively high temperatures would reduce the potential for formation of intermediate products which might cause reversion, but would also result in excessive oxygen consumption becuase of the oxygen demand exerted by formation of sodium sulfate and oxidation of phenolic lignin. An approximate liquor temperature range of 170 to 190°F would probably be optimum for maximum oxidation efficiency for sodium sulfide without either excessive oxygen consumption or increased reversion potential.

(3) Effect of Liquid pH

Considerations from reaction chemistry indicated that the pH of weak black liquor to have a potential impact on both the black liquor oxidation process and operation of the Kraft recovery system. Particular concerns regarding the effect of liquid pH on the black liquor oxidation process were the rate of sodium sulfide oxidation, the rate of sodium thiosulfate oxidation, and the rate of sodium sulfate formation. The major concern with

regard to the Kraft recovery system involved the potential effects of changes in liquid pH upon the solubility of phenolic lignin in black liquor, particularly as its solids concentration was increased. Decreases in lignin solubility with reductions in pH could result in precipitation of the organic solids on heat transfer surfaces of the multiple effect evaporators, thus increasing steam requirements. Lignin precipitation could also cause plugging of liquor spray guns with resultant upsetting of recovery furnace operation.

The oxidation reactions taking place would tend to cause a change in the pH of the weak black liquor which depended on reaction time. The major chemical reaction which tended to increase the pH of black liquor was the oxidation of sodium sulfide to form sodium thiosulfate, resulting in the liberation of sodium hydroxide (Reaction 29). A reaction of major importance tending to produce reduction in black liquor pH was the oxidation of sodium thiosulfate to sodium sulfate, resulting in the consumption of sodium hydroxide (Reaction 32). An additional reaction tending to cause a reduction in black liquor pH was the oxidation of phenolic lignin to various organic acids and eventually carbon dioxide and water. The major variables appearing to affect the change in pH of weak black lqiuor were the initial ratio of sodium sulfide to sodium thiosulfate, the amount of oxygen added, and factors affecting formation of sodium sulfate.

Initial experiments were involved with determination of the effect of reaction time on changes in liquid pH during weak black liquor oxidation with molecular oxygen. Results from a number of studies indicated a reduction of approximately 0.1 to 0.3 pH units for the weak black liquor across the plug flow reactor during the oxidation process. The change in liquir pH with reaction time for a typical run has been illustrated in

Figure 52, indicating a reduction of approximately 0.3 pH units, in agreement with findings by Lindholm and Stockman (121). These findings were directly applicable only to the particular mill installation which used low sulfidity black liquor with a relatively high ratio of sodium thiosulfate to sodium sulfide of 0.3 to 1.0 in the unoxidized weak black liquor. These findings were in marked contrast to those described by Galeano and Amsden (103), who reported an increase of 0.1 to 0.3 pH units during the oxidation process. Their studies were performed on weak black liquor with a high inlet sodium sulfide concentration and a low ratio of thiosulfate to sulfide of 0.1 to 0.2.

Experiments were made where the pH of weak black liquor was varied by addition of measured amounts of hydrochloric acid upstream of the point of oxygen addition. The effect of reaction time on liquid pH was then determined by a series of analyses in parallel with the respective chemical analyses of the black liquor samples. The pH of weak black liquor as a function of reaction time was also measured to provide additional background information regarding the chemistry of the oxidation processes.

Results indicated that the change in liquid pH resulted in effects upon the oxidation rates of sodium sulfide, sodium mercaptide, and sodium thiosulfate, the rate and amount of sodium sulfate formation and the total sulfur balance. Decreasing the pH of weak black liquor from 12.9 to 10.5 caused a substantial reduction in the primary initial reaction rate constant for sodium sulfide oxidation. The effect was particularly pronounced for liquid pH values below 11.4, as shown in Figure 53. One possible reason for the decrease in initial zero order reaction rate was that the relative catalytic effect of the lignin monomers was reduced at the lower pH values. This occurred because of increased stability of the aromatic ring structures

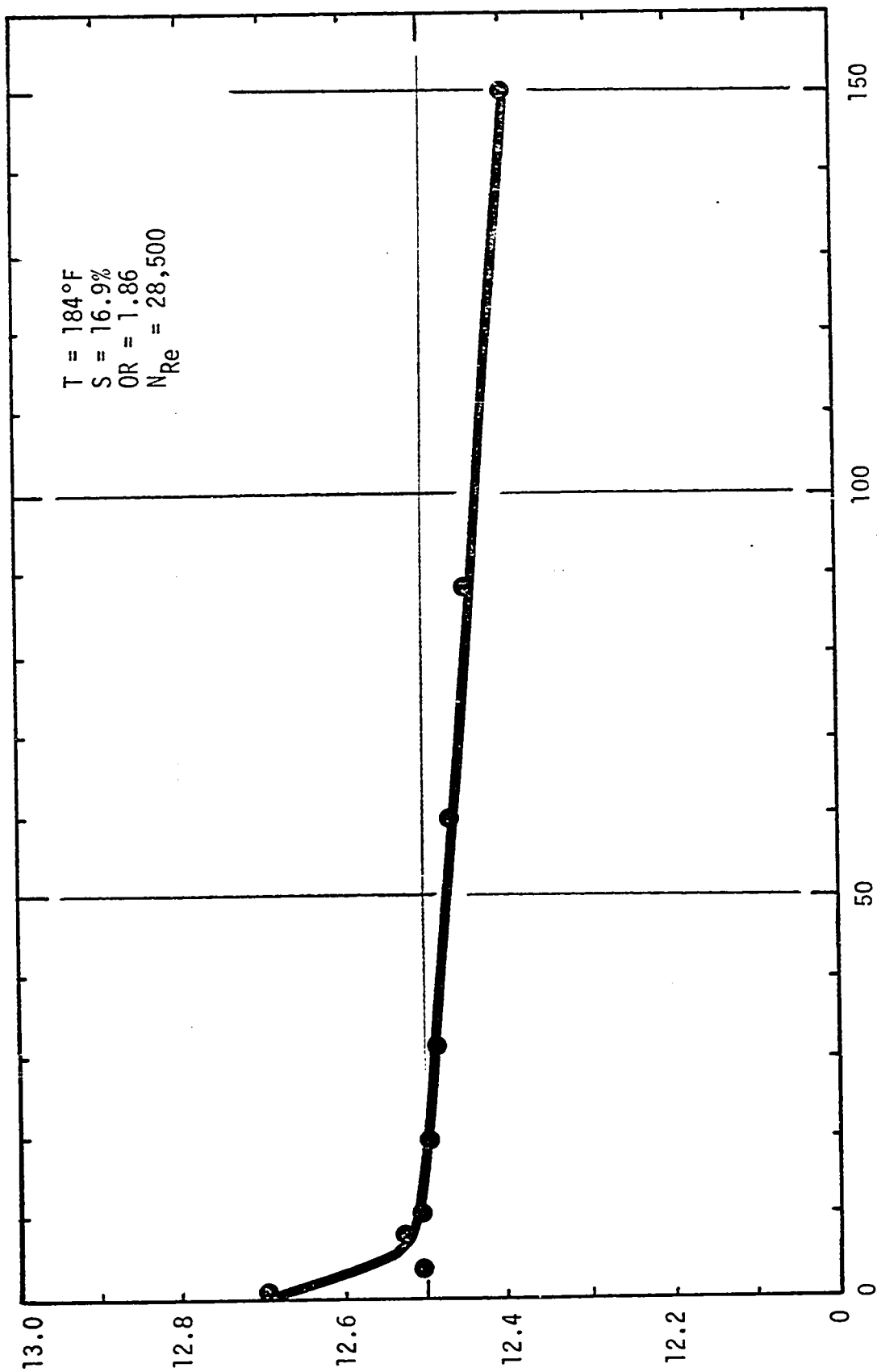


FIGURE 52. EFFECT OF WEAK BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN ON LIQUID pH

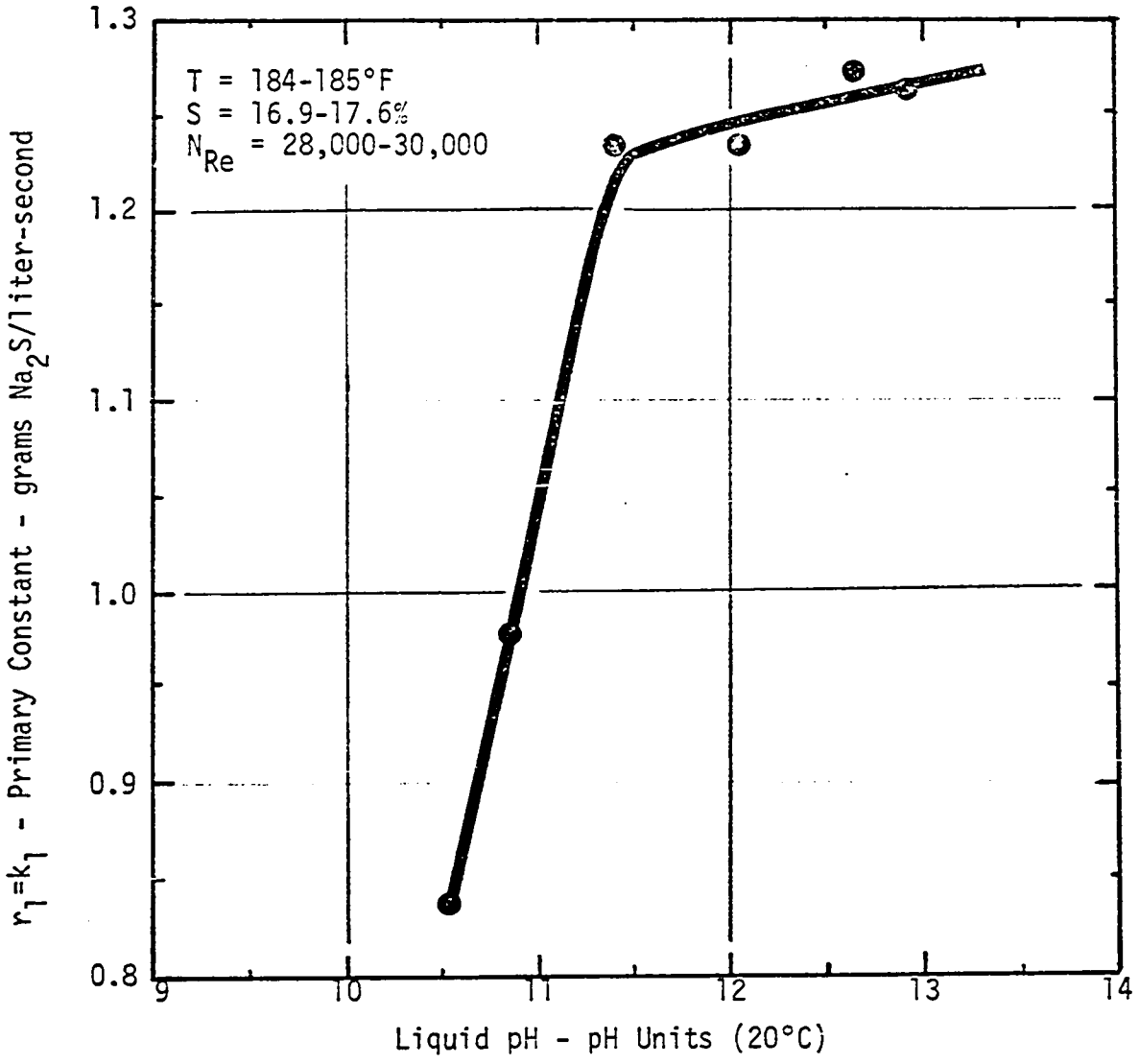


FIGURE 53. EFFECT OF LIQUID pH ON PRIMARY Na_2S OXIDATION RATE IN WEAK BLACK LIQUOR

in the less alkaline liquid media because of reduced ionization of the phenolic groups. A second possible reason was that the sulfide ion was the reactive species instead of hydrosulfide ion.

There was little discernible effect upon the secondary rate constant for sodium sulfide oxidation with change in liquid pH, probably because the low concentration of sodium sulfide was the important variable in the first order reaction. In addition, a slight increase in oxidation efficiency was noted across the plug flow reactor (point zero to ten) with increase in liquid pH for sodium sulfide, and a significant increase for sodium mercaptide, as shown in Table 39. It was also noted that the decrease in pH below 12.0 resulted in the liberation of small amounts of hydrogen sulfide and significant quantities of methyl mercaptan, along with decreases in both primary and secondary rate constants for sodium mercaptide oxidation. Lignin precipitation from black liquor samples was observed in increasing quantities as the liquid pH was reduced below 12.0.

TABLE 39. EFFECT OF LIQUID pH ON Na_2S AND $NaSCH_3$ OXIDATION EFFICIENCIES IN WEAK BLACK LIQUOR.

Liquid pH	Oxidation Efficiency-%	
	Na_2S	$NaSCH_3$
12.9	99.4	90.0
12.0	99.2	80.0
10.9	98.5	75.0

Alteration of the liquid pH resulted in changes in the reaction rate constants for sodium thiosulfate reactions and sodium sulfate formation, as shown in Table 40. Little change was noted in the primary constant for initial sodium thiosulfate formation with pH. However, substantial reductions

were observed in the rate constant for sodium thiosulfate oxidation (k_6), plus both primary and secondary rate constants for sodium sulfate formation with decreasing pH. These findings tended to verify considerations from reaction chemistry where increased liquor pH provided greater driving force for sodium sulfate formation, as shown in Figure 54.

TABLE 40. EFFECT OF LIQUID pH ON $Na_2S_2O_3$ AND Na_2SO_4 REACTION RATES IN WEAK BLACK LIQUOR.

Liquid pH	Sodium Thiosulfate		Sodium Sulfate	
	Primary (k_5) gm $Na_2S_2O_3$ / liter-sec	Secondary (k_6) 1/second	Primary (k_7) gm Na_2SO_4 / liter-sec	Secondary (k_8) liter bl / gm Na_2SO_4-sec
12.9	+1.060	0.00017	±0.138	-0.00013
12.0	+0.823	0.00007	+0.088	-0.00003
10.9	+1.060	0.00006	+0.028	-0.00001

It was also observed that decreasing the liquid pH resulted in increased amounts of total sulfur (by chemical addition of that initially present) which could not be accounted for by analyses for sulfide, polysulfide, thiosulfate, sulfite, and sulfate constituents, as listed in Table 41.

TABLE 41. EFFECT OF LIQUID pH ON TOTAL SULFUR BALANCE ACROSS PLUG FLOW REACTOR DURING WEAK BLACK LIQUOR OXIDATION.

Liquid pH	Total Sulfur Ratio S_{11}/S_0
12.9	0.950
12.0	0.745
10.9	0.703

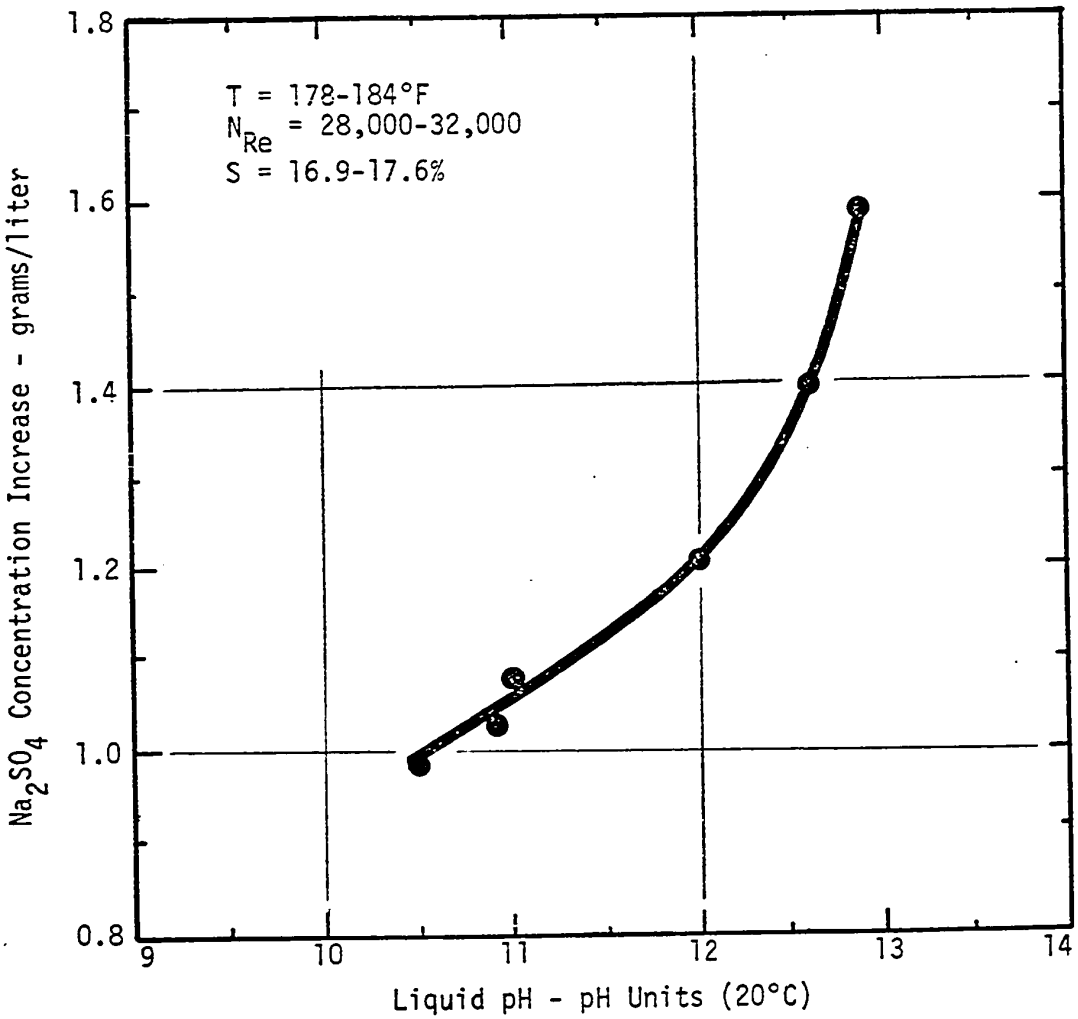


FIGURE 54. EFFECT OF LIQUID pH ON Na_2SO_4 INCREASE IN WEAK BLACK LIQUOR

These findings pointed to the increased potential for formation of intermediate reaction products such as various forms of sodium polythionates at lower liquid pH values.

Liquid pH has been observed to have an effect of black liquor oxidation reactions by several investigators. Alferova and Titova (78) found that the initial rate of sodium sulfide oxidation was increased substantially with increasing pH in a batch reactor, along with greater formation of sodium sulfate and decomposition of sodium thiosulfate, in agreement with findings of the present study. Avrahami and Golding (142) observed that the rate of sodium sulfide oxidation increased over the range from pH 11 to 13, and that sodium thiosulfate became more predominant with increasing pH over the competing forms of sodium trithionate and tetrathionate.

The significance of liquid pH as a reaction variable was to maintain it within a certain range to inhibit potential problems from occurring, either in terms of oxidation efficiency or process economics. It was necessary to maintain the pH of weak black liquor above 11.5 to prevent a reduction in sodium sulfide oxidation efficiency and above 12.0 to inhibit the potential for precipitation of lignin and evolution of methyl mercaptan. It was also necessary to maintain the pH of weak black liquor below 12.6 to inhibit the potential formation of excessive quantities of sodium sulfate, with a resultant increase in oxygen consumption requirements. It appeared that a liquor pH range from 12.0 to 12.6 was optimum for effective oxidation of sodium sulfide without excessive lignin precipitation or oxygen consumption requirements. Findings pointed to the prospective use of petroleum refinery spent caustic solutions or other highly alkaline waste liquids as potential sources of sodium and sulfur makeup chemical which also provided high alkalinities.

(4) Effect of Sodium Thiosulfate

Increasing the inlet concentration of sodium thiosulfate in weak black liquor would be expected to have several effects on the oxidation process. First, it would decrease the oxidation rate for sodium sulfide because of reduced concentration driving force. Second, it would increase the tendency for sodium sulfate formation because of greater inlet reaction concentration. Third, it would increase the drop in liquid pH across the plug flow reactor during the oxidation process because of additional sulfate formation. The problem of sodium thiosulfate concentration in weak black liquor was of particular importance where it was desired to upgrade the performance of existing air oxidation units.

A series of experiments were made where variable quantities of sodium thiosulfate solution were added to weak black liquor upstream of the point of oxygen introduction. The effect of inlet sodium thiosulfate concentration on the black liquor oxidation process was then determined as a function of reaction time by a series of chemical analyses. Results indicated that increasing the inlet sodium thiosulfate concentration from three to twelve grams per liter with other variables held constant caused a greater drop of 0.10 to 0.25 pH units across the plug flow reactor. These findings pointed to a reduction in liquid pH by consumption of sodium hydroxide with oxidation of sodium thiosulfate to sodium sulfate. It was not possible to make sodium sulfate analyses because of an interference with the analytical technique which occurred at elevated sodium thiosulfate concentrations.

The inlet concentration of sodium thiosulfate in weak black liquor was increased in successive tests from three to twenty grams per liter to determine its effect on the rate and overall efficiency of sodium sulfide oxidation. Results indicated a substantial reduction in the primary and secondary rate constants for sodium sulfide oxidation, as shown in Table 42.

TABLE 42. EFFECT OF INLET $Na_2S_2O_3$ CONCENTRATION ON Na_2S OXIDATION RATES IN WEAK BLACK LIQUOR.

$Na_2S_2O_3$ Concentration gm/liter	Reaction Rates	
	Primary (k_1) gm Na_2S/liter-sec	Secondary (k_2) l/seconds
3.25	1.21	0.00654
11.78	1.15	0.00325
20.00	0.82	0.00053

The probable reason for the decrease in reaction rate constants with increasing inlet sodium thiosulfate concentration in weak black liquor was as follows. It was only possible to evaluate the overall rate constant for sodium sulfide oxidation to sodium thiosulfate by experimental measurements, while the overall reaction rate was in actuality the difference between the forward and reverse reactions. As equilibrium was approached at increasing reaction product ($Na_2S_2O_3$) concentrations, the net difference between the forward and reverse reactions was reduced, resulting in a decreased overall sulfide oxidation rate. These results pointed to the necessity for determining design reaction rate constants for particular operating conditions at individual mills by specific pilot scale studies prior to construction of full-scale units.

An additional result of increasing inlet sodium thiosulfate concentration was that the overall efficiency of sodium sulfide oxidation across the plug flow reactor was reduced, as shown in Table 43. The above tests were made across the plug flow reactor for a reaction time of aprpoximately three minutes. The probable reason for the decreases in overall oxidation efficiency was that the reaction product increase reduced the net concentration driving force.

TABLE 43. EFFECT OF INLET $Na_2S_2O_3$ CONCENTRATION ON Na_2S OXIDATION EFFICIENCY IN WEAK BLACK LIQUOR.

$Na_2S_2O_3$ Concentration gm/liter	Concentration Ratio C_s/C_o	Oxidation Efficiency %
3.25	0.010	99.0
11.78	0.017	98.3
20.00	0.037	96.3

The importance of inlet sodium thiosulfate concentration on the black liquor oxidation process was particularly in the upgrading of existing air oxidation units by addition of molecular oxygen to the liquid or with black liquors of low sulfidities. It would probably be desirable to introduce oxygen to the inlet black liquor stream upstream of the air oxidation system to take advantage of the rapid mass transfer. Oxygen addition to the inlet stream would also alleviate potential problems associated with substantial oxidation of sodium thiosulfate to sodium sulfate in the exit stream, resulting in decreased liquid pH, possible lignin precipitation, reduced sulfide oxidation rates, plus excessive oxygen consumption requirements.

Murray (148) observed that increasing sodium thiosulfate concentration reduced the overall rate of sodium sulfide oxidation, but no specific values were presented. His findings were in agreement with the above results.

(5) Effect of Wood Species

The effect of changes in wood species upon the oxidation of black liquor was not investigated as a part of the present research because the Simpson Lee Kraft pulp mill employed a constant wood furnish of 50 percent Douglas Fir (softwood), 50 percent Black Cottonwood (hardwood). Changes in wood species would be expected to produce differences in the reaction rate

constants and retention time requirements in order to achieve effective oxidation of sodium sulfide, so that pilot studies would have to be run at individual mills to obtain accurate design information. The use of softwoods such as Southern yellow pines would be expected to result in a lesser catalytic effect on the initial sodium sulfide oxidation rate because of the less complicated and more stable aromatic ring structure, thus requiring greater system retention times. However, softwoods would also contain less sodium mercaptide, which would result in a slightly lower oxygen demand and reduced chances for evolution of methyl mercaptan or dimethyl disulfide from the black liquor. Freedman (84) previously reported that the rate of sodium sulfide oxidation was slower with Southern pine than Northern hardwood weak black liquors with oxygen.

E. Strong Black Liquor Studies

A series of experiments were made regarding the oxidation of sodium sulfide in strong black liquor with the pilot scale plug flow reactor in a manner similar to those previously described for wea- black liquor. Particular emphasis was placed on determination of specific variables on chemistry and kinetics of sodium sulfide oxidation in strong black liquor. The effect of the oxidation reactions for other constituents present in the strong black liquor was also of interest. It was not possible to obtain reliable measurements for sodium mercaptide concentration in strong black liquor because of difficulties with the analytical technique, and that a major portion of that initially present in weak black liquor had been removed during the multiple effect evaporation process. Process variables investigated included the following: 1) liquid temperature; 2) solids concentration; 3) oxygen ratio; 4) contactor configuration; 5) inlet sodium sulfide concentration for liquor "polishing" studies.

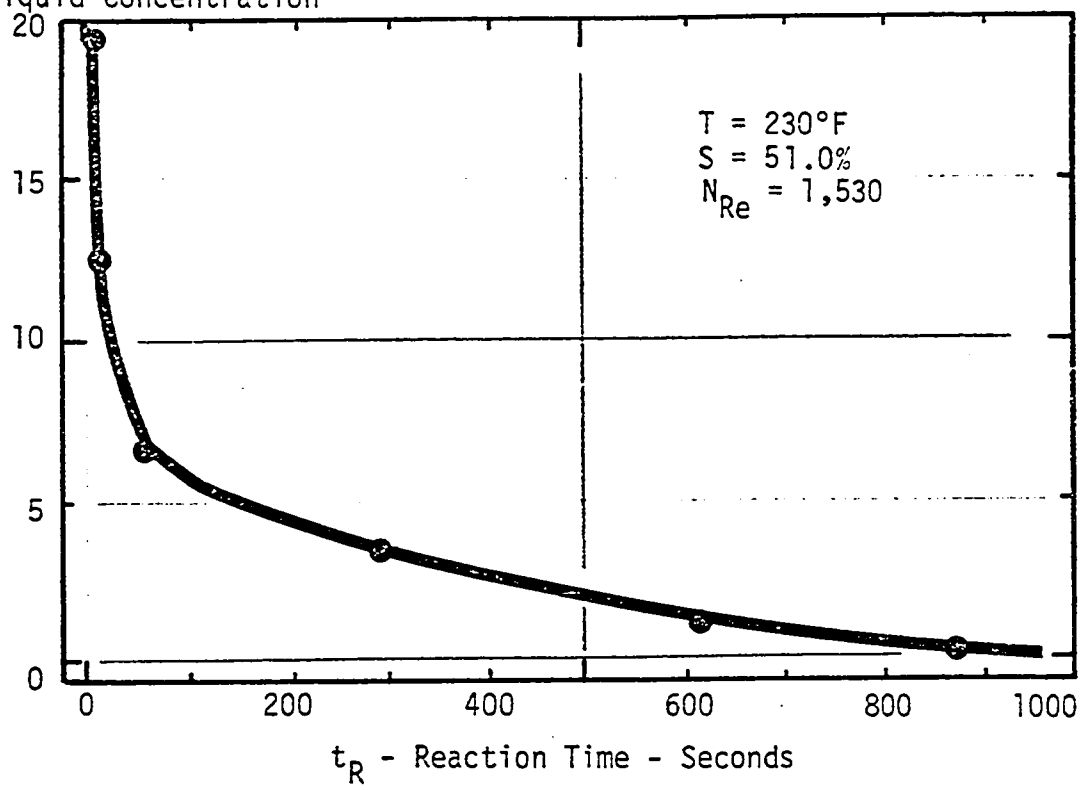
1. Reaction Kinetics

a. Sodium Sulfide

The rate of sodium sulfide oxidation in strong black liquor followed a three step pattern similar to weak black liquor with increasing reaction time. The initial period of five to ten seconds was characterized by a relaitvely rapid decrease in sodium sulfide concentrations which under some circumstances approached being a zero order reaction for concentrations greater than approximately ten grams per liter. The transition period following the initial reaction period of five to ten seconds up to a reaction time of 60 to 120 seconds and was characterized by a gradually decreasing rate of sodium sulfide oxidation. The third region was characterized by a relatively slow decrease in sodium sulfide concentration which appeared to approximate a first order reaction in sodium sulfide concentration, as illustrated in Figure 55.

The major difference between weak and strong black liquor was that the region of relatively slow sodium sulfide oxidation was predominant at concentrations below five to eight grams per liter in strong liquir, as compared to values of 0.10 to 0.25 for weak black liquor. The result was that substantially longer retention times were required for equivalent degrees of sodium sulfide oxidation in strong black liquor than with weak black liquor. A possible reason for the difference was that there was relatively less catalytic effect exerted upon the sodium sulfide oxidation in the initial reaction phase by organic constituents in the black liquor such as phenolic lignin. A possible reason was that there was greater oxygen demand exerted by oxidation of organic constituents such as phenolic lignin at greater temperatures in the more concentrated strong black liquor. The oxidation of organic constituents thus acted to compete for available oxygen instead of catalyzing the oxidation of sodium sulfide.

a. Liquid Concentration



b. Concentration Ratio

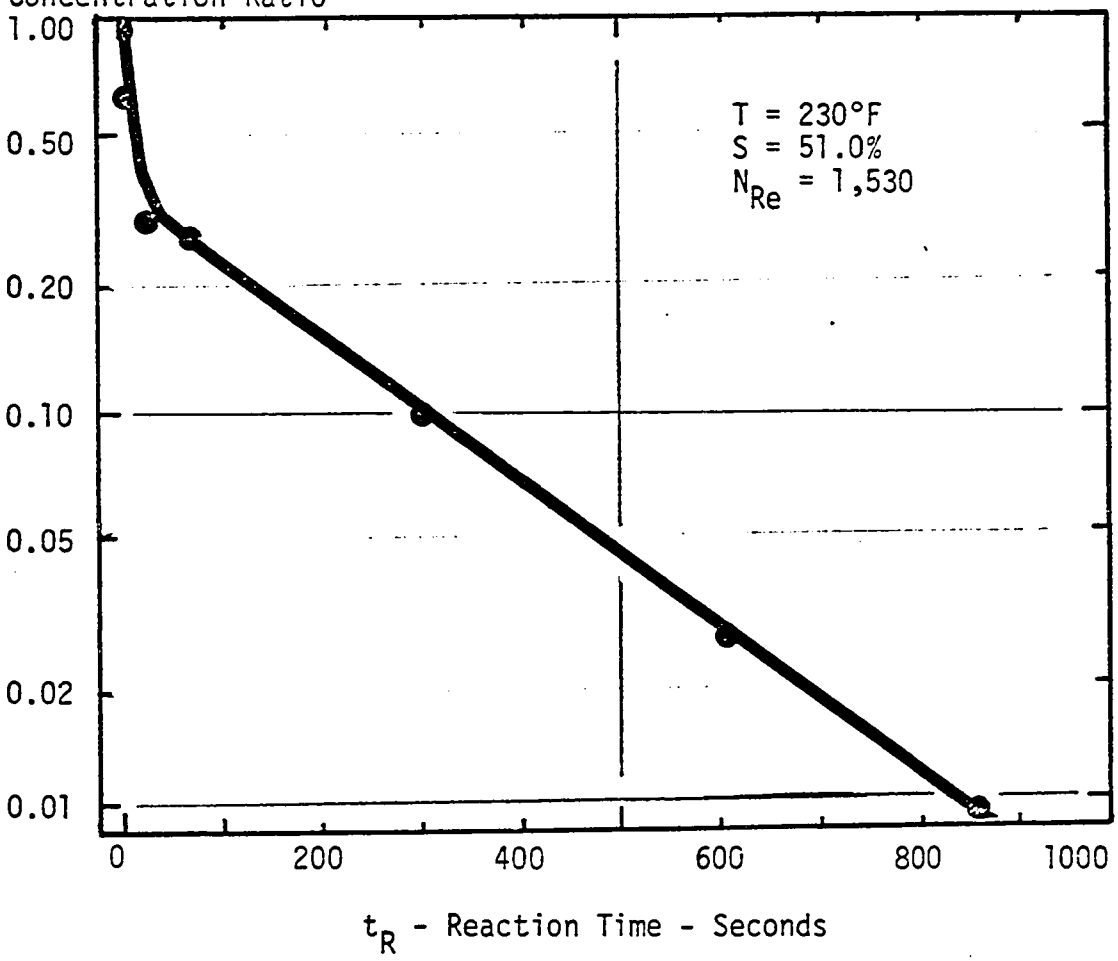


FIGURE 55. Na_2S OXIDATION IN STRONG BLACK LIQUOR.

Reaction rate constants for the oxidation of sodium sulfide were determined by graphical means from data obtained by chemical analyses in a manner previously described. A summary of primary (k_1) and secondary (k_2) reaction rate constants for sodium sulfide oxidation has been presented in Table 44.

TABLE 44. REACTION RATES FOR Na_2S OXIDATION IN STRONG BLACK LIQUOR.

Constant	Order	Units	Mean	Maximum	Minimum
Primary (k_1)	0	$\frac{\text{gm } Na_2S}{\text{liter b.l.-sec}}$	-0.688	-1.172	-0.234
	0	$\frac{\text{lb } Na_2S}{\text{gal b.l.-hour}}$	-20.60	-35.50	-7.03
Secondary (k_2)	1	1/seconds	-0.00238	-0.00458	-0.00067
	1	1/minutes	-0.143	-0.275	-0.040
$t_{1/2}$	1	seconds	381	1035	153

Note: Values for k_2 were calculated to base "e" logarithms.

The primary reaction rate constants obtained for the initial reaction period were dependent upon oxygen mass transfer, and were particularly affected by factors such as oxygen ratio, liquid temperature, and solids concentration. Secondary reaction rate constants dependent on the chemical reaction rate were found to be dependent on liquid temperature and possibly oxygen ratio.

Morgan and Murray (159) reported that the oxidation of sodium sulfide with air in strong black liquor followed consecutive zero and first order reactions, but did not list values for the respective constants. They observed that the overall rate of sodium sulfide oxidation in a completely mixed reactor decreased logarithmically with decreasing outlet concentration on a logarithmic basis. These findings pointed out the increasing importance

of the slow secondary first order reaction when it was desired to produce high degree sodium sulfide oxidation efficiencies, which would require extended retention times. No published values have been reported for oxidation rates and overall oxidation efficiencies for sodium sulfide in strong black liquor with molecular oxygen.

b. Sodium Polysulfide

A limited amount of experimental data showed that concentrations of sodium polysulfide in strong black liquor ranged from one to four grams per liter. These values were substantially greater than the levels of 0.05 to 0.5 grams per liter observed for weak black liquor. It was not possible to make calculations of reaction rate constants for changes in sodium polysulfide concentrations. It was observed that sodium polysulfide concentrations tended to increase from initial levels during the initial reaction period and then return to the initial concentration with increasing retention time. No information was available in the literature regarding sodium polysulfide concentrations in strong black liquor.

c. Sodium Sulfite

A limited amount of experimental data indicated that sodium sulfite concentrations in strong black liquor were extremely small, generally ranging from undetectable to approximately 0.3 grams per liter. Results indicated that minimum sodium sulfite concentrations corresponded to maximum sodium polysulfide concentrations in strong black liquor. No information regarding sodium sulfite concentrations for strong liquor was available in the literature.

d. Sodium Thiosulfate

Results indicated sodium thiosulfate was the primary reaction product of sodium sulfide oxidation in strong black liquor. The increase in sodium

thiosulfate concentration with increasing reaction time appeared to follow a three step sequence which inversely paralleled the oxidation of sodium sulfide. The initial step was a rapid increase in sodium thiosulfate concentration during the initial reaction period of five to ten seconds. The primary initial increase in sodium thiosulfate concentration approximated a zero order reaction which paralleled decreases in sodium sulfide. The initial reaction period was followed by a transition region characterized by a decreasing rate of sodium thiosulfate formation. The final reaction period occurred after approximately five minutes of reaction time, and approximated a second order reaction, as shown in Figure 56.

Values for the primary (k_5) and secondary (k_6) rate constants for sodium thiosulfate formation for the single test were as follows: 1) primary (k_5) - 0.940 grams $Na_2S_2O_3$ per liter black liquor per second; 2) secondary (k_6) 0.79×10^{-5} liters of black liquor per gram $Na_2S_2O_3$ per second. There was an insufficient amount of data to draw firm conclusions regarding the respective rates of sodium thiosulfate formation in strong black liquor, and no comparative values for reaction rates were available in the literature. The slow sodium thiosulfate increase during prolonged reaction times for strong liquor oxidation was in marked contrast to the slow decrease in thiosulfate levels during prolonged oxidation of weak black liquor with oxygen. These findings pointed to inhibition of subsequent sodium sulfate formation during strong black liquor oxidation with oxygen.

e. Sodium Sulfate

It was not possible to observe any significant increases in sodium sulfate concentrations in strong black liquor during any of the tests, even at the prolonged reaction times or at the elevated temperatures employed. This finding was in marked contrast to results obtained for oxidation of

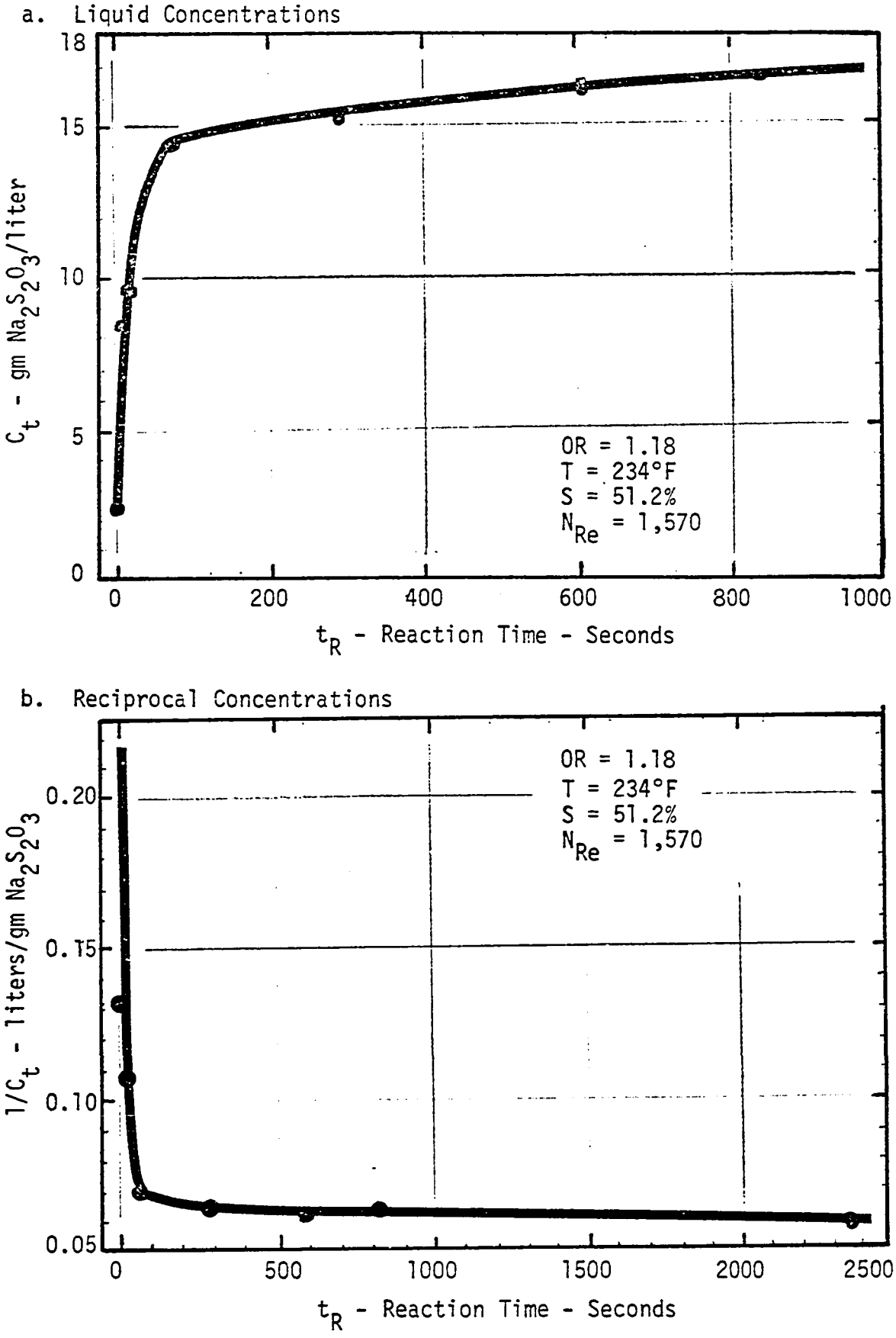


FIGURE 56. $Na_2S_2O_3$ FORMATION IN STRONG BLACK LIQUOR.

weak black liquor, and had three possible explanations. The first reason was that the oxidation of strong black liquor operated in a relatively oxygen-starved condition because of the difficulties in achieving effective oxygen mass transfer into the highly viscous liquid, with the possibility for substantial oxygen uptake by organic constituents such as phenolic lignin at elevated temperatures. The second possible reason was that the presence of sodium polysulfide in relatively high concentrations increased the chance that any sodium sulfite formed by oxidation of sodium thiosulfate would react rapidly with polysulfide. The result was the possible regeneration of sodium thiosulfate and sodium sulfide, with resultant inhibition of sodium sulfate formation. No comparative information was available in the literature regarding sodium sulfate formation during strong black liquor oxidation with oxygen.

f. Total Sulfur

Results of two studies indicated that for strong liquor it was possible to account for a greater portion of the sulfur initially present as the reaction progressed by means of the chemical analyses employed than with weak black liquor as listed in Table 45. A possible reason was that the higher temperatures employed for strong black liquor oxidation of 220 to 240°F tended to provide sufficient energy to the system to cause certain unstable reaction intermediate forms of polysulfide or polythionate ions to be oxidized to more stable products such as sodium thiosulfate. No comparative information was available in the literature.

2. Process Variables

Studies were made with the particular objectives of determining the effects of several variables on the overall efficiency and rate of sodium

TABLE 45. EFFECT OF REACTION TIME ON TOTAL SULFUR BALANCE DURING STRONG BLACK LIQUOR OXIDATION WITH OXYGEN.

Reaction Time	Concentration as Sulfur-gm S/liter						Sulfur Ratio
Seconds	Na_2S	Na_2S_2	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4	Total	S_t/S_o
0	7.730	1.272	0.895	0.032	1.027	10.956	1.000
7	4.380	0.630	3.550	0.056	0.845	9.461	0.864
26	2.362	1.920	3.820	0.048	1.117	9.267	0.846
68	1.233	1.813	5.890	0.016	1.152	10.104	0.946
292	2.018	2.183	6.080	0.000	1.100	11.381	1.037
603	0.428	2.200	6.700	0.048	1.700	10.546	0.953
838	0.310	0.972	6.510	0.064	1.062	8.918	0.812
2380	1.282	1.260	6.770	0.897	1.050	11.259	1.026

sulfide oxidation in strong black liquor. Variables of particular interest included the following: 1) Reynolds number; 2) liquid temperature; 3) solids concentration; 4) oxygen ratio; 5) contactor configuration; 6) inlet sodium sulfide concentration.

a. Effect of Reynolds Number

Results from previous studies indicated that it was desirable to maintain liquid Reynolds numbers above approximately 40,000 to maximize the rate of oxygen mass transfer into black liquor. Previous calculations indicated that it would be extremely difficult to obtain liquid Reynolds numbers above 20,000 with strong black liquor because of its high viscosity, even for full scale installations. Liquid Reynolds numbers during the pilot scale studies ranged between 1,000 and 2,500, and indicated the expected difficulties of oxygen mass transfer into strong black liquor.

Once the sodium sulfide concentration in strong black liquor dropped below five to eight grams per liter, the oxidation of sodium sulfide became an essentially first order reaction where oxygen mass transfer was not the rate-limiting process. Liquid Reynolds number was of considerable importance in the oxidation process only at relatively high sodium sulfide concentrations above five to eight grams per liter. It would be important for strong black liquor oxidation with molecular oxygen only where weak black liquor was not being oxidized, and where the inlet sodium sulfide concentration was relatively high, such as Kraft mills with high sulfidities on those employing Kamyr continuous digesters. No information was available in the literature regarding the effects of liquid Reynolds number on strong black liquor oxidation with oxygen.

b. Effect of Liquid Temperature

The temperature of strong black liquor was found to affect both the primary and secondary overall rate constants for sodium sulfide oxidation, and the sodium sulfide oxidation efficiency across the plug flow reactor, as listed in Table 46. The primary rate constant (k_1), dependent largely on oxygen mass transfer, was found to increase with temperature, in marked contrast to findings observed for weak black liquor. The probable reason for the increase with temperature was that the liquor viscosity was reduced sufficiently to increase the rate of oxygen mass transfer to overcome the contrary effect of reduced gas solubility with increasing temperature. The secondary rate constant (k_2) was primarily a function of the rate of the chemical oxidation reaction, and was found to increase with temperature in agreement with kinetic theory. A slight increase in the overall sodium sulfide oxidation efficiency was also observed at the highest temperature, probably because of the increased reaction rates.

TABLE 46. EFFECT OF TEMPERATURE ON REACTION RATE AND OVERALL EFFICIENCY FOR Na_2S OXIDATION IN STRONG BLACK LIQUOR.

Liquid Temperature °F	Oxidation Rates		Oxidation Efficiency %
	Primary (k_1) gm Na_2S/liter-sec	Secondary (k_2) l/seconds	
215	0.234	0.00105	97.9
220	0.405	0.00136	97.9
230	0.983	0.00199	99.1

Findings pointed to the necessity for maintaining strong black liquor at maximum temperatures to facilitate optimum rates of sodium sulfide oxidation. However, practical temperature increase probably had a maximum upper limit in terms of economics because excessive oxygen consumption required for oxidation of organic constituents in black liquor such as phenolic lignin and gas solubility. Heating of strong black liquor upstream of the oxidation unit was one possibility for maintaining a maximum rate of both oxygen mass transfer and sodium sulfide oxidation in the highly viscous liquid. No specific comparative values were available from published literature regarding temperature effects upon strong black liquor oxidation with oxygen. Smith (106) observed a substantial increase in the rate of sodium sulfide oxidation with air with increasing temperatures with refinery spent caustic liquids, particularly during the initial reaction period at concentrations above 0.5 grams per liter.

c. Effect of Solids Concentration

Increasing the solids concentration with other variables held constant was found to affect both the primary rate constant (k_1) and the overall efficiency of sodium sulfide oxidation as listed in Table 47. The above

TABLE 47. EFFECT OF SOLIDS CONCENTRATION REACTION RATE AND OVERALL EFFICIENCY FOR Na_2S OXIDATION IN STRONG BLACK LIQUOR.

Solids Concentration % by wt.	Primary Rate ($r_1=k_1$) gm Na_2S/liter-sec	Oxidation Efficiency %
51.2	1.172	97.9
53.3	0.405	83.8

experiments were performed at a temperature of 234°F, Reynolds number of 1,550, liquor retention times of approximately fifteen minutes, and oxygen ratios between 1.05 and 1.18. The probable reason for the decreases in rate constant and oxidation efficiency was that the strong liquor viscosity increased sufficiently to reduce the rate of oxygen mass transfer. The increase in black liquor viscosity would act to allow oxygen bubble size to increase and increase the ability of the liquid film to resist rupture. These findings were in basic agreement with results reported at a previous National Council symposium (93) where solids concentrations of greater than approximately 52 percent were found to inhibit oxygen mass transfer into strong black liquor. The results pointed to the necessity for controlling solids concentration to below 52 percent by weight to facilitate effective oxidation of strong black liquor with molecular oxygen.

d. Effect of Oxygen Ratio

The oxygen ratio, or amount of oxygen added compared to that required for stoichiometric conversion of sodium sulfide to thiosulfate, was observed to affect the efficiency of oxygen utilization and sodium sulfide oxidation, plus the primary and secondary rate constants for sodium sulfide oxidation. The tests for oxygen ratio were all made with liquid retention times of

approximately fifteen minutes, temperatures between 215 and 235°F, and liquid Reynolds numbers between 1,000 and 1,500.

The trends of decreasing oxygen utilization and increasing sodium sulfide oxidation efficiency with increasing oxygen ratio were notes for both weak and strong black liquor. The major difference was that values for both oxygen utilization and oxidation efficiency were lower for strong black liquor at equivalent oxygen ratios than for weak liquor. Results indicated that the maximum values for sodium sulfide oxidation efficiency were observed at oxygen ratios between 1.2 and 1.4, in agreement with findings for weak black liquor, as shown in Figures 57 and 58.

Values observed for the primary and secondary reaction rate constants of sodium sulfide oxidation were both found to be at a maximum for values between 1.2 and 1.4. The findings were in basic agreement with those observed for weak black liquor. At lower oxygen ratios the system became starved for oxygen, with resultant decrease in reaction rates. At higher oxygen ratios, sufficient oxygen was probably present to result in oxidation of sodium thiosulfate to sodium sulfite, which could then react with sodium polysulfide to regenerate sodium sulfide and reduce the overall (removal minus formation) rate of sodium sulfide oxidation.

These findings pointed to the necessity for careful control of the amount of oxygen added as comapred to that required for oxidation of sodium sulfide. Inadequate oxygen supply would mean incomplete oxidation of sodium sulfide while excess amounts of oxygen would mean both an economic drawback and potential problems with reduction in overall oxidation efficiency. The findings were generally in agreement with those observed for the effect of oxygen ratio on weak black liquor oxidation. No directly comparable values were available for the effect of oxygen ratio on strong black liquor oxidation with molecular oxygen.

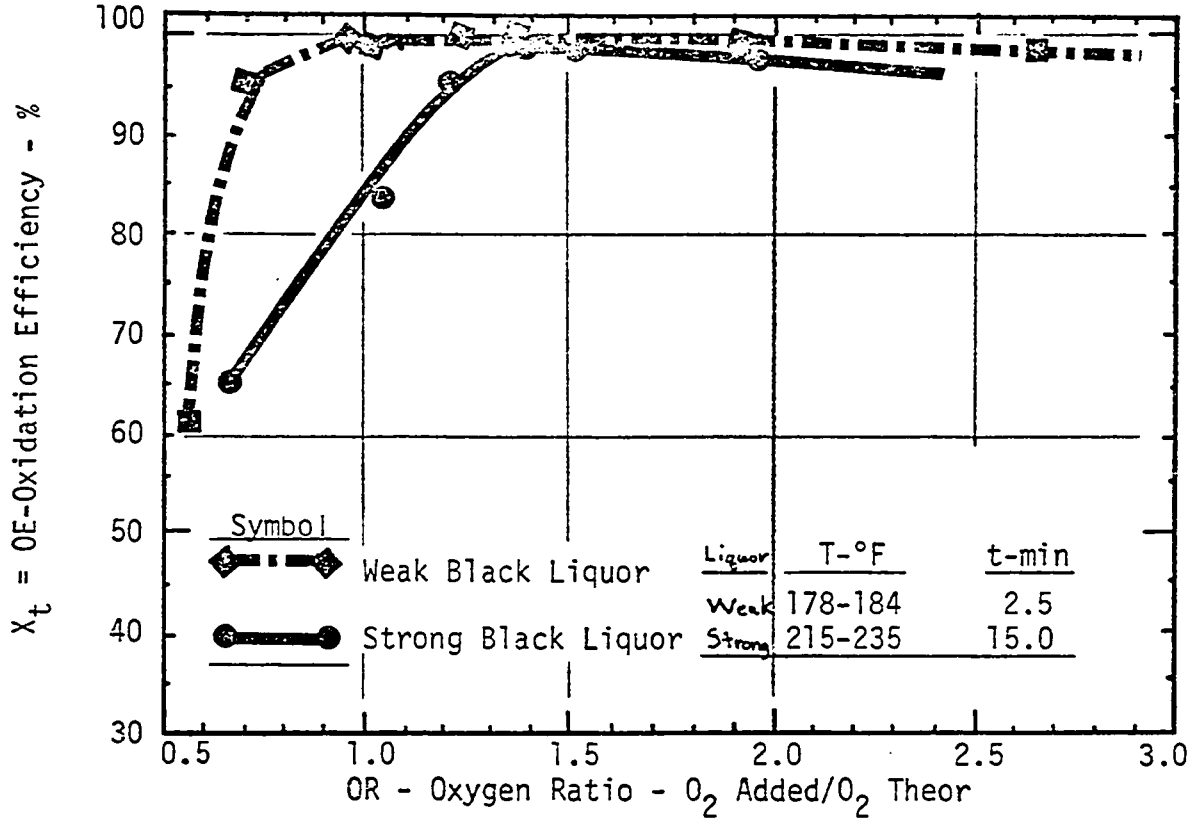


FIGURE 57. EFFECT OF OXYGEN RATIO ON Na_2S OXIDATION EFFICIENCY IN BLACK LIQUOR

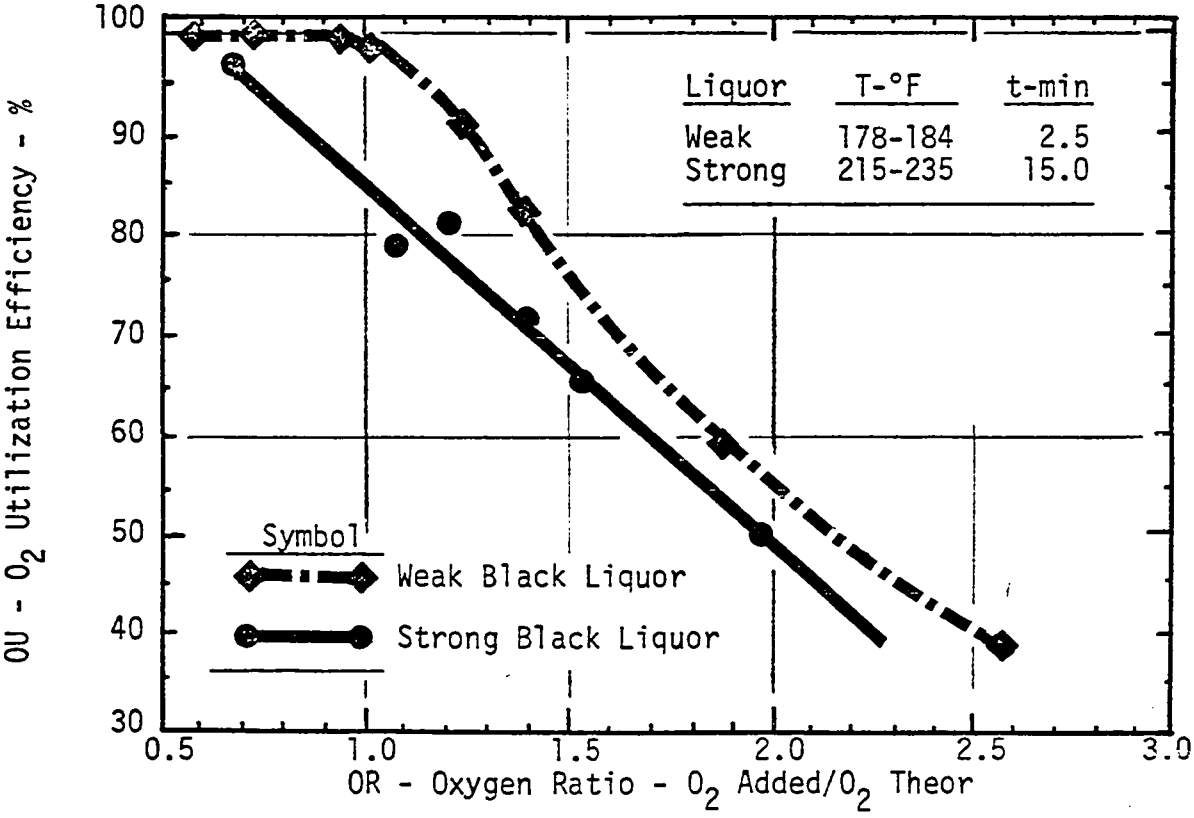


FIGURE 58. EFFECT OF OXYGEN RATIO ON OXYGEN UTILIZATION EFFICIENCY IN BLACK LIQUOR

e. Effect of Contactor Configuration

Tests were made where the configuration of the contactor for introducing oxygen into strong black liquor was changed to determine its effect upon the rate and efficiency of sodium sulfide oxidation. The normal configuration involved a horizontal 3/8 inch pipe of fifteen foot length with a retention time of five to ten seconds, depending on liquid flow rate. The modifications to the inlet contactor configuration employed a "U"-shaped section following the introduction of oxygen where the black liquor flowed in a vertical downward direction through a series of expansion chambers and then upward in a two inch diameter pipe to facilitate increased gas bubble retention time. In addition, the method oxygen introduction could be changed by using either an axially located porous gas dispersion cylinder or four open tubes located axially in a downward vertical direction.

Results indicated that there was a slight effect on the overall efficiency of sodium sulfide oxidation in terms of both the method of oxygen introduction and the contactor flow direction. The axially located porous gas dispersion cylinder proved to be more effective for introducing oxygen to strong black liquor than the four axially located open inlet tubes. The probable reason was that the initial bubble sizes produced were smaller with the porous cylinders than the open tubes and there was a greater degree of initial mixing. The use of cocurrent oxygen and strong liquor flow in a downward vertical direction also appeared to improve the overall efficiency of sodium sulfide oxidation as compared to horizontal flow alone, primarily because of the increased bubble retention time and the avoidance of stratified flow. However, these modifications only slightly changed the sodium sulfide oxidation efficiency because strong black liquor oxidation was primarily

limited by the rate of the chemical oxidation reactions at concentrations below five grams per liter, and was limited by mass transfer at the relatively high inlet concentrations.

f. Strong Liquor Polishing

A test was run regarding the effectiveness of using molecular oxygen for oxidizing strong black liquor which had been previously undergone oxidation with molecular oxygen. The purpose of "polishing" the strong black liquor was to counteract potential reversion to sodium sulfide during multiple effect evaporation, where relatively low inlet concentrations of one to three grams per liter could be expected. The strong black liquor at relatively high concentrations was initially oxidized with molecular oxygen by one passage through the pilot scale reactor to reduce its inlet concentration to the range of interest. The partially oxidized liquor was then pumped from storage through the plug flow reactor for subsequent oxidation of the remaining sodium sulfide. It was only possible to run one sample because of the severe pumping problems which developed for the partially oxidized liquor upon cooling.

Results for the single test at an oxygen ratio of 2.7 that reduction of the sodium sulfide present would require a retention time of between fifteen and twenty minutes to reduce the sodium sulfide concentration to below 0.05 grams per liter from an inlet concentration of 2.5 grams per liter. It was possible that substantially more oxygen would be required than the stoichiometric requirement for sodium sulfide oxidation to sodium thiosulfate, but additional tests would be necessary. As the rate of sodium sulfide oxidation at low concentrations was primarily limited by the rate of the chemical reactions occurring, it was also possible to perform the oxidation of strong black liquor in some type of completely mixed tank or to use

atmospheric oxygen in place of molecular oxygen. However, such a tank might require an agitator or other moving parts, and would present the potential for both additional expense and considerable mechanical problems.

F. Special Studies

1. Lignin Oxidation

A series of analyses were made to determine the effect of reaction time on weight loss of organic materials such as phenolic lignin during black liquor oxidation with molecular oxygen. Tests were made by weighing the amounts of organic material collected by filtration from a series of black liquor samples following acidification to cause lignin precipitation. A single series of tests were made for one run each for both weak and strong black liquor. The test procedure used would not give exact figures for the change in lignin content of black liquor, but would provide approximations of any weight changes taking place. The material collected included both lignin and other filterable materials.

Results of the studies at the respective operating conditions indicated the overall weight loss of filterable material from black liquor was approximately ten percent for weak black liquor and fifteen percent for strong black liquor. The decrease in lignin content of the black liquor with increasing reaction time appeared to follow a pattern similar to oxidation of sodium sulfide, as shown in Figure 60. The findings for weak black liquor were verified by separate analyses of organic solids content of the samples. Both weak and strong black liquor displayed the pattern of a rapid initial weight loss, a transition period, and a final period of relatively slow decrease in weight. Possible reasons noted for the greater weight loss noted with strong than weak black liquor was the higher concentrations and greater temperatures represented the potential for greater attack on the

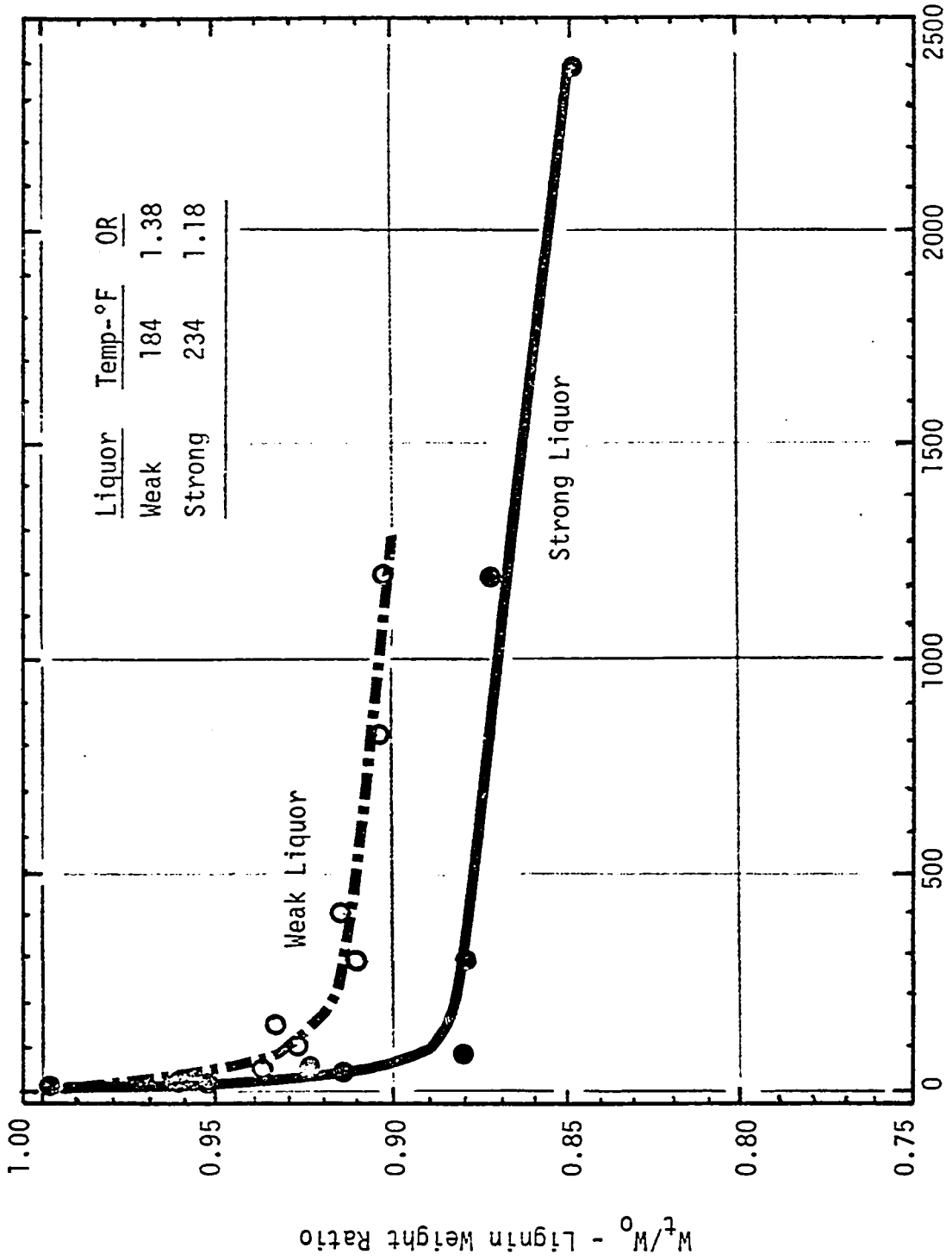


FIGURE 59. LIGNIN WEIGHT REDUCTION DURING BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN

lignin monomers. The relative attack of oxygen on phenolic lignin would be expected to increase with liquid temperature and pH, and for certain wood species. No directly comparable values for lignin weight loss were available in the literature.

The significance of the weight loss of filterable organic material, of which lignin was a major constituent, was that it was necessary to add a sufficient amount of oxygen to account for lignin oxidation. The amount of oxygen necessary to compensate for lignin oxidation and still achieve effective sodium sulfide removal could be as much as ten to twenty percent of that required for sulfide oxidation. The potential oxygen demand exerted by lignin and other organic constituents would probably increase with increasing temperature, and would be a greater problem for strong than weak black liquor. The additional oxygen demand exerted by phenolic lignin would tend to make black liquor oxidation with molecular oxygen less attractive from an economic standpoint. The wood species employed would probably have an important impact on the amount of lignin oxidation taking place. Hardwoods with complex ring structures would probably display the greatest susceptibility to oxidation.

2. Liquor Heating Value

Successive tests were made of the respective heating values for the inlet and outlet samples of strong black liquor used in the previous lignin oxidation determinations by means of oxygen bomb colorimetry. Results indicated a reduction of approximately six percent in the heat of combustion for strong black liquor from 5,239 to 4,932 BTU per pound during the oxidation process. These findings were in basic agreement with values previously reported by Lindholm and Stockman (121), except that they reported reductions of 2.0 to 3.6 percent in heating value for weak black liquor. The losses in

liquor heating value were less than the lignin weight loss, indicating that other materials in black liquor contributing to the heat of combustion, such as soluble organic materials to hemicelluloses and sugars, were not as easily oxidized. The major significance of the loss in heat of combustion for strong black liquor was that it would cause a slight reduction in the amount of heat available in the recovery furnace, and could be a particular drawback for strong black liquor oxidation with molecular oxygen. The effect would also be a function of wood species.

3. Tall Oil Recovery

A test was made to determine the effect of weak black liquor oxidation with molecular oxygen on tall oil yield. The procedure used for isolating tall oil employed filtration of lignin from black liquor, washing and extraction of tall oil from the aqueous phase with petroleum ether. Samples were taken from the respective inlet and outlet points of the plug flow reactor prior to analyses. Results indicated a slight increase in the amount of tall oil recovered of between five and ten percent. The tall oil fraction in the reactor exit sample separated from the ether and aqueous phases more rapidly and more easily than from the reactor inlet sample. The increase in tall oil yield during weak black liquor oxidation with molecular oxygen was in basic agreement with findings previously reported by Galeano and Amsden (103), though smaller than the approximately fifteen percent they observed.

The potential increase in tall oil yield was of considerable importance in enhancing the economic feasibility of black liquor oxidation with molecular oxygen. Small increases in tall oil yield would be of considerable importance in determining whether the process was economically attractive. The above experiments were made with wood species displaying relatively low tall oil

yields, and were not considered as being either representative or conclusive. Considerable additional experimentation would be required at Southern Kraft mills pulping substantial quantities of pine wood species where relatively high tall oil yields could be expected. Particular attention should be given to the following: 1) the mechanism of increase in tall oil yield, either physical or chemical, or both; 2) factors tending to cause an increase in tall oil yield; 3) the possible deterioration of tall oil quality (93); 4) the possible use of nitrogen gas as an inert flotation-aiding medium.

4. Liquor Temperature Change

The oxidation of black liquor with molecular oxygen appeared to have a definite effect on the temperature change across the plug flow reactor. A temperature increase of five to ten degrees Fahrenheit (2 to 5°C) was noted across the plug flow reactor during weak black liquor oxidation with oxygen based on inlet sodium sulfide concentrations from four to seven grams per liter. The primary reason for the temperature increase was the heat released by the oxidation of sodium sulfide to sodium thiosulfate and other exothermic reactions occurring. The temperature increase would be primarily dependent on the inlet sodium sulfide concentration, the amount of oxygen added, and the surface area of the reactor available for heat transfer. The temperature increases reported for weak black liquor oxidation with molecular oxygen was less than the 18°F previously reported by Freedman (84). The probable reason was the relatively low inlet sodium sulfide concentrations at the mill where studies were made and the greater reactor surface area available for heat transfer. The significance of the findings was that the sensible heat requirement for heating black liquor to the boiling point during multiple effect evaporation was reduced, with a corresponding decrease in evaporator steam requirements.

The oxidation of strong black liquor with molecular oxygen resulted in a temperature decrease of between twelve and twenty degrees Fahrenheit across the plug flow reactor. The probable reason for the decrease was because the rate of the sodium sulfide oxidation was much lower at equivalent concentrations than in weak black liquor, and was not primarily limited by oxygen mass transfer. The unabsorbed and unreacted oxygen gas dispersed in the strong black liquor then acted to evaporate water from the black liquor with resultant cooling. Cooling the strong black liquor caused its viscosity to increase and make the liquid more difficult to pump, and also increased the sensible heat requirements during direct contact evaporation with recovery furnace flue gas. The potential for additional corrosion existed in precipitator and ductwork surfaces with the cooler flue gas stream, and the potential for malfunctioning of direct contact evaporators and liquor guns by the more viscous liquid. The findings were in agreement with previous observations by Miller (102).

5. Sodium Sulfide Reversion

Though not a function of the present research, observations regarding the reversion of sodium sulfide in black liquor were made from observed findings. It was normally possible to observe the onset of reversion to sodium sulfide within 30 minutes for weak black liquor, and within 45 minutes of reaction time for strong black liquor. Reversion within fifteen minutes was noted for weak black liquor during storage following oxidation on two different occasions. The amount of sodium sulfide reversion per unit time appeared to be far greater for strong black liquor than for weak black liquor, possibly because of the greater sodium polysulfide concentrations. For strong black liquor, the amount of sodium sulfide reversion also tended to increase with increasing oxygen ratios above 1.4, possibly because of the reaction

between sodium polysulfide and sulfite to form sodium thiosulfate and regenerate sodium sulfide.

The significance of sodium sulfide reversion was that it was necessary to have extremely short retention times for storage facilities following the introduction of oxygen into black liquor. For strong black liquor oxidation systems using molecular oxygen, a maximum storage retention time of 30 to 60 minutes would be necessary. For weak black liquor oxidation systems, it would be desirable to have either an extremely short retention time of 15 to 30 minutes prior to evaporation, or prolonged retention times of eight to twelve hours in an existing weak liquor storage tank in order to avoid potential reversion problems. Additional studies would be necessary to ascertain the best means for counteracting reversion to sodium sulfide in the weak black liquor oxidation systems at full scale installations.

G. Experimental Errors

1. Flow Measurements

A series of 30 tests each were made at constant flow settings for both oxygen and black liquor to determine the variability of measurements. Results for oxygen at a constant mean flow rate of 1.180 cubic feet per minute with an average deviation of 0.005 cubic feet per minute, with a resultant potential variation in measurement of 0.4 percent. Results for a constant setting of mean flow rate for weak black liquor of 3.40 gallons per minute indicated a mean deviation of 0.05 gallons per minute for an average error of 1.5 percent in measurements. It was concluded that variations in measurements for both oxygen and weak black liquor were not significant in terms of potential experimental errors.

2. Total Sulfur

Attempts were made to determine the potential errors in chemical analyses by means of a material balance. The total sulfur content of weak black liquor samples from one test run by means of additive chemical analyses for the respective inorganic constituents (sulfide, polysulfide, thiosulfate, sulfite, sulfate) was compared to results obtained by means of total sulfur analyses. Results indicated an average absolute difference between total sulfur content of black liquor solids by chemical addition and by separate combustion iodometric analyses averaged approximately 4.8 percent for all of the samples tested, as shown in Table 48. Results indicated that the total sulfur contents by additive chemical analyses were slightly higher than by separate analyses for sulfur contents, indicating that a certain degree of sulfur volatilization in the samples might be occurring, particularly during storage prior to analyses. Organic sulfur compounds were not included in the calculations, as they were not extensively characterized by chemical analyses and were more volatile than the forms of inorganic sulfur present. They were probably removed by heating during the drying step prior to analyses.

The total amount of sulfur present by both types of analyses generally appeared to decrease with increasing retention time up to 143 seconds and then to increase, indicating that the sulfur which could not be accounted for was a function of retention time. The trend was verified by separate analyses of the inorganic ash contents of respective black liquor samples. The exact nature of the intermediate products which were not accounted for was unknown, but it was suspected that they were either volatile, or could undergo decomposition to either volatile or otherwise undetectable products. It was suspected that various forms of sodium polythionates and polysulfides

comprised a portion of these nondetected products, but separate studies would be necessary to determine their exact nature. The fact that it was not possible to completely account for all of the sulfur present in weak black liquor during oxidation with oxygen has also been observed by Ricca (97), Galeano and Amsden (103), plus Sakhuja and Basu (98), with similar values for the discrepancies.

Relatively close agreement (less than five percent difference) was obtained between total sulfur content of black liquor by addition of separate chemical analyses for sulfide, polysulfide, thiosulfate, sulfite, and sulfate, and by specific analyses for total sulfur content of black liquor solids. Experimental errors would be systematic in nature, dependent on analytical methods employed. Additional work would be necessary to develop suitable techniques for total sulfur analysis in black liquor. It was the author's conclusion that additional work would be necessary to develop accurate, reproducible, specific and rapid analytical techniques for measurement of specific sulfur compounds in black liquor.

TABLE 48. COMPARATIVE TOTAL SULFUR ANALYSES IN WEAK BLACK LIQUOR.

Point	Retention Time Seconds	Total Sulfur-gm S/liter Chemical Addition	Total Sulfur-gm S/liter Sulfur Analysis	Difference $\frac{S_{c_a}}{S_{s_a}}$	Difference Absol. Value
0	0.0	3.85	3.79	1.020	2.0
1	3.4	3.81	3.65	1.043	4.3
2	8.1	3.80	3.70	1.025	2.5
3	13.0	3.63	3.58	1.013	1.3
4	21.2	3.65	3.48	1.048	4.8
5	33.6	3.43	3.80	0.903	9.7
6	50.0	3.82	3.58	1.068	6.8
7	82.0	3.56	3.65	0.976	2.4
8	143.0	3.43	3.68	0.930	7.0
9	295.0	3.52	3.44	1.023	7.7
10	410.0	3.44	3.63	0.948	5.2
11	1180.0	3.67	3.52	1.038	3.8
			Average -	1.004	4.8

TABLE 49. EFFECT OF REACTION TIME ON TOTAL SULFUR CONTENT OF WEAK BLACK LIQUOR.

Point	Retention Time Seconds	Total Sulfur Ratio-S_t/S_o		Ash Content	
		Chemical Addition	Sulfur Analysis	grams Ash / liter	A_t/A_o
0	0.0	1.000	1.000	59.90	1.000
1	3.4	0.987	0.962	49.95	0.833
2	8.1	0.986	0.975	50.70	0.846
3	13.0	0.941	0.944	50.75	0.848
4	21.2	0.946	0.917	50.20	0.838
5	33.6	0.890	1.003	50.60	0.846
6	50.0	0.992	0.944	50.23	0.837
7	82.0	0.925	0.963	50.85	0.850
8	143.0	0.888	0.971	50.65	0.847
9	295.0	0.914	0.907	50.42	0.904
10	410.0	0.892	0.957	54.30	0.915
11	1180.0	0.952	0.928	54.20	0.905
Average	—	0.943	0.955	—	0.873

VII. ECONOMIC ANALYSIS

A. Oxygen Consumption

1. Black Liquor Oxidation

The ultimate feasibility for using molecular oxygen for black liquor oxidation was primarily dependent on the quantity used. Previous results indicated that a quantity of oxygen of about 1.2 times the stoichiometric amount for oxidation of sodium sulfide to sodium thiosulfate would be sufficient for weak black liquor. For strong black liquor polishing it was probable that a quantity of oxygen of two to three times the stoichiometric amount for oxidation of sodium sulfide to sodium thiosulfate might be required. The quantities of oxygen required per unit of production in terms of increasing concentration have been illustrated in Figure 60 for weak black liquor oxidation and Figure 61 for strong black liquor polishing. Calculations were based on typical black liquor characteristics at Kraft mills in the Southeastern United States.

2. Alternative Oxygen Uses

Use of molecular oxygen for additional uses in Kraft pulp mills besides black liquor oxidation enhanced its potential uses because of the lower unit costs associated with economies of scale from greater oxygen consumption rates. The total oxygen use for black liquor oxidation might be 70 to 90 pounds per ton of pulp with comparable figures of 35 for biological waste treatment, 40 for pulp bleaching, and 50 for recovery furnace addition. A summary of the total oxygen consumption requirements for particular oxygen uses as a function of pulp production has been presented in Figure 62.

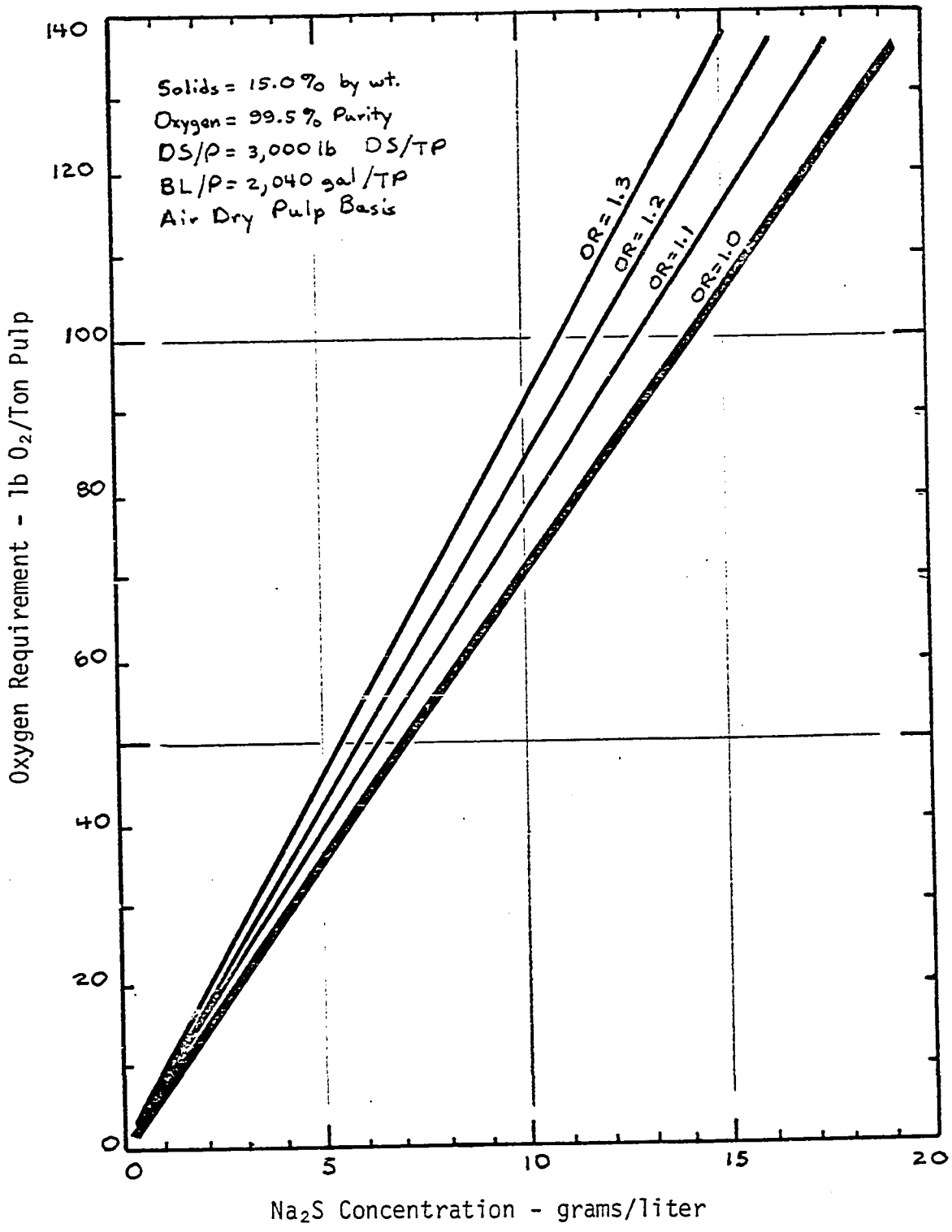


FIGURE 60. OXYGEN REQUIREMENTS FOR Na_2S OXIDATION IN WEAK BLACK LIQUOR.

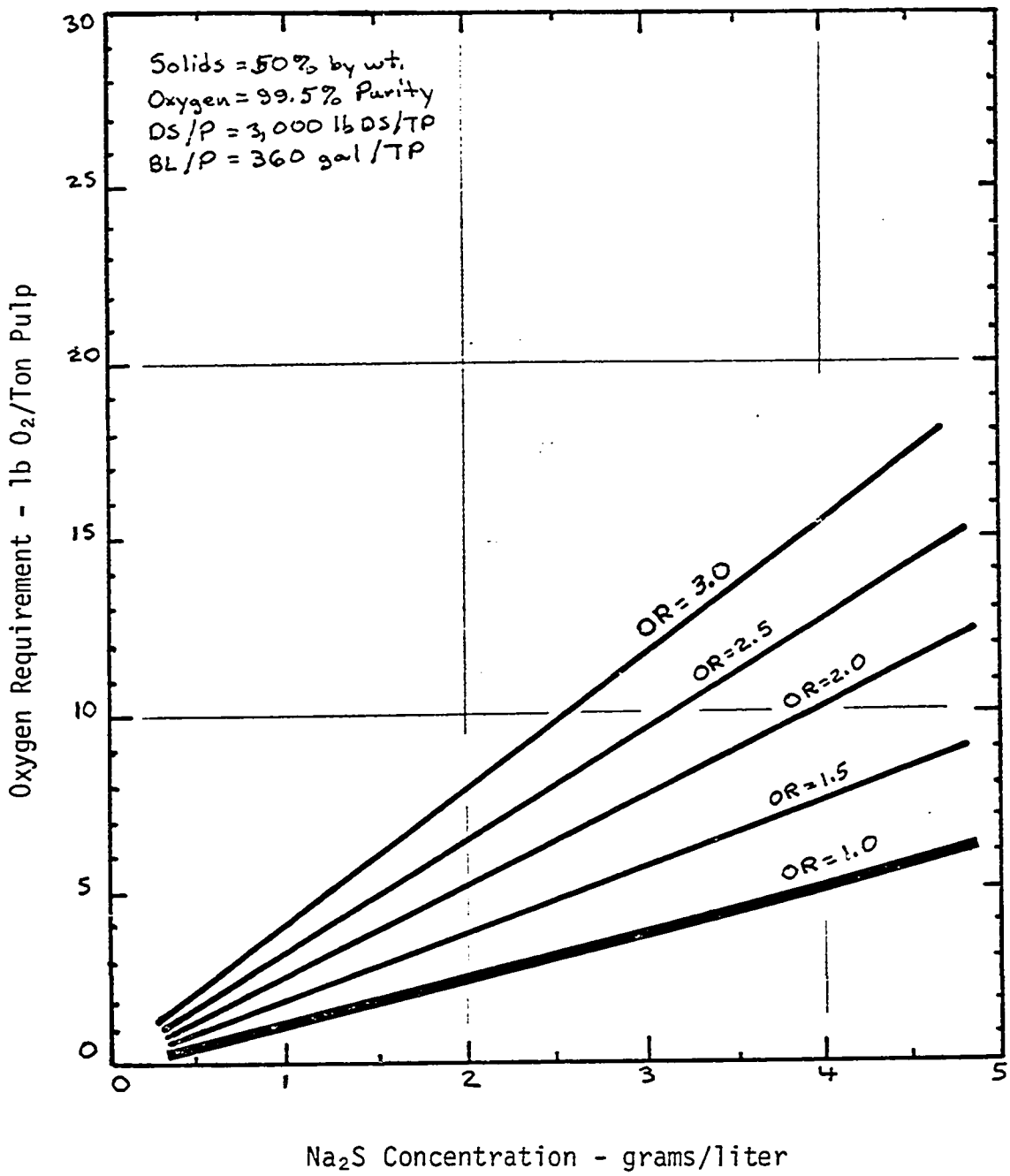


FIGURE 61. OXYGEN REQUIREMENTS FOR STRONG BLACK LIQUOR POLISHING.

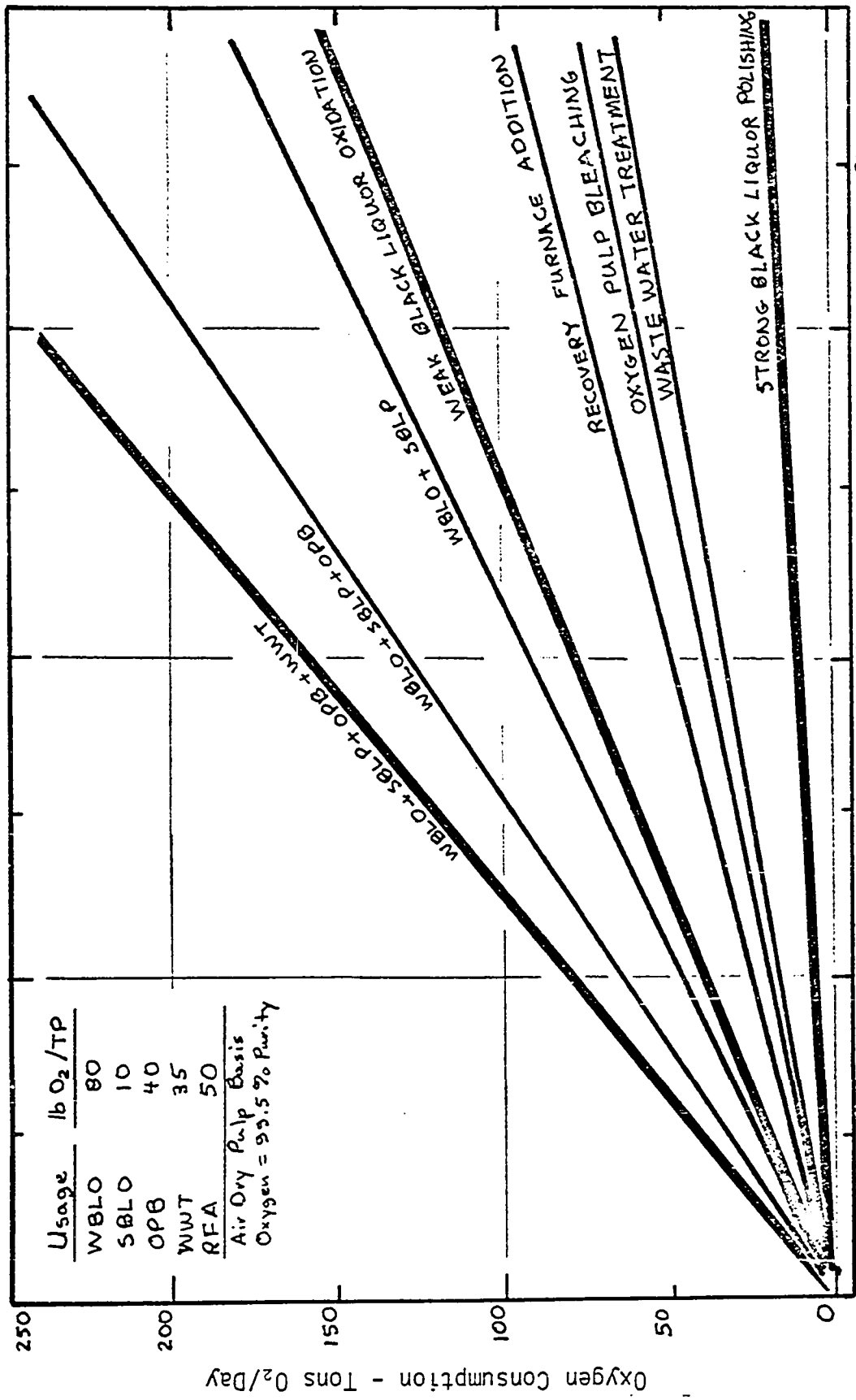


FIGURE 62. EFFECT OF PULP PRODUCTION ON OXYGEN CONSUMPTION.

B. Chemical Cost Credits

1. Tall Oil

The use of black liquor oxidation with molecular oxygen provided a means for reducing the rate of sodium sulfate makeup and increase the tall oil yield. The effect of increased tall oil yield on the reduction in process operating cost has been presented in Figure 63, for a tall oil price of 50 dollars per ton. Relatively small increases in tall oil yield of ten to fifteen pounds per ton of pulp would substantially enhance the potential economic attractiveness of using molecular oxygen for black liquor oxidation. The possibility of using nitrogen as a flotation aid to increase tall oil yield without causing potential effects by oxidation would be a suitable subject for further investigation.

2. Lime Addition

Black liquor oxidation would tend to produce an increase in the sulfidity levels of both green and white liquors. The increase would cause a decrease in lime makeup rate in the causticizing section of two to five pounds per ton of pulp, depending on the increase in percent sulfidity. For a lime cost of approximately fifteen dollars per ton as calcium oxide, the chemical savings would be approximately one to four cents per ton of pulp produced. The savings would only be observed if the sulfidity level were allowed to increase. A reduction in lime mud processing rate of ten to fifteen pounds per ton of pulp might be observed, but it was not possible to estimate this saving in terms of net operating cost for the overall process.

3. Sodium-Sulfur Makeup

Black liquor oxidation caused the retention of sulfur in the chemical recovery system instead of releasing it to the atmosphere. The retention of sulfur provided the potential for reduction in sodium sulfate chemical makeup requirement, but also provided the potential for increased sulfidity levels and

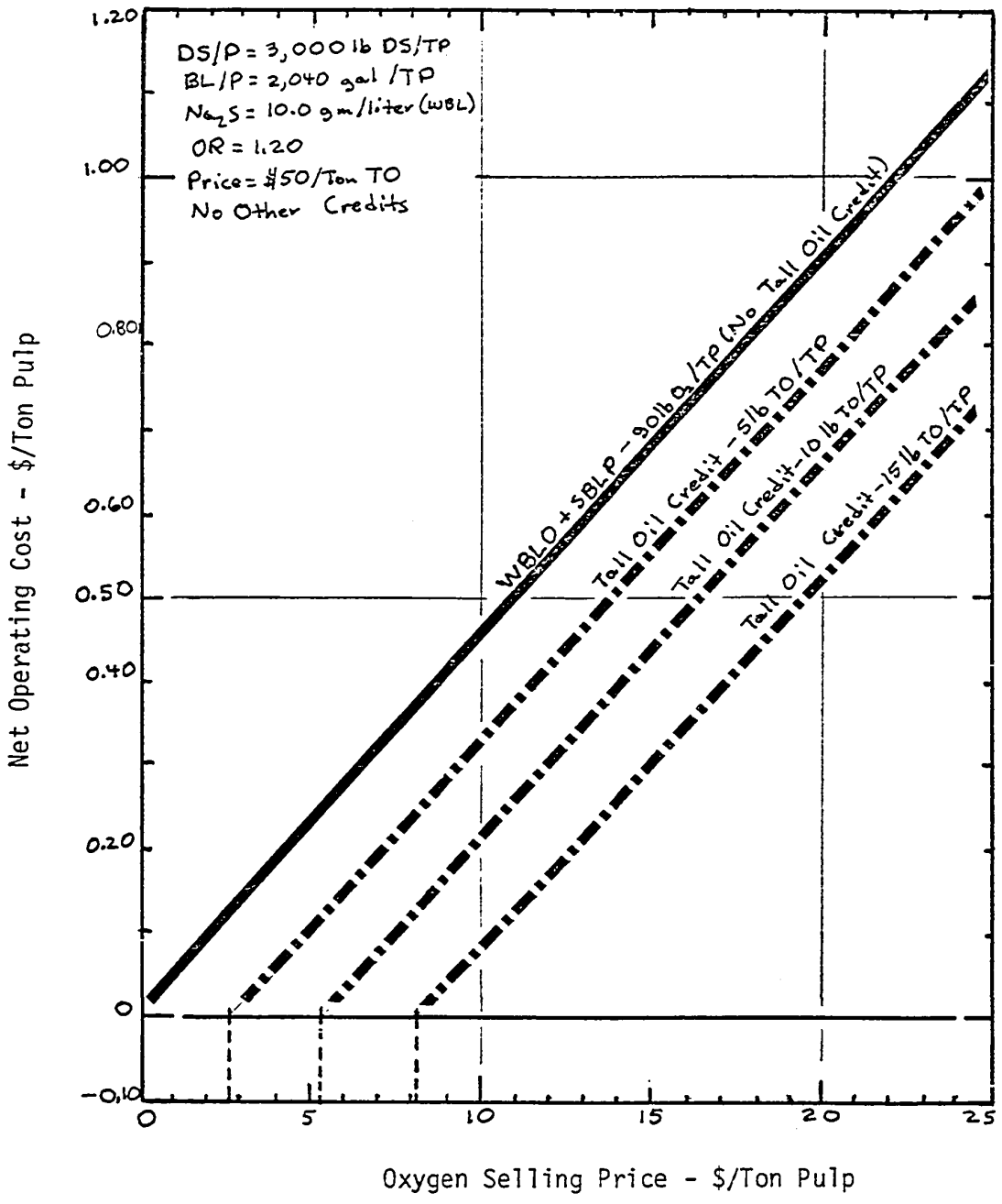


FIGURE 63. EFFECT OF TALL OIL YIELD ON NET OPERATING COST FOR BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN.

resultant greater potential for release of sulfur gas emissions. It would then become necessary to add sodium in the form of sodium hydroxide or other forms to maintain constant sodium - sulfur ratios and liquor sulfidity levels, nullifying any potential cost savings. Values for chemical savings in sodium sulfate makeup requirement of 30 to 60 pounds per ton have been reported in the literature, but it was questionable whether actual cost savings resulted. Increased sodium retention in the chemical recovery system would help to maintain constant sulfidity levels, particularly with increased brown stock washer efficiency and recovery furnace particulate collection efficiency. The possibility existed for addition of alkaline extraction stage bleachery effluent in bleached Kraft pulp mills to maintain a proper sodium-sulfur chemical balance. An additional method for maintaining high black liquor pH values and provide for sodium and sulfur chemical makeup requirements was to employ spent caustic liquids from petroleum refineries. The technique was particularly feasible for mills located near large petroleum or petrochemical complexes, such as in Texas and Louisiana. Considerable study would be required to accurately define the potential effects of alternative chemical makeup sources and black liquor oxidation on chemical balances in the Kraft recovery system.

C. Process Economics

1. Operating Costs

The major economic factor for black liquor oxidation systems employing molecular oxygen was the net operating cost, particularly for the cost of the oxygen. The major factors affecting the unit cost for oxygen were the sodium sulfide concentration, the amount of black liquor per unit of production, the oxygen ratio required, and the total oxygen consumption for the mill. A summary of unit production costs for weak black liquor oxidation with molecular

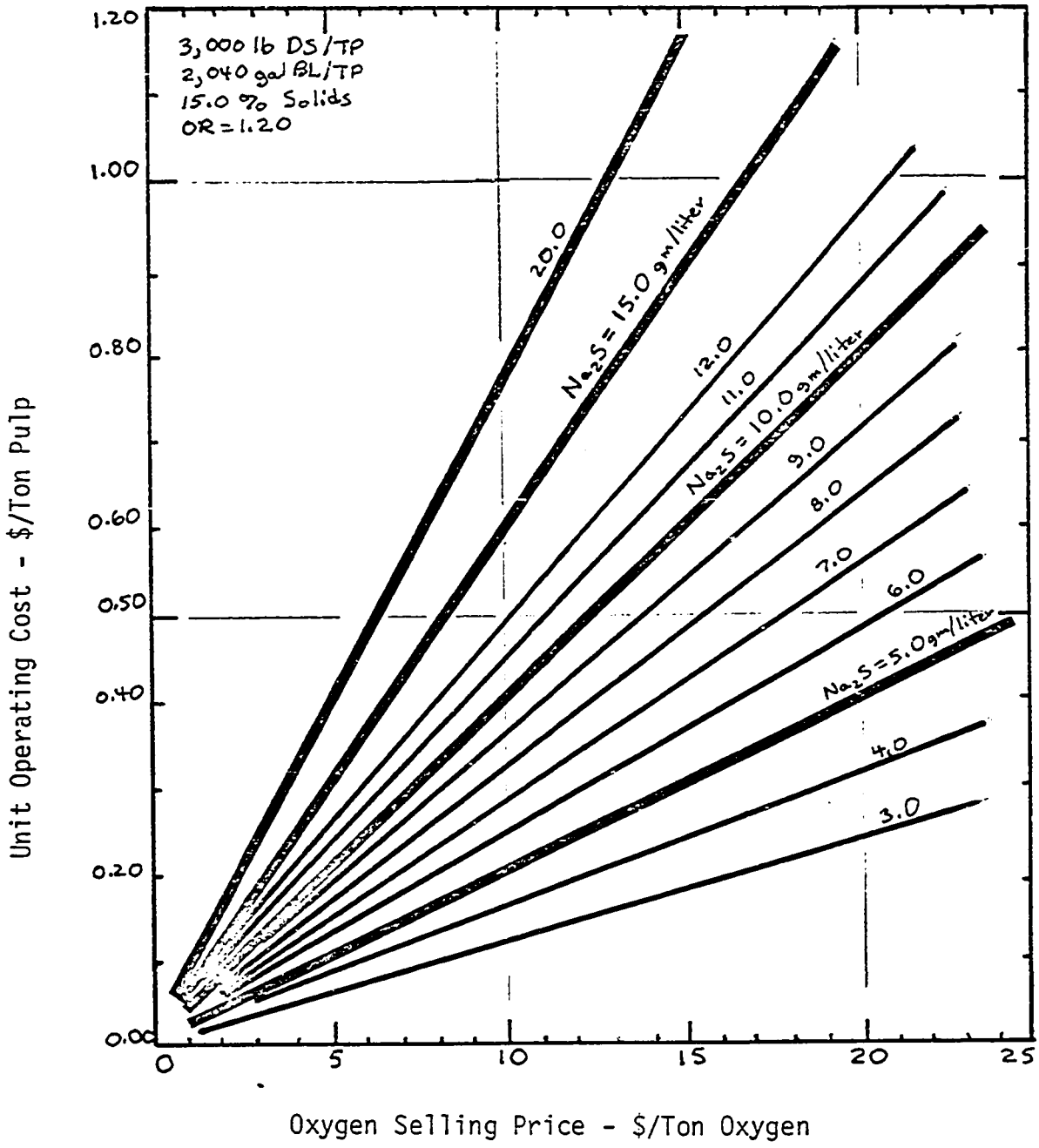


FIGURE 64. UNIT PRODUCTION COSTS FOR WEAK BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN.

oxygen as a function of sodium sulfide concentration and oxygen selling price has been presented in Figure 64.

Other factors also influenced process operating costs. Additional operating costs were for the additional electric power requirements to overcome the additional pressure drop because of two phase gas-liquid flow, and for periodic maintenance and repairs. Maintenance costs would be higher for systems employing mild carbon steel than stainless steel piping. Repayment of principal plus interest for capital investment and equipment would be an additional cost factor. Major possibilities for operating cost credits included the following: 1) increases in tall oil yield; 2) decreases in chemical makeup rate for sodium sulfate (or other sodium-sulfur addition forms) and calcium oxide; 3) reduced scaling and corrosion for multiple effect evaporator surfaces; 4) reduced steam requirements during multiple effect evaporation because of weak black liquor heating and improved heat transfer rates. The last benefit would be partially or fully offset by decreases in black liquor heating value, which would result in reduced heat release for steam generation in the recovery furnace.

A summary of estimates for the respective operating cost debits and credits has been presented in Table 50, based on projections for a 1,000 ton pulp per day Kraft pulp mill.

2. Capital Costs

A major advantage of using molecular oxygen for black liquor oxidation was that it required only a minimal capital investment, as the system could often be installed within the piping of an existing mill. The system design would be for a two stage system where the major portion of the oxidation would be performed in weak black liquor, with only polishing of the strong black liquor to counteract sodium sulfide reversion. Each of the stages would employ an inlet

TABLE 50. OPERATING COST FACTORS FOR BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN.

Expense	Cost Item	Amount lb/TP	Cost Range $/Ton Pulp
Debits	Oxygen Cost		
	Weak Black Liquor	20-120	0.10-1.50
	Strong Black Liquor	1-15	0.01-0.25
	Electric Power (hp/TPD)	0.05-0.15	0.01-0.03
	Operating and Maintenance	0.5-1.0 man hr/wk	0.01-0.02
	Total Cost	-	0.13-1.80
Credits	Tall Oil	0-20	0.00-0.50
	Calcium Oxide	2-5	0.01-0.04
	Salt Cake*	0-30	0.00-0.30
	Total Credit	-	0.01-0.84

* Estimated as actual savings.

section where oxygen was introduced to the black liquor, a section of piping in a plug flow configuration for oxygen mass transfer to be completed, and a storage tank to provide sufficient retention time for the chemical reactions to proceed to completion. A summary of the estimated capital costs for systems constructed of both stainless and carbon steels has been presented in Table 51, based on projections for a 1,000 ton pulp per day mill.

Total capital costs were substantially less for systems constructed of mild carbon steel than stainless steel, but might require greater maintenance because of corrosion in the highly alkaline liquid. A useful compromise might be piping constructed of stainless steel, with storage tanks constructed of mild steel. It might not be necessary to construct a storage tank for weak black liquor if an existing tank could be used, particularly if oxygen could be allowed to purge through the black liquor for extensive periods of eight to twelve hours. Total capital costs for black liquor oxidation systems would be expected to vary from 35 to 120 dollars per ton of pulp per day installed capacity, depending on the equipment and piping requirements, and the mill pulping capacity.

3. Comparative Investments

The capital investment required for installation of a black liquor oxidation system using molecular oxygen would be substantially lower than strong black liquor with air, replacement of the direct contact evaporator with an indirect contact evaporation system, or construction of a new recovery furnace, as listed in Table 52. Insufficient information was available to make accurate comparisons of operating costs, though the use of molecular oxygen was potentially the largest unless economics of scale existed, and process credits were possible.

TABLE 51. ESTIMATED CAPITAL COSTS FOR BLACK LIQUOR OXIDATION SYSTEMS USING MOLECULAR OXYGEN.[1]

Reactor Section	Weak Liquor System-$/TPD		Strong Liquor System-$/TPD	
	Carbon Steel	Stainless Steel	Carbon Steel	Stainless Steel
Liquid Pumping	2-3	2-3	1-2	1-2
Oxygen Injection	1-2	1-2	1-3	1-3
Piping Section[2]	2-5	12-25	3-5	5-10
Storage Tank	10-20	25-50[3]	5-10	13-25[4]
Total Cost	15-30	40-80	10-20	20-40

Notes: 1. All cost figures are in dollars per ton pulp per day capacity.
2. Liquid retention times of 30 to 60 seconds.
3. Liquid retention times of 15 to 30 minutes.
4. Liquid retention times of 30 to 60 minutes.
5. Cost data from references (183) and (184).

TABLE 52. COMPARATIVE ESTIMATED INITIAL CAPITAL INVESTMENTS FOR ALTERNATIVE RECOVERY FURNACE ODOR CONTROL METHODS.

System	Capital Investment-$/TPD
Black Liquor Oxidation-Oxygen	35-120
Strong Black Liquor Oxidation-Air	500-800
Direct Contact Evaporator Replacement	1,000-2,000
New Recovery Furnace Construction	5,000-10,000

D. Potential Markets

1. Molecular Oxygen

The total potential market for oxygen sales to the pulp and paper industry in the Southeastern United States could be as much as two million tons per year, as listed in Table 53.

TABLE 53. POTENTIAL MARKET FOR OXYGEN SALES TO PAPER INDUSTRY IN THE SOUTHEASTERN UNITED STATES

Process Application	Consumption lb O_2/TP	Potential Market Tons O_2/Year[1]
Black Liquor Oxidation	80	860,000
Recovery Furnace Addition	50	535,000
Waste Water Treatment	35	380,000
Oxygen Pulp Bleaching[2]	40	225,000
Total	-	2,000,000

Notes: 1. Based on capacity of 60,000 tons pulp per day and 360 days per year of operation.

2. Assuming 50 percent of production employs bleaching.

Based on the average unit price of ten to twenty dollars per ton of oxygen, a potential market of ten to twenty million dollars existed for oxygen sales, with approximately forty percent for black liquor oxidation. Subsequent trends such as other industrial uses for oxygen, municipal waste water treatment, coal gasification, and oxygen pulping would tend to increase the potential for oxygen usage in the paper industry. The prospective use of oxygen at Kraft pulp mills in the Southeastern United States was made promising by their relatively large capacities and the possibility of increased tall oil yields.

2. Nitrogen Applications

The use of oxygen in the paper industry would be enhanced by the ability to employ nitrogen as a byproduct. Possible uses in the pulp mills would be to assist in tall oil flotation and to replace air in pneumatic process instrumentation systems. The location of nitrogen-consuming industries adjacent to pulp mills would also enhance its economic attractiveness.

3. Refinery Spent Caustic

Spent caustic liquids from petroleum refineries were previously listed as a means for supplying the necessary sodium and sulfur makeup chemicals for the Kraft recovery system. Spent caustic liquids also provided the necessary alkalinity to maintain sulfidity balance, maximize sodium sulfide removed during black liquor oxidation, and minimize hydrogen sulfide emissions during direct contact evaporation of black liquor. The spent caustic liquids were normally waste products from petroleum refinery and other petrochemical operations which would otherwise have to be disposed of. Their use as a makeup chemical was particularly suitable for Kraft pulp mills along the Gulf of Mexico located near petroleum refineries in the States of Texas, Louisiana, Mississippi, Alabama, and Florida, where transportation costs would not be excessive. The potential market for refinery spent caustic was approximately one million tons per year as equivalent sodium sulfate, or 600,000 tons per year as equivalent sodium hydroxide.

VIII. SUMMARY AND CONCLUSIONS

A. Overall Findings

Results of the pilot scale tests showed that oxidation of weak black liquor with molecular oxygen was feasible in a plug flow reactor, but could only be used for polishing of strong black liquor to counteract sodium sulfide reversion. The rate of sodium sulfide oxidation in weak black liquor was primarily limited by oxygen mass transfer except for low concentrations, while sodium sulfide oxidation in strong black liquor was inhibited by the rate of a relatively slow chemical reaction except at high concentrations. Two stage systems would be applicable for both weak and strong black liquor oxidation with molecular oxygen. Each system would employ in series a plug flow reactor section for oxygen mass transfer into the black liquor, followed by a storage tank of sufficient retention time for the oxidation reactions to proceed to completion. Systems could be installed at minimal capital costs, and operating costs could be minimized at large Kraft pulp mills in the Southeastern United States, particularly where increased tall oil yields could be obtained.

B. Preliminary Experiments

1. Laboratory Studies

Initial laboratory studies were devoted to determination of information regarding oxygen absorption into and sodium sulfide oxidation in weak black liquor. The absorption of oxygen occurred in more than one rate regime, and materials in black liquor other than sodium sulfide and sodium mercaptide were found to exert an oxygen demand, which could occur over an extended period of

time. Batch reactor tests indicated that sodium sulfide oxidation in weak black liquor occurred in two different reaction rate sequences separated by a transition region. The initial region was a relatively rapid reaction at high concentrations, which approximated a zero order reaction primarily dependent on oxygen mass transfer rate. The final region at low concentrations approximated a slow first order reaction dependent on the chemical oxidation rate, where a liquor retention time of twenty minutes was necessary to achieve a sodium sulfide oxidation efficiency of 99 percent. Reaction rates for sodium sulfide oxidation during the initial reaction period observed from batch studies of either oxygen absorption or sodium sulfide oxidation were much lower than values for the plug flow reactor, probably because of lower turbulence levels. As a result, it was not possible to directly apply the results of laboratory findings of initial oxidation rates, as a substantial overestimation of retention time requirements would then result.

2. Mass Transfer Studies

Mass transfer studies involved observations for both the oxygen-water system and oxygen dispersion into weak black liquor. Visual and photographic studies were made of oxygen dispersion into water in cocurrent horizontal two phase gas-liquid flow in transparent plastic pipes. Results indicated it was necessary to maintain a liquid Reynolds number of 40,000 or greater immediately downstream of the point of oxygen introduction into the liquid phase. The high turbulence levels promoted minimum oxygen bubble diameters of 0.1 to 0.2 millimeters in the froth regime of two phase gas-liquid flow necessary for maximum interfacial contact areas and resultant maximum oxygen mass transfer into the liquid phase. The findings of liquid Reynolds numbers above 40,000 for effective oxygen mass transfer were verified by subsequent tests in weak black liquor, where it was observed that the inlet pipe diameter immediately

downstream of the point of oxygen introduction should be as small as possible. It was also observed that introduction of oxygen to a liquid flowing in a pipe resulted in a two-to-three fold increase in the resultant head loss in the piping immediately downstream of the point of injection. For a given liquid flow rate, the pressure drop change increased with increasing gas flow rate and decreasing pipe diameter.

C. Reaction Kinetics

The reactions undergone during black liquor oxidation with molecular oxygen in the plug flow reactor all proceeded through successive three step sequences of rapid reactions, transition periods, and slow reactions. The initial reaction period was normally characterized by rapid reactions during the initial five to ten seconds, and was followed by the transition period of decreasing reaction rate during the next 60 to 300 seconds of reaction time, depending upon the reaction. The final reaction period occurred following the transition period of 60 to 300 seconds and was characterized by slow, relatively constant reaction rates. A summary of reaction rate constants sodium sulfide, sodium mercaptide, sodium thiosulfate, and sodium sulfate for weak and strong black liquor oxidation with molecular oxygen has been presented in Table 54. A summary of half-lifes observed for first order-type oxidation of sodium sulfide, sodium mercaptide, and sodium thiosulfate for prolonged retention times has been presented in Table 55.

1. Weak Black Liquor

The oxidation of sodium sulfide in weak black liquor was primarily limited by the rate of oxygen mass transfer at concentrations greater than approximately 0.5 grams per liter, and by the rate of the chemical reaction at concentrations below 0.2 grams per liter. The initial oxidation reaction was an

TABLE 54. SUMMARY OF OVERALL REACTION RATE CONSTANTS FOR BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN.

a. Weak Black Liquor

Compound	Constant	Order	Units	Mean	Maximum	Minimum
Na_2S	k_1	0	$\frac{gm\ Na_2S}{liter\text{-}sec}$	-1.150	-1.483	-0.432
	k_2	1	$\frac{1}{min}$	-0.188	-0.462	-0.058
Na_2SCH_3	k_3	0-Var	$\frac{gm\ Na_2SCH_3}{liter\text{-}sec}$	-0.110	-0.271	-0.013
	k_4	1	$\frac{1}{min}$	-0.133	-0.512	-0.019
$Na_2S_2O_3$	k_5	0	$\frac{gm\ Na_2S_2O_3}{liter\text{-}sec}$	+1.048	+1.340	+0.427
	k_6	1	$\frac{1}{min}$	-0.017	-0.042	-0.004
Na_2SO_4	k_7	0	$\frac{gm\ Na_2SO_4}{liter\text{-}sec}$	+0.119	+0.290	+0.010
	k	2	$\frac{liter\ bl}{gm\ Na\ SO\text{-}min}$	-0.004	-0.008	-0.001

b. Strong Black Liquor

Na_2S	k_1	0	$\frac{gm\ Na_2S}{liter\text{-}sec}$	-0.688	-1.172	-0.234
	k_2	1	$\frac{1}{min}$	-0.143	-0.275	-0.040
$Na_2S_2O_3$	k_5	0	$\frac{gm\ Na_2S_2O_3}{liter\ bl\text{-}sec}$	+0.940	-	-
	k_6	2	$\frac{liter\ bl}{gm\ Na_2S_2O_3\text{-}sec}$	-0.79×10^{-5}	-	-

TABLE 55. SUMMARY OF REACTANT HALF-LIFE VALUES DURING BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN.

Liquor	Compound	$t_{1/2}$-Reactant Half-Life-Seconds		
		Mean	Maximum	Minimum
Weak	Na_2S	326	1,260	90
	$NaSCH_3$	611	2,160	81
	$Na_2S_2O_3$	3,300	11,500	153
Strong	Na_2S	381	1,035	153

extremely rapid zero order reaction which predominated during the first five to ten seconds. It was probably catalyzed by the presence of organic materials in the black liquor such as phenolic lignins, an effect which would vary with the wood species and pulping conditions employed. The rate of sodium sulfide oxidation was a relatively slow first order reaction at lower concentrations where a retention time of 15 to 45 minutes was necessary to reduce its concentration to below 0.05 grams per liter, for oxidation efficiencies of 99 percent or greater.

Sodium thiosulfate was the primary reaction product of sodium sulfide oxidation, and the presence of sodium sulfide inhibited the oxidation of sodium mercaptide and sodium thiosulfate. Most of the sodium sulfate formed appeared to be produced during the initial reaction period from the sodium thiosulfate initially present in a rapid zero order reaction, followed by a slow second order increase in concentration. Sodium thiosulfate concentration appeared to rapidly increase to a maximum and then undergo a slow first order decrease in concentration with prolonged reaction times. The decomposition of sodium thiosulfate appeared to be the slowest reaction (from half-life determinations), which would explain the fact that thiosulfate accumulation was noted during black liquor oxidation.

A possible explanation for the reversion of sodium sulfide was the oxidation of sodium thiosulfate to sulfite, followed by reaction with sodium polysulfide to regenerate sodium sulfide and thiosulfate. It was not possible to account for all of the sulfur initially present, and intermediate products such as polythionates may have been forming during the oxidation process, and may have contributed to the reversion problems.

Sodium mercaptide oxidation followed a pattern similar to that of sodium sulfide with consequtive rapid zero order and slow first order reactions,

except that the reactions tended to be slower. The presence of sodium sulfide tended to inhibit the oxidation of sodium mercaptide in weak black liquor, particularly during conditions of relative oxygen starvation.

2. Strong Black Liquor

The oxidation of sodium sulfide in strong black liquor was limited by the rate of oxygen mass transfer only at concentrations above approximately eight grams per liter. It was limited by the rate of the chemical oxidation reaction at sodium sulfide concentrations below five grams per liter, requiring storage retention times of 30 to 60 minutes in order to reduce sodium sulfide levels below 0.05 grams per liter. Sodium thiosulfate was the primary reaction product of sodium sulfide oxidation, and appeared to increase rapidly during the initial reaction period. The rapid reaction was followed by a slow second order reaction with prolonged reaction times, as compared to a decrease with weak black liquor. It was not possible to observe significant increases in sodium sulfate concentrations during any of the strong black liquor oxidation studies. Sodium polysulfide concentrations in strong black liquor were substantially higher than in weak black liquor, and the amount of sodium sulfide reversion was much greater than for weak black liquor. It was possible to account for most of the inlet sulfur by additive chemical analyses for strong black liquor, in contrast to findings for weak black liquor.

Several problems were noted during strong black liquor oxidation with molecular oxygen which made its use less desirable than for weak black liquor. Substantial reversion to sodium sulfide could occur, particularly for storage periods of more than one hour. A considerable weight loss from lignin oxidation was observed, along with an accompanying decrease in liquor heating value. Cooling of strong black liquor was also observed, making the liquid more difficult to pump. Oxygen mass transfer into strong black liquor was

made difficult by its high viscosity, and the overall sodium sulfide oxidation rate became limited by a slow first order chemical reaction at concentrations below five grams per liter. In addition, no benefits of weak black liquor oxidation would be obtained. Therefore, it was concluded that strong black liquor oxidation with molecular oxygen should only be performed as a polishing step to counteract sodium sulfide reversion.

D. Process Variables

1. Reynolds Number

It was necessary to maintain liquid Reynolds numbers above 40,000 to maximize the rate of oxygen mass transfer into black liquor. Weak black liquor oxidation with molecular oxygen was feasible in a plug flow reactor because liquid Reynolds numbers were normally well above 40,000 in full scale systems. It was normally impossible for the liquid Reynolds number of strong black liquor to be above 20,000 in a plug flow reactor because of its high viscosity, particularly for solids concentrations above 52 percent by weight. Considerable difficulties with oxygen mass transfer into strong black liquor were to be expected, and were observed. The possible use of agitated completely mixed reactors provided an alternative method for introducing oxygen to strong black liquor, but would involve greater capital and operating costs, moving parts, and the potential for considerable mechanical problems.

2. Oxygen Pressure

Increases in oxygen total and partial pressure of the incoming gas stream both produced slight increases in the sodium sulfide oxidation rate during the initial reaction period. It was desirable to maintain a maximum total oxygen inlet pressure to maximize the initial oxygen mass transfer, except that pressures much above 50 psig would require additional compressor capacity and increased operating costs. Reducing the oxygen partial pressure from 99.5 to

to 80 percent caused only a slight decrease in initial sodium sulfide reaction rates, but produced a considerable increase in foaming potential. A lower limit of 90 percent purity for oxygen produced in molecular sieve adsorption plants was necessary to prevent excessive foaming, though some increase in tall oil yield might be a side benefit of using the lower purity oxygen.

3. Oxygen Ratio

Oxygen ratio, plus liquid temperature and pH, and sodium thiosulfate concentration were found to be important variables in determining the overall efficiency of sodium sulfide oxidation, and the respective reaction rates. The oxidation of sodium sulfide in weak black liquor with oxygen was found to be a relatively selective reaction. The overall oxidation efficiencies and respective primary and secondary rate constants for sodium sulfide oxidation were found to be a maximum at oxygen ratios between 1.2 and 1.4 for both weak and strong black liquor, with reduced efficiencies at both higher and lower oxygen ratios. Inadequate oxygen supply was the reason for the decrease at lower values, while the oxidation of sodium thiosulfate to sulfite with subsequent reaction with polysulfide to regenerate sodium sulfide possibly caused the decrease at higher oxygen ratios. It was observed that adding large excess quantities of oxygen did not necessarily improve the overall sodium sulfide oxidation.

4. Liquid Temperature

Liquid temperature changes produced a complex series of effects on both weak and strong black liquor oxidation with molecular oxygen. For weak black liquor, increases in liquid temperature resulted in decreased primary initial rate because of either lower gas solubility or greater lignin oxidation, and increased secondary rate for sodium sulfide oxidation because of greater Kinetic energy. Increased liquid temperatures also resulted in greater degrees of

sodium thiosulfate oxidation and sodium sulfate formation with prolonged retention times, and would probably result in greater lignin oxidation. For strong black liquor, the initial sodium sulfide oxidation rate increased with increasing temperature because of greater oxygen mass transfer at lower liquid viscosity, while the secondary oxidation rate increased with increasing temperature in accordance with kinetic theory. Temperature ranges of 170 to 190°F for weak liquor, and 230 to 240°F for strong liquor would be optimum black liquor oxidation with molecular oxygen in plug flow reactors.

5. Liquid pH

The overall efficiency of sodium sulfide and sodium mercaptide oxidation was found to increase with increasing liquid pH. Substantial reductions in the primary initial rate of sodium sulfide oxidation were noted for liquid pH values below 11.5, while lignin precipitation became apparent for pH values below 12.0. It was also observed that the amount of sodium thiosulfate oxidation and sodium sulfate formation increased substantially at pH values above 12.6. Increased lignin oxidation would be expected with increasing liquor pH because of increased ionization of the phenolic groups, which would also increase the relative catalytic effect on the sulfide oxidation reaction. Slight decreases in liquor pH were noted during the oxidation process, but the change in pH during the oxidation process would be primarily dependent on the inlet ratio of sodium sulfide to sodium thiosulfate, and the oxygen ratio. An optimum pH range of 12.0 to 12.6 would be suitable for black liquor oxidation with molecular oxygen.

6. Sodium Thiosulfate

Increased sodium thiosulfate concentration caused a considerable decrease in the rate and overall efficiency of sodium sulfide oxidation in weak black liquor. When existing black liquor oxidation systems using air were to be

upgraded by addition of molecular oxygen, it was desirable to add the oxygen to the inlet liquor line to the existing tower to take advantage of rapid mass transfer and alleviate potential excessive oxygen consumption from thiosulfate oxidation.

7. Liquor Solids

It was important to control the solids content of strong black liquor for polishing with strong black liquor to below 52 percent, with an optimum range of 48 to 50 percent by weight. Increased liquor viscosities at greater solids concentrations would otherwise reduce the rate of oxygen mass transfer into strong black liquor.

E. Design Criteria

Plug flow reactor systems employing molecular oxygen were suitable for both weak black liquor oxidation and strong black liquor polishing. A full scale installation for a Kraft pulp mill would employ successive weak and strong black liquor oxidation systems in series as shown in Figure 65.

1. Physical System

Both the weak and strong black liquor oxidation systems would consist of two stages as follows: 1) an inlet plug flow reactor section for oxygen mass transfer into the black liquor; 2) a storage tank of sufficient retention time for the chemical oxidation reactions to be completed. The oxidations systems would each consist of four basic components as follows: 1) black liquor pumping system upstream of oxygen addition; 2) system for oxygen injection into black liquor; 3) plug flow reactor piping system for oxygen mass transfer; 4) liquor storage tank to provide sufficient retention time for the oxidation reactions to proceed to completion.

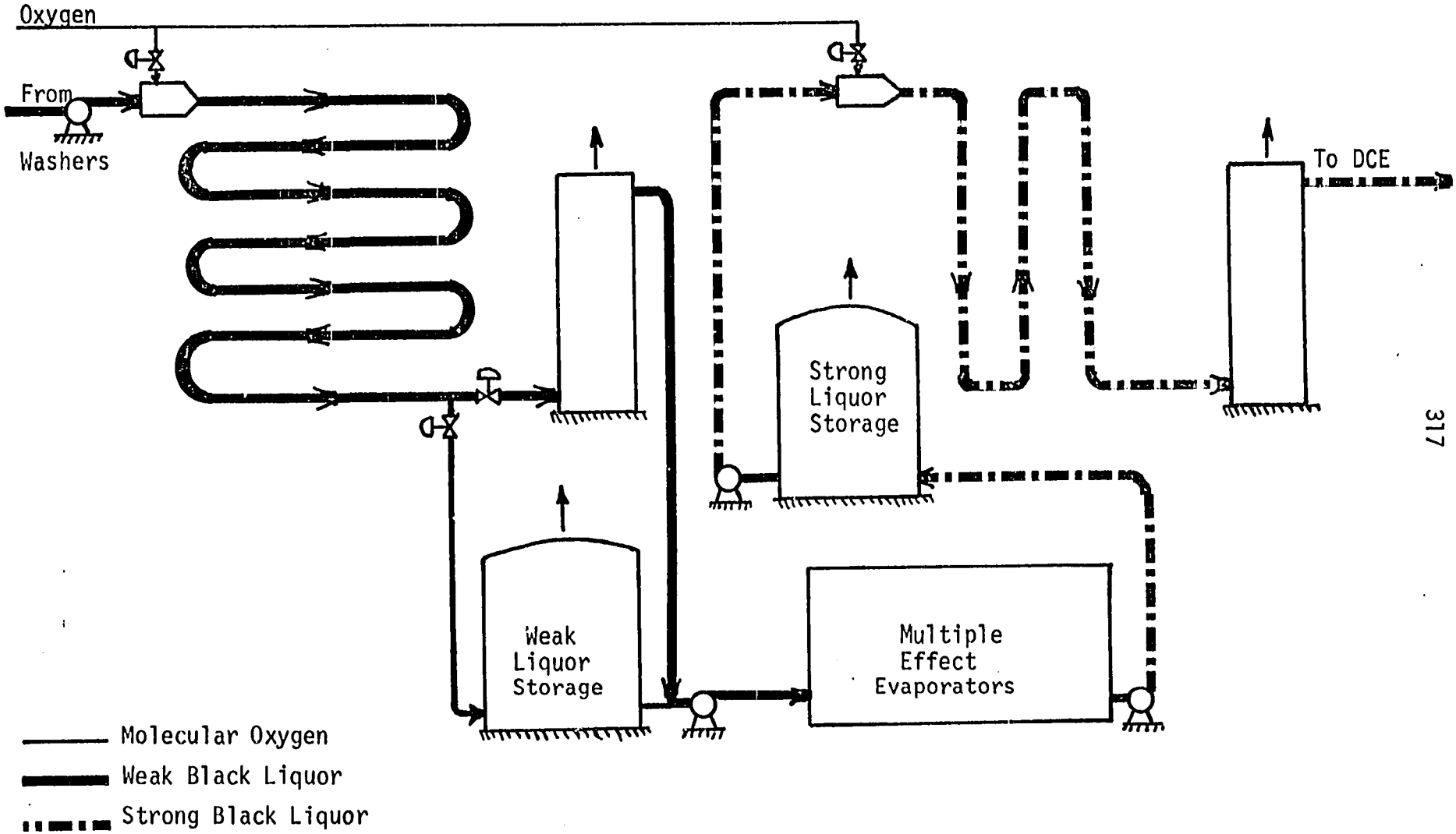


FIGURE 65. FULL SCALE TWO STAGE SYSTEM FOR WEAK AND STRONG BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN.

a. Liquor Pumping

It was necessary to provide additional liquor pumping capacity to provide for the additional pressure drop caused by the occurrence of two phase gas-liquid flow. Providing for two to three times the pressure drop for black liquor flowing alone at constant liquid flow rates in the pipe section immediately downstream of the point of oxygen injection to avoid potential problems with cavitation of metal surfaces and pump overheating.

b. Oxygen Injection

Oxygen was to be injected into the black liquor through a porous ceramic dispersion cylinder of 50 to 100 micron porosity at a loading rate of 50 to 150 feet per minute (cfm/sf) in order to produce a froth of small diameter bubbles. The porous dispersion cylinder was located axially in an expansion section of pipe of three to four times the diameter of the exit pipe. The expansion section was located immediately downstream of a bend in the inlet liquor piping to facilitate accessibility for cleaning and maintenance. It was probably advisable to employ oxygen injector systems in series for inlet sodium sulfide concentrations above 7.5 grams per liter to avoid excessive pressure drops because of high oxygen-to-liquor ratios immediately downstream of the point of introduction.

c. Piping Section

It was necessary to provide sufficient retention time in the plug flow reactor (pipeline) section for the initial and transition regimes of sodium sulfide oxidation kinetics, where oxygen mass transfer was an important factor. The piping system would normally involve consequtive sections of small and large diameter pipes in a telescoping arrangement to provide a balance between high turbulence levels, sufficient retention time, and minimum pressure drops.

It was necessary to have accurate knowledge of the primary reaction rates for sodium sulfide oxidation to provide for the proper length for the small diameter initial pipe section, where oxygen mass transfer was of critical importance. The initial pipe section would normally be of six to eight inch diameter with a retention time of five to ten seconds. The larger diameter pipe could be of larger diameter to provide a retention time of 60 to 120 seconds during the transition period in going from a zero to first order reaction, where oxygen mass transfer was still a factor in terms of reaction Kinetics.

d. Storage Tank

The primary purpose of the storage tanks was to provide a retention time sufficient for effective (99 percent or greater) oxidation of sodium sulfide to take place, but not so long as to allow either excessive sodium sulfate formation to occur or sodium sulfide reversion to take place. The necessary retention time was primarily determined by the first order rate constant for sodium sulfide oxidation at low concentrations. It was necessary to modify the inlet system for liquor introduction to the bottom of the storage tank to facilitate dispersion of any unabsorbed oxygen into small bubbles, particularly at high liquid flow rates where retention times might not be sufficient. The liquid and oxygen were allowed to percolate in an upward direction for 30 to 40 feet to facilitate maximum oxygen absorption and maximum retention time with minimum short circuiting. It was necessary to vent offgases from the storage tanks as a safety feature to prevent possible explosions during multiple effect evaporation with weak liquor, and to alleviate pumping problems for strong black liquor.

2. Process Parameters

It was desired to achieve a sodium sulfide oxidation efficiency of 99

percent or greater for both weak and strong black liquor oxidation, with sodium sulfide concentrations in both exit liquids following storage of 0.01 to 0.02 grams per liter to minimize potential odor problems. A summary of the respective design criteria for plug flow reactor systems employing molecular oxygen has been presented in Table 56. It was emphasized that specific criteria would have to be developed for each mill because of individual variations in wood species and pulping conditions between mills, and the values listed were intended as approximations only.

F. Process Economics

Results of the studies indicated that black liquor oxidation with molecular oxygen could be performed on an economical basis for oxygen costs of below between ten and twelve dollars per ton. The process became attractive if increases in tall oil yield or other process credits were observed, if the net operating cost could be reduced to below 10 to 15 cents per ton of pulp. Lignin oxidation and sodium sulfate formation could result in an additional oxygen consumption of ten to 15 percent in weak black liquor, while lignin oxidation in strong black liquor could result in an additional oxygen consumption of ten to 25 percent for strong black liquor. Plug flow reactor systems could be installed in Kraft pulp mills at capital costs ranging from 35 to 120 dollars per ton pulp per day capacity, a substantially lower investment than for alternative methods for recovery furnace odor control. Potential oxygen sales to the pulp and paper industry for black liquor oxidation and other uses could amount to between one and two million tons per year, with a market value of ten to twenty million dollars on an annual basis.

TABLE 56. DESIGN CRITERIA OF PLUG FLOW REACTOR SYSTEMS FOR BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN.

Classification	Item	Units	Weak Black Liquor Oxidation	Strong Black Liquor Polishing
Performance	Na_2S Efficiency	%	99+	99+
	Na_2S Outlet	gm/liter	0.01-0.02	0.01-0.02
Liquor	Reynolds Number	-	100,000	10,000-20,000
	Velocity	ft/sec	5-15	3-10
	Temperature	°F	170-190	230-240
	Liquid pH	-	12.0-12.6	12.0-13.0
	Solids	% by wt.	-	48-51
Oxygen	Oxygen Ratio	Actual/Theor.	1.1-1.3	1.2-2.5
	Total Pressure	psig	30-50	30-60
	Partial Pressure	% Purity	90-99.5	90-99.5
Retention Time (Liquor Basis)	Piping Section	seconds	60-120	60-180
	Storage Tank	minutes	15-45	30-60

IX. RECOMMENDATIONS

Several areas related to the present research are in need of further investigation, including additional work with black liquor oxidation, Kraft recovery process economics, alternative oxygen uses, nitrogen applications, and analytical techniques.

A. Kraft Process

The major areas of additional study for black liquor oxidation with molecular oxygen are as follows. It is necessary to evaluate from full scale tests whether a very short (15 to 45 minutes) or very long (8 to 12 hours) is required for weak black liquor storage following the plug flow reactor to minimize potential sodium sulfide reversion problems. Full scale tests are also necessary to determine the exact oxygen consumption and retention time requirements for strong black liquor polishing to counteract sulfide reversion. Specific pilot scale tests are necessary at each mill to accurately determine the respective rate constants for sodium sulfide oxidation and other reactions necessary for the subsequent design of full scale installations because of differences in wood species, pulping conditions, and operating parameters between mills. The unknown products of partial oxidation of sodium sulfide, such as polythionates and polysulfides, should be further characterized in terms of their potential impact on reversion phenomena. The effect of wood species, temperature, pH and solids concentration should be further investigated in terms of oxygen consumption requirements as a competing side reaction.

The potential impact of black liquor oxidation on the overall operation in terms of operating and maintenance costs can only be investigated for a full scale installation over a long period of time. The effect of black

liquor oxidation on actual chemical makeup requirements must be evaluated from an economic standpoint, particularly in terms of using alternative sources of sodium and sulfur, such as refinery spent caustic or alkaline bleachery effluent. The effect of weak black liquor oxidation with oxygen should be evaluated in terms of the overall heat economy of the Kraft recovery system and multiple effect evaporator operation and maintenance as a possible means for reducing overall operating costs. The effect of black liquor oxidation with oxygen on tall oil recovery should be evaluated over an extended time period to provide an accurate index of potential operating cost credits.

B. Alternative Applications

Alternative uses of oxygen and nitrogen in a pulp and paper mill or nearby applications enhances the economic attractiveness of using molecular oxygen for black liquor oxidation. The potential uses of oxygen for addition to recovery furnaces and lime kilns, for condensate liquid treatment, and with pulping all require additional investigation. Nitrogen may find potential application as an aid in increasing tall oil yields by flotation without causing deterioration in quality. Nitrogen may find application as a replacement for air in pneumatic process instruments because of the absence of humidity and oxygen necessary to enhance corrosion.

C. Analytical Techniques

Analytical techniques are another area requiring additional investigation. Measurement of sodium sulfide at low concentrations is still lacking a completely satisfactory method. Other wet chemical techniques for measurement of sodium polysulfide, sodium sulfite, sodium sulfate, and perhaps thiosulfate could be improved in terms of either their accuracy or the time required for analyses. A particular need in evaluating the efficiency of black liquor

oxidation with molecular oxygen is the development of a continuous process monitor for sodium sulfide concentrations which is accurate, reliable, reproducible, inexpensive, and suitable for extended operation by mill personnel. Possible alternatives are either measurement of sodium sulfide in the liquid phase following dilution or measurement in the gaseous phase following acidification of the sodium sulfide and evolution as hydrogen sulfide.

A liquid stream of black liquor may be diluted to the proper conditions with sodium hydroxide and water, and either oxidation-reduction potential or sulfide ion-specific electrodes used to provide an indicator of sodium sulfide concentration. Problems of severe operating conditions such as high temperatures, pH's and solids concentrations may limit use of liquid phase measurements. Gaseous phase measurement of hydrogen sulfide on total sulfur (as sulfur dioxide) may also provide potential use for sodium sulfide monitoring, following acidification of the gas and evolution by purging with nitrogen. Systems such as electrochemical potential cells, flame photometric detectors, coulometric titration cells, or ultraviolet spectrometry may then be used to measure the hydrogen sulfide content of the offgas as an indicator of sodium sulfide concentration, but lignin precipitation, bubble occlusion and detector interferences such as moisture may limit suitability of the technique.

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XI. APPENDICES

APPENDIX A

NOMENCLATURE

1. English Letter Symbols

A = Total gas-liquid interfacial contact area in square feet.

a = Gas-liquid interfacial contact area in square feet of surface per cubic foot or 1/feet.

A_p = Cross-sectional area (flow) of pipe in square feet.

b = Rate constant for oxygen absorption in grams Na_2S per liter-atmosphere.

C = Reactant concentration in moles per unit volume or mass per unit volume.

$(C_{O_2})_i$ = Dissolved oxygen concentration at gas-liquid interface in pound-moles per cubic foot.

$(C_{O_2})_l$ = Dissolved oxygen concentration in bulk liquid phase in pound-moles per cubic foot.

(C_{O_2}) = Dissolved oxygen concentration at saturation in the liquid corresponding to oxygen partial pressure $(p_{O_2})_g$ in pound-moles per cubic foot.

C_o = Initial reactant concentration at time zero in grams per liter or other units.

C_t = Reactant concentration at time t in grams per liter or other units.

C_{Na_2S} = Sodium sulfide concentration in grams per liter on other units.

$C_{Na_2S_2}$ = Sodium polysulfide concentration (as Na_2S_2) in grams per liter or other units.

$C_{Na_2S_2O_3}$ = Sodium thiosulfate concentration in grams per liter or other units.

$C_{Na_2SO_3}$ = Sodium sulfite concentration in grams per liter or other units.

$C_{Na_2SO_4}$ = Sodium sulfate concentration in grams per liter or other units.

C_s = Total sulfur concentration in grams sulfur per liter or other units.

C_{s_o} = Inlet concentration of reactant "s" in pound-moles per gallon.

D_L = Diffusivity of gas in the liquid in square centimeters per second.

1. English Letter Symbols (continued)

D_M = Molecular diffusivity of oxygen in the liquid phase in square feet per second.

D_T = Turbulent diffusivity of oxygen in the liquid phase in square feet per second.

dC_s = Change in concentration of reactant "s" across element dV in pound-moles per gallon.

dV = Differential volume element in gallons.

$\frac{dO_2}{dt}$ = Rate of oxygen mass transfer across gas-liquid boundary in pound-moles per second.

E = Fractional change in volume during reaction period.

E_a = Energy of activation in gram-calories per gram-mole.

HO = Henry's law constant for oxygen in atmospheres per mole-fraction.

k = Reaction rate constant for chemical reaction in variable units.

k_A = Specific rate parameter

k_B = Specific rate parameter.

K_G = Overall mass transfer coefficient on gas basis in pound-moles of oxygen per square foot atmosphere-second.

k_G = Individual mass transfer coefficient across gas film in pound-moles of oxygen per square foot-atmosphere-second.

K_L = Overall mass transfer coefficient on liquid basis in feet per second.

k_L = Individual mass transfer coefficient across liquid film in feet per second or other units.

k_o = Reaction rate constant at base temperature T_o in variable units.

k_T = Reaction rate constant at temperature T in variable units.

k_1 = Primary initial reaction rate constant for sodium sulfide oxidation in grams Na_2S per liter black liquor per second or other units.

k_2 = Secondary reaction rate constant for sodium sulfide oxidation in 1/seconds or other units.

1. English Letter Symbols (continued)

k_3 = Primary initial reaction rate constant for sodium mercaptide oxidation in grams $NaSCH_3$ per liter black liquor per second.

k_4 = Secondary reaction rate constant for sodium mercaptide oxidation in grams $NaSCH_3$ per liter black liquor per second.

k_5 = Primary initial reaction rate constant for sodium thiosulfate formation in grams Na S O per liter black liquor per second or other units.

k_6 = Secondary reaction rate constant for sodium thiosulfate reaction in 1/seconds.

k_7 = Primary initial reaction rate constant for sodium sulfate formation in grams Na_2SO_4 per liter black liquor per second or other units.

k_8 = Secondary reaction rate constant for sodium sulfate formation in liters of black liquor per gram Na_2SO_4 per second.

L = Liquid flow rate through reactor in gallons per minute or other units.

l = Pipe length in feet.

m = Amount of reactant in grams or pounds.

M_G = Gaseous superficial mass velocity in pounds per square foot per hour.

M_L = Liquid superficial mass velocity in pounds per square foot per hour.

N = Number of moles of reactant in gram-moles or pound-moles.

n = Order of a chemical reaction.

P = Total pressure of gas stream in atmospheres or pounds per square inch.

p_{O_2} = Partial pressure of oxygen above a liquid in atmospheres.

$(p_{O_2})_g$ = Partial pressure of oxygen in the bulk gas stream in atmospheres.

$(p_{O_2})_l$ = Partial pressure of oxygen at the gas-liquid interface in atmospheres.

R = Universal gas constant (1,982 gram-calories per gram-mole-°K).

1. English Letter Symbols (continued)

r = Reaction rate for reactant in moles per unit volume per unit time.

$-r_s$ = Rate of disappearance of reactant "s" in pound-moles per gallon per minute or other units.

r_1 = Primary initial rate of Na_2S oxidation in grams Na_2S per liter black liquor per second or other units.

r_2 = Secondary rate of Na_2S oxidation in grams Na_2S per liter black liquor per second or other units.

r_3 = Primary initial rate of $NaSCH_3$ oxidation in grams $NaSCH_3$ per liter black lqiuor per second or other units.

r_4 = Secondary rate of $NaSCH_3$ oxidation in grams $NaSCH_3$ per liter black liquor per second or other units.

r_5 = Primary initial reaction rate for sodium thiosulfate formation in grams $Na_2S_2O_3$ per liter black liquor per second or other units.

r_6 = Secondary reaction rate for sodium thiosulfate formation reaction in grams $Na_2S_2O_3$ per liter black liquor per second or other units.

r_7 = Primary initial reaction rate for sodium sulfate formation in grams Na_2SO_4 per liter black liquor per second or other units.

r_8 = Secondary reaction rate for sodium sulfate formation in grams Na_2SO_4 per liter black liquor per second or other units.

s = Surface renewal rate in 1/seconds.

S_o = Initial total sulfur concentration at time zero in grams sulfur per liter black liquor.

S_t = Total sulfur concebtration at time t/in grams sulfur per liter black liquor.

T = Temperature of black liquor in °F or °K.

t = Reaction time in seconds or other units.

t_1 = Primary initial reaction period in seconds or minutes.

t_2 = Transition period of reaction in seconds or minutes.

t_3 = Secondary reaction period in seconds or minutes.

$t_{1/2}$ = Half-life of reactant in seconds or minutes.

1. English Letter Symbols (continued)

U_L = Liquid velocity in feet per second or feet per minute.

V = Volume of system in cubic feet, gallons, or liters.

V_o = Volume of system at time zero in gallons.

V_t = Volume of system at time t in gallons.

W_o = Lignin weight at time t in grams.

X = Fraction of reactant converted to products.

x = Hypothetical film thickness in feet.

x_{O_2} = Mole fraction of oxygen in liquid phase in moles per mole.

X_s = Fractional conversion of reactant "s."

X_t = Fractional conversion of reactant at time t.

2. Greek Letter Symbols

Λ = Gas and liquid density parameter.

μ_L = Liquid viscosity in centipose.

ρ_G = Density of gas stream in pounds per cubic foot.

ρ_L = Density of liquid stream in pounds per cubic foot.

ρ_m = Molar density of liquid phase in total pound-moles per cubic foot.

σ = Surface tension of liquid in dynes per centimeter.

τ = Space time in seconds or other units.

Ψ = Liquid viscosity and density parameter.

3. Double Letter Symbols

OA = Oxygen addition rate to black liquor in pounds O_2 per minute.

OC = Oxygen consumption rate in black liquor in pounds O_2 per minute.

OE = Oxidation efficiency in percent.

3. Double Letter Symbols (continued)

OR = Oxygen ratio.

OT = Theoretical oxygen requirement in pounds per minute.

OU = Oxygen utilization efficiency in percent.

$$OR = \frac{OA}{OT} \; ; \; OU = \frac{OC}{OA} \times 100$$

APPENDIX B

SUMMARY OF LABORATORY AND MASS TRANSFER STUDY DATA

1. LABORATORY STUDIES OF OXYGEN ABSORPTION INTO BLACK LIQUOR

a. Constant Pressure Variable Volume Reactor

Unmodified, T = 24°C		Acidified, T = 26°C		Unmodified, T = 80°C	
Time minutes	Uptake ml O_2	Time minutes	Uptake ml O_2	Time minutes	Uptake ml O_2
0	0	0	0	0	0
2	3	2	7	4	20
7	12	4	11	6	23
9	21	6	15	8	30
12	28	8	19	10	34
15	38	10	22	12	38
18	48	12	24	14	42
21	57	14	26	16	46
24	67	16	29	18	51
27	77	18	31	20	56
30	86	20	33	22	62
33	95	22	34	24	67
36	102	24	36	26	73
39	110	26	37	29	80
42	117	28	39	31	85
45	124	30	41	33	89
48	131	32	42	35	93
51	137	34	44	37	96
54	145	36	45	38	98
57	150	38	47	42	101
60	155	40	48	44	103
63	160	42	50	46	104
66	163	44	51	49	105
69	164	46	53	51	107
74	165	48	54	54	110
80	166	50	56	56	113
90	171	52	57	59	116
97	176	54	59	61	119
105	181	56	58	64	122
120	194	58	61	70	128
130	202	60	62	74	132
140	203	65	65	79	135
150	207	70	68	84	136
160	212	75	71	89	137
170	215	80	75	94	138
180	220	85	76	99	140
		90	78	104	144
		95	81	109	146
		100	84	114	149
		105	86	119	152
		110	89	124	155
		115	91	129	156
		120	94	134	158
		152	109	139	161
		155	110	144	163
		160	111	149	165
		165	113	154	167
		170	115	159	169
		175	117	164	170
		180	118	169	173
		185	120	174	175
		190	121	179	177
		195	123	184	179
		200	124	189	180
				194	180
				199	181

b. Constant Volume - Variable Pressure Reactor

V_{BL} = 500 ml, T = 24°C

Time minutes	Pressure psig	Change psig
0	40.0	0.0
2	37.5	2.5
4	35.0	5.0
5	34.0	6.0
6	33.5	6.5
7	33.0	7.0
8	32.5	7.5
10	32.0	8.0
12	31.2	8.8
14	30.5	9.5
15	30.2	9.8
17	30.0	10.0
19	29.7	10.3
20	29.5	10.5
25	28.5	11.5
30	28.0	12.0
35	27.0	13.0
40	26.5	13.5
45	26.0	14.0
50	25.5	14.5
55	25.0	15.0
60	24.5	15.5
65	24.2	15.8
70	23.8	16.2
100	20.2	19.8
105	19.5	20.5
110	18.0	22.0
115	17.0	23.0
120	16.0	24.0
125	15.5	24.5
140	13.5	26.5
145	13.2	26.8
150	12.8	27.2
155	12.0	28.0
160	11.5	28.5
165	11.0	29.0
170	10.5	29.5
175	10.2	29.8
180	10.0	30.0
200	8.2	31.8
205	7.8	32.2
210	7.2	32.8
215	6.2	33.8
220	5.5	34.5
225	5.2	34.8
230	4.8	35.2
235	4.4	35.6
240	4.0	36.0

2. LABORATORY BATCH STUDIES OF SODIUM SULFIDE AND MERCAPTIDE OXIDATIONS

a. Sodium Sulfide:

Reaction Time minutes	Initial Potential mV	Titrant Volume ml	Concentration gm Na_2S / liter 6.1	Concentration Ratio C_+/C_o
0.0	-780	7.75	5.85	1.000
0.5	-775	4.50	3.40	0.581
1.0	-770	3.25	2.54	0.434
1.5	-740	2.00	1.52	0.259
2.0	-730	1.50	1.14	0.194
5.0	-380	1.35	0.26	0.045
10.0	-340	0.20	0.15	0.026
18.0	-280	0.10	0.07	0.013

b. Sodium Mercaptide:

Reaction Time minutes	Initial Potential mV	Titrant Volume ml	Concentration gm $NaSCH_3$ / liter b.l.	Concentration Ratio C_+/C_o
0.0	-170	1.80	2.45	1.000
0.5	-160	1.75	2.37	0.966
1.0	-160	1.50	2.03	0.828
1.5	-170	1.35	1.82	0.743
2.0	-170	1.25	1.69	0.690
5.0	-155	1.00	1.35	0.551
10.0	-160	0.80	1.08	0.440
18.0	-160	0.60	0.81	0.330

3. PHOTOGRAPHIC STUDIES OF OXYGEN BUBBLE DIAMETERS

a. Experimental Test Conditions

Test	D_p inches	L_w gal/min	N_{Rel}	Qo_2 cf/min	Q/A cfm/sf	Flow Regime	d_b-Bubble Diameter-mm Mean	Max	Min
1	3/4	9.55	34,200	9.31	101	(B)	1.3	2.4	0.4
2	3/4	9.65	34,500	0.50	164	(B)	1.5	2.8	0.6
3	3/4	9.74	34,800	0.50	164	(B)	0.7	1.4	0.8
4	3/4	9.74	34,800	0.78	255	(F)	0.4	0.9	0.1[3]
5	3/4	7.23	25,800	0.78	255	(A)	1.6	2.6	0.5
6	3/4	7.35	26,300	1.05	344	(S)	---	---	---
7	3/4	7.00	25,000	1.05	344	(S)	---	---	---
8	3/4	Blank	------	----	---	------	---[3]	---	---[3]
9	1/2	8.85	47,500	0.34	249	(F)	0.1[3]	0.4	0.1[3]
10	1/2	8.50	45,500	0.58	425	(F)	0.1[3]	0.3	0.1[3]
11	1/2	8.15	44,000	0.88	645	(F)	0.1[3]	0.5	0.1[3]
12	1/2	7.92	42,700	1.14	846	(F)	0.1[3]	0.4	0.1[3]
13	1/2	6.78	36,500	0.34	249	(B)	0.6	1.1	0.2
14	1/2	6.65	35,600	0.58	425	(B)	0.5	1.3	0.1
15	1/2	6.55	35,000	0.88	645	(B)	0.4	0.9	0.1
16	1/2	4.60	24,500	0.34	249	(B)(A)	0.9	2.4	0.2
17	1/2	4.50	24,000	0.58	425	(B)(A)	0.8	2.4	0.3
18	1/2	4.35	23,200	0.88	645	(B)(A)	0.7	1.4	0.1
19	1/2	4.25	22,700	1.14	836	(B)(A)	0.8	1.5	0.1
20	1/2	2.40	17,000	0.34	249	(A)	1.5	3.0	0.4
21	1/2	2.40	17,000	0.58	425	(A)	1.1	1.6	0.4
22	1/2	2.40	17,000	0.88	645	(A)(B)	0.9	1.8	0.2
23	3/8	7.93	57,200	0	0	------	---[3]	---	---[3]
24	3/8	7.22	52,500	0.34	446	(F)	0.1[3]	0.2	0.1[3]
25	3/8	6.65	49,000	0.58	760	(F)	0.1[3]	0.3	0.1[3]
26	3/8	6.32	46,000	0.88	1,153	(F)	0.1[3]	0.2	0.1[3]
27	3/8	6.10	44,000	1.14	1,495	(F)	0.1[3]	0.2	0.1[3]
28	3/8	6.32	46,000	0.34	446	(F)	0.1[3]	0.3	0.1[3]
29	3/8	5.85	42,200	0.58	760	(F)	0.1[3]	0.3	0.1[3]
30	3/8	5.75	41,800	0.88	1,153	(F)	0.1[3]	0.3	0.1[3]
31	3/8	5.30	38,500	1.14	1,495	(F)(B)	0.1[3]	0.4	0.1[3]
32	3/8	4.37	34,500	0.34	446	(B)	0.2	0.6	0.1[3]
33	3/8	4.02	29,200	0.58	760	(B)	0.3	0.7	0.1
34	3/8	3.80	27,500	0.88	1,153	(B)	0.2	0.5	0.1
35	3/8	3.57	25,500	1.14	1,495	(B)(A)	0.2	0.4	0.1
36	3/8	2.30	16,000	0.34	446	(A)	0.8	1.5	0.2
37	3/8	2.20	15,500	0.58	760	(A)	0.7	1.3	0.2
38	3/8	2.20	15,500	0.88	1,153	(A)	0.6	1.2	0.2
39	3/8	2.20	15,500	1..4	1,495	(A)(B)	0.5	1.2	0.2

Notes:
1. Liquid is water at 10°C.
2. Two phase flow regimes:
   (A) - Annular Flow; (F) - Froth Flow
   (B) - Bubble Flow; (S) - Stratified Flow
3. Bubble diameters are at lower limit of resolution of 0.1 millimeters or less.

b. Bubble Diameter Frequency Distribution

Test	Total Count	Oxygen Bubble Diameter Interval - Millimeters										
		0.0-0.2	0.3-0.4	0.5-0.6	0.7-0.8	0.9-1.0	1.1-1.2	1.3-1.4	1.5-1.6	1.7-1.8	1.9-2.0	2.0 +
1	32	0	2	1	5	4	4	3	6	5	1	1
2	34	0	0	1	1	3	2	7	3	11	2	4
3	33	2	8	10	3	3	5	2	0	0	0	0
4	33	13	8	5	6	1	0	0	0	0	0	0
5	18	0	0	3	1	1	0	3	1	1	2	5
13	30	2	6	10	8	3	1	0	0	0	0	0
14	44	7	15	8	8	2	2	2	0	0	0	0
15	34	8	14	7	4	1	0	0	0	0	0	0
16	47	3	10	5	6	3	3	6	4	5	1	1
17	38	0	9	9	7	1	3	4	2	2	0	1
18	32	3	4	10	10	2	2	1	0	0	0	0
19	30	4	3	5	6	2	3	5	2	0	0	0
20	30	0	1	4	6	1	1	3	1	3	2	8
21	30	0	1	3	5	3	5	10	3	0	0	0
22	34	1	7	6	5	2	4	4	3	2	0	0
32	38	28	9	3	0	0	0	0	0	0	0	0
33	32	11	12	8	1	0	0	0	0	0	0	0
34	34	26	7	1	0	0	0	0	0	0	0	0
35	31	22	9	0	0	0	0	0	0	0	0	0
36	31	1	3	4	8	8	3	2	2	0	0	0
37	30	1	4	9	6	4	4	2	0	0	0	0
38	37	4	10	7	8	6	2	0	0	0	0	0
39	21	3	11	4	1	1	1	0	0	0	0	0

Note: Only estimates were made for the tests in the froth regime of two phase gas-liquid flow.

4. STUDIES OF FLUID RESISTANCE DURING TWO PHASE FLOW

a. 1/2 Inch Pipe

L_{BL}		Q=0	Q_o=0.6 cfm Q/A=284 fpm		Q_o=1.5 cfm Q/A=710 fpm		Q_o=2.4 cfm Q/A=1140 fpm		Q_o=3.2 cfm Q/A=1510 fpm	
gal/min	$\frac{gal}{sf\text{-}min}$	dP in Hg	dP in Hg	$\frac{dP_{tp}}{dP_{bl}}$	dP in Hg	$\frac{dP_{tp}}{dP_{bl}}$	dP in Hg	$\frac{dP_{tp}}{dP_{bl}}$	dP in Hg	$\frac{dP_{tp}}{dP_{bl}}$
1.0	473	2.0	6.0	3.00	8.5	4.25	4.0	2.00	7.0	3.50
2.1	994	2.5	10.0	4.00	14.0	5.58	10.5	4.20	14.5	5.58
3.2	1515	3.0	15.0	5.00	18.5	6.16	18.8	6.00	23.0	7.65
4.2	1990	5.5	20.0	3.64	21.5	3.91	28.0	5.09	30.5	5.55
5.3	2510	8.5	24.0	2.83	30.5	3.60	36.0	4.24	36.5	4.30
6.3	2920	13.0	30.0	2.31	36.0	2.77	----	----	----	----
7.3	3460	18.5	35.5	1.92	----	----	----	----	----	----
7.7	3650	26.0	----	----	----	----	----	----	----	----
8.8	4160	30.5	----	----	----	----	----	----	----	----

b. One Inch Pipe

L_{BL}		Q/A=0 Q=0	Q_o=0.6 cfm Q/A=100 fpm		Q_o=1.5 cfm Q/A=250 fpm		Q_o=2.4 cfm Q/A=400 fpm		Q_o=3.2 cfm Q/A=533 fpm	
gal/min	$\frac{gal}{sf\text{-}min}$	dP in Hg	dP in Hg	$\frac{dP_{tp}}{dP_{bl}}$	dP in Hg	$\frac{dP_{tp}}{dP_{bl}}$	dP in Hg	$\frac{dP_{tp}}{dP_{bl}}$	dP in Hg	$\frac{dP_{tp}}{dP_{bl}}$
1.0	167	0.1	4.0	40.00	4.0	40.00	7.0	70.00	8.0	80.00
2.1	350	0.2	5.0	25.00	6.0	30.00	10.0	50.00	11.5	57.50
3.2	533	0.5	6.5	13.00	10.0	20.00	12.5	25.00	15.5	31.00
4.2	700	1.5	8.5	5.67	12.5	8.33	15.5	10.30	17.5	11.67
5.3	883	2.0	10.0	5.00	14.5	7.25	17.5	8.75	20.5	10.25
6.3	1050	5.0	12.5	2.50	16.5	3.30	20.5	4.10	23.5	4.70
7.3	1220	7.0	14.5	2.07	19.5	2.78	22.5	3.21	27.5	3.92
8.3	1380	9.0	17.0	1.89	22.0	2.43	----	-----	----	-----
9.3	1550	12.5	18.5	1.48	----	-----	----	-----	----	-----

c. Effect of Pipe Diameter

1/2 Inch Pipe		3/4 Inch Pipe		1 Inch Pipe	
L_{BL} gal/min	dP in Hg	L_{BL} gal/min	dP in Hg	L_{BL} gal/min	dP in Hg
1.0	8.5	1.0	4.0	1.0	3.0
2.1	14.0	2.1	7.3	2.1	6.0
3.2	18.5	3.2	8.5	3.2	10.0
4.2	21.5	4.2	12.0	4.2	12.5
5.3	30.5	5.3	15.5	5.3	14.5
6.3	36.0	6.3	18.5	6.3	16.5
6.5	37.5	6.9	20.5	7.3	19.5
				8.3	22.0

APPENDIX C.

SUMMARY OF PILOT SCALE TEST DATA

KEY TO PURPOSE OF TEST RUNS

Weak Black Liquor

Symbol	Test Program	Run
PR	Preliminary Test Runs	1, 2, 3, 4, 5
ORW	Oxygen Ratio Tests	6, 7, 8, 9, 10, 11, 12, 13, 25, 30
TP	Oxygen Total Pressure	21, 22, 23, 24, 25
PP	Oxygen Partial Pressure	25, 33, 34
LT	Liquor Temperature Runs	25, 26, 27, 28, 29
PH	Liquid pH Adjustment	31, 32, 40, 42, 43, 44
RN	Liquid Reynolds Number	35, 36, 37, 38, 39
TS	Sodium Thiosulfate Addition	50, 51, 52

Strong Black Liquor

Symbol	Test Program	Run
ORS	Oxygen Ratio Tests	14, 15, 16, 17, 18, 19, 20
LP	Strong Liquor Polishing	46, 47
CC	Contactor Configuration	48, 49

1. SUMMARY OF PILOT SCALE TEST OPERATING CONDITIONS

	Black Liquor Flow						Oxygen Flow				
Run	Flow gal/min	Solids % by wt.	P_o psig	T_o °F	T_s °F	-	Q cf/min	P_o psig	T_o °F	Q/A ft/min	Test
1	4.70	17.0	-	180	-	33,000	2.72	22	76	1,290	PR
2	4.80	17.1	-	184	-	33,500	1.73	26	78	820	PR
3	5.85	17.5	-	184	-	40,000	1.77	30	78	840	PR
4	6.15	17.5	-	180	-	43,000	1.24	31	78	590	PR
5	1.50	17.3	-	185	186	23,000	1.50	30	63	1,130	PR
6	3.10	16.9	20.0	184	190	28,000	1.50	30	65	1,130	OR
7	3.30	16.9	21.0	178	181	28,500	1.20	30	63	900	OR
8	4.05	16.9	21.0	180	182	35,000	0.91	30	67	684	ORW
9	4.30	17.7	17.0	180	177	37,000	0.63	30	72	473	ORW
10	2.30	16.4	21.0	183	185	20,000	0.63	30	72	473	ORW
11	4.47	17.2	22.5	180	184	39,000	0.87	30	70	653	ORW
12	3.82	17.2	23.5	181	186	33,000	1.02	30	65	767	ORW
13	3.50	16.9	23.0	180	187	30,500	1.14	30	60	857	ORW
14	1.33	51.6	20.0	228	208	1,350	1.68	30	74	1,260	ORS
15	1.52	53.3	20.5	234	218	1,550	1.15	30	65	864	ORS
16	1.18	50.3	16.5	215	200	1,220	1.68	30	70	1,260	ORS
17	1.23	51.1	17.0	220	205	1,260	1.61	30	74	1,210	ORS
18	1.60	51.1	16.5	220	208	1,740	0.87	30	70	653	ORS
19	1.49	51.0	21.0	230	214	1,530	1.68	30	56	1,260	ORS
20	1.56	51.2	22.0	234	216	1,570	1.61	30	60	1,210	ORS
21	3.51	17.0	22.0	180	187	30,500	1.19	25	76	895	TP
22	3.72	16.8	22.0	184	189	32,000	1.02	60	74	767	TP
23	3.60	17.2	21.5	184	188	34,000	1.02	50	78	767	TP
24	3.72	17.2	21.5	184	188	33,500	1.02	40	80	767	TP
25	3.15	16.9	20.5	184	188	28,000	1.17	30	62	880	LT
26	3.00	17.5	22.5	203	203	31,000	1.17	30	63	880	LT
27	3.80	16.4	21.5	170	179	32,500	1.18	30	80	887	LT
28	3.72	16.5	20.5	154	160	32,000	1.17	30	57	880	LT
29	3.70	16.5	21.0	139	145	32,000	1.17	30	58	880	LT
30	3.80	17.9	19.5	184	188	33,000	0.87	30	66	653	ORW
31	3.40	17.6	23.5	185	189	29,500	1.17	30	78	880	pH
32	3.40	17.6	27.0	185	189	29,500	1.17	30	65	880	pH
33	3.51	18.1	26.5	184	190	30,000	1.18	30	67	887	PP
34	3.49	18.1	28.5	184	189	30,000	1.18	30	68	887	PP
35	1.32	18.5	6.0	182	169	11,500	0.35	30	66	263	RN
36	2.25	18.5	11.0	185	180	19,500	0.57	30	67	438	RN
37	2.84	18.4	17.5	184	188	25,000	0.87	30	67	654	RN
38	4.40	18.4	30.0	184	192	38,000	1.47	30	67	1,110	RN
39	3.50	18.4	22.5	184	190	30,000	1.18	30	67	887	RN
40	3.70	17.3	23.0	174	182	32,000	1.17	30	72	880	pH
41	3.70	17.3	24.5	174	182	32,000	1.17	30	67	880	pH
42	3.72	17.3	24.0	174	180	32,000	1.17	30	69	880	pH
43	3.72	17.4	24.0	174	180	32,000	1.17	30	65	880	pH
44	3.72	17.3	22.0	173	180	32,000	1.17	30	72	880	pH
45	1.15	53.6	14.5	221	208	1,170	1.17	30	77	880	LP
46	2.16	53.6	8.5	190	182	2,160	0.18	30	82	887	LP
47	2.16	53.6	13.0	184	176	2,160	0.58	30	62	447	LP
48	1.25	52.5	13.0	230	208	1,000	1.17	30	75	555	CC
49	1.25	54.8	13.5	227	208	1,000	1.17	30	63	555	CC
50	2.63	17.4	15.0	184	186	24,000	1.15	30	76	867	TS
51	2.63	17.4	17.0	180	184	24,000	1.17	30	78	880	TS
52	2.63	16.6	16.0	184	187	24,000	1.17	30	68	880	TS

2. SUMMARY OF SODIUM SULFIDE AND SODIUM MERCAPTIDE CONCENTRATIONS

a. Weak Black Liquor

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
1	0	0.0	3.350	1.000	1.400	1.000	PR
	1	3.2	0.386	0.113	1.260	0.896	
	2	16.2	0.000	0.000	1.126	0.798	
	3	54.0	0.000	0.000	1.700	0.500	
	4	91.8	0.000	0.000	0.420	0.300	
2	0	0.0	3.200	1.000	1.950	1.000	PR
	1	3.0	0.390	0.122	1.680	0.862	
	2	10.0	0.230	0.071	-----	-----	
	3	16.0	0.160	0.050	1.400	0.718	
	4	54.0	0.080	0.025	1.120	0.574	
	5	91.0	0.040	0.012	0.420	0.216	
3	0	0.0	3.280	1.000	1.120	1.000	PR
	1	2.6	0.310	0.063	0.560	0.500	
	2	6.7	0.160	0.032	0.230	0.250	
	3	13.1	0.080	0.019	0.560	0.500	
	4	49.4	0.040	0.010	0.210	0.188	
4	0	0.0	2.810	1.000	0.700	1.000	PR
	1	2.4	0.896	0.318	0.630	0.900	
	2	6.2	0.585	0.208	0.430	0.700	
	3	12.2	0.429	0.153	0.490	0.700	
	4	40.8	0.156	0.055	0.420	0.600	
	5	69.4	0.156	0.055	0.420	0.600	
5	0	0.0	6.000	1.000	1.353	1.000	PR
	1	3.5	2.000	0.333	0.810	0.597	
	2	6.7	0.380	0.063	0.540	0.398	
	3	9.9	0.260	0.043	0.410	0.303	
	4	18.9	0.230	0.038	0.370	0.273	
	5	33.4	0.210	0.035	0.350	0.258	
	6	68.6	0.190	0.032	0.310	0.229	
	7	103.8	0.150	0.025	0.270	0.199	
	8	174.2	0.110	0.018	0.200	0.148	

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
6	0	0.0	6.000	1.000	1.353	1.000	ORW
	1	2.9	2.000	0.333	0.810	0.600	
	2	7.2	0.380	0.063	0.540	0.400	
	3	11.5	0.260	0.043	0.410	0.304	
	4	19.0	0.230	0.038	0.370	0.275	
	5	31.0	0.210	0.035	0.350	0.260	
	6	59.5	0.190	0.032	0.310	0.230	
	7	88.0	0.150	0.025	0.270	0.200	
	8	145.0	0.110	0.018	0.200	0.148	
7	0	0.0	4.336	1.000	1.560	1.000	ORW
	1	3.3	0.230	0.053	0.810	0.518	
	2	7.8	0.150	0.035	0.340	0.218	
	3	12.4	0.140	0.032	0.200	0.128	
	4	20.0	0.130	0.030	0.310	0.199	
	5	32.0	0.110	0.025	0.270	0.173	
	6	47.5	0.100	0.023	0.230	0.148	
	7	78.0	0.030	0.018	0.200	0.128	
	8	137.0	0.070	0.016	0.180	0.113	
8	0	0.0	4.830	1.000	1.420	1.000	ORW
	1	2.6	1.670	0.345	1.220	0.858	
	2	6.3	0.230	0.046	0.540	0.380	
	3	10.3	0.170	0.035	0.360	0.253	
	4	16.4	0.160	0.033	0.310	0.218	
	5	26.0	0.150	0.031	0.300	0.211	
	6	38.5	0.130	0.027	0.280	0.197	
	7	63.5	0.110	0.023	0.270	0.190	
	8	112.0	0.080	0.016	0.260	0.183	
9	0	0.0	5.800	1.000	1.560	1.000	ORW
	1	2.5	3.480	0.600	1.490	0.954	
	2	6.0	3.150	0.545	1.350	0.864	
	3	9.5	3.030	0.524	1.490	0.954	
	4	15.4	2.950	0.510	1.420	0.908	
	5	24.6	2.650	0.458	1.350	0.863	
	6	36.5	2.570	0.444	1.220	0.780	
	7	60.0	2.430	0.420	1.220	0.780	
	8	106.0	2.270	0.392	1.220	0.780	

Run	Point	Time Sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
10	0	0.0	7.080	1.000	1.150	1.000	ORW
	1	4.7	2.580	0.365	1.090	0.950	
	2	11.2	0.950	0.134	1.020	0.887	
	3	17.3	0.190	0.027	0.410	0.355	
	4	28.8	0.150	0.021	0.400	0.350	
	5	46.0	0.150	0.021	0.340	0.295	
	6	68.2	0.130	0.018	0.470	0.410	
	7	122.0	0.110	0.016	0.340	0.295	
	8	198.0	0.080	0.011	0.270	0.235	
11	0	0.0	6.140	1.000	1.690	1.000	ORW
	1	2.4	3.220	0.522	1.420	0.938	
	2	5.8	2.980	0.468	1.350	0.797	
	3	9.2	1.900	0.309	1.760	1.040	
	4	14.7	1.140	0.186	1.350	0.797	
	5	23.7	1.330	0.216	1.220	0.720	
	6	35.0	0.570	0.093	1.690	1.000	
	7	57.5	0.270	0.044	0.540	0.318	
	8	100.0	0.230	0.037	0.470	0.278	
12	0	0.0	6.270	1.000	1.353	1.000	ORW
	1	2.8	2.830	0.451	1.220	0.903	
	2	6.8	1.530	0.246	1.080	0.800	
	3	10.8	0.310	0.049	0.640	0.470	
	4	17.4	0.270	0.043	0.610	0.450	
	5	27.5	0.150	0.024	0.470	0.350	
	6	41.0	0.110	0.018	0.430	0.320	
	7	67.5	0.100	0.016	0.370	0.270	
	8	118.0	0.080	0.012	0.200	0.150	
13	0	0.0	6.050	1.000	1.220	1.000	ORW
	1	3.1	1.440	0.238	1.083	0.887	
	2	7.4	0.340	0.056	0.744	0.610	
	3	11.7	0.151	0.025	0.678	0.554	
	4	18.8	0.114	0.019	0.338	0.278	
	5	30.5	-----	-----	-----	-----	
	6	45.0	0.091	0.015	0.312	0.255	
	7	73.5	0.076	0.012	0.271	0.222	
	8	130.0	0.053	0.009	0.244	0.200	

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
21	0	0.0	6.150	1.000	1.220	1.000	TP
	1	3.0	1.520	0.246	1.082	0.888	
	2	7.3	0.266	0.043	0.743	0.610	
	3	11.5	0.132	0.021	0.305	0.250	
	4	18.8	0.114	0.018	0.271	0.222	
	5	30.0	0.098	0.016	0.264	0.216	
	6	44.3	0.091	0.015	0.244	0.200	
	7	72.0	0.083	0.014	0.257	0.211	
	8	128.0	0.076	0.012	0.237	0.195	
	9	264.0	0.060	0.010	0.176	0.144	
	10	354.0	0.056	0.009	0.169	0.138	
22	0	0.0	5.500	1.000	1.220	1.000	TP
	1	2.9	1.740	0.316	1.080	0.888	
	2	6.9	0.189	0.034	0.743	0.610	
	3	11.0	0.151	0.028	0.270	0.222	
	4	17.7	0.136	0.025	0.263	0.216	
	5	28.5	0.132	0.024	0.250	0.205	
	6	42.0	6.128	0.023	0.243	0.199	
	7	68.0	0.114	0.021	0.236	0.194	
	8	120.0	0.095	0.017	0.236	0.194	
	9	248.0	0.076	0.014	0.203	0.166	
	10	344.0	0.057	0.010	0.169	0.138	
	11	985.0	0.095	0.017	0.197	0.161	
23	0	0.0	6.880	1.000	1.220	1.000	TP
	1	2.7	3.320	0.520	1.290	1.057	
	2	6.5	1.890	0.276	1.020	0.837	
	3	10.3	1.320	0.193	1.150	0.943	
	4	16.7	0.833	0.122	0.950	0.780	
	5	26.5	0.577	0.083	0.680	0.558	
24	0	0.0	6.880	1.000	1.220	1.000	
	1	2.8	3.100	0.452	1.290	1.057	

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
25	0	0.0	6.250	1.000	1.353	1.000	LT
	1	3.4	2.120	0.339	1.290	0.950	
	2	8.1	0.228	0.036	0.813	0.600	
	3	13.0	0.152	0.024	0.372	0.275	
	4	21.2	0.133	0.021	0.339	0.250	
	5	33.6	0.121	0.019	0.325	0.240	
	6	50.0	0.114	0.018	0.305	0.225	
	7	62.0	0.095	0.015	0.271	0.200	
	8	143.0	0.076	0.012	0.237	0.175	
	9	295.0	0.057	0.009	0.203	0.150	
	10	410.0	0.038	0.006	0.135	0.100	
	11	1180.0	0.076	0.012	0.170	0.125	
26	0	0.0	6.050	1.000	1.353	1.000	LT
	1	3.6	2.345	0.388	1.220	0.900	
	2	8.6	0.246	0.041	1.050	0.775	
	3	13.6	0.189	0.031	0.338	0.250	
	4	22.0	0.170	0.028	0.305	0.225	
	5	35.0	0.151	0.025	0.271	0.200	
	6	52.0	0.133	0.022	0.271	0.200	
	7	86.0	0.113	0.019	0.271	0.200	
	8	151.0	0.095	0.016	0.271	0.200	
	9	310.0	0.076	0.013	0.237	0.175	
	10	432.0	0.057	0.009	0.237	0.175	
	11	1230.0	0.095	0.016	0.237	0.175	
27	0	0.0	6.930	1.000	1.353	1.000	LT
	1	2.8	2.945	0.425	1.353	1.000	
	2	6.8	1.817	0.262	1.353	1.000	
	3	10.8	0.454	0.064	1.220	0.900	
	4	17.7	0.303	0.044	0.982	0.725	
	5	28.0	0.246	0.035	0.914	0.675	
	6	41.5	0.227	0.033	0.372	0.275	
	7	68.0	0.170	0.025	0.372	0.275	
	8	121.0	0.151	0.022	0.372	0.275	
	9	247.0	0.133	0.019	0.372	0.275	
	10	343.3	0.114	0.016	0.339	0.250	
	11	985.0	0.170	0.025	0.407	0.300	

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
28	0	0.0	6.130	1.000	1.353	1.000	LT
	1	2.9	1.882	0.307	1.220	0.900	
	2	7.0	0.378	0.062	1.080	0.800	
	3	11.0	0.189	0.032	0.404	0.300	
	4	18.0	0.170	0.028	0.371	0.275	
	5	28.6	0.151	0.025	0.337	0.250	
	6	42.5	0.132	0.022	0.303	0.225	
	7	69.5	0.113	0.018	0.270	0.200	
	8	123.0	0.095	0.015	0.236	0.175	
	9	252.0	0.076	0.012	0.202	0.150	
	10	350.0	0.057	0.009	0.236	0.175	
	11	1000.0	0.076	0.012	0.202	0.150	
29	0	0.0	6.120	1.000	1.353	1.000	LT
	1	2.9	2.160	0.351	1.285	0.950	
	2	7.0	1.020	0.166	1.015	0.750	
	3	11.0	0.227	0.047	0.406	0.300	
	4	18.0	0.208	0.034	0.305	0.225	
	5	28.5	0.170	0.028	0.271	0.200	
	6	42.5	0.152	0.025	0.237	0.175	
	7	69.5	0.132	0.021	0.237	0.185	
	8	123.0	0.114	0.019	0.237	0.175	
	9	252.0	0.094	0.015	0.237	0.175	
	10	350.0	0.076	0.012	0.203	0.150	
	11	1000.0	0.094	0.015	0.237	0.175	
30	0	0.0	6.280	1.000	1.220	1.000	ORW
	1	2.8	2.880	0.458	1.220	1.000	
	2	6.8	1.667	0.266	1.082	0.890	
	3	10.8	1.137	0.181	1.082	0.890	
	4	17.5	0.831	0.132	1.082	0.890	
	5	27.8	0.723	0.115	1.015	0.834	
	6	41.5	0.378	0.060	1.082	0.890	
	7	68.0	0.303	0.048	0.812	0.666	
	8	119.0	0.265	0.042	1.150	0.944	
	9	245.0	0.227	0.036	1.015	0.834	
	10	342.0	0.265	0.042	0.744	0.610	
	11	975.0	0.378	0.060	0.744	0.610	

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
31	0	0.0	4.840	1.000	0.677	1.000	pH
	1	3.2	0.908	0.188	0.339	0.500	
	2	7.6	0.133	0.027	0.068	0.100	
	3	12.0	0.114	0.023	0.068	0.100	
	4	19.5	0.095	0.020	0.034	0.050	
	5	31.0	0.057	0.012	0.034	0.050	
	6	46.2	0.076	0.016	0.068	0.100	
	7	72.7	0.076	0.016	0.068	0.100	
	8	133.0	0.057	0.012	0.102	0.150	
	9	278.0	0.057	0.012	0.237	0.350	
	10	382.0	0.038	0.008	0.135	0.200	
	11	1090.0	0.133	0.027	0.102	0.150	
32	0	0.0	4.920	1.000	0.540	1.000	pH
	1	3.2	1.820	0.370	0.270	0.500	
	2	7.6	0.378	0.077	0.135	0.250	
	3	12.0	0.132	0.027	0.034	0.062	
	4	19.5	0.114	0.023	0.068	0.125	
	5	31.0	0.095	0.019	0.068	0.125	
	6	46.2	0.095	0.019	0.068	0.125	
	7	72.7	0.086	0.017	0.081	0.150	
	8	133.0	0.076	0.015	0.102	0.187	
	9	278.0	0.057	0.012	0.102	0.187	
	10	382.0	0.076	0.015	0.135	0.250	
	11	1090.0	0.876	0.015	0.170	0.312	
33	0	0.0	5.000	1.000	1.490	1.000	PP
	1	3.1	1.175	0.235	1.220	0.818	
	2	7.4	0.227	0.045	0.474	0.318	
	3	11.7	0.189	0.038	0.474	0.318	
	4	18.9	0.114	0.023	0.304	0.205	
	5	30.2	0.095	0.019	0.304	0.205	
	8	129.0	0.076	0.015	0.237	0.159	
	10	370.0	0.057	0.011	0.203	0.136	
34	0	0.0	5.000	1.000	1.490	1.000	PP
	1	3.1	1.400	0.280	1.350	0.904	
	2	7.4	0.834	0.167	1.290	0.865	
	3	11.7	0.208	0.042	0.508	0.340	
	4	18.9	0.132	0.027	0.372	0.250	
	5	30.2	0.095	0.019	0.305	0.204	
	8	129.0	0.076	0.015	0.237	0.159	
	10	370.0	0.057	0.011	0.203	0.136	

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
35	0	0.0	5.380	1.000	1.353	1.000	RN
	1	8.2	4.540	0.844	1.353	1.000	
	2	19.7	2.120	0.384	1.200	0.900	
	3	32.0	1.475	0.362	0.610	0.450	
	4	50.0	1.325	0.246	0.475	0.350	
	8	345.0	1.440	0.268	1.150	0.850	
36	0	0.0	5.380	1.000	1.353	1.000	RN
	1	4.8	3.030	0.564	1.220	0.900	
	2	11.5	-----	-----	-----	-----	
	3	18.3	2.570	0.477	1.220	0.900	
	4	29.3	2.230	0.415	0.950	0.700	
	8	202.0	0.378	0.071	0.542	0.400	
37	0	0.0	5.380	1.000	1.353	1.000	RN
	1	3.8	2.660	0.494	1.083	0.800	
	2	9.1	2.280	0.424	1.220	0.900	
	3	14.3	2.200	0.409	1.083	0.800	
	4	23.2	1.062	0.198	0.677	0.500	
	8	160.0	0.246	0.046	0.508	0.375	
38	0	0.0	5,380	1.000	1.353	1.000	RN
	1	2.4	1.780	0.331	0.880	0.650	
	2	5.8	0.265	0.049	0.880	0.650	
	3	9.3	0.171	0.032	0.440	0.325	
	4	13.5	0.151	0.028	0.407	0.300	
	8	103.0	0.114	0.021	0.068	0.050	
39	0	0.0	5.380	1.000	1.353	1.000	RN
	1	3.1	2.160	0.402	0.948	0.700	
40	0	0.0	5.040	1.000	1.150	1.000	pH
	1	3.0	1.892	0.374	1.082	0.940	
	4	17.8	0.132	0.026	0.304	0.264	
	8	122.0	0.064	0.013	0.149	0.129	

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
42	0	0.0	4.920	1.000	0.541	1.000	pH
	1	3.0	2.380	0.483	0.541	1.000	
	4	17.8	0.151	0.306	0.473	0.870	
	8	122.0	0.076	0.015	0.203	0.374	
43	0	0.0	4.280	1.000	0.406	1.000	pH
	1	3.0	1.665	0.388	0.406	1.000	
	4	17.8	0.170	0.040	0.812	2.000	
	8	122.0	0.095	0.022	0.068	0.167	
44	0	0.0	5.800	1.000	1.282	1.000	pH
	1	3.0	1.630	0.280	1.150	0.900	
	4	17.8	0.113	0.019	0.135	0.105	
	8	122.0	0.057	0.010	0.068	0.053	
50	0	0.0	5.640	1.000	1.290	1.000	TS
	1	4.0	1.060	0.188	1.220	0.947	
	2	9.7	0.340	0.060	1.082	0.840	
	3	15.5	0.170	0.030	0.507	0.394	
	4	25.0	0.152	0.027	0.394	0.264	
	8	172.0	0.095	0.017	0.203	0.158	
51	0	0.0	5.640	1.000	1.290	1.000	TS
	1	4.0	1.365	0.242	1.220	0.947	
	2	9.7	0.378	0.067	1.220	0.947	
	3	15.5	0.265	0.047	1.150	0.890	
	4	25.0	0.227	0.040	0.947	0.733	
	8	172.0	0.208	0.037	0.847	0.656	
52	0	0.0	5.640	1.000	1.290	1.000	TS
	1	4.0	0.833	0.147	0.676	0.524	
	4	25.0	0.152	0.027	0.271	0.210	
	8	172.0	0.057	0.010	0.169	0.131	

b. Strong Black Liquor

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
14	0	0.0	17.800	1.000	4.070	1.000	ORS
	1	8.1	13.430	0.756	3.730	0.916	
	2	19.4	11.350	0.639	3.390	0.833	
	3	31.0	10.020	0.564	3.390	0.833	
	4	49.5	9.640	0.543	2.710	0.667	
	5	79.5	8.700	0.490	3.730	0.916	
	6	117.0	7.940	0.447	-----	-----	
	7	192.0	6.420	0.362	-----	-----	
	8	342.0	5.670	0.320	-----	-----	
15	0	0.0	17.500	1.000	3.560	1.000	ORS
	1	7.2	14.770	0.843	3.390	0.952	
	2	17.2	14.200	0.810	3.390	0.952	
	3	27.2	12.020	0.686	3.320	0.932	
	4	43.8	11.830	0.676	3.390	0.952	
	5	70.0	11.630	0.665	3.320	0.932	
	6	103.0	10.890	0.621	3.050	0.856	
	7	170.0	10.220	0.584	2.270	0.637	
	8	300.0	9.000	0.514	2.040	0.573	
	9	623.0	4.730	0.270	2.040	0.573	
	10	863.0	2.840	0.162	2.040	0.573	
	11	2450.0	1.420	0.081	1.520	0.428	
16	0	0.0	17.600	1.000	3.306	1.000	ORS
	3	34.8	9.450	0.536	3.306	1.000	
	8	385.0	5.670	0.322	3.306	1.000	
	9	835.0	0.755	0.043	0.507	0.153	
	10	1120.0	0.377	0.021	Tr	Tr	
	11	3150.0	4.900	0.278	2.375	0.703	
17	0	0.0	18.400	1.000	3.390	1.000	ORS
	8	375.0	7.100	0.385	3.390	1.000	
	9	780.0	1.330	0.072	1.357	0.400	
	10	1080.0	0.378	0.021	0.169	0.050	
	11	3080.0	2.650	0.144	1.185	0.350	

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
18	0	0.0	20.000	1.000	3.380	1.000	ORS
	8	285.0	9.430	0.471	3.300	1.000	
	10	820.0	7.160	0.358	3.380	1.000	
	11	2320.0	5.840	0.292	2.700	0.898	
19	0	0.0	19.700	1.000	2.880	1.000	ORS
	1	7.3	12.500	0.633	2.710	0.940	
	3	27.5	8.150	0.413	2.710	0.940	
	5	70.5	7.290	6.369	2.880	1.000	
	8	305.0	3.600	0.182	0.680	0.236	
	9	627.0	0.568	0.029	Tr	Tr	
	10	870.0	0.189	0.009	Tr	Tr	
	11	2475.0	0.284	0.014	Tr	Tr	
20	0	0.0	18.850	1.000	2.040	1.000	ORS
	1	7.0	10.700	0.566	2.040	1.000	
	3	26.3	5.770	0.306	2.380	1.165	
	5	68.0	5.670	0.301	2.380	1.165	
	8	292.0	4.920	0.261	1.695	0.833	
	9	603.0	1.042	0.055	0.339	0.167	
	10	838.0	0.757	0.040	0.508	0.249	
	11	2380.0	3.130	0.166	2.380	1.165	
46	0	0.0	2.650	1.000	-----	-----	LP
	1	5.0	2.270	0.855	-----	-----	
	4	30.0	2.085	0.785	-----	-----	
	8	210.0	1.705	0.643	-----	-----	
	10	600.0	1.325	0.500	-----	-----	
47	0	0.0	2.440	1.000	-----	-----	LP
	1	5.0	1.420	0.582	-----	-----	
	4	30.5	0.757	0.310	-----	-----	
	8	212.0	0.520	0.213	-----	-----	
	10	605.0	0.189	0.078	-----	-----	

Run	Point	Time sec	Sodium Sulfide Concen gm/liter	Sodium Sulfide C_t/C_o	Sodium Mercaptide Concen gm/liter	Sodium Mercaptide C_t/C_o	Test
48	0	0.0	15.500	1.000	-----	-----	CC
	A	31.8	9.060	0.584	-----	-----	
	B	58.0	4.530	0.292	-----	-----	
	1	69.5	3.780	0.244	-----	-----	
	4	113.8	2.460	0.159	-----	-----	
	8	416.0	1.040	0.067	-----	-----	
	10	1080.0	0.280	0.018	-----	-----	
49	0	0.0	15.700	1.000	-----	-----	CC
	A	31.8	9.620	0.612	-----	-----	
	B	58.0	5.850	0.372	-----	-----	
	1	69.5	4.900	0.312	-----	-----	
	4	113.8	3.120	0.199	-----	-----	
	8	416.0	1.330	0.085	-----	-----	
	10	1080.0	0.566	0.036	-----	-----	

3. INORGANIC SULFUR COMPOSITION OF BLACK LIQUOR SAMPLES

a. Weak Black Liquor

Run	Point	Time sec	Concentration - Grams/Liter Na_2S	Na_2S_2	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4	Liquid pH	Test
6	0	0.0	6.00	-----	2.40	0.03	0.62	12.70	ORW
	1	3.4	2.00	-----	6.50	0.03	1.47	12.50	
	2	8.3	0.38	-----	6.90	0.06	1.50	12.53	
	3	13.2	0.26	-----	6.75	0.03	1.62	12.50	
	4	21.3	0.23	-----	6.80	0.03	1.45	12.50	
	5	34.0	0.21	-----	----	----	1.82	12.48	
	6	51.0	0.19	-----	6.75	0.03	1.63	12.47	
	7	83.0	0.15	-----	6.50	0.06	1.58	12.45	
	8	147.0	0.11	-----	6.20	0.03	1.66	12.40	
25	0	0.0	6.250	0.296	2.320	0.032	0.710	12.90	LT
	1	3.4	2.120	0.510	5.925	0.000	1.380	12.92	
	2	8.1	0.228	0.161	8.060	0.032	1.460	12.85	
	3	13.0	0.152	0.120	7.440	0.048	1.930	12.87	
	4	21.2	0.133	0.067	7.440	0.063	2.120	12.85	
	5	33.6	0.121	0.215	6.820	0.032	2.100	12.83	
	6	50.0	0.114	0.456	7.440	0.048	2.070	12.82	
	7	82.0	0.095	0.133	7.130	0.096	2.100	12.80	
	8	143.0	0.076	0.039	6.975	0.032	2.290	12.78	
	9	295.0	0.057	0.174	6.820	0.063	2.370	12.80	
	10	410.0	0.038	0.094	6.975	0.032	2.290	12.82	
	11	1180.0	0.076	0.215	7.130	0.096	2.390	12.84	
26	0	0.0	6.050	0.402	5.880	0.063	1.220	-----	LT
	1	3.6	1.665	0.430	9.600	0.044	2.200	-----	
	2	8.6	0.246	0.385	9.750	0.094	2.230	-----	
	3	13.6	0.189	0.358	9.750	0.126	2.370	-----	
	4	22.0	0.170	0.400	9.750	0.189	2.420	-----	
	5	35.0	0.151	0.372	9.600	0.220	2.640	-----	
	6	52.0	0.133	0.272	9.150	0.094	2.640	-----	
	7	86.0	0.113	0.358	8.840	0.126	2.630	-----	
	8	151.0	0.095	0.287	8.670	0.189	2.650	-----	
	9	310.0	0.076	0.444	8.520	0.220	2.280	-----	
	10	432.0	0.057	0.330	8.900	0.063	2.690	-----	
	11	1230.0	0.095	0.430	9.300	0.189	2.720	-----	
27	0	0.0	6.930	0.172	4.460	0.000	0.710	-----	LT
	1	2.8	2.945	0.298	7.425	0.000	0.780	-----	
	2	6.8	1.817	0.136	8.333	0.031	1.045	-----	
	3	10.8	0.454	0.115	9.250	0.063	1.190	-----	
	4	17.7	0.303	0.107	8.333	0.252	1.387	-----	
	5	28.0	0.246	0.115	8.035	0.189	1.550	-----	
	6	41.5	0.227	0.079	8.333	0.157	1.760	-----	
	7	68.0	0.170	0.086	8.333	0.126	-----	-----	
	8	121.0	0.151	0.050	8.333	0.095	1.780	-----	
	9	247.0	0.133	0.036	7.140	0.189	1.820	-----	
	10	343.0	0.114	0.036	7.730	0.252	1.920	-----	
	11	985.0	0.170	0.036	6.855	0.252	2.050	-----	
28	0	0.0	6.130	0.301	5.400	0.000	1.250	-----	LT
	1	2.9	1.882	0.186	3.280	0.000	1.425	-----	
	2	7.0	0.378	0.237	10.500	0.032	1.500	-----	
	3	11.0	0.189	0.294	10.500	0.000	-----	-----	
	4	18.0	0.170	0.145	9.900	0.000	1.570	-----	
	5	28.6	0.151	0.043	9.580	0.063	1.900	-----	
	6	42.5	0.132	0.093	9.900	0.063	1.960	-----	
	7	69.5	0.113	0.093	9.580	0.095	2.000	-----	
	8	123.0	0.095	0.152	9.900	0.095	2.130	-----	
	9	252.0	0.076	0.115	9.900	0.126	-----	-----	
	10	350.0	0.057	0.158	9.580	0.063	2.290	-----	
	11	1000.0	0.076	0.029	9.580	0.032	2.290	-----	

Run	Point	Time sec	Concentration - Grams/Liter Na_2S	Na_2S_2	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4	Liquid pH	Test
29	0	0.0	6.120	0.086	4.340	0.063	0.723	-----	LT
	1	2.9	2.160	0.202	5.580	0.000	0.750	-----	
	2	7.0	1.020	0.100	5.580	0.000	0.800	-----	
	3	11.0	0.227	0.115	5.580	0.000	0.819	-----	
	4	18.0	0.208	0.100	5.270	0.000	1.120	-----	
	5	28.5	0.170	0.202	5.270	0.000	1.150	-----	
	6	42.5	0.152	0.301	5.270	0.000	1.160	-----	
	7	69.5	0.132	0.072	5.270	0.000	1.190	-----	
	8	123.0	0.114	0.029	4.960	0.000	1.220	-----	
	9	252.0	0.094	0.086	4.960	0.000	1.230	-----	
	10	350.0	0.076	0.115	4.960	0.000	1.280	-----	
	11	1000.0	0.094	0.086	4.650	0.000	1.270	-----	
30	0	0.0	6.280	0.509	5.100	0.000	1.480	12.68	ORW
	1	2.8	2.880	0.467	8.680	0.063	2.300	12.60	
	2	6.8	1.667	0.454	9.600	0.000	2.590	12.58	
	3	10.8	1.137	0.496	10.250	0.063	2.950	12.60	
	4	17.5	0.831	0.454	10.400	0.000	3.000	12.65	
	5	27.5	0.723	0.482	10.850	0.000	3.300	12.67	
	6	41.5	0.378	0.398	10.400	0.000	3.250	12.68	
	7	68.0	0.303	-----	10.850	0.000	3.380	12.68	
	8	119.0	0.265	0.426	10.400	0.000	3.200	12.63	
	9	245.0	0.227	0.454	3.900	0.000	3.220	12.65	
	10	342.0	0.265	0.425	10.550	0.000	-----	12.68	
	11	975.0	0.378	0.722	10.250	0.000	3.290	12.62	
31	0	0.0	4.840	0.517	4.030	0.032	1.760	12.00	pH
	1	3.2	0.908	0.654	6.665	0.063	2.040	11.82	
	2	7.6	0.133	0.485	7.000	0.032	2.330	11.88	
	3	12.0	0.114	0.353	6.820	0.032	2.560	11.85	
	4	19.5	0.095	0.604	6.500	0.000	2.660	11.80	
	5	31.0	0.057	0.402	6.350	0.000	2.620	11.63	
	6	46.2	0.076	0.287	6.300	0.032	2.790	11.65	
	7	72.7	0.076	0.525	6.260	0.000	2.810	11.65	
	8	133.0	0.057	0.396	6.250	0.000	2.840	11.65	
	9	278.0	0.056	0.323	6.200	0.000	2.960	11.65	
	10	382.0	0.038	0.396	6.200	0.000	2.810	11.65	
	11	1090.0	0.133	0.234	5.900	0.000	2.850	11.55	
32	0	0.0	4.920	0.517	4.030	0.000	1.840	10.90	pH
	1	3.2	1.820	0.366	7.440	0.000	1.930	10.90	
	2	7.6	0.378	0.453	6.820	0.000	2.580	10.82	
	3	12.0	0.132	-----	6.520	0.032	2.760	11.15	
	4	19.5	0.114	0.366	6.200	0.000	2.870	-----	
	5	31.0	0.095	0.624	6.200	0.000	2.870	10.85	
	6	46.2	0.095	0.436	6.200	0.000	2.770	10.88	
	7	72.7	0.086	0.358	6.040	0.000	2.830	10.95	
	8	133.0	0.076	0.430	5.890	1.000	2.850	11.00	
	9	278.0	0.057	0.358	5.560	0.000	2.720	10.90	
	10	382.0	0.076	0.301	5.890	0.000	2.830	10.85	
	11	1090.0	0.076	0.294	5.560	0.000	2.850	10.85	
50	0	0.0	5.640	0.220	11.780	0.063	-----	12.85	TS
	1	4.0	1.060	0.179	16.720	0.000	-----	12.80	
	4	25.0	0.152	0.138	14.270	0.063	-----	12.65	
	8	172.0	0.095	0.179	13.000	0.032	-----	12.60	
51	0	0.0	5.640	0.440	20.000	0.063	-----	12.85	TS
	1	4.0	1.365	0.302	22.000	0.000	-----	12.78	
	4	25.0	0.227	0.234	22.000	0.032	-----	12.75	
	8	172.0	0.208	0.165	25.750	0.000	-----	12.75	
52	0	0.0	5.640	0.204	3.250	0.000	1.660	12.85	TS
	1	4.0	0.833	0.179	6.800	0.063	1.700	12.90	
	4	25.0	0.152	0.426	6.800	0.000	2.250	12.80	
	8	172.0	0.057	0.179	7.120	0.000	2.370	12.75	

b. Strong Black Liquor

Run	Point	Time sec	Concentration - Grams/Liter Na_2S	Na_2S_2	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4	Liquid pH	Test
20	0	0.0	18.850	2.187	2.210	0.126	4.520	------	ORS
	1	7.0	10.700	1.084	8.760	0.220	3.760	------	
	3	26.3	5.770	3.300	9.440	0.189	4.960	------	
	5	68.0	5.670	3.120	14.560	0.063	5.120	------	
	8	292.0	4.920	3.740	15.020	0.000	4.880	------	
	9	603.0	1.042	3.780	16.580	0.189	5.200	------	
	10	838.0	0.757	1.782	16.100	0.252	4.720	------	
	11	2380.0	3.130	2.165	16.720	0.357	4.600	------	
47	0	0.0	2.440	2.025	14.400	0.000	8.910	------	LP
	1	5.0	1.420	1.890	15.000	0.000	8.890	------	
	4	30.5	0.757	0.890	16.960	0.000	8.870	------	
	8	212.0	0.520	1.958	16.000	0.008	9.310	------	
	10	605.0	0.189	2.300	17.000	0.016	9.310	------	

4. SUMMARY OF INORGANIC SULFUR COMPOSITION

a. Weak Black Liquor

Run	Point	Time sec	Concentration as Sulfur - gm S/liter Na_2S	Na_2S_2	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4	T.I.S.	S_t/S_o	Test
6	0	0.0	2.46	-----	0.97	0.01	0.14	-----	-----	ORW
	1	3.7	0.82	-----	2.63	0.01	0.33	-----	-----	
	2	8.3	0.15	-----	2.78	0.02	0.34	-----	-----	
	3	13.2	0.11	-----	2.76	0.01	0.36	-----	-----	
	4	21.3	0.09	-----	2.75	0.01	0.33	-----	-----	
	5	34.0	0.08	-----	----	----	0.41	-----	-----	
	6	51.0	0.08	-----	2.73	0.01	0.37	-----	-----	
	7	83.0	0.06	-----	2.63	0.02	0.36	-----	-----	
	8	147.0	0.05	-----	2.52	0.01	0.37	-----	-----	
25	0	0.0	2.560	0.158	0.941	0.032	0.162	3.853	1.000	LT
	1	3.4	0.870	0.273	2.400	0.000	0.266	3.809	0.989	
	2	8.1	0.093	0.086	3.263	0.032	0.329	3.803	0.988	
	3	13.0	0.062	0.064	3.015	0.048	0.435	3.634	0.942	
	4	21.2	0.055	0.037	3.015	0.063	0.477	3.648	0.947	
	5	33.6	0.050	0.115	2.763	0.032	0.484	3.444	0.896	
	6	50.0	0.047	0.244	3.015	0.048	0.489	3.843	0.999	
	7	82.0	0.039	0.071	2.885	0.096	0.496	3.587	0.932	
	8	143.0	0.031	0.021	2.825	0.032	0.516	3.425	0.890	
	9	295.0	0.023	0.093	2.763	0.063	0.534	3.476	0.902	
	10	410.0	0.016	0.050	2.825	0.032	0.516	3.439	0.892	
	11	1180.0	0.031	0.115	2.885	0.096	0.539	3.666	0.952	
26	0	0.0	2.480	0.417	2.380	0.016	0.275	5.568	1.000	LT
	1	3.6	0.683	0.550	3.882	0.011	0.496	5.622	1.010	
	2	8.6	0.101	0.508	3.945	0.024	0.502	5.080	0.912	
	3	13.6	0.078	0.366	3.945	0.032	0.534	4.955	0.890	
	4	22.0	0.070	0.417	3.945	0.047	0.542	5.021	0.900	
	5	35.0	0.062	0.442	3.882	0.055	0.594	5.034	0.903	
	6	52.0	0.055	0.375	3.710	0.024	0.594	4.758	0.855	
	7	86.0	0.046	0.317	3.580	0.032	0.592	4.567	0.821	
	8	151.0	0.039	0.334	3.510	0.047	0.597	4.517	0.812	
	9	310.0	0.032	0.358	3.450	0.055	0.514	4.409	0.792	
	10	432.0	0.023	0.358	3.380	0.016	0.605	4.382	0.778	
	11	1230.0	0.039	0.378	3.765	0.047	0.612	4.830	0.867	
27	0	0.0	2.840	0.100	3.285	0.000	0.318	5.543	1.000	LT
	1	2.8	1.208	0.167	3.740	0.000	0.176	5.291	0.955	
	2	6.8	0.745	0.779	4.200	0.009	0.236	5.268	0.953	
	3	10.8	0.187	0.067	4.650	0.016	0.471	5.391	0.964	
	4	17.7	0.124	0.062	4.200	0.064	0.197	4.647	0.844	
	5	28.0	0.101	0.067	4.045	0.048	0.350	4.611	0.834	
	6	41.5	0.093	0.046	4.200	0.040	0.400	4.779	0.864	
	7	68.0	0.070	0.050	4.200	0.032	0.425	4.777	0.862	
	8	121.0	0.062	0.029	4.200	0.024	0.401	4.716	0.852	
	9	247.0	0.055	0.021	3.600	0.048	0.355	4.079	0.737	
	10	343.0	0.047	0.021	3.900	0.064	0.298	4.330	0.782	
	11	985.0	0.070	0.021	3.445	0.064	0.461	4.061	0.735	
28	0	0.0	2.515	0.018	2.185	0.000	0.282	5.000	1.000	LT
	1	2.9	0.771	0.011	3.700	0.000	0.338	4.880	0.977	
	2	7.0	0.155	0.014	4.260	0.008	0.270	4.707	0.943	
	3	11.0	0.078	0.017	4.260	0.000	0.228	4.583	0.916	
	4	18.0	0.070	0.008	4.000	0.000	0.354	4.432	0.886	
	5	28.6	0.062	0.003	3.880	0.016	0.428	4.389	0.877	
	6	42.5	0.054	0.005	4.000	0.016	0.392	4.467	0.894	
	7	69.5	0.046	0.005	3.880	0.024	0.416	4.371	0.875	
	8	123.0	0.039	0.009	4.000	0.024	0.441	4.513	0.903	
	9	252.0	0.031	0.007	4.000	0.032	0.831	4.901	0.973	
	10	350.0	0.023	0.009	3.880	0.016	0.516	4.444	0.888	
	11	1000.0	0.031	0.002	3.880	0.008	0.464	4.385	0.877	

Run	Point	Time sec	Concentration as Sulfur - gm S/liter Na_2S	Na_2S_2	$Na_2S_2O_3$	Na_2S_3	Na_2SO_4	T.I.S.	$\frac{S_t}{S_o}$	Test
29	0	0.0	2.515	0.033	1.760	0.016	0.163	4.437	1.000	LT
	1	2.9	0.884	0.116	2.240	0.000	0.169	3.409	0.760	
	2	7.0	0.418	0.183	2.240	0.000	0.180	3.021	0.675	
	3	11.0	0.093	0.167	2.240	0.000	0.184	2.684	0.600	
	4	18.0	0.085	0.183	2.140	0.000	0.252	2.660	0.594	
	5	28.5	0.070	0.058	2.140	0.000	0.259	2.527	0.565	
	6	42.5	0.062	0.100	2.140	0.000	0.261	2.563	0.573	
	7	69.5	0.054	0.158	2.140	0.000	0.268	2.620	0.584	
	8	123.0	0.047	0.108	2.019	0.000	0.275	2.440	0.544	
	9	252.0	0.039	0.141	2.010	0.000	0.277	2.467	0.550	
	10	350.0	0.031	0.058	2.010	0.000	0.299	2.387	0.533	
	11	1000.0	0.039	0.108	1.885	0.000	0.286	2.318	0.516	
30	0	0.0	2.580	0.172	1.150	0.000	0.276	4.178	1.000	ORW
	1	2.8	1.180	0.272	1.957	0.016	0.518	3.943	0.947	
	2	6.8	0.683	0.264	2.162	0.000	0.584	3.693	0.880	
	3	10.8	0.465	0.288	2.310	0.016	0.694	3.773	0.900	
	4	17.5	0.341	0.264	2.340	0.000	0.714	3.659	0.872	
	5	27.5	0.296	0.280	2.445	0.000	0.766	3.787	0.905	
	6	41.5	0.155	0.231	2.340	0.000	0.732	3.458	0.825	
	7	68.0	0.124	0.240	2.445	0.000	0.761	3.570	0.852	
	8	119.0	0.109	0.248	2.340	0.000	0.662	3.359	0.802	
	9	245.0	0.071	0.264	2.227	0.000	0.683	3.245	0.775	
	10	342.0	0.109	0.247	2.380	0.000	0.635	3.371	0.805	
	11	975.0	0.155	0.420	2.310	0.000	0.654	3.539	0.844	
31	0	0.0	1.985	0.301	1.633	0.008	0.397	4.324	1.000	pH
	1	3.2	0.372	0.380	2.700	0.016	0.460	3.928	0.910	
	2	7.6	0.055	0.282	2.835	0.008	0.525	3.705	0.857	
	3	12.0	0.047	0.205	2.760	0.000	0.575	3.587	0.853	
	4	19.5	0.039	0.351	2.630	0.000	0.598	3.618	0.837	
	5	31.0	0.023	0.234	2.570	0.008	0.590	3.425	0.793	
	6	46.2	0.031	0.167	2.550	0.000	0.627	3.375	0.780	
	7	72.7	0.031	0.305	2.535	0.000	0.631	3.502	0.811	
	8	133.0	0.023	0.230	2.530	0.000	0.639	3.422	0.793	
	9	278.0	0.023	0.188	2.500	0.000	0.666	3.377	0.780	
	10	382.0	0.016	0.230	2.500	0.000	0.631	3.377	0.780	
	11	1090.0	0.055	0.142	2.380	0.000	0.641	3.210	0.745	
32	0	0.0	2.020	0.301	1.632	0.000	0.414	4.367	1.000	pH
	1	3.2	0.726	0.213	3.010	0.000	0.434	4.403	1.010	
	2	7.6	0.155	0.250	2.760	0.000	0.581	3.746	0.857	
	3	12.0	0.054	-----	2.640	0.008	0.621	-----	-----	
	4	19.5	0.047	0.213	2.510	0.000	0.646	3.416	0.781	
	5	31.0	0.039	0.363	2.510	0.000	0.646	3.558	0.813	
	6	46.2	0.039	0.254	2.510	0.000	0.624	3.427	0.785	
	7	72.7	0.035	0.208	2.445	0.000	0.637	3.325	0.761	
	8	133.0	0.031	0.250	2.383	0.000	0.641	3.305	0.757	
	9	278.0	0.023	0.208	2.230	0.000	0.612	3.073	0.703	
	10	382.0	0.031	0.175	2.383	0.000	0.637	3.226	0.739	
	11	1090.0	0.031	0.171	2.230	0.000	01641	3.073	0.703	
52	0	0.0	2.312	0.120	1.315	0.000	0.375	4.122	1.000	TS
	1	4.0	0.341	0.104	2.750	0.016	0.384	3.595	0.870	
	4	25.0	0.062	0.248	2.758	0.000	0.510	3.578	0.866	
	8	172.0	0.023	0.104	2.890	0.000	0.533	3.550	0.860	

b. Strong Black Liquor

Run	Point	Time sec	Concentration as Sulfur - gm S/liter Na_2S	Na_2S_2	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4	T.I.S.	$\frac{S_t}{S_o}$	Test
20	0	0.0	7.730	1.272	0.895	0.032	1.027	10.956	1.000	ORS
	1	7.0	4.380	0.630	3.550	0.056	0.845	9.451	0.864	
	3	26.3	2.362	1.920	3.820	0.048	1.117	9.267	0.846	
	5	68.0	1.233	1.813	5.890	0.016	1.152	10.104	0.926	
	8	292.0	2.018	2.183	6.080	0.000	1.100	11.378	1.040	
	9	603.0	0.428	2.200	6.700	0.048	1.170	10.546	0.963	
	10	838.0	0.310	0.972	6.510	0.064	1.062	8.918	0.814	
	11	2380.0	1.282	1.260	6.770	0.891	1.050	11.253	1.028	
47	0	0.0	1.000	1.180	5.830	0.000	2.004	10.014	1.000	LP
	1	5.0	0.582	1.100	6.070	0.000	2.000	9.752	0.961	
	4	30.5	0.310	1.100	6.970	0.000	1.993	10.378	1.022	
	8	212.0	0.213	1.140	6.460	0.002	2.100	9.915	0.978	
	10	605.0	0.058	1.340	6.880	0.004	2.100	10.382	1.025	

5. SUMMARY OF LIGNIN WEIGHT ANALYSES

a. Weak Black Liquor - Run No. 25

Point	Reaction Time Seconds	Net Weight Grams	Weight Ratio W_t/W_o
0	0	1.3045	1.000
1	3	1.1932	0.915
2	8	1.2541	0.961
3	13	1.2079	0.925
4	21	1.2020	0.921
5	34	1.2177	0.932
6	50	1.2050	0.924
7	82	1.2085	0.925
8	143	1.2195	0.934
9	295	1.1876	0.910
10	410	1.1930	0.915
11	1180	1.1785	0.902

b. Strong Black Liquor - Run No. 20

Point	Reaction Time Seconds	Net Weight Grams	Weight Ratio W_t/W_o
0	0	8.5493	1.000
1	7	7.9920	0.935
3	26	7.9478	0.928
5	68	7.2804	0.852
8	292	7.3129	0.856
9	603	7.9976	0.925
10	838	7.4446	0.872
11	2380	7.2294	0.848

APPENDIX D

KRAFT PULP MILL PRODUCTION IN THE UNITED STATES

1. KRAFT PULP MILL PRODUCTION IN THE UNITED STATES (1968).

State	City	Company	Pulp Production (Tons/Day) Unbleached	Bleached	Wood Species (%) Softwood	Hardwood
Alabama	Brewton	Container Corp. of America	900	400	75	25
	Coosa Pines	Kimberly-Clark Corp.	630	630	64	36
	Demopolis	Gulf States Paper Corp.	400	375	60	40
	Jackson	Allied Paper Corp.	520	475	40	60
	Mahrt	Georgia Kraft Company	900	0	90	10
	Mobile	International Paper Co.	1,050	450	77	23
	Mobile	Scott Paper Company	1,400	1,300	73	27
	Montgomery	Union Camp Corp.	870	0	93	7
	Naheola	American Can Co.	970	970	60	40
	Selma	Hammermill Paper Co.	430	400	75	25
	Pine Hill	MacMillan United, Inc.	900	0	95	5
	Tuscaloosa	Gulf States Paper Corp.	500	0	90	10
Arizona	Snowflake	Southwest Forest Industries	320	65	100	0
Arkansas	Ashdown	Great Northern Nekoosa	430	400	65	35
	Camden	International Paper Co.	700	0	93	7
	Crossett	Georgia Pacific Corp.	640	120	100	0
	Morrilton	Arkansas Kraft Corp.	350	0	88	12
	Pine Bluff	Weyerhaeuser Company	200	0	100	0
	Pine Bluff	International Paper Co.	1,300	1,170	70	30

1. KRAFT PULP MILL PRODUCTION IN THE UNITED STATES (1968)(continued)

State	City	Company	Pulp Production (Tons/Day) Unbleached	Bleached	Wood Species (%) Softwood	Hardwood
California	Anderson	Simpson Lee Paper Company	165	150	100	0
	Antioch	Fibreboard Corporation	750	160	100	0
	Fairhaven	Crown Simpson Pulp Co.	550	500	100	0
	Samoa	Georgia Pacific Corp.	550	500	100	0
Florida	Fernandina	Container Corp. of America	825	0	95	5
	Foley	Buckeye Cellulose Corp.	950	860	85	15
	Jacksonville	Alton Box Board Co.	675	0	90	10
	Jacksonville	St. Regis Paper Co.	1,300	0	60	40
	Palatka	Hudson Pulp and Paper Co.	950	400	60	40
	Panama City	International Paper Co.	1,410	735	50	50
	Pensacola	St. Regis Paper Co.	300	260	88	12
	Port St. Joe	St. Joe Paper Co.	1,700	500	90	10
Georgia	Augusta	Continental Can Co.	750	700	60	40
	Brunswick	Brunswick Pulp and Paper Co.	1,290	1,195	61	39
	Cedar Springs	Great Northern Paper Co.	1,700	0	99	1
	Jesup	ITT-Rayonier, Inc.	675	675	90	10
	Macon	Georgia Kraft Company	875	0	85	15
	Port Wentworth	Continental Can Co.	625	0	95	5
	Riceboro	Interstate Paper Corp.	450	0	95	5
	Rome	Georgia Kraft Company	1,500	0	90	10

1. KRAFT PULP MILL PRODUCTION IN THE UNITED STATES (1968)(continued)

State	City	Company	Pulp Production (Tons/Day) Unbleached	Pulp Production (Tons/Day) Bleached	Wood Species (%) Softwood	Wood Species (%) Hardwood
Georgia (continued)	St. Marys	Gilman Paper Co.	900	350	80	20
	Savannah	Union Carbide Corp.	2,700	0	95	5
	Valdosta	Owens-Illinois, Inc.	770	0	95	5
Idaho	Lewiston	Potlatch Forests, Inc.	840	800	100	0
Kentucky	Hawesville	Western Kraft Corp.	300	0	0	100
	Wickliffe	Westvaco Corp.	600	600	50	50
Louisiana	Bastrop	International Paper Co.	1,200	1,100	45	55
	Bogalusa	Crown Zellerbach Corp.	1,350	140	99	1
	DeRidder	Boise Cascade Corp.	600	0	100	0
	Elizabeth	Calcasieu Paper Co.	250	0	90	10
	Hodge	Continental Can Co.	500	0	100	0
	Pineville	Pineville Kraft Corp.	850	0	100	0
	Port Hudson	Louisiana Forest Prod.	550	510	15	85
	St. Francisville	Crown Zellerbach Corp.	550	500	60	40
	Springhill	International Paper Co.	1,650	1,000	70	30
	West Monroe	Olin Kraft, Inc.	1,066	0	77	23

1. KRAFT PULP MILL PRODUCTION IN THE UNITED STATES (1968)(continued)

State	City	Company	Pulp Production (Tons/Day) Unbleached	Pulp Production (Tons/Day) Bleached	Wood Species (%) Softwood	Wood Species (%) Hardwood
Maine	Cumberland Mills	Scott Paper Co.	270	250	30	70
	Jay	International Paper Co.	525	470	65	35
	Lincoln	Lincoln Pulp Co.	225	210	0	100
	Old Town	Penobscot Company	375	350	10	90
	Rumford	Oxford Paper Co.	560	525	35	65
	Woodland	Georgia Pacific Corp.	550	500	70	30
Maryland	Luke	Westvaco Corp.	740	740	30	70
Michigan	Escanaba	Mead Corp.	300	300	50	50
	Filer City	Packaging Corp. of America	200	184	50	50
	Muskegon	Scott Paper Co.	240	225	36	64
Minnesota	Cloquet	Potlatch Forests, Inc.	325	305	60	40
	Intern. Falls	Boise Cascade Corp.	250	250	50	50
Mississippi	Monticello	St. Regis Paper Co.	1,690	0	100	0
	Moss Point	International Paper Co.	730	660	55	45
	Natchez	International Paper Co.	1,000	1,000	19	81
	Vicksburg	International Paper Co.	985	300	85	15

KRAFT PULP MILL PRODUCTION IN THE UNITED STATES (1968)(continued)

State	City	Company	Pulp Production (Tons/Day) Unbleached	Pulp Production (Tons/Day) Bleached	Wood Species (%) Softwood	Wood Species (%) Hardwood
Montana	Missoula	Hoerner Waldorf Corp.	1,200	250	100	0
New Hampshire	Berlin	Brown Company	615	500	35	65
New York	Ticonderoga	International Paper Co.	500	500	0	100
North Carolina	Canton	U.S.P.-Champion Papers	1,290	1,290	60	40
	Plymouth	Weyerhaeuser Co.	1,180	450	80	20
	Riegelwood	Riegel Paper Corp.	1,070	1,070	50	50
	Roanoke Rapids	Hoerner Waldorf Corp.	900	0	88	12
Ohio	Chillicothe	Mead Corp.	650	600	0	100
Oklahoma	Valliant	Weyerhaeuser Co.	1,200	-	-	-
Oregon	Albany	Western Kraft Corp.	500	0	100	0
	Gardiner	International Paper Co.	545	0	100	0
	Halsey	American Can Co.	300	300	100	0
	St. Helens	Boise Cascade Corp.	800	650	100	0
	Springfield	Weyerhaeuser Co.	1,150	0	100	0
	Wauna	Crown Zellerbach Corp.	800	550	85	15

1. KRAFT PULP MILL PRODUCTION IN THE UNITED STATES (1968)(continued)

State	City	Company	Pulp Production (Tons/Day) Unbleached	Bleached	Wood Species (%) Softwood	Hardwood
Pennsylvania	Johnsonburg	New York and Penn. Co.	170	160	0	100
	Roaring Spring	Combined Paper Mills	195	180	50	50
	Spring Grove	P. H. Glatfetter Co.	550	500	50	50
	Tyrone	Westvaco Corp.	160	152	30	70
South Carolina	Catawba	Bowaters Corp.	860	860	88	12
	Charleston	Westvaco Corp.	1,850	0	80	20
	Florence	South Carolina Ind.	600	0	90	10
	Georgetown	International Paper Co.	1,550	340	79	21
Tennessee	Calhoun	Bowaters Corp.	520	490	100	0
	Counce	Tenn. River P. & P. Co.	700	0	91	9
Texas	Evadale	Eastex, Inc.	1,200	1,000	58	42
	Houston	Southland Paper Mills	450	100	100	0
	Lufkin	Southland Paper Mills	325	300	100	0
	Orange	Owens-Illinois, Inc.	1,000	0	100	0
	Pasadena	USP-Champion Papers	805	805	70	30
	Texarkana	International Paper Co.	650	650	100	0

1. KRAFT PULP MILL PRODUCTION IN THE UNITED STATES (1968)(continued)

State	City	Company	Pulp Production (Tons/Day) Unbleached	Pulp Production (Tons/Day) Bleached	Wood Species (%) Softwood	Wood Species (%) Hardwood
Virginia	Covington	Westvaco Corp.	950	850	34	66
	Franklin	Union Camp Corp.	1,100	940	43	57
	Hopewell	Continental Can Co.	900	0	100	0
	West Point	Chesapeake Corp. of Va.	1,050	0	88	12
Washington	Camas	Crown Zellerbach Corp.	780	780	100	0
	Everett	Weyerhaeuser Co.	440	400	85	15
	Longview	Longview Fibre Co.	1,800	400	100	0
	Longview	Weyerhaeuser Co.	695	650	91	9
	Port Townsend	Crown Zellerbach Co.	420	0	100	0
	Tacoma	St. Regis Paper Co.	930	145	100	0
	Wallula	Boise Cascade Corp.	410	0	100	0
Wisconsin	Kaukouna	Thilmany Pulp and Paper Co.	380	90	100	0
	Mosinee	Mosinee Paper Mills	175	0	80	20
	Nekoosa	Great Northern Nekoosa	340	315	75	25
	Wisconsin Rapids	Consolidated Papers, Inc.	360	333	33	67

Reference: Hendrickson, E. R., Roberson, J. E., and Koogler, J. B., "Control of Atmospheric Emissions in the Wood Pulping Industry," volume 1, Final Report, Control No. CPA 22-69-18, U. S. Dept. of Health, Education, and Welfare, National Air Pollution Control Administration, Raleigh, North Carolina, March 15, 1970, pp. A-2 to A-31.

2. PRODUCTION FOR KRAFT PULP MILLS IN THE SOUTHEASTERN UNITED STATES

State	Kraft Pulp Production - Tons Pulp Per Day							
	0-500	501-750	751-1000	100 -1250	1251-1500	1501-2000	2001-3000	Total
Alabama	2	4	4	1	1	0	0	12
Arkansas	3	2	0	0	2	0	0	7
Florida	2	1	3	0	2	1	0	9
Georgia	1	3	4	0	1	2	1	12
Kentucky	1	1	0	0	0	0	0	2
Louisiana	0	4	1	2	1	1	0	9
Maryland	0	1	0	0	0	0	0	1
Mississippi	0	1	1	1	0	1	0	4
North Carolina	1	1	1	2	1	0	0	6
Oklahoma	1	0	0	0	0	0	0	1
South Carolina	1	1	0	0	0	2	0	4
Tennessee	0	2	0	0	0	0	0	2
Texas	2	1	2	1	0	0	0	5
Virginia	0	0	2	2	0	0	0	4
Total	14	21	18	9	8	7	1	78

VITA

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Birthdate:	February 19, 1940
Birthplace:	Ames, Iowa
Parents:	Hal Bluford Harrison Cooper Zerelda Edith Nicholson
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	University of Washington Seattle, Washington M.S., Civil Endineering, 1966
	University of Washington Seattle, Washington Ph.D., Civil Engineering, 1972
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