White liquor oxidation in a pilot plant pipeline reactor

Ronald W. Thring, Victor C. Uloth, Gilles M. Dorris, Thomas S. Galvin, Derek Hornsey, and John R. Ayton

ABSTRACT: An in-line pilot reactor studied the effects of operating variables on sulfide conversion and oxygen utilization efficiency. The study examined conversion with varying oxygen to sulfide molar ratios. Clarified white liquor without black liquor catalyst oxidized as effectively under pressure as white liquor containing lime mud. Increasing the oxygen to sulfide molar ratio gave declining oxygen utilization efficiencies due to poor gas and liquid mixing. Thiosulfate was the primary oxidation product under all experimental conditions using no foreign catalyst. Much longer retention times would be necessary to convert the sulfide to sulfate.

KEYWORDS: Alkalis, oxidation, pilot plants, pipelines, reaction time, reactors, thiosulfates, white liquors.

White liquor can be an inexpensive source of sodium hydroxide for the purification of flue gases, for oxygen delignification, and for caustic extraction stages in kraft pulp bleaching. A major problem with the use of white liquor, however, is the formation of hydrogen sulfide when the liquor pH drops below 10. Even when the pH of the process is above 10, the sulfide in white liquor can adversely affect the brightness and viscosity of softwood kraft pulp. This happens in pulping and bleaching processes using oxygen *(1, 2)* and in bleaching sequences using chlorine or chlorine dioxide (*2, 3)*. Converting the sulfide to thiosulfate in an oxidation stage can eliminate these problems *(1, 2, 4)*. It is possible to use purchased caustic (NaOH), white liquor, and oxidized white liquor interchangeably in the medium consistency oxygen delignification of eucalyptus pulp *(5)*. Using oxidized white liquor as a source of alkali for oxygen delignification is, however, often necessary to preserve the mill's chemical balance without the need for purchased chemicals *(1, 2, 6)*. While white liquor routinely oxidized in large stirred-tank reactors using air with black liquor as a catalyst *(2)*, recent reports show that white liquor oxidizes more quickly, more completely, and more cheaply using oxygen in an in-line or serpentine type reactor *(4)*. Although an in-line reactor might be a low cost alternative for white liquor oxidation, little data is available on the effects of design and operating variables on white liquor oxidation or oxygen utilization efficiency.

This paper reports on pilot plant data obtained from a prototype serpentine pipeline reactor used to study the effects of operating variables on the complete oxidation of white liquor. Potential benefits resulting from the use of a pipeline reactor vs. conventional air oxidation in stirred-tank reactors include the following *(4)*:

- No foaming
- No total reduced sulfur (TRS) emissions
- No requirement for foreign catalysts or heat input

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- A smaller unit, if space constraints are important
- Reduced capital and maintenance costs that are partially offset by increased operating costs.

Table I summarizes the potential reactions occurring during white liquor oxidation. An earlier paper discusses these in greater detail *(7)*.

I. Potential reactions during white liquor oxidation

Polysulfide production

$$4NaHS + O_2 \rightarrow 2Na_2S_2 + 2H_2O$$

$$18NaHS + 7O_2 \rightarrow 4Na_2S_{4.5} + 10NaOH + 2H_2O^*$$

Thiosulfate production

$$2NaHS + 2O_2 \rightarrow Na_2S_2O_3 + H_2O$$

$$Na_2S_2 + 3/2\ O_2 \rightarrow Na_2S_2O_3$$

$$4Na_2S_{4.5} + 11O_2 + 10NaOH \rightarrow 9Na_2S_2O_3 + 5H_2O^*$$

Sulfite production

$$Na_2S_2O_3 + O_2 + 2NaOH \rightarrow 2Na_2SO_3 + H_2O$$

Sulfate production

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

$$NaHS + 2O_2 + NaOH \rightarrow Na_2SO_4 + H_2O$$

*Typical reactions during polysulfide liquor production

Experimental

Reactor description

Figure 1 provides a schematic diagram of the pilot plant reactor in the kraft mill used for this study. White liquor from the mill's No. 3 causticizer containing lime mud at approximately 100 g/L is pumped through a vertically mounted serpentine pipeline. The flow rates are as high as 225 L/min at a maximum pressure of 1200 kPa. The 35.1 mm ID pipeline is 150 meters long. The oxidized liquor discharges into the fourth causticizer. It is possible to inject oxygen, air, or a mixture of both at four separate points along the reactor. One can withdraw cooled liquor samples before and after each of the gas spargers. Cooling tubes at the outlet of the reactor reduce the liquor temperature and prevent liquor flashing when the heat generated by the exothermic oxidation reaction increases the liquor temperature above its atmospheric boiling point. Electronic instrumentation consists of liquor flowmeters, gas flowmeters, and flow control valves. These require frequent maintenance in the hot, dusty recausticization environment. A barrel and stop watch checked liquor flows in each run. Simple rotameters and manual valves replaced the electronic gas flowmeters and flow control valves late in the trials.

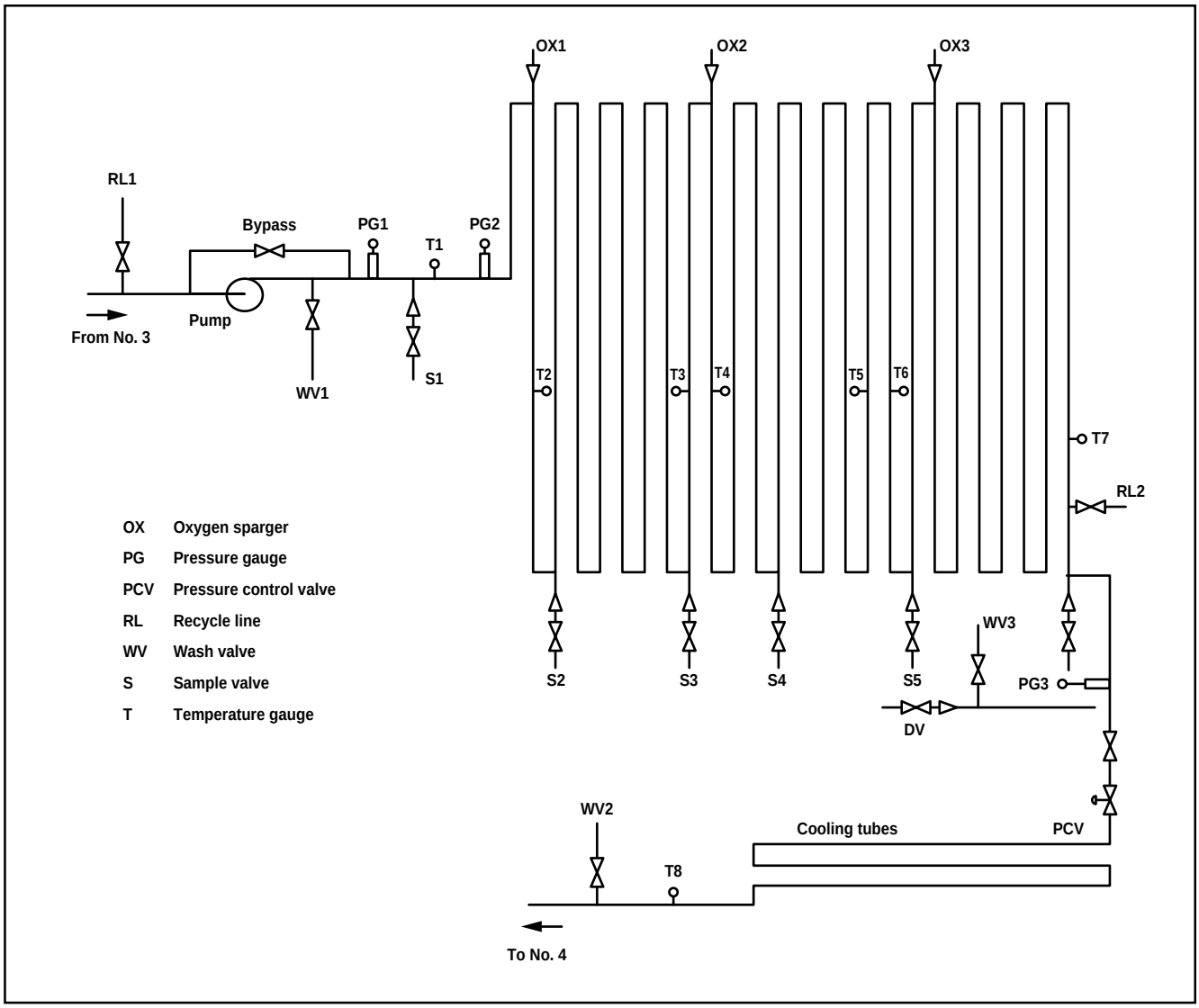
Operation

Beginning a run involved priming the pump with water and switching it on. The feed liquor valve on the bottom of the No. 3 causticizer was then opened, and the water was turned off. Air or oxygen flow at a rate close to that anticipated for the run then began. Measuring the liquor flow rate into the fourth causticizer using a barrel and a stopwatch provided settings for the desired liquor flow rate and reactor operating pressure. Adjusting this flow used two control valves. One was at the pump discharge for pressure control, and the other was at the end of the pipeline reactor.

After obtaining constant liquor flow, adjusting the appropriate flowmeter and automated flow control valve or throttling valves on each injector allowed fine tuning of the desired feed gas flow at each injection point. In most of the trials, the total gas flow rate to the reactor was equally split between the last three injection points. After 5–10 min of steady operation, temperature and pressure readings through the pipeline reactor were recorded. Liquor samples of approximately 250 mL volume were then taken at each sampling point for analyses. Potentiometric titration with HgCl using a sulfide ion electrode determined the sulfide content *(8)*. Modified procedures presented in a separate report determined the thiosulfate, polysulfide, and sulfate contents *(7)*.

Liquor flow rates varied from 30

1. Schematic diagram of the pipeline reactor



L/min to 225 L/min while reactor pressure varied between 500 kPa and 1200 kPa (60–160 psig). It was not possible to sustain lower liquor flow rates due to pump cavitation. Operating pressures varied over the full 500–1200 kPa range at low gas to liquor flow rates. As the gas flow rates increased to provide complete oxidation, however, line pressure losses increased. At oxygen to sulfide molar ratios greater than the stoichiometric requirement for oxidation of sulfide to thiosulfate (1.0), the gas to liquor volume ratio at reactor inlet conditions was greater than 1.4. There were line pressure losses as high as 270 kPa. At oxygen to sulfide molar ratios above 1.0, operating pressures therefore only varied from 600 kPa to 1200 kPa.

Results and discussion

To establish optimum operating conditions for the complete oxidation of white liquor, the study examined the effects of several operating variables. These were total oxidant gas flow rate, type of oxidant gas (oxygen or air and oxygen gas mixtures), reactor pressure, retention time, and gas to liquid volume ratio (or oxygen to sulfide mole ratio). The two parameters used to characterize oxidation efficiency were sulfide conversion and oxygen utilization efficiency. Equations 1 and 2 provide the definitions for these terms:

$$SC = 100\{1 - [(Na_2S)_f/(Na_2S)_i]\} \quad (1)$$

$$OUE = [100(O_s - O_u)]/O_s \quad (2)$$

where

SC = sulfide conversion, %

$(Na_2S)_f$ = final sulfide content

$(Na_2S)_i$ = initial sulfide content

OUE = oxygen utilization efficiency, %

O_s = oxygen supplied

O_u = oxygen used.

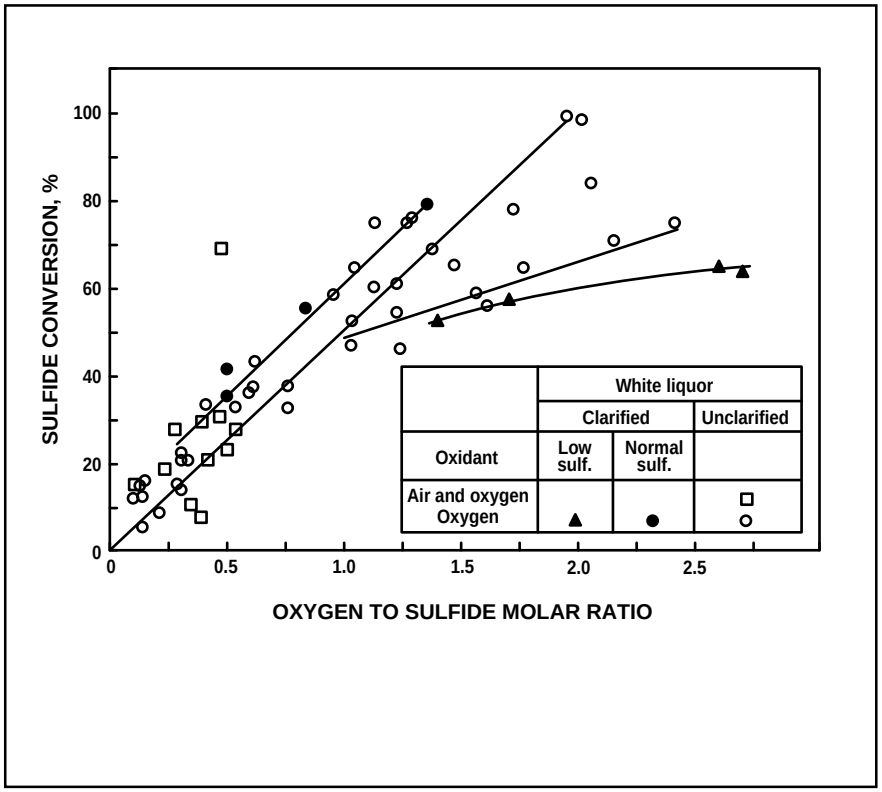
Chemical analyses on the feed and oxidized white liquor samples allowed calculation of the oxygen use from the stoichiometry illustrated in Table I.

Factors affecting sulfide conversion

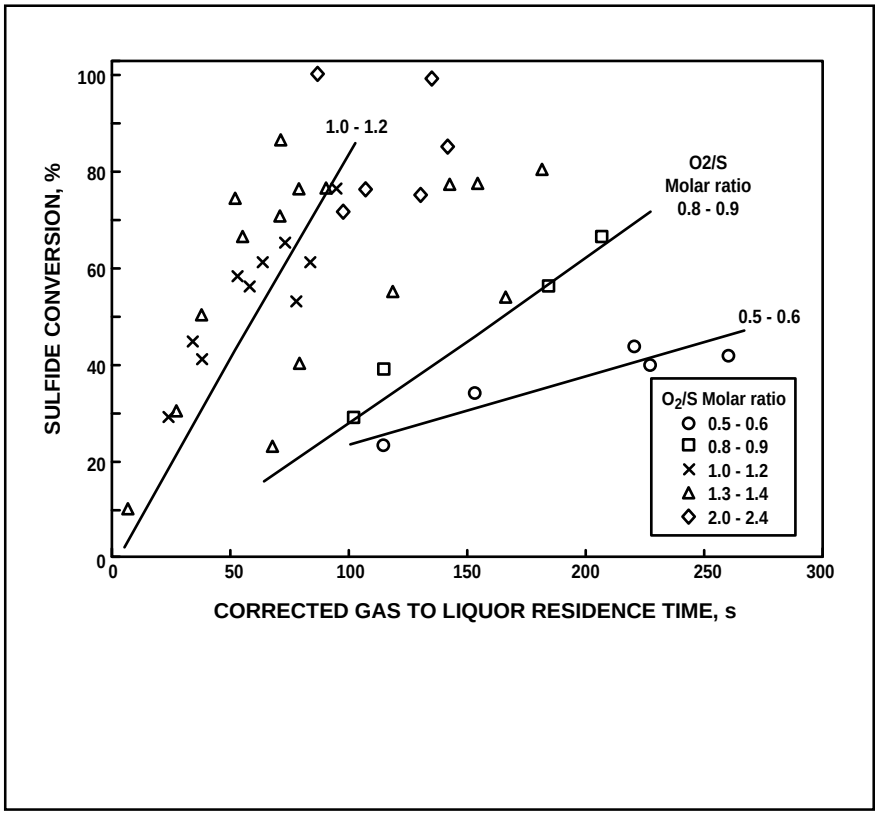
The stoichiometric oxygen to sulfide molar ratio for conversion of sulfide to thiosulfate is 1.0. **Figure 2** indicates that the conversion of sulfide increased linearly with the oxygen to sulfide molar ratio up to a value of 0.8–1.2 when using either pure oxygen or an air and oxygen mixture as the oxidant gas. With increasingly higher mole ratios using oxygen only, sulfide conversion efficiency was erratic. For this reactor, most of the highest conversions were in the 65–90% range. In two runs, sulfide conversion reached a high of 96–100%, but oxygen to sulfide molar ratios of approximately 2 were necessary to achieve almost complete oxidation. High gas flow rates with oxygen supply greater than stoichiometric were apparently required for complete oxidation to thiosulfate under the conditions in these trials.

The noticeable variability in the data at high gas to liquid flow ratios results from poor oxygen mass transfer due to insufficient gas and liquid mixing, reduced oxygen solubility, or both. In barrel and stop watch flow checks, liquor flow was erratic under these conditions with gas pockets punctuating periods of liquor flow. In pilot plant studies of gas mixing in pulp suspensions *(9)*, there was segregated flow when the gas to liquor volume ratio exceeded 0.49. With an oxygen to sulfide molar ratio of 1.0, the gas to liquor volume ratio at reactor inlet conditions was approximately 1.4. The gas to liquor volume ratio at each injector would be near 0.47 assuming all the gas reacted between injection points. Another possible source of variability in the data is the temperature increase accompanying oxidation. This is proportional to sulfide con-

2. Effect of the molar ratio of oxygen to sulfide on sulfide conversion using pure oxygen and mixtures of air and oxygen as the oxidant gas



3. Sulfide conversion vs. corrected residence time for increasing molar ratios of oxygen to sulfide using oxygen only



II. Changes in liquor composition upon oxidation with air and oxygen or pure oxygen in the pilot plant pipeline reactor

Run no. and conditions	*Sample point*	*Sodium sulfide, Na_2S, g Na_2O/L*	*Sodium thiosulfate, $Na_2S_2O_3$, g S/L*	*Sodium sulfate, Na_2SO_4, g S/L*	*Sodium polysulfide (PS), Na_2S_x where x = 2–6, g S/L*	*Na_2S + $Na_2S_2O_3$ + Na_2SO_4 + PS, g S/L*
58 (Air and oxygen)	S1	39.3	5.0	1.8	0.6	27.7
O_2/S molar ratio: 0.5	S2	38.2	5.2	1.9	1.0	27.8
Inlet pressure: 1070 kPa	S3	33.6	6.6	1.7	1.7	27.4
Retention time to S6: 90 s	S4	31.6	7.4	1.7	2.1	27.5
	S5	28.1	8.9	1.8	2.9	28.1
	S6	24.5	10.0	1.8	3.7	28.2
97 (Oxygen only)	S1	39.1	3.1	1.7	0	25.0
O_2/S molar ratio: 0.9	S4	27.4	5.8	3.2	0.3	23.5
Inlet pressure: 1120 kPa	S6	18.4	8.7	3.3	1.5	23.0
Retention time to S6: 131 s						
66 (Oxygen only)	S1	36.3	4.8	1.9	1.2	26.8
O_2/S molar ratio: 1.2	S4	16.1	11.3	3.3	0.8	23.7
Inlet pressure: 1050 kPa	S6	14.2	13.5	3.5	0.7	25.0
Retention time to S6: 64 s						
20 (Oxygen only)	S1	34.5	6.4	2.0	1.1	27.3
O_2/S molar ratio: 1.4	S4	17.1	12.8	2.6	0.7	24.9
Inlet pressure: 1090 kPa	S6	10.5	15.8	2.9	0.6	24.7
Retention time to S6: 90 s						

version. As the oxygen to sulfide molar ratio increased, the temperature rise through the reactor up to 40°C increased markedly. If the chemical reactions are very fast, the oxygen mass transfer rate would limit the total oxidation rate. As the solubility of oxygen in white liquor decreases with increasing temperature, changes in the operating temperature could affect the oxidation efficiency. Evidence presented in a previous paper *(7)* also indicated that liquors produced by oxidation under pressure were metastable. Upon acidification, polysulfides formed probably by rearrangement of various sulfur anions. It is possible that these side reactions or simple polysulfide reversion at high temperatures significantly reduced the total rate of sulfide conversion. Increased oxygen to sulfide ratios therefore led to large temperature increases. These increases reduced oxygen solubility and increased the oxygen demand exerted by competing side reactions.

To assess the effect of lime mud on white liquor oxidation under pressure, two series of trials used clarified liquor containing less than 100 ppm of suspended solids. Figure 2 also illustrates the results of these trials. At the same sulfidity, clarified and unclarified white liquor oxidized with equal efficiency. Caustic enriched, clarified white liquor of low sulfidity oxidized less efficiently than white liquor at normal sulfidity containing lime mud. This was likely due to the reduced concentration driving force. These trials and further laboratory tests at atmospheric pressure have shown that lime mud does not significantly affect the kinetics of oxidation except to increase the selectivity of the oxidation reaction for polysulfide formation *(7)*. Earlier trials in the pipeline reactor demonstrated that increased selectivity for production of polysulfide resulting from the presence of lime mud was lost when the reaction was carried out at high temperature and pressure. Even with very high de-

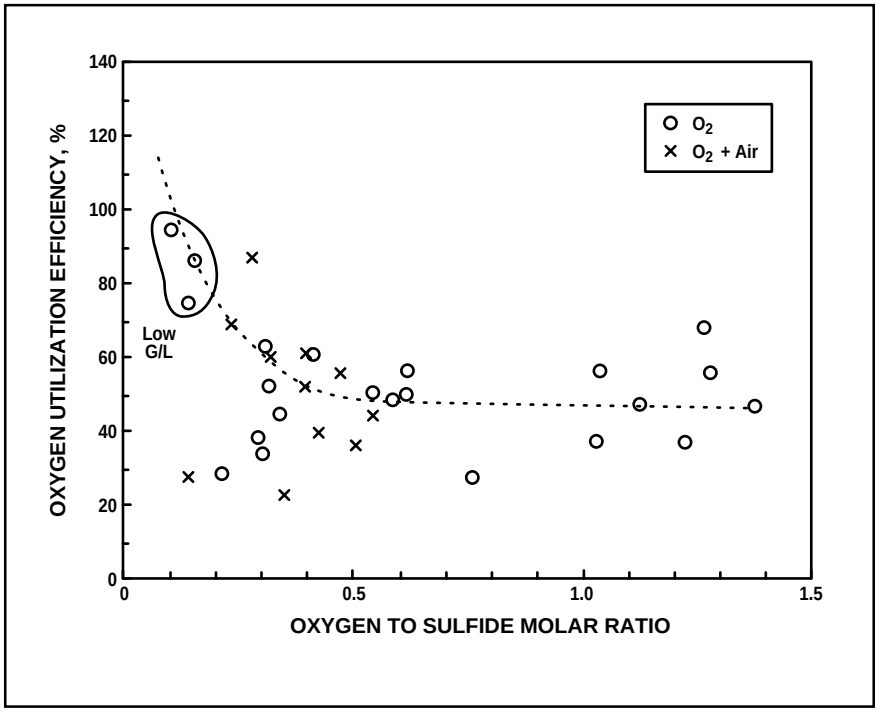
grees of sulfide conversion, **Table II** shows that thiosulfate was the primary oxidation product in these pilot plant trials *(7)*. Very little sulfate (1.6 g/L as S, maximum) formed in contrast to results reported for another pressurized oxygen oxidation system *(4)*. While increasing the operating pressure from 500 kPa to 1200 kPa (60 to 160 psig) should have increased the rate of oxygen mass transfer and resulted in higher oxidation rates, such a clearly identifiable trend did not occur due to wide scatter in the experimental data. Pressure did not affect the products of the oxidation reactions *(7)*.

To determine the effect of retention time, **Fig. 3** shows a plot of sulfide conversion in trials with and without lime mud as a function of the corrected residence time. The corrected residence time came from gas and liquor flow rates using the changes in liquor sulfide content to estimate oxygen consumption and average flow rates between sample points. This assumes that all the consumed sulfide converted to thiosulfate using one mole of oxygen per mole of sulfide. Since the sulfide could also form polysulfide with a lower oxygen consumption, this may overestimate oxygen consumption and retention time. Analyses of pilot plant samples from trials with lime mud present, however, indicated that little true polysulfide forms during oxidation under pressure *(7)*. This is particularly true when the oxygen to sulfide molar ratio exceeds 0.6 as Table II shows. Retention time estimates are therefore reasonable. The ideal gas law allowed correction of gas volumes for pressure changes through the pipeline reactor.

Fig. 3 illustrates that increasing the oxygen to sulfide molar ratios from 0.5 to 1.2 consistently increased the rate of sulfide conversion. At an oxygen to sulfide molar ratio between 1.3 and 2.0, results became very erratic as poor gas and liquid mixing began to affect reactor performance seriously. The highest oxidation rates consistently occurred at oxygen to sulfide molar ratios near 1.1 (0–20% excess oxygen). Extrapolation of this curve predicts that retention times of approximately 3 min will be necessary for more than 90% oxidation efficiency at an oxygen to sulfide molar ratio close to stoichiometric. With these results, a retention time of 4.0–6.0 min with multiple spargers (6–10) to ensure good gas and liquid mixing should allow over 90% sulfide conversion at oxygen to sulfide molar ratios near 1.0. Pump cavitation problems prevented tests at lower liquor flow rates. It was not possible to confirm the predicted conditions necessary for nearly complete oxidation. At higher oxygen to sulfide molar ratios, complete sulfide oxidation occurred with retention times as low as 80 s. Results at these high gas flow rates were erratic, however, due to poor gas and liquid mixing.

Liquor temperatures increased as much as 40°C during runs in which sulfide conversion exceeded 80%. If the oxidized white liquor did not go directly to the oxygen delignification stage, a pressurized storage tank or liquor cooling before storage would be necessary to prevent flashing.

4. Effect of molar ratio of oxygen to sulfide on oxygen utilization efficiency using pure oxygen and mixtures of air and oxygen



Oxygen utilization efficiency

Figure 4 shows that oxygen utilization was greatest at low gas to liquid volume ratios. This is equivalent to low oxygen to sulfide mole ratios. These low ratios naturally gave low sulfide conversions of less than 20%. Oxygen utilization efficiency decreased rapidly with increasing oxygen to sulfide molar ratios and remained approximately constant at 40–50% at ratios above 0.4 under the conditions used in these pilot trials. If the oxygen and sulfur reaction is fast, as Fig. 3 suggests, then the decline in oxygen utilization efficiency with increasing gas to liquid volume ratios is primarily a reflection of poor gas and liquid mixing efficiencies. For a given oxygen to sulfide mole ratio, addition of feed gas either as pure oxygen or as an air and oxygen mixture did not seem to have significant impact on the oxygen utilization efficiency. Results with air and oxygen mixtures are, however, more erratic than those

with oxygen alone. The larger gas volumes that must mix with liquor in the air and oxygen trials create gas and liquid mixing problems at much lower oxygen to sulfide molar ratios.

Conclusions

From the work presented in this paper, it is possible to draw the following conclusions:

- The pipeline reactor is an effective tool for white liquor oxidation, since oxidation under pressure proceeds much more quickly than oxidation at atmospheric conditions. Retention times of at least 3 min appear necessary for complete oxidation at oxygen to sulfide molar ratios close to stoichiometric (1.0).
- Increasing oxygen to sulfide molar ratios decreased the retention times necessary for sulfide conversion. Complete conversion of sulfide to thiosulfate occurred with retention times as low as 80 s using oxygen to sulfide molar ratios near 2.0. Much longer retention times would be necessary to convert the sulfide to sulfate. Results at high oxygen to sulfide molar ratios greater than 1.3 were erratic due to poor gas and liquid mixing.
- Lime mud does not significantly affect the kinetics of oxidation in a pressurized pipeline reactor. Clarified white liquor can oxidize as effectively and as quickly under pressure as white liquor containing lime mud.
- Pressure had little effect on the rate of reaction over the 500–1200 kPa range used in these trials.
- Oxygen utilization efficiencies decreased rapidly due to poor gas and liquid mixing as the oxygen to sulfide molar ratio increased.
- An on-line serpentine reactor would appear to offer a low cost alternative to conventional stirred-tank oxidation using air. Nonplugging spargers, multiple (6-10) gas injection points, and a retention time of 4-6 min would be necessary for near complete sulfide oxidation at oxygen to sulfide molar ratios close to stoichiometric. The lower capital costs for an in-line reactor would be partially offset by higher operating costs due to the need to use oxygen in this reactor. TP

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