

ABSTRACT

The prototype mill-scale installation of a new, low-cost process for the production of polysulfide (PS) liquor is described. The system was retrofitted into a kraft mill by modifying only one of the mill's four causticizers. Batch trials were conducted using two different impellers—with oxygen, oxygen–nitrogen mixtures, and air—to convert a portion of the sodium sulfide in white liquor to PS. The mill trial results were very similar to those obtained in the laboratory using samples of the mill's green liquor and reburtn lime.

Using small amounts of manganese to improve the process selectivity with oxygen, over 7 g/L of PS (as sulfur) was produced with only 45 min retention time. Using air, 6.8–8.4 g/L of PS were produced in 90–120 min. Process liquor and lime analyses indicated that the added Mn stayed with the lime mud and was retained in the lime cycle. The added Mn caused no operating problems in recaust. Numerous batch tests were completed with each gas to optimize process conditions and to develop engineering data that will facilitate effective process control and process installation in additional mills. PS liquors produced in the batch trials were used in pilot-plant pulping trials that confirmed the expected yield increases relative to conventional kraft pulping.

Application:

Polysulfide liquor can be used in traditional kraft cooking to either increase production or lower organic load in the effluent. This paper outlines a method for effectively producing polysulfide liquor in an existing recausticizing line.

THE BENEFITS OF USING polysulfide liquor in the kraft pulping process have been known for at least 30 years (1). The presence of polysul-

Mill-scale implementation of Paprican's process for polysulfide liquor production in kraft mill causticizers, Part 1: Batch trials and process optimization

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fides in the cooking liquor permits an increase in the pulping yield at a given blow kappa number (1–3) and/or a reduction in the pulp kappa number from the digester without a loss in yield (3, 4).

A major impediment to recycling bleach plant effluents to the kraft recovery system is the additional load of organic material that must be processed in the recovery boiler. About 70% of recovery boilers in North America are running at full thermal capacity and cannot accommodate additional load. Using polysulfide (PS) liquor would reduce the thermal load on the boiler from pulping (5). This could allow some organic material from bleaching or oxygen delignification to be accommodated in the mill's chemical recovery system without reducing pulp production capacity. Polysulfide pulping thus provides the kraft pulping industry with a flexible tool for reducing effluent discharge, while at the same time providing economical benefit through savings in the consumption of wood (5) or bleaching chemicals.

Sodium polysulfides can be produced by adding sulfur to white liquor (WL). Since this would upset the sodium/sulfur balance in the mill, this method of PS production cannot be used, except possibly for short-term trials (4). Sodium polysulfides may also be produced by oxi-

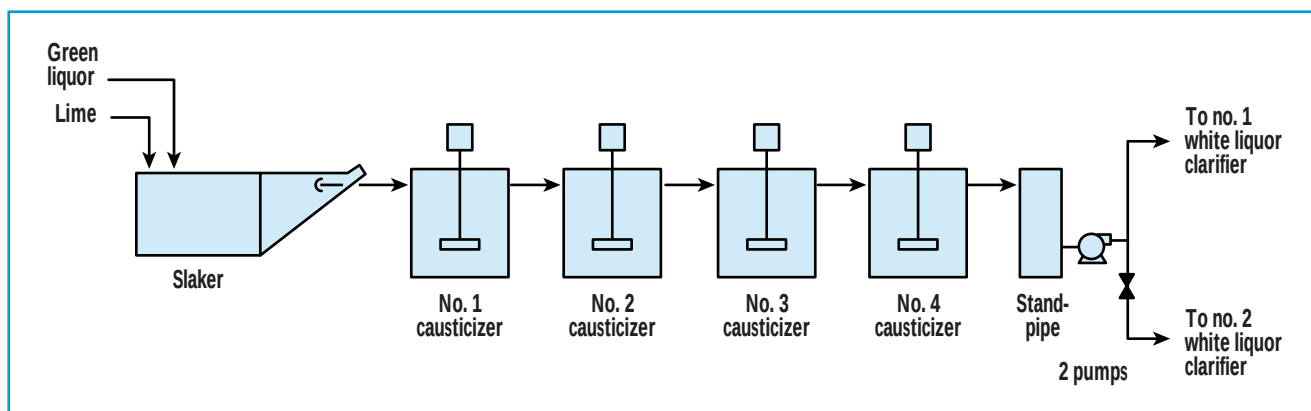
dizing the sodium sulfide in the normal kraft cooking liquor (white liquor) using air or oxygen (6–9). Since sodium thiosulfate is also produced as a coproduct, a successful process must have enhanced polysulfide production and limited thiosulfate production (e.g., selectivity must be high). To achieve a high selectivity, a catalyst must be used during the oxidation reaction (6–9).

The new Paprican polysulfide technology (PAPRILOX™) is based on the discovery that the lime mud found in a typical mill's causticizers is an extremely good PS catalyst. Extensive laboratory (10) and pilot-plant (11) trials have established that high selectivity can be achieved and that either air or oxygen can be used. It has also been discovered that the addition of a small amount of manganese dioxide (MnO_2) will enhance the formation of PS (10, 11).

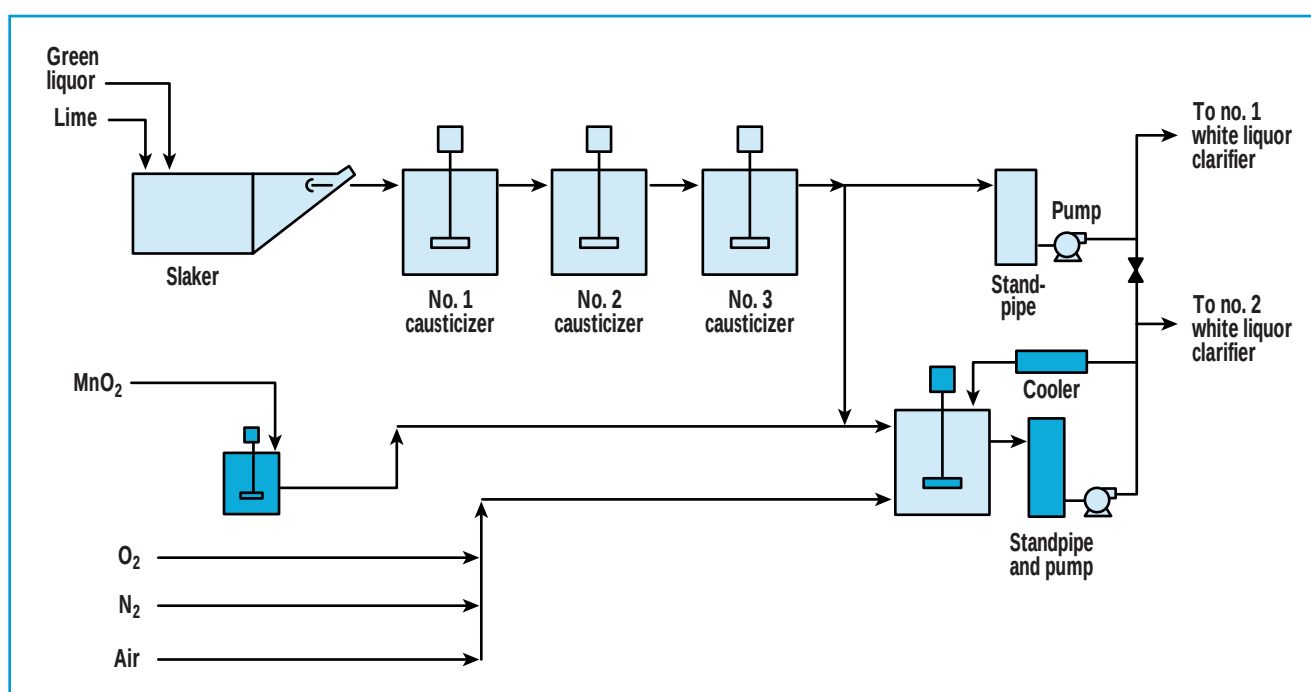
With Paprican's discovery, a process can now be retrofitted into the existing causticizing system of a pulp mill rather than requiring a completely new unit operation. The process has the benefits of low capital investment (11) and simple operation.

BACKGROUND

Laboratory testing (1:100,000 scale) and pilot trials (1:100 scale) have already established the initial operat-



1. Present Eddy Forest Products causticizing system



2. Eddy Forest Products—full-scale trial

ing parameters needed for the process to be successful. The next step, which is reported in this paper, was demonstration trials using a full-scale (1:1-scale) causticizer. These trials were required to investigate and finalize the equipment configuration and operating parameters under actual mill production conditions.

The demonstration trials involve a three-phase program. The first phase was a series of individual batch tests designed to investigate and optimize the process parameters and equipment selection. Phase two is a 2–3-month trial designed to

demonstrate and to study the impact of using polysulfide for pulp and paper production at the mill. The fact that the partner mill produces several grades of specialty papers on site will allow complete evaluation of the impact of PS on both paper machine operability and final paper properties. In the third phase, the polysulfide system will be modified to become a permanent installation.

The main questions that needed to be answered in producing high-quality PS liquor in a full-scale system, which could not be answered in the laboratory or pilot plant, are as

follows:

- What is the impact of full-scale liquor height on the selectivity and yield of the desired reaction?
- How consistent is the operation under full-scale mill conditions?
- What is the required gas flow rate and distribution?
- What is the amount of makeup MnO_2 catalyst needed, i.e., what is the recovery level in full-scale continuous operation?
- Are the proposed impeller designs and agitator speeds adequate to facilitate polysulfide gen-

eration without impairing lime mud quality?

- What are the effects of polysulfide on fine and specialty paper quality in mill operation?

PROCESS DESCRIPTION

The Eddy Forest Products Ltd. (EFPL) causticizing system consists of four causticizers in series after the slaker, where reburnt lime is added to green liquor to produce an 8–10% slurry (Fig. 1). Each causticizer is an agitated tank, 18 ft in diameter by 16 ft high, overflowing to the next in line. To produce PS with the Paprican process, one or more of the causticizers are converted to a PS reactor by adding a larger agitator, modifying the internals to permit gas distribution under the new agitator, and sealing the causticizer to prevent gas leaks. For the Phase 1 batch trials, EFPL converted only its No. 4 causticizer to allow isolation from the rest of the recaust line (Fig. 2). For these trials, the system allowed sparging with either oxygen, air, or oxygen–nitrogen mixtures.

Since the gas bubbles lower the existing slurry density, the agitator speed must be increased to prevent solids settling. The agitator's other main purpose is to provide intimate contact between the gas bubbles, lime particles, and white liquor. A large, variable-speed motor and drive were installed to allow us to evaluate different impellers and the effect of increased mixing speed on polysulfide formation and selectivity. A small MnO_2 handling and slurring system would normally be installed, but for the batch trials, a temporary drum system was used.

Since a conventional causticizer operates very close to its liquor boiling point, a liquor cooling system was required to remove the heat of reaction. This required a new pump tank and the use of an existing transfer pump and heat exchanger, plus the installation of local instrumentation.

After successful batch trials were completed in February 1998, we began the design of a continuous system that reuses the converted polysulfide reactor. During the continuous trials, the modified No. 4 causticizer will provide sufficient polysulfide liquor (approx. 50% of WL capacity) for the mill's batch digesters only. The mill expects to split the liquor flow after the No. 2 causticizer, with one half going to the No. 3 causticizer and the other half going to the No. 4 causticizer or polysulfide reactor. Liquor from each of these causticizers will then be pumped to separate white and orange (polysulfide) liquor clarifiers. With half the white liquor going to the No. 4 causticizer, the liquor retention time in the PS reactor will be about 55 min.

Note that the process equipment that is downstream of the No. 4 causticizer will now contain polysulfide liquor (termed *orange liquor* because of its color), e.g., the clarifier/storage tank will now contain orange liquor. The mill will now have both "white liquor" and "orange liquor" lines.

Experimental program

Laboratory tests. Samples of green liquor and reburnt lime were sent from the mill to Paprican in late 1995 and early 1997. These samples were used in laboratory tests to establish the expected optimum process conditions. This allowed a preliminary estimate of the MnO_2 addition rate and retention time necessary in the full-scale causticizer to produce polysulfide liquors suitable for cooking. Additional green liquor and reburnt lime samples were also taken during the full-scale mill trials. These were used in laboratory tests to provide a direct comparison to the full-scale test results.

In all of the laboratory tests, a Rushton or disc impeller was used for liquor, lime mud, and gas mixing. The gases were sparged into the

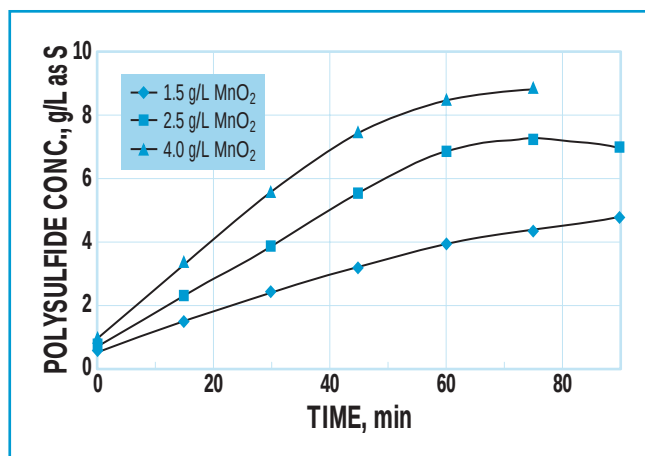
reactor below the impeller using a sintered metal sparger containing 0.2- μm pores. The impeller was operated at a rotational speed calculated to produce a tip velocity comparable to that observed in the full-scale causticizer.

In all of the lab tests, 55 g of the mill's reburnt lime were added to an 800-mL sample of the mill's green liquor at 90–95°C. The solution was slaked for 15 min and then causticized for a further 45 min before adding the desired dose of MnO_2 and starting to sparge with oxygen or air. Samples for analysis were withdrawn every 10–15 min. Further details on the laboratory test procedures are provided in an earlier publication (10).

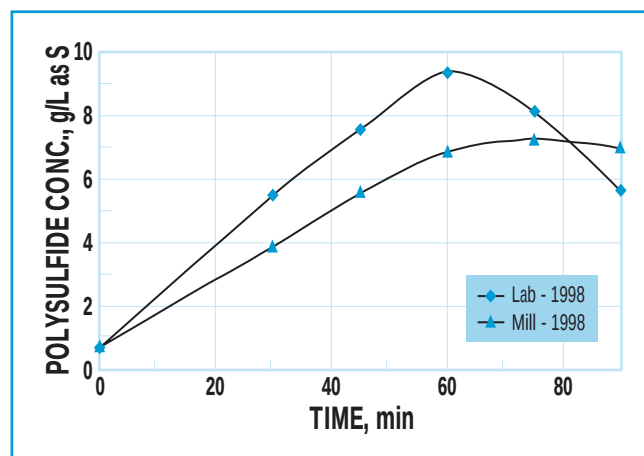
Full-scale trials. The mill's No. 4 causticizer was taken out of service in late 1997 and converted to serve as the polysulfide reactor over the next few months. The mill ran without it until the batch PS trials began in February 1998. Although not required for production, when each batch test was completed, the PS reactor was returned to service as a causticizer.

Oxygen was supplied from a liquid storage tank mounted on a mobile trailer complete with ambient air vaporizers and a pressure-reducing station. Also located adjacent to the trailer was a liquid nitrogen storage tank with vaporizers and a pressure-reducing station. The entire assembly was installed close to the causticizer building.

For the Rushton turbine agitator, oxygen was added in about equal volumes to four injectors located close to the bottom of the causticizer and underneath the turbine. The oxygen was added through spring injectors that were (12) designed to open when oxygen pressure was applied and to close when the pressure was lowered. This was to prevent a backflow of the slurry into the oxygen supply pipes, which could eventually



3. Polysulfide generation using Rushton agitator with oxygen—effects of manganese dioxide concentration



4. Polysulfide generation for E.B. Eddy: Laboratory vs. mill-scale trials (2.5 g/L MnO₂-oxygen)

lead to blockage. A contoured agitator was then installed to determine the effects of impeller type, mixing speed, and lower power requirements on the PS production rate and process selectivity. Oxygen, air, and oxygen-nitrogen mixtures were added through a set of four different nozzles.

To begin a batch test, liquor flow to the No. 4 causticizer (PS reactor) was stopped by opening the bypass from the No. 3 causticizer directly to the standpipe and closing the valves isolating the No. 4 causticizer. Immediately after isolating the reactor, a sample of liquor was withdrawn from the causticizer, via the cooling circulation loop, for settling tests and analysis. The required dosage of MnO₂ was slurried with water in the preweighed barrels and pumped into the No. 4 causticizer using an air-driven pump. Cooling water was typically used on the liquor heat exchanger to lower the reactor temperature to about 90°C. After the manganese was added, a second sample of liquor was withdrawn from the causticizer for settling tests and analysis. The reactor mixing speed was set, and gas flow (oxygen, mixed oxygen and nitrogen, or air) to the causticizer was initiated. This is time zero in the PS-vs.-time graphs or in estimating retention time requirements for PS liquor production. The gas flow was fine-tuned and set to

the desired flow rate within 5 min of initiating gas flow. Samples of liquor were then taken from the causticizer for analysis every 15–30 min. Liquor recirculation flow to the PS reactor and cooling water flow to the heat exchanger were generally adjusted during the oxygen runs to keep the reactor temperature below 99°C. When air was used for liquor oxidation, no cooling was required.

Oxygen utilization was measured by the Helium Tracer Test (13). This consists of continuously adding a measured volume of helium gas to the oxygen gas downstream from the pressure-reducing station. As helium does not react in the causticizer and has a very low solubility, it stays with the unreacted oxygen and is vented. By measuring the helium and oxygen concentrations in the vent gases, and from knowledge of the helium flow rate, it is possible to calculate the oxygen vented. Knowing the oxygen flow added, it is possible to determine the oxygen utilized. This method has been widely used to measure oxygen utilization in the oxygen extraction and delignification stages (14).

Once the batch was complete, a third liquor sample was taken for additional settling tests. The valves isolating the No. 4 causticizer were opened, and the causticizer was returned to service. When two batch tests were run on the same day, at

least 90 min (i.e., three times the causticizer's retention time) was allowed between batches. This ensured that the PS liquor from the first batch was effectively flushed from the reactor before starting the next.

Batch trials were conducted to examine the effect of impeller type, mixing speed, gas sparging rate, and manganese dioxide and oxygen concentrations on the reaction rate, selectivity, and oxygen utilization.

Sample analyses. Liquor samples from both the laboratory and full-scale trials were first filtered to remove suspended lime mud particles. The polysulfide concentration in each sample was determined using a gravimetric method that has been shown to agree well with the more commonly employed chromatographic and titrimetric methods, when synthetic white liquor samples are tested (15). However, with oxidized liquors, the gravimetric results were sometimes higher than those obtained by titrimetric methods, particularly at high polysulfide concentrations. The accuracy of various methods for determining polysulfide is currently under investigation. The sodium carbonate, sodium hydroxide, and sodium sulfide concentrations in each liquor were determined using an automatic titrator and a modified version (15) of the standard ABC test (16).

Results and discussion

Earlier laboratory tests using samples of reburnt lime and green liquor, from the Espanola mill, showed that it was possible to produce 6.5–7.8 g/L of polysulfide (PS) in 30–45 min when sparging oxygen. With air, 6.6–8.9 g/L of PS (as sulfur) were produced with retention times of 60–90 min. The use of air instead of oxygen approximately doubled the retention time requirements for any given concentration of polysulfide. Both the selectivity and peak PS concentrations obtained with a given liquor were increased when air was employed. The current commercial processes for polysulfide liquor production, such as the Moxo process (6, 7) and the Chiyoda process (8, 9), typically produce 5.5–7.0 g/L of PS (17). This is with selectivities of 60–70% using air as the oxidant (17).

Effect of MnO_2 dosage

In the initial pure oxygen full-scale trials (No. 1 through 4), we evaluated the Rushton (disc) impeller, which is similar to that employed in both the pilot (11) and laboratory (10) tests. When the MnO_2 dosage was increased from 1.5 to 4.0 g/L in a series of three tests, the peak PS concentration increased from 4.8 to 8.8 g/L (Fig. 3). The rate of PS production and the selectivities also increased as the MnO_2 dosage was increased. In the remaining full-scale trials, the MnO_2 dosage rate was kept constant at 2.5 g/L.

In laboratory tests with green liquor and reburnt lime samples taken during the full-scale trials, by adding 2.5 g/L of MnO_2 , we were able to produce 6.0–9.3 g/L of PS in 35–60 min (Fig. 4). In the full-scale trials, also illustrated in Fig. 4, we were able to produce 6.0–7.2 g/L PS in 50–70 min. At any given PS concentration, the selectivities observed in the full-scale reactor, when using pure oxygen, were slightly lower than those observed in the laboratory.

Using air, we were able to produce peak PS concentrations of up to 11 g/L in both the laboratory and the full-scale reactor. We found that 135 min were required in the laboratory, while 210 min were required in the full-scale reactor. Using air, the selectivities observed in the laboratory and full-scale reactors were nearly identical at any given PS concentration. The shorter retention time requirements obtained in the laboratory, using both air and oxygen, probably reflect the better gas dispersion, which resulted from the use of sintered metal spargers. The lower peak PS concentrations observed in the full-scale oxygen trials reflect both less-efficient gas mixing and the effect of higher oxygen partial pressure due to the increased liquid height. Earlier pilot-plant trials in a pipeline reactor (18) similarly showed that the peak PS concentration was decreased as the oxygen or reactor pressure was increased.

Impact of impeller type

In the next series of full-scale tests, the use of a contoured impeller (designed specifically for improved gas-liquid mixing) was evaluated with pure oxygen. We found that the mixing speed and gas flow rate had little effect on the rate of PS formation when using this impeller. Also, with either higher mixing speeds or gas flow, the peak PS concentration and the process selectivity both decreased slightly. At optimum conditions, the performance of the contoured impeller was very similar to that of the Rushton, or disc, impeller. However, the contoured impeller had a much lower power requirement than the Rushton impeller, and the contoured unit's power requirements were much less sensitive to the gas flow rate as well. For these reasons, the contoured impeller was used in the rest of the full-scale trials.

Impact of oxygen concentration

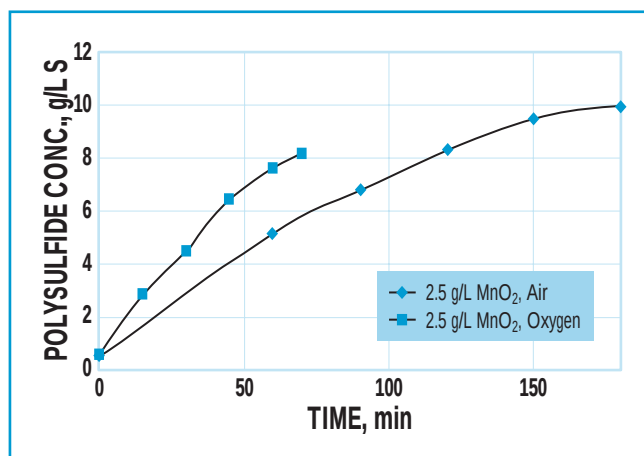
E.B. Eddy is currently installing an ozone stage in its bleach plant as part

of a modernization program. The company plans to use the off-gas from the ozone stage for polysulfide liquor production. This ozone vent gas will contain 80–85% oxygen by volume. To evaluate the effect of oxygen purity on the retention time requirements and process selectivity, we ran a series of oxygen concentration trials. In these trials, nitrogen was used to dilute pure oxygen to concentrations down to 64%. The absolute oxygen flow rate (standard liters per minute) was kept nearly constant through this series of tests with the contoured impeller. As expected, dilution of the oxygen increased the peak PS concentrations and selectivity, relative to those obtained when using pure oxygen. Quite surprisingly, however, with low dilution factors, the retention time requirements were very similar to, or even slightly lower than, those required when using pure oxygen. Using a 74% oxygen/26% nitrogen blend, with only 45 min retention time, we were able to produce 8.0 g/L of PS with good selectivity. With the oxygen diluted to 64%, it took 75 min to produce 8.1 g/L of PS.

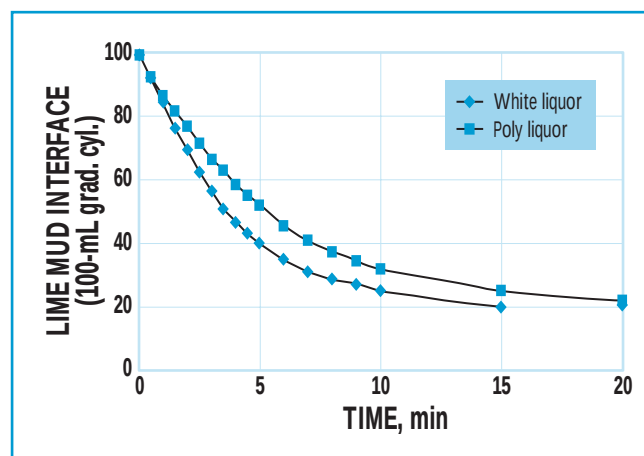
One method to control the oxygen concentration in the gas mixture going to the polysulfide reactor is to use an air aspirator (eductor) with the compressed ozone off-gas as the motivator. By adjusting the oxygen concentration, we can maintain the peak PS production efficiency when liquor flow rates, and subsequent retention times, are varied as a result of recaust operating problems or production rate changes.

Air trials

In the final series of trials, the use of air with the contoured impeller was investigated. As in the oxygen trials with both the Rushton and contoured agitators, increasing the mixing speed had a small positive effect on the rate of PS production. Higher speed also decreased the selectivity. This was probably a result of



5. Polysulfide generation with air and oxygen in full-scale trials



6. Lime mud settling rates using Rushton agitator—effects of oxidation. Scale: 1.83 cm per 10-mL increment.

increased mass transfer to the liquor and higher dissolved oxygen. The theory suggested is that thiosulfate is a reaction with dissolved oxygen in the liquor, and PS is a reaction at the catalyst surface with gaseous oxygen. Increasing the air flow rate to an apparent optimum increased the rate of PS production and the peak PS concentrations. It is likely that the contoured impeller can only effectively disperse a certain gas flow, and air flow rates in excess of this optimum are counterproductive. Near the optimum air flow rate, 6.8–8.4 g/L of PS were produced in 90–120 min (see Fig. 5). The retention times required to produce a given concentration of PS when using air were, thus, about twice those required when using oxygen. We predicted this from both the earlier laboratory (10) and pilot-plant (11) tests. The use of air also eliminated the need to recirculate and cool the liquor in the reactor. As heat lost in saturating the vent gas with water vapor exceeded the heat of reaction, the reactor temperature typically decreased slightly during the air runs.

Typical operating parameters and product liquor analyses obtained when using oxygen, oxygen–nitrogen mixtures, or air for liquor oxidation are summarized in Table I.

Oxygen utilization efficiencies

Oxygen utilization efficiencies (i.e.,

Parameter	GAS USED FOR WHITE LIQUOR OXIDATION			
	Initial white liquor	Pure oxygen	74% O ₂ /26% N ₂ (by vol.)	Air
Retention time, min	-	45	45	120
Oxygen utilization efficiency, %	-	81–91	77–88	>65
Na ₂ S, g/L as Na ₂ O	34.0	15.6	12.3	12.9
NaOH, g/L as Na ₂ O	68.0	78.1	82.7	87.4
Active alkali, g/L as Na ₂ O	102	93.7	95.0	100.3
Total titratable alkali, g/L as Na ₂ O	110	106.1	102.8	108.0
Sulfidity, % on TTA	30.9	14.7	12.0	11.9
(% on AA)	(33.3)	(16.6)	(12.9)	(12.9)
Polysulfide, g/L as S	0.5	6.5	7.8	8.4

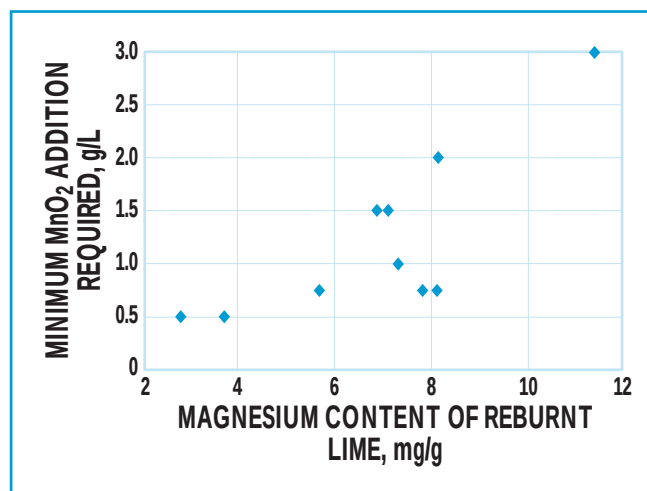
1. Typical operating parameters and product polysulfide liquors resulting from the use of different gas mixtures in the full-scale batch trials

how much of the oxygen added is actually consumed in the reactor) during these trials were estimated by two techniques. In the first method (13), we injected helium into the feed gas and used the measured changes in helium concentration to calculate the oxygen consumption. In the second method, we used the changes in liquor composition and reaction stoichiometry to calculate oxygen use. We then divided the calculated consumption by the oxygen mass flow rate to estimate the oxygen utilization efficiency. Both methods indicated that the oxygen utilization efficiencies in these trials were much higher than the 50% estimated

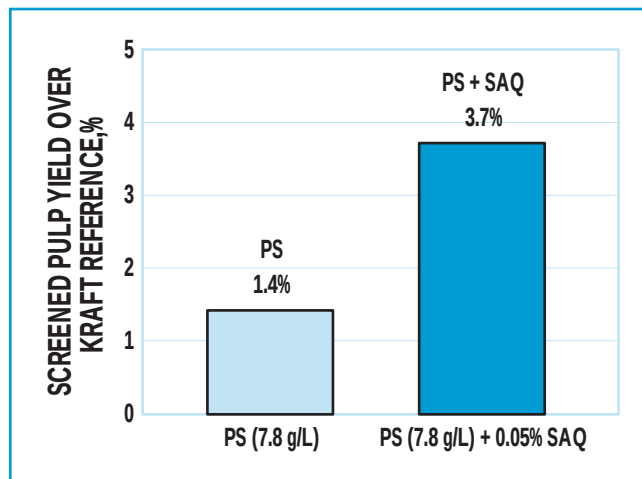
in our pilot-plant trials (11). Oxygen utilization efficiencies during the oxygen trials, the oxygen–nitrogen trials, and the air trials were estimated at 81–91%, 77–88%, and greater than 65%, respectively.

Mud settling trials

The impact of the modified impellers, liquor recirculation for cooling, and gas sparging on the lime mud settling rates was also evaluated in laboratory tests using liquor samples taken during the batch trials. We found that neither of the impellers nor liquor recirculation had a significant impact on the lime mud settling rate. Mixing speed also had only a very small effect on settling with either



7. Effect of reburnt lime magnesium content on manganese dioxide requirements for the PAPRILOX process (estimated minimum required to produce 7 g/L of PS at 70% selectivity)



8. Yield increases in pilot-plant cooks on mixed dense hardwoods

impeller. Gas sparging, however, decreased the lime mud settling rate typically by 15–20% (see Fig. 6). The decrease in lime mud settling rate is similar to that which we observed in both the laboratory and pilot-plant trials (10–20%) (10, 11). The fact that the reductions in settling rate are at the high end of the observed range is probably due to some overliming at Espanola, where the causticizing efficiencies were very high. Calcium hydroxide (present as a result of overliming) is much softer than calcium carbonate and is probably disintegrated more by gas sparging. The lime mud settling rates even after gas sparging were, however, always still in an acceptable range (1.5–2.0 cm/min) (19). The recaust operators only observed problems with white liquor clarity on one day when they were overliming (the causticity was as high as 87%).

Fate of MnO₂

Over a period of 17 days, we added about 4 metric tons of MnO₂ to the mill's lime mud system. We asked the operators to monitor the recaust system for any problem signs, such as increased dusting or other changes in their operation. To check dusting, the operators took routine samples of the scrubber slurry every 2 hours and monitored the settled solids content. As the water flow to the kiln

scrubber was generally constant, an increase in dusting would be expected to result in an increase in the slurry solids content. In the week preceding the trials, and throughout the trials, the scrubber slurry settled solids content ranged from 0.6 to 13 mL/L. While the captured solids and reburnt lime became noticeably darker throughout the trials, indicating that the added Mn was retained in the lime cycle, no operating problems were reported. This also confirms the results of a shorter-term trial conducted at a British Columbia kraft mill to determine the fate of Mn added to improve the selectivity (20).

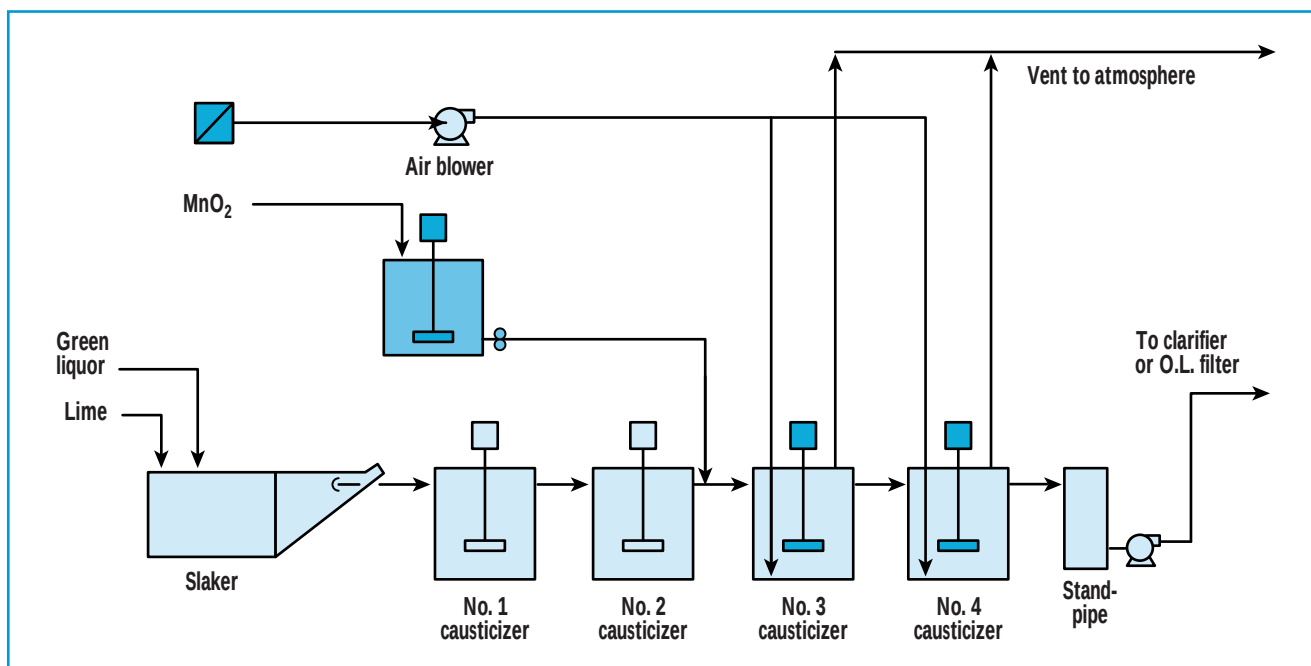
We sampled reburnt lime and scrubber slurry at E.B. Eddy before the trials began, midway through the trials, and at the end of the trials. Analyses on these samples were expected to provide an estimate of how quickly the manganese would accumulate in the lime cycle and the level of makeup that might be required under steady-state conditions. Some mechanical problems with the conveyor to one of the reburnt lime silos, however, resulted in a significant amount of lime going to landfill for a few days. As a result, we could not confirm our previous estimate of the manganese retained in the system (20).

Analyses on settled orange liquors from six of our polysulfide batch tests at Espanola showed Mn concentrations of 4.6–11.9 mg/L. This indicating again (20) that greater than 99% of the Mn stayed with the lime mud. Since the tests showed that manganese was not leaving in the white liquor or kiln dust (scrubber slurry tests), we are confident that any losses will be low.

Shortly after the batch trials were completed, the mill began to observe scale deposits in a number of areas where it previously had no apparent scaling problems. Analysis of these scales, however, established that they were not related to the polysulfide trials but more to upset conditions, such as overliming in the recaust plant.

Effect of magnesium

A unexpected trend was found when comparing the data of the magnesium (Mg) concentrations in reburnt lime samples, taken during the batch trials, to past analyses on samples from Espanola. A reburnt lime sample sent to us in 1995, for the original laboratory evaluations of our polysulfide process, contained 7,300 mg/kg or ppm of Mg. A second sample in early 1997 contained 11,400 ppm of Mg, while samples of reburnt lime taken during the February 1998 trials contained 12,000–14,500 ppm of Mg. It appears, therefore, that Mg is accu-



9. PAPRILOX™—air system

mulating in the lime cycle at Espanola. The 1997 reburnt lime sample from Espanola had the highest levels of Mg observed by Paprican's Prince George laboratory in analyses of lime samples taken from 10 kraft mills; the Mg level at Espanola is now even higher.

Our laboratory tests on green liquors and reburnt lime samples from various mills, summarized in **Fig. 7**, indicate that we need to use higher concentrations of Mn when the mill's lime contains higher concentrations of Mg. We believe that Mg acts to stabilize Mn as MnO , which is formed when MnO_2 reacts with NaHS to produce polysulfide. At this time, we are uncertain of the exact mechanism for deactivating MnO_2 by Mg. A similar reaction has been reported in hydrogen peroxide bleaching of kraft pulp (21). We found that the Mg concentration in a sample of Espanola's clarified green liquor was only 0.2 mg/L or ppm—much lower than the 2.5–16 ppm normally observed at Canadian kraft mills (22). E.B. Eddy's own, earlier Mg balances also showed that most of the Mg dropped out in the green liquor dregs. These observations lead us to suspect that the Mg in the

Espanola lime cycle may be input with the purchased lime. Analysis of some hard-scale samples taken from one of the causticizers contained more than 32% Mg [equivalent to greater than 75% as $\text{Mg}(\text{OH})_2$]. We believe this also indicates high levels of Mg in the lime cycle.

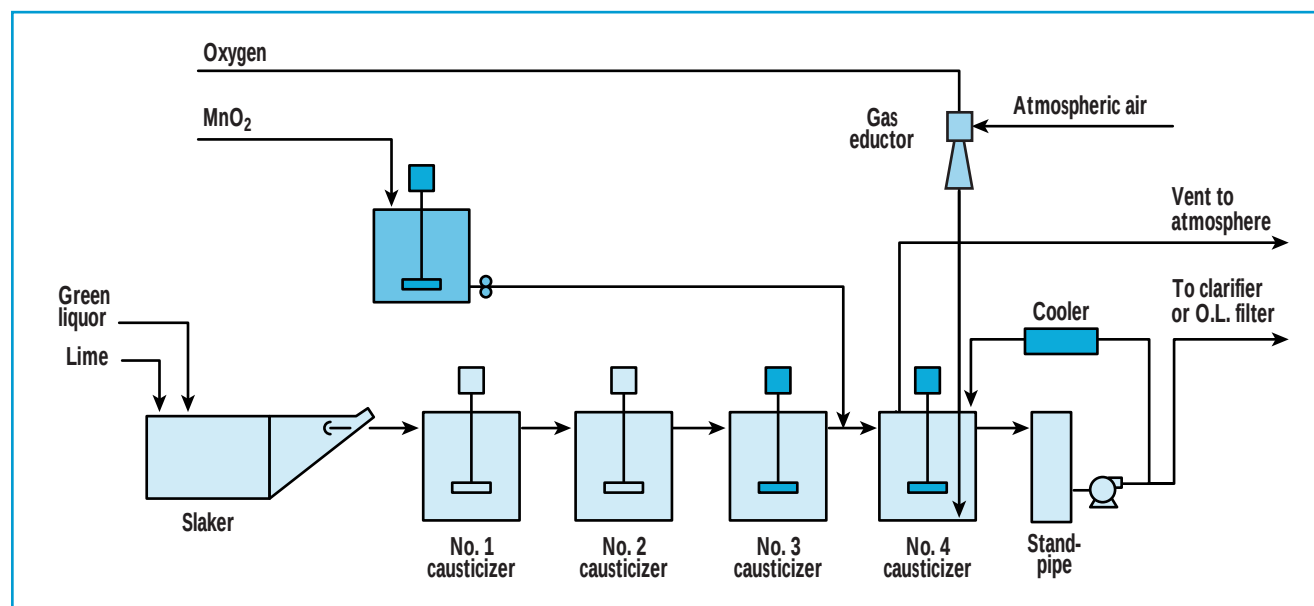
It is worth noting that besides its impact on the polysulfide process, magnesium can also cause other problems in the recaust plant. Concentrations of greater than 2% MgO in lime have been reported (23) to hamper lime mud settling and filtration; we are now seeing concentrations just over this 2% threshold at Espanola. In addition, Mg can reduce the settling properties and filterability of green liquor dregs (23, 24), causing problems in the lime kiln and with dirt in bleached pulp. It may be worthwhile to look at means, such as aluminum salt addition (25), to more effectively purge Mg from the recaust cycle. This would reduce the amount of Mn that must be used for polysulfide liquor production and avoid other potential operating problems. If the major source of Mg is makeup lime, it may be appropriate to find a new source/supplier with a lower Mg content.

Pulping results

Polysulfide liquors produced in the batch trials, and samples of the mill's white liquor, were used in pilot-plant pulping trials on chip samples from the mill. Typical results are summarized in **Fig. 8**. With a 1.4% PS charge (as S) on wood, the pulp yield, relative to a conventional kraft cook on a mixture of dense hardwood, was increased by 1.4%. This was at a typical permanganate number target of 10.5. This yield increase is similar to that which would typically result if synthetic polysulfide solutions were used for cooking (1–4, 26). Using 1.4% PS and 0.05% soluble anthraquinone (SAQ) on wood, the yield increase was 3.7%, confirming the synergistic effects on pulp yield often reported when using PS and AQ together (27).

Conceptual design and future plans

After completing laboratory, pilot-plant, and full-scale trials, we now have sufficient information to design systems for various mill configurations. One of our most important discoveries is that liquor and lime muds from different kraft mills are not the same when it comes to efficiently producing orange liquor in the causticizers. Laboratory simulations can



10. PAPRILOX™—diluted oxygen system

be used to establish important parameters, such as the initial MnO₂ concentrations, preliminary gas flows, etc. Lab trials can also be used to uncover potential anomalies that will minimize full-scale problems or to indicate when further investigations are required.

Air can be used for the polysulfide system (Fig. 9) but will typically require modifying more than one of the causticizers. The actual number of causticizers that require conversion will depend on each mill's operation and the retention time in each of its causticizers. Figure 9 shows a simplified scheme where two causticizers need to be modified. A blower package provides the required air, while an MnO₂ handling system is used to store/transport and slurry the required secondary catalyst.

The use of pure oxygen is not recommended due to lower selectivities. However, we found that diluting oxygen with air did provide another oxidant that could be used successfully. Figure 10 shows a scheme that could be used to produce polysulfide in only one causticizer. The pressurized oxygen is used with an eductor to draw in the necessary outside air for the dilution. An alternative would be to simply use instrument air if it is

available. Note that, unlike the air system, the heat of reaction must be removed using a liquor cooler.

As previously mentioned, the future plans for the Paprican PS process have been identified as phase two and phase three. At the time of writing, June 1998, the engineering to modify the batch unit into a continuous PS reactor system is almost complete. When finished, this system will provide the mill with about half of its white liquor production as orange liquor. We expect to be operating the PS process at the time of the TAPPI Pulping Conference and should be able to provide some information about continuous operations.

CONCLUSIONS

We reached the following conclusions based on our work:

- The equipment that was installed met the requirements for the batch trials, and this same equipment can be reused, with additional equipment, for the future continuous trials.
- Although there may be excessive magnesium in the lime cycle at Espanola and this required higher concentrations of manganese dioxide than originally estimated

from laboratory studies, we achieved results similar to those obtained in the laboratory trials. That is, we could produce 7 g/L of polysulfide liquor in less than 60 min.

- The time needed to produce 6–7 g/L of PS is the same, or less, for diluted oxygen (ozone vent) as it was for pure oxygen.
- To produce the PS liquor at target concentrations (7 g/L as S), the mill would require approximately one causticizer for oxygen (or diluted oxygen) and two causticizers for air.
- Manganese dioxide remained in the system, and there was only a small increase in the manganese concentration in the orange liquor product.
- The contoured agitator and the Rushton agitator both produced PS, at the same rate and selectivities, but the contoured agitator had a lower power consumption. Also, the rotational speed required to maintain the solids in suspension and produce small gas bubbles was independent of the gas flow rate when the contoured impeller was used.
- The oxygen consumption during the oxygen trials, the

nitrogen-oxygen trials, and the air trials was estimated at 81–90%, 77–88%, and greater than 65%, respectively. Oxygen consumption was much higher than in the pilot trials (50%), and thus less oxygen will be wasted by venting from the full-scale system.

- The lime mud settling rate was reduced by 15–20% as a result of gas sparging. Although slightly lower than existing settling rates, this reduction was predicted on the basis of both laboratory and pilot-plant trial results.

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The batch trials at the mill were considered by the team members to be successful, and one of the primary reasons was the cooperation that was given to us by the mill personnel. Specially notable were Nick Cefaratti and Wayne Kutschke, who provided the necessary equipment or people at very short notice. The pipefitter/welder teams always produced superior work. The operators did not complain when asked for help and often came looking for things to do in order to help us.

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