Production of polysulfide liquor in a kraft mill's causticizers

VIC ULOTH, GILLES DORRIS, RON THRING, ROB HOGIKYAN, JIM WEARING, LARRY TENCH, AND JACK AYTON

ABSTRACT

Polysulfide can be added in kraft pulping to improve the hemicellulose yield. To produce polysulfide in the mill, a portion of the sulfide in white liquor can be oxidized. Batch and continuous pilot plant trials at two kraft mills confirmed the technical feasibility of using lime mud as the primary oxidation catalyst. With oxygen and air as oxidants and with small amounts of MnO_2 added, a cooking liquor was produced with polysulfide concentrations suitable for pulping.

Application:

If the pulp yield is increased by 2%, the capital costs of the system would be paid back in 2–5 months in a kraft mill producing 1000 tons/day.

THE USE OF POLYSULFIDE LIQUOR (orange liquor) has grown in recent years. Companies have developed catalyzing agents that oxidize some of the sulfur in the white liquor to form polysulfides. The catalyzing agents eliminate the need to add elemental sulfur to kraft liquor to generate the polysulfide sulfur species (1). Mead Corp., with its Moxy Process (2, 3), and Chiyoda International (4, 5) have been active in the area of on-site polysulfide generation. Today, there are about eight mills that employ the polysulfide pulping process. All of these are in Japan and Europe, where wood costs are, or at least used to be, higher than in North America.

Of all the known processes for on-site production of polysulfide, only those that use an activated carbon catalyst have reached commercial status *(4–6)*. Activated carbon is relatively expensive, and very clear white liquor (with suspended solids of less than 5 ppm) is required with current commercial processes. The liquor must be clear to minimize the deactivation of the catalyst, to restrict bed plugging, and to limit the pressure drop across the catalyst bed *(4, 5)*.

To reduce the capital cost of currently available oxidizing systems and to find a way to avoid the use of expensive and problematic carbon catalysts, researchers at Paprican sought an alternative method of producing polysulfide liquor. Laboratory oxidation experiments *(6)* indicated that the presence of lime mud particles in white liquor could increase the formation of polysulfides. Would it be practical to use lime mud particles as an inexpensive alternative to the use of commercial carbon catalysts? Laboratory experiments indicated that lime mud did in fact represent another method for producing polysulfide liquor.

Based on these findings, Paprican developed and patented a process in which the oxidation catalyst—lime mud—is already an inherent part of the causticizing cycle *(7)*. One of the proposed approaches is to carry out the oxidation directly in a kraft mill's causticizers, where total retention times generally vary between 70 and 180 min *(6)*. Pilot plant studies were undertaken at a Paprican member company kraft mill. There were two main goals. The first was to quantify the effects of operating variables on the kinetics and selectivity of polysulfide production using lime mud as a catalyst. The second goal was to develop engineering data that would permit the design of a full-scale process.

Continuous trials were conducted at a second member company kraft mill. Results from the trials at the two mills were used to scale-up the design and to evaluate the economics of the process. Paprican's process design and economic analysis were subsequently reviewed and revised by two commercial partners selected to supply the technology to interested kraft mills. The results of these studies are summarized here.

BACKGROUND

Polysulfide stabilizes the terminal reducing groups of polysaccharides against alkaline reactions. It protects the end groups against peeling and slows the degradation of hemicellulose. The result is a higher yield at a given kappa number *(8–10)* or, as an option, a lower kappa number at a fixed pulp yield *(1, 10)*.

An increase in softwood pulp yield of about 1% can be expected for each 1% of polysulfide sulfur applied in the cooking liquor, up to a maximum of about 8% *(11)*. Let us assume that wood costs $150 per bone-dry metric ton and that the yield increases by 1.5%. We would expect savings of no less than $7.00 per metric ton of pulp in changing kraft pulping over to polysulfide pulping.[1]

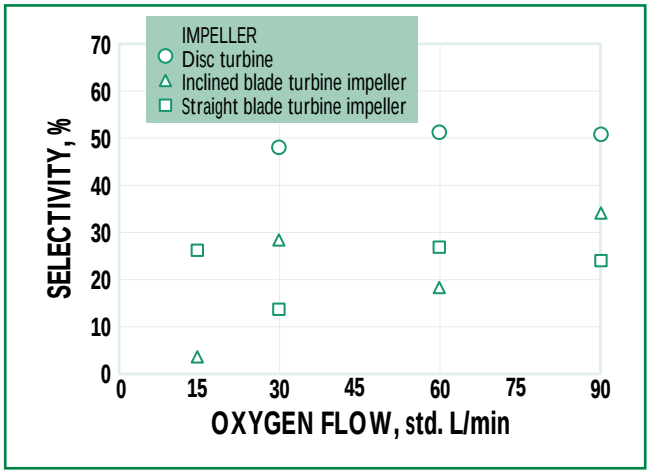
The properties of tensile strength, bursting strength, and folding endurance of polysulfide pulps are at least equivalent to those of conventional kraft pulps at equal kappa number *(1, 9–11)*. The polysulfide pulp

[1] When polysulfides are added to kraft liquor, the rate of delignification does not change appreciably *(8, 11)*. Active alkali charges may have to be increased slightly (by 0.5–1.0% on o.d. wood) when polysulfides are produced by partial oxidation of white liquor.

	Disc	Flat	Dual*
Stirrer diameter			
in.	11	11	11
cm	27.94	27.94	27.94
Blade length			
in.	2.75	4.5	4.5
cm	6.985	11.43	11.43
Disc diameter			
in.	7	…	…
cm	17.78	…	…
Blade width			
in.	2	2	2
cm	5.08	5.08	5.08
Blade pitch, °	…	…	45

*Dual-turbine, inclined.

I. Types and dimensions of stirrers



I. Effect of oxygen flowrate and the type of impeller on the selectivity of the conversion of sulfide to polysulfide

may be equal or slightly lower [up to 14% lower *(1)*] in tear strength than a conventional kraft pulp at the same kappa number *(9–11)*.

The loss in tear strength at kappa numbers greater than 20 is at least partially compensated for by higher pulp tensile strength *(9–11)*. Plane stress fracture toughness should prove to be more reliable than out-of-plane tear strength in evaluating pulp strength for product use *(12)*. However, no research on fracture toughness has been published comparing kraft, polysulfide, and oxygen-delignified pulps.

Anthraquinone is another pulping additive that is economical and has little negative effect on the physical properties of pulp. When anthraquinone (AQ) is added to polysulfide liquor, the yield increases at least additively at a given kappa number for softwoods and hardwoods *(10, 13, 14)*. Others report a synergistic effect when AQ is added to polysulfide *(1, 14, 15)*. If the effect is synergistic, then the yield increase observed when the two additives are used together is greater than the sum of the yield increases observed when the two additives are used independently.

A study by Weyerhaeuser *(1)*, with a furnish made up of 75% Douglas Fir and 25% Lodgepole pine chips, showed a synergistic effect that increased with kappa number over the kappa number range of 15–30. The pulps produced using polysulfide and soluble anthraquinone had the same yield at kappa no. 17–20 as the pulps from a conventional kraft process at kappa no. 30 *(1, 10)*. Polysulfide or polysulfide–AQ pulping could thus be considered an alternative process that would lower the lignin loading on the bleach plant without increasing the organic loading on the chemical recovery system.

In mills where the lower kappa numbers reached in oxygen delignification of kraft pulps are necessary, polysulfide or polysulfide–AQ pulping could be used to increase pulp yield. Changing over to the process would reduce the organic loading on the recovery furnace. The change would also minimize the production loss arising from the recycling of effluents from the oxygen delignification process in recovery-limited mills.

EXPERIMENTAL PROCEDURES

Equipment

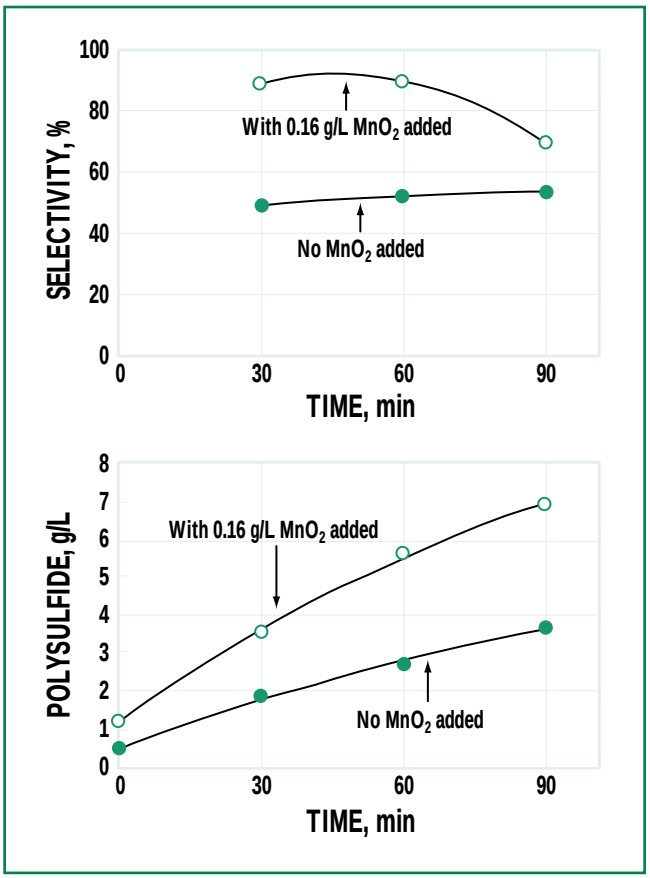
A pilot plant reactor designed to simulate air sparging or oxygen sparging of a causticizer was installed in two kraft mills. The reactor was employed in batch trials in the first mill; in the second mill, it was used both in batch trials and in continuous trials.

The vessel was a flat-bottomed cylindrical tank, 1.080 m in diameter by 1.022 m deep, fabricated from 304-L stainless steel pipe. The reactor was equipped with four baffles 0.102 m wide, spaced at equal distances. The slurry was agitated by a turbine impeller mounted on a vertical shaft. The impeller type used was one of three types of standard geometric configuration for which **Table I** presents engineering details. A steam jacket around the vessel minimized heat losses and helped keep the liquor temperature in the range of 90–100°C during each run.

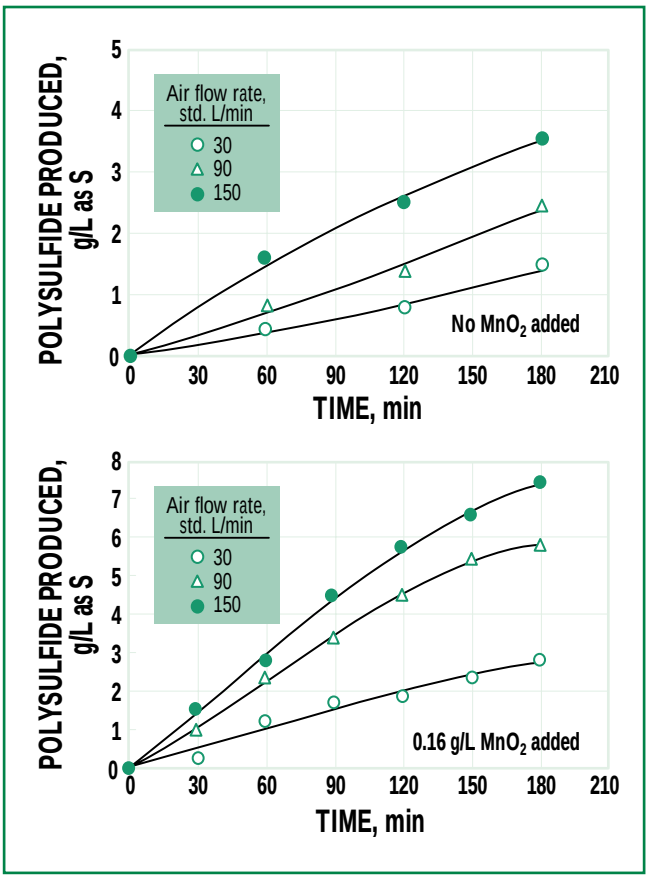
Procedures

In batch tests at the first mill, white liquor, containing lime mud particles, was pumped at about 60 L/min from the No. 3 causticizer directly into the 940-L pilot plant causticizer. To restrain lime mud particles from settling and plugging the gas spargers, we started the agitator as soon as the blades of the impeller were completely immersed in liquor. When the liquor level reached the desired height (about 0.65 m), pumping was stopped, mixing was halted, and the height of liquor was accurately measured.

The mixer was started again, and the flowrate of the gas (air or oxygen) was set to the desired value. The



2. Effect of MnO_2 addition on the conversion of sulfide to polysulfide (oxygen flowrate: 60 std. L/min)



3. Effect of MnO_2 addition and air flowrates on the conversion of sulfide to polysulfide

flowrate was measured using a calibrated Fisher Porter magnetic flowmeter. During a typical run, readings of the gas flowrate, gas pressure, and liquor temperature were recorded every 15 min. Every 30 min, samples of the liquor were drawn off for polysulfide and sulfide analysis. In many runs, the lime mud slurry was spiked with small amounts of MnO_2, which was added batchwise as a suspension in water prior to starting the run.

At the second mill, a few batch tests were performed before a continuous run was started. In both types of test, white liquor containing lime mud particles was diverted to the pilot plant reactor from an adjacent surge tank off the No. 4 causticizer. The liquor was fed by gravity to the reactor, but the time required to fill the reactor to the operating height was always less than that required in the first mill. Batch operating procedures at the second mill were essentially identical to those followed at the first mill.

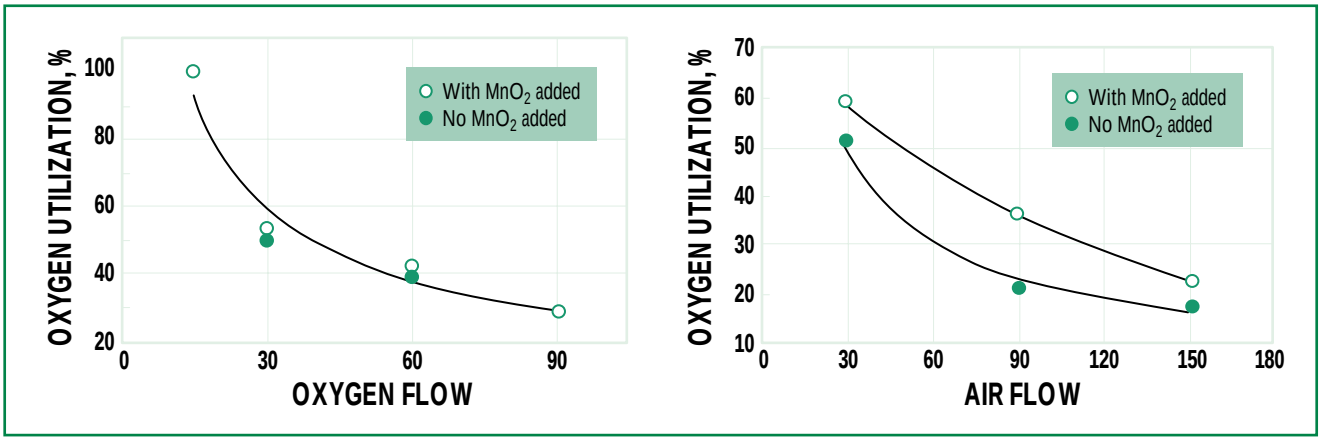
In the continuous run, the white liquor contained lime mud and was spiked with MnO_2. This slurry was oxidized with oxygen at a rate of flow set on the basis of the batch tests. The goal was to produce polysulfide at a concentration greater than the 6 g/L (as sulfur). With a retention time approximating that in the mill's final three causticizers (80–90 min), a concentration of 6 g/L is required for cooking.

After 80 min, the gravity feed line was opened, and the feed flow was adjusted to about 6.8 L/min with a control valve in the feed line. MnO_2 flow to the reactor was initiated and adjusted so that it corresponded to 0.16–0.18 g/L MnO_2 in the feed liquor. The MnO_2 was added as a slurry (380 g/L) in water using a peristaltic pump.

The discharge pump was started, and the discharge flow was adjusted with valves in a recirculation line and in the discharge line back to a large process pump. This pump transferred about 3000 L/min of white liquor from the No. 4 causticizer to the white liquor clarifier. Every hour, we measured and recorded the liquor level in the reactor, the reactor temperature, the gas flowrate and pressure, the MnO_2 slurry flowrate, the feed liquor flowrate, and the product liquor flowrate.

The flowrates of the feed liquor and product liquor were adjusted as required to be nearly equal. Every hour, 250-mL samples of the feed and product liquors were taken. A portion of each sample was combined in a separate flask. Once the flask contained portions of three samples, representing a 3-h period, this composite sample was analyzed for sulfide and polysulfide.

After 18 h of running in the continuous mode, feed and product liquor flowrates were reduced in order for us



4. Effect of MnO_2 addition and either the oxygen flowrate (top) or the air flowrate (bottom) on the efficiency of oxygen utilization

to examine the effects of longer retention times and over-oxidation. After 9 h at these conditions, the flowrates of the feed and product liquors were increased. This change in flowrates allowed us to examine the effect of reduced retention times and made it easier to compare data from the batch and continuous runs.

Analysis of liquors

Analytical methods have already been described for determining polysulfides, sulfide, thiosulfate, and effective and active alkali in unoxidized and oxidized liquors *(16, 17)*. Liquors sampled from the pilot plant reactor were first filtered to remove suspended mud particles. The concentration of polysulfide was determined at the mill site by a gravimetric method. Sulfide was determined by titrating with $HgCl_2$ in a potentiometric titration using a sulfide-ion-selective electrode *(16, 17)*.

Mathematical expressions

The efficiency of oxidation processes in producing polysulfides rather than thiosulfate is expressed in terms of polysulfide yield *(Y)* and polysulfide selectivity *(SEL)*. *Y* is defined as 100 times the concentration of polysulfides formed (g/L) divided by initial sulfide concentration (g/L). *SEL* is defined as 100 times the concentration of polysulfides formed (g/L) divided by the concentration of sulfides converted (g/L).

As used here, the term "sulfide" conforms to the conventional definition. However, the sulfide ions in white liquor hydrolyze to hydrosulfide ions prior to oxidation *(6, 16, 17)*.

RESULTS AND DISCUSSION

All commercial processes based on activated carbon catalysts operate with a polysulfide selectivity of 60–80%. These commercial processes produce 6–7 g/L of polysulfide, corresponding to a maximum polysulfide yield of 33–45% when 55–60% of the hydrosulfide ions have been oxidized to form polysulfide and thiosulfate ions. The pilot plant trials were conducted to define the operating conditions necessary to maximize polysulfide selectivity and to obtain a polysulfide yield greater than 35% with selectivities greater than 60%.

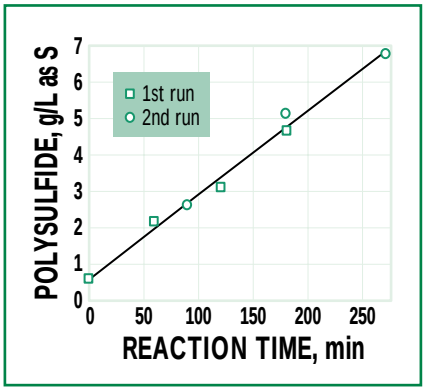
Figure 1 illustrates the effect of the oxygen flowrate and the type of impeller on reaction selectivity in the simulated causticizer. The type of impeller used for mixing affected selectivity dramatically. When a disc impeller was used in place of a straight-blade turbine impeller, polysulfide selectivity increased from 25–35% to about 50% at high rates of oxygen flow. Straight blade impellers are commonly used in causticizers, but the disc impeller maximizes the mixing of gas and liquid. Similar results were observed in laboratory tests *(6, 7)*. These observations suggest that selectivity is strongly dependent on the hydrodynamics and flow pattern in the agitated slurry.

Oxygen as the oxidizing agent

When oxygen was used for producing polysulfide liquor, the maximum selectivity was about 50%. Laboratory studies *(6, 7)* showed a similar upper limit for selectivity with oxygen. However, small additions of a metal oxide catalyst, MnO_2, increased the maximum concentration of polysulfide and the reaction selectivity. Similarly, a very small dosage of MnO_2 (0.16 g/L, or about 0.1% Mn on mud solids) dramatically increased the reaction selectivity in pilot plant trials, regardless of the type of impeller used. This effect with the disc impeller is illustrated in the upper graph of **Fig. 2**, which shows that MnO_2 addition increases selectivity from 50% to more than 70%.

In all experiments in which MnO_2 was added to the reactor, selectivity decreased with increasing reaction time. This finding suggests that the deactivation of (MnO_2) catalyst or the sequential oxidation of polysulfide to thiosulfate could limit the maximum concentration of polysulfide that can be obtained in a process using oxygen. Laboratory studies have also shown, however, that 70–80% of the catalytic effect of the added MnO_2 is maintained when the lime mud is recovered, washed, calcined, and used again in slaking and causticizing *(6)*.

Oxidation studies in a pressurized pipeline reactor *(16–18)* indicated that very little polysulfide is formed and that the oxidation of sulfide to thiosulfate can occur rapidly. Such an



5. Production of polysulfide as a function of reaction time in repeat pilot plant trials, using a disc impeller and air at 150 std. L/min for oxidation, with no MnO_2 added

Oxidant	MnO_2 addition, g/L	Gas flowrate, std. L/min	Reaction time to reach 6 g/L, min	Reaction selectivity at 6 g/L, %
Air	0	30	540	70
	0.16	30	360	93
	0	90	430	85
	0.16	90	190	100
	0	150	255	95
	0.16	150	130	100
Oxygen	0	15	520	25
	0	30	280	40
	0.16	30	135	75
	0	60	195	40
	0.16	60	80	70
	0	90	135	50
	0.16 *	90	65	80

*Batch test at second mill.
All other test results are for the first mill.

II. The effects of gas flowrate and MnO_2 addition on polysulfide production in a pilot plant causticizer

environment is oxygen-enriched, as opposed to the case of air being used as the oxidant. When lime mud is used as a catalyst, sulfide oxidizes to polysulfide at the catalyst surface, whereas sulfide or polysulfide oxidizes to thiosulfate in the bulk liquid *(6)*. Thus, the higher oxygen partial pressures or higher oxygen solubility in the process probably result in the direct oxidation of sulfide to thiosulfate or in the further oxidation of polysulfide to thiosulfate in the bulk liquid.

As the results in Fig. 2 suggest, the rate of this second reaction may become significant when the polysulfide concentration is increased. Furthermore, the maximum polysulfide concentration attainable in the process will be lower when oxygen rather than air is used as an oxidant. As illustrated in the lower graph, however, polysulfide was produced at concentrations greater than 6 g/L with MnO_2 addition and a reaction time of 70–90 min. Corresponding selectivities were greater than 70%. Therefore, the criteria for a commercial process are satisfied.

Air as the oxidant

Figure 3 shows the effects of adding manganese dioxide when air is used as the oxidant. With air, the rates of polysulfide formation are much lower than with oxygen. With oxygen as the oxidant and MnO_2 added, only 70 min of reaction time was required to produce 6 g/L of polysulfide (as sulfur), at a flowrate of 60 std. L/min. (Fig. 2, bottom). At high air flowrates, even with MnO_2, it took over 120 min of reaction time to produce polysulfide liquor at cooking liquor concentrations (Fig. 3, bottom). With no manganese dioxide added, reaction times of over 240 min were required when air was used, even at high gas flowrates (Fig. 3, top).

All selectivities were greater than 80% when air was used for producing polysulfide in the simulated causticizer. Higher air flowrates generally increased selectivity, probably as a result of increased turbulence. These generally higher selectivities for air instead of oxygen indicate that selectivity increases as the oxygen partial pressure decreases. This finding suggests, again, that polysulfide is an intermediate in a series of reactions, with high oxygen partial pressure promoting the oxidation of the desired polysulfide intermediate.

Oxygen utilization efficiencies

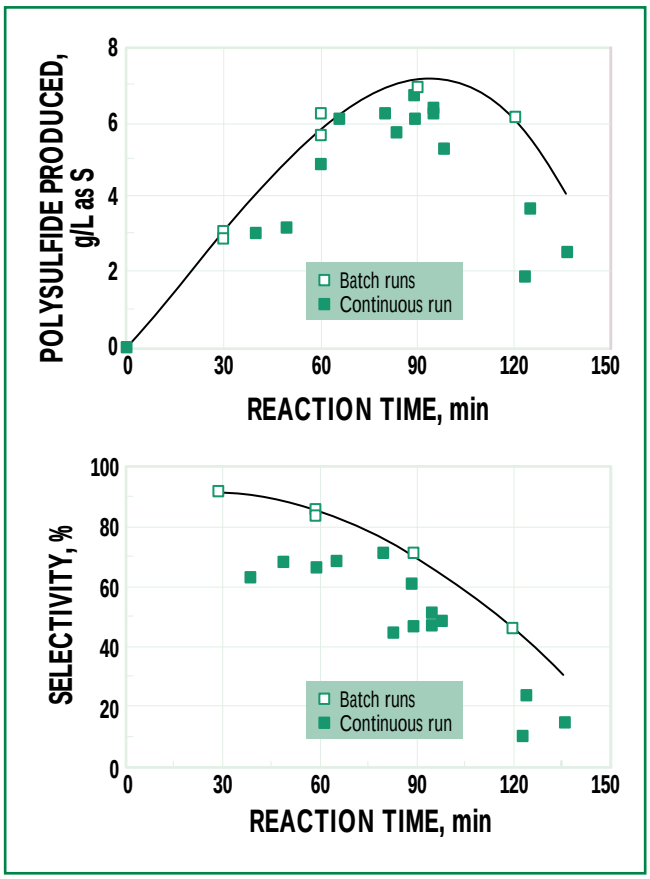
Oxygen utilization efficiencies were calculated from the changes in liquor composition. These efficiencies, for the case of the disc impeller, are presented in **Fig. 4** as a function of gas flowrate.

For the upper graph in Fig. 4, oxygen was used as the oxidant. When manganese dioxide was added, there was no significant effect on the utilization efficiency; the manganese dioxide simply increased the reaction selectivity. Note also that oxygen utilization efficiencies are only 30–55% when oxygen is used at flowrates that give good selectivity.

With air, manganese dioxide increased oxygen utilization efficiencies slightly, as illustrated in the lower graph. When air is used as the oxidant, manganese dioxide increases the reaction rate, so more of the oxygen in an air bubble can be utilized in the reaction as the air bubble rises through the reactor.

Reliability of the data

As illustrated in **Fig. 5**, good reproducibility was obtained between runs. The polysulfide concentration in liquors fed to the pilot plant causticizer varied from 0.3 g/L to 1.1 g/L (as sulfur). This variability indicates that up to 6% of the hydrosulfide ions in white liquor were already oxidized by air drawn unintentionally into the causticizers. Dorris observed similar tendencies in analyzing liquor samples from the slaker and the last causticizer in another Canadian mill *(6)*.



6. Comparison of batch and continuous trials on polysulfide production and selectivity as a function of reaction time during trials at the second mill

Selectivity and reaction time

In a commercial polysulfide cooking process, polysulfide must be produced at a concentration of 6 g/L or greater for a yield greater than about 33% with a selectivity of greater than 60%. Since we propose to perform this oxidation directly in a kraft mill's causticizers, we had to consider that the 0.3–1.1 g/L of polysulfide in pilot plant feed liquors may not be present in the feed liquor of the commercial process. For this reason, the time to produce 6 g/L of polysulfide and the selectivity at 6 g/L were the most useful indicators of the feasibility of the proposed process.

Pilot plant results with respect to these two parameters are summarized in **Table II** for the disc impeller. At the first mill, reaction times of about 4 h were necessary when air was used as the oxidant. The addition of small amounts of manganese dioxide (0.16 g/L) cut the reaction time by nearly 50%, to about 130 min. When oxygen was used as the oxidant, manganese dioxide had to be added to get acceptable selectivity. Using oxygen with manganese dioxide, liquor with a polysulfide concentration of greater than 6 g/L was prepared with reaction times of 65–85 min.

Retention times in causticizing usually vary between 100 min and 180 min *(6)*, so it should be possible to produce polysulfide liquor directly in a kraft mill's causticizers. More retention time could be required in some mills, depending on which gas is chosen for oxidation and depending on its flowrate.

As the rates of gas flow were increased in our study, lower retention times were required. The use of higher oxygen flowrates might allow a mill to produce polysulfide in the existing causticizers without adding causticizers to increase reaction time. Reduced system capital costs would be offset, however, by higher operating costs arising from less efficiency in oxygen utilization and by the cost of the increased power required for mixing.

The benefit of increasing gas flowrates also declines with increasing gas flowrates. In other words, at a higher gas flowrate, a percent increase in gas flowrate does not reduce the retention time by as much as it would at lower rates of gas flow. As a result, there are limits to this trade-off between capital and operating costs.

Continuous runs

Figure 6 summarizes the pilot plant runs at the second mill. In all of these trials, high oxygen flowrates were employed, and manganese dioxide was added. At an oxygen flowrate of 90 std. L/min, polysulfide at a concentration of 6.6 g/L was produced in only 65 min, at a selectivity of 80% in the batch runs (Table II).

Using oxygen with MnO_2 added, polysulfide at concentrations of greater than 6 g/L was consistently produced in both the batch trials and continuous runs with retention times between 60 min and 100 min. With retention times up to 90 min, selectivities were generally 60–70% in the continuous runs and were slightly higher in the batch runs. Note that the low selectivities at lower retention times in the continuous mode were probably exaggerated by high levels of residual thiosulfate remaining in the reactor as a result of the high-retention-time operation immediately preceding.

As Fig. 6 shows, laboratory or pilot plant data from batch tests can be used to predict performance for a continuous system. Each of the points for the continuous runs in these graphs represents a 3-h composite liquor sample. The pilot plant was thus operated in a continuous mode for about 40 h.

The optimum reaction time is a function of the oxygen flowrate (Table II). If the oxygen flowrate is controlled as a function of the rate of liquor flowing into the causticizers, polysulfide production and selectivity can be maintained at the peak illustrated in Fig. 6.

OBSERVATIONS ON SCALING UP THE PROCESS

Air or oxygen sparging of the causticizer has a number of potentially important effects in addition to producing polysulfides. These side ef-

fects include:

- Reduced mixer speed
- Higher liquor level
- Greater turbulence
- Higher liquor temperature
- Sparger plugging.

Reduced mixer speed. The additional mixing required to disperse gas bubbles reduced the operating mixer speed for the fixed-horsepower mixer. With no gas sparging, the pilot plant mixer operated at close to 300 rpm. The speed of the impeller tip was about the same as that of the impeller tip in the full-scale causticizers at a mixing speed of 80 rpm. At high gas loading, the pilot plant mixer operated at only 200–225 rpm.

Consequently, larger mixer motors would be required in the causticizers. If these motors were designed to keep the tip speed from dropping, gas dispersion would probably be substantially better than it was in our pilot plant runs. Higher efficiencies of oxygen utilization and increased reaction rates could be anticipated.

Higher liquor level. The liquor height in the simulated causticizer increased by about 10% at high rates of gas flow. Similar but larger increases are usually observed in white liquor oxidation reactors, in which gas-to-liquor volume ratios are also much higher. Because liquor flows by gravity from one causticizer to the next, this height increase would reduce actual retention times in sparged causticizers by about 10%.

Greater turbulence Gas dispersion causes extreme turbulence. The greater turbulence breaks lime mud particles into smaller sizes and reduces the rate of lime mud settling. Reductions in settling rate of 10–30% were observed in the batch runs. In the continuous trials, where a portion of the liquor was recirculated through a discharge pump and a severely throttled valve, settling rates were reduced by up to 45%.

	Air	Oxygen	O_2 with recycle[a]
Heat of reaction	13.7	13.7	13.7
Heat loss in vent gas[b]	11.7	5.7	0.9
Heat to raise causticizer temp. by 5°F	2	2	2
Heat removed by recirculating-gas cooler	0	0	1.3
Heat removed by white liquor cooler	0	6	9.5

[a]Nitrogen is vented to maintain oxygen at a concentration of 85%, assuming vacuum swing absorption (VSA) feed at 93% purity.
[b]Gases exit from the air oxidation at 190°F and 75% water saturation. Gases exit from oxygen oxidation at 200°F and 75% water saturation.

III: Heat balances for the 1000-ton/day mill, in millions of BTUs per hour

After gas sparging, the lime muds formed a more compact bed, and the cake porosity was reduced by 4–8%. The settling rates after gas sparging were still within the range normally observed in Canadian kraft mills [1.0–4.0 cm/min *(19)*]. Any reduction in settling rate would be partially offset by a more compact mud bed. Consequently, it is unlikely that gas sparging would result in a significant increase in suspended solids in the clarified liquor.

Lime mud settling rates routinely varied by 200–300% for liquor samples going to the pilot plant reactor. The 10–30% reductions in settling rate caused by the process would seem to be insignificant for this reason as well.

Particle size analyses also indicated that gas sparging did not decrease the average diameter of lime mud particles by more than the 2-µm change generally observed across each causticizer. Gas sparging simply resulted in slightly higher percentages of finer-diameter particles, which settle more slowly.

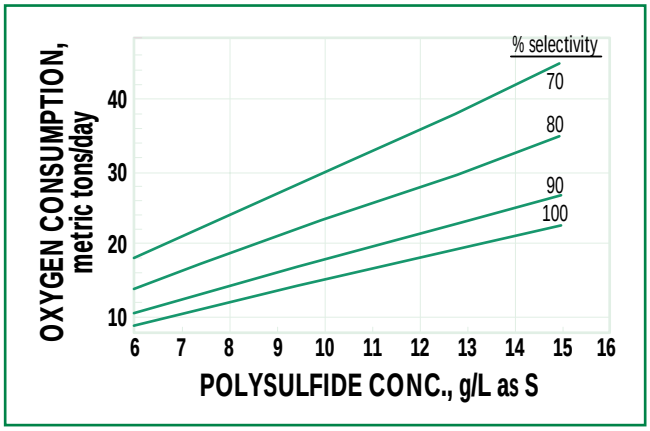
Higher liquor temperature Gas sparging of the simulated causticizer increased the liquor temperature. The temperature of 88–90°C at the start of a run rose to 92–95°C in the first half hour of a batch trial. Liquor temperatures stabilized in the 92–95°C range because the heat losses from the simulated causticizer then equalled the heat generated by the exothermic oxidation of sulfide to polysulfide and thiosulfate.

Calculations indicated that heat generated by the exothermic chemical reactions *(20)* would just about equal heat losses to evaporate water and saturate the unconsumed gases at about 88°C when air was used for sulfide oxidation. The results of these calculations are summarized in **Table III**. A slight excess in heat would be consumed by higher heat losses from the causticizers or by the green liquor cooler being operated to reduce the feed temperature to the slaker.

When oxygen is used as the oxidant, excess heat is generated, and liquor cooling would be necessary. Causticizers operate close to the white liquor boiling point, and an increase in operating temperature could cause the liquor to boil over. Liquor would have to be recirculated through heat exchangers on the first sparged causticizer.

Recirculation might further reduce the rate of mud settling, however. That would make it necessary to increase the area in the white liquor clarifier or install pressure filters, to ensure good quality in the orange liquor. The use of pressure filters would have the added advantage of shortening the time of orange liquor storage, minimizing the degradation of polysulfide in storage. After 24 h, at a storage temperature of 70°C, polysulfide loses 0.30 g/L; at 80°C, it loses 0.70 g/L. (These losses were measured in laboratory experiments.)

Sparger plugging The sintered metal spargers used in most of the pilot plant trials were observed to plug rapidly with lime mud. After 6–8 h of operation, the gas pressures needed to maintain high gas flowrates



7. The theoretical oxygen requirements for a 1000-ton/day mill as a function of the process selectivity and the equilibrium concentration of polysulfide produced

	Capital costs, $	Annual operating costs, $
Oxygen, no recycle	1,500,000 – 2,000,000	1,169,000
Oxygen with recycle	2,000,000 – 2,500,000	835,000
Air	2,500,000 – 3,000,000	495,000

Oxygen costs were assumed to be $65 per metric ton.
Power costs were assumed to be $0.038 per kW·h.

IV. Capital and operating cost estimates for polysulfide liquor production in the causticizers of a 1000-ton/day kraft mill

would increase from 55–65 kPa to 340–400 kPa. To reduce maintenance requirements and improve the technical feasibility of the process, nonplugging spargers were necessary.

Canadian Liquid Air, an active collaborator in the pilot plant trials, developed a nonplugging sparger that had a low pressure loss. We tested this sparger in later batch trials and continuous runs. In a continuous run of over 36 h, the gas pressure to deliver 90 std. L/min of oxygen to the simulated causticizer increased from 37 kPa to only 48 kPa. Over the last 12 h of the run, the pressure increased only slightly.

PROCESS DESIGN SCALE-UP

The results of the pilot plant trials at the two mills were used to upgrade the design for a full-scale plant. Capital and operating costs were estimated for both air and oxygen systems. For both systems, we assumed that manganese dioxide would have to be used to reduce reaction times and to increase reaction selectivity.

Laboratory experiments have shown that 70–80% of the catalytic effect of the added manganese dioxide is maintained when the lime mud is recovered, washed, calcined, and used again in slaking and causticizing *(6)*. Nevertheless, we calculated operating costs by assuming that additions of 0.16 g/L of a low-grade MnO_2 would be necessary on a continuous basis.

MnO_2 products of various purities are available, with costs ranging from $0.28/kg (84% pure) to $6.60/kg (99.9% pure). A low-grade MnO_2 was adequate for once-through pilot plant trials. Nonprocess elements could build up in recausticizing on a continuous basis, however, making it necessary to use a very pure grade. The operating cost assumed for MnO_2 would permit continuous addition of an 84% pure MnO_2 at 0.16 g/L or the on-going replacement of 25% of the originally added MnO_2 with a 98% pure form.

Laboratory tests at Paprican indicated that 98% of the added MnO_2 goes with the settled lime mud. More than 98% of the manganese input to a fiber line comes from the wood supply *(21)*, and only about 30% of that input passes into the bleach plant with the brownstock *(21)*. Consequently, the slight increases in manganese input arising from this polysulfide process are not likely to be detectable. As long as peroxide stages in a totally chlorine-free bleach plant are preceded by an effective acid wash or chelation stage, the use of manganese in the Paprican process should have no effect on the peroxide-stage performance.

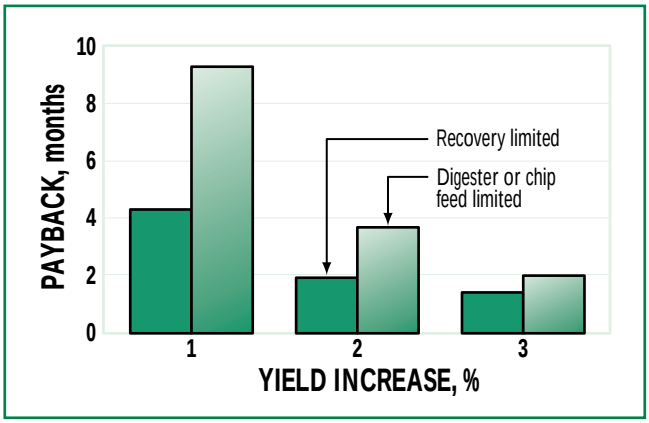
A vintage 1967 kraft mill was chosen as the test subject for scaling up the design and analyzing the economics involved *(22)*. Originally designed to produce 750 tons/day of bleached market kraft pulp, the mill is currently producing 1000 tons/day. Retention times in the original three causticizers total only 75 min—a worst-case type of analysis.

With oxygen, a reaction time of 75 min would be necessary to generate polysulfide liquor at cooking liquor concentrations (Table II and Fig. 6). Oxygen was added only to the existing No. 2 and 3 causticizers, and a new stainless steel causticizer was added to the line to give the required reaction time.

With air, a reaction time of 130 min would be necessary, and two new causticizers would be added. These two would operate in parallel with the existing No. 1 causticizer, as the first stage in the polysulfide plant.

In both systems, liquor would flow by gravity to the new causticizers but would be pumped back to the old No. 2 causticizer. By leaving the existing No. 1 causticizer untouched in the case study for oxygen and by providing additional reaction time in both

KEYWORDS
Bibliographies, causticizers, chemical reactions, chemical reactors, cooking liquors, economic analysis, economics, feasibility, kraft mills, manganese compounds, manganese dioxide, mills (factories), mud, oxidation, oxides, pilot plants, plant departments, polysulfides, pulp mills, reaction time, selectivity, sulfides, sulfur compounds, time, white liquor mud, white liquors.



8. Effect of the pulping yield increase from polysulfide pulping and the mill's capacity limitation on the payback period

	Capital cost,[a] $	Net annual benefit,[b] $	Payback, months
Case A—Recovery Limited Mill			
Air	2,750,000	11,827,000	2.8
Oxygen	1,750,000	11,153,000	1.9
Case B—Digester or Chip Feed Limited Mill			
Air	2,750,000	6,365,000	5.2
Oxygen	1,750,000	5,691,000	3.7

[a]Averages of capital cost estimates from Table IV.
[b]Derived using calculations illustrated by Blain and Holton (*32*).

V. Economic analysis of polysulfide liquor production processes

case studies, we would minimize any adverse effects on causticizing efficiency.

New stainless steel causticizers, if used for the first reactors in the polysulfide plant, would satisfy considerations about corrosion. Studies indicate that polysulfide can be corrosive at a concentration of 1–2 g/L in white liquor *(23, 24)*. At higher concentrations, polysulfide has been found to passivate carbon steels and to actually lower corrosion rates in digesters *(24)*. The first reactor in the polysulfide plant would be expected to produce liquor with a polysulfide concentration of 2.0–2.5 g/L. Therefore, the first reactors would have to be constructed of stainless steel to minimize corrosion, particularly during process startups and shutdowns, when the polysulfide concentration would pass through the range of corrosivity.

Design scale-up was based on the results of pilot plant tests with an oxygen flow of 60 std. L/min and an air flow of 150 std. L/min (Table II). A constant volume of gas was maintained per volume of liquor per minute. Several studies have shown that this basis is the most rigorous method of scale-up for gas dispersion in agitated tanks *(25–27)*. Reactor height was assumed to have no affect on the efficiency of oxygen utilization. An oxygen utilization efficiency of 50% was thus estimated from the pilot plant data.

Figure 7 presents the theoretical oxygen requirements for a 1000-ton/day mill, as a function of the process selectivity and the concentration of polysulfide produced. Mixer horsepower requirements for complete gas dispersion and complete solids suspension in each reactor, using disc impellers, were initially calculated using correlations from the pertinent literature *(28–30)*.

After Paprican's initial economic analysis of the process *(22)*, Kvaerner Chemetics was asked to review both the scale-up calculations and cost estimates. The mixing horsepower requirements and costs of new impellers, new motors, additional reactors, and so forth were requested from equipment suppliers. No additional clarifier capacity or buildings were assumed necessary in this analysis.

ECONOMIC EVALUATION

The capital and operating costs for three alternatives are summarized in **Table IV**. Additional details on two of these cost estimates were provided in an earlier publication *(22)*.

The capital cost for the air system is Can$2.5–3.0 million. This amount is substantially less than the capital cost of Can$5.5 million (US$4 million) for a commercial polysulfide production process utilizing an activated carbon catalyst *(31)*. The use of oxygen for polysulfide liquor generation allows further savings in capital cost and improved payback (**Table V**). The annual operating costs for the Paprican process utilizing oxygen, at $65 per metric ton, are slightly higher than those estimated for the Chiyoda process, but capital cost savings in excess of three million dollars still make the developed process economically attractive.

The net annual benefits and payback periods of Table V are based on a 2% gain in yield over conventional kraft pulping. We assumed a pulp price of $575 per metric ton, with a net profit of $350 per incremental metric ton. Case A is for a mill limited by the capacity of its recovery boiler. Case B is for a mill limited by its digester capacity or its chip-feed system. For these calculations, we took averages from Table IV as the capital costs.

Only 50% of the oxygen sparged into the causticizers is used in producing polysulfide liquor in the designed process. Vent gas from the causticizers would be saturated with water vapor but would contain little in terms of organics or noncondensible gases, since the primary reactions in the causticizers involve oxidation of inorganic sulfides. Moisture could be easily removed from the flue gas using demisters and condensers, and the gas could be recompressed and used again. Recycling the oxygen gas would require sealing around the reactors (and impeller shafts) to minimize oxygen losses or air infiltration, a liquid ring compressor, and demisters and condensers. Adding these features would increase the process capital costs by about $0.5 million but would

reduce annual operating costs by about $335,000/year (Table IV). Oxygen recycling would thus have an attractive payback and would further improve process economics. Alternatively, a portion of the oxygen from causticizer sparging could be used for oxygen-enrichment of the lime kiln combustion air to increase kiln capacity.

If these estimates are to be compared with those published earlier by Paprican *(20)*, then some differences should be mentioned. Here, the cost estimates for the air-based system are slightly lower. We decided to start air sparging in the existing No. 1 causticizer and eliminate one new causticizer, because the doubling of the retention time would more than compensate for any impact on causticizing efficiency. By contrast, the capital costs for the oxygen-based system without recycle are slightly higher than our earlier estimates *(20)*. This difference arises from including the heat exchanger, a more elaborate system for MnO_2 addition (to minimize occupational exposure), and added safeguards (sealing, oxygen compatible lubricants, etc.) identified by the commercial partners.

Even with only 50% oxygen utilization, assuming a 2% increase in pulp yield, the process has payback periods of 1.9–3.7 months, depending on the exact mill bottleneck (digester, recovery boiler, or chip feed system). Even if pulp yield is increased by only 1%, payback periods of 3.8–9.3 months are possible (**Fig. 8**). If polysulfide or polysulfide–AQ cooking were used to lower the kappa number of pulp entering the bleach plant, the system costs should be compared to those for an alkaline extraction stage, mini-oxygen delignification, or oxygen delignification. Capital costs for each of these systems would be $15–35 million for a 1000-ton/day kraft mill.

High oxygen purity is not essential for polysulfide liquor production by the Paprican process. As the oxygen purity decreases, the retention time required will increase. Higher dosages of MnO_2 can be employed, however, to reduce the retention time requirements *(6, 7)*. It may thus be possible to use the vent gases from oxygen delignification or ozone generation to produce polysulfide liquor *(33)*. The integration of the Paprican process with oxygen delignification and ozone bleaching can provide good economic returns. As effluent systems are closed to a higher degree, such a combined process can minimize the impact of closure on the recovery boiler *(33)* and help to maintain mill production capacity.

CONCLUSIONS

Pilot plant studies of a process patented by Paprican have confirmed the technical feasibility of producing polysulfide liquor at cooking liquor concentrations in a kraft mill's causticizers. Lime mud is used as the primary oxidation catalyst.

Small amounts of manganese dioxide should be added to increase reaction selectivity when oxygen is used as the oxidant. MnO_2 reduces the reaction time required when either air or oxygen is used as the oxidant.

With oxygen as the gas and with manganese dioxide added, polysulfide liquor suitable for pulping was produced within short reaction times in trials at two mills. With air, longer reaction times were required, but selectivities were higher.

Continuous pilot plant trials confirmed the fact that laboratory or pilot plant data using batch tests could be used to accurately predict the performance for a continuous system. The trials at the mills produced engineering data from which capital and operating costs were estimated. Whether air or oxygen is used as the oxidant, the economics are attractive for the Paprican process for generating polysulfide liquor in a mill's causticizers. **TJ**

Uloth is senior process engineer at Paprican, Prince George, B.C. Dorris is senior scientist and head of the chemicals recycling section at Paprican, 570 St. John's Blvd., Pointe Claire, PQ. Ron Thring was with Paprican but is now professor of chemical engineering at the University of New Brunswick, Fredericton. Hogikyan is assistant research assistant at Paprican in Vancouver. Wearing is also at Paprican in Vancouver as associate director of the Vancouver laboratory and head of the chemical technology section. Larry Tench is manager, process engineering with Kvaerner Chemetics Inc., 1818 Cornwall Ave., Vancouver, B.C. Jack Ayton is gas applications manager, Air Liquid Canada, 8390 Manitoba Street, Vancouver, B.C.

The authors would like to thank Canadian Liquid Air for donating oxygen, gas flowmeters, and gas sparging equipment for the pilot plant trials. We greatly appreciated the assistance and helpful suggestions offered by Derek Hornsey and Gord Homer of Canadian Liquid Air and by Norbert Eckert, Andre Jankowski, and Stuart Harper of Kvaerner Chemetics.

We wish to express our gratitude to the technical, steam and recovery, and maintenance staffs at Cariboo Pulp, Quesnel, and Canfor, Prince George, for all the assistance they provided during these trials. The interest, encouragement, and assistance of Tom Galvin and Magnus Vinje at Cariboo and Ed Dylke at Canfor made these pilot plant trials possible. The skilled technical assistance of Ed Stafford is also gratefully acknowledged.

Parts of this paper have been previously published by Pulp and Paper Canada. *We thank their editorial staff and the Technical Section of CPPA for permission to republish this paper.*

Received for review Aug. 26, 1996.

Accepted March 14, 1997.

Presented at the TAPPI 1996 Pulping Conference.

Selected as the Weatherhorn Award winner by the Alkaline Pulping Committee as its choice for the outstanding paper from that conference.

LITERATURE CITED

1. Mayovsky, J., *Proceedings of the 1992 Pan-Pacific Pulp and Paper Technology Conference*, p. A1. Japan TAPPI
2. Smith, G. C., Knowles, S. E., and Green, R. P., *Paper Trade J.* 159(13): 38(May 1975).
3. Smith, G. C. and Sanders, F.W., U.S. pat. 4,024,229(1977).
4. Nakamura, M. and Ono, T., *TAPPI 1988 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 407.
5. Lightfoot, W. E., *Pulp & Paper* 64(1): 88(1990).
6. Dorris, G. M., *Pulp Paper Can.* 95(10): 44(1994).
7. Dorris, G. M., U.S. pat. 5,082,526(1992).
8. Alfredsson, B. and Samuelson, O., *Svensk Papperstid.* 72(11): 361(1969).
9. *Pulp and Paper Manufacture, Vol. 5: Alkaline Pulping* (Kocurek, M.J., Ed.), The Joint Textbook Committee of the Pulp and Paper Industry, 1989, p. 114.
10. Pekkala, O., *Paperi Puu* 5: 385(1986).
11. Scoop, I.W., *The Paper Industry* 233(July 1961).
12. Seth, R. S., Robertson, A. G., Mai, Y.-W., and Hoffmann, J. D., *Tappi J.* 76(2): 109(1993).
13. Green, R. P. and Smith, G. C., *TAPPI 1983 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 79.
14. *New trend of cooking with the quinone additive*, Kawaski Kasei Chemicals Ltd., Tokyo, 1990.
15. Kleppe, P. J., *Paperi Puu* 63(4): 204(1981).
16. Dorris, G. M. and Uloth, V. C., *J. Pulp Paper Sci.* 20(8): J211(1994).
17. Dorris, G. M. and Uloth, V. C., *J. Pulp Paper Sci.* 20(9): J242(1994).
18. Thring, R.W., Uloth, V. C., Dorris, G. M., Galvin, T. S., Hornsey, D., and Ayton, J., *Tappi J.* 78(1): 107(1995).
19. Dorris, G. M. and Allen, L. H., *TAPPI 1992 Recovery Operations Short Course Notes*, TAPPI PRESS, Atlanta, 1992, p. 17.
20. Ayala, V., O'Czerny, A., Zanchin, R., Magnotta, V., and Zierdt, J. R., *TAPPI 1990 Oxygen Delignification Conference Proceedings*, TAPPI PRESS, Atlanta, p. 153.
21. Bryant, P. S., Robarge, K., and Edwards, L. L., *Tappi J.* 76(11): 148(1993).
22. Uloth, V. C., Dorris, G. M., Thring, R. W., Hogikyan, R. M., and Wearing, J. T., *CPPA 1995 81st Annual Meeting Proceedings*, CPPA, Montreal, p. A141.
23. Ahlers, P., *Proceedings of the 1983 International Symposium on Corrosion in the Pulp and Paper Industry*, Swedish Corrosion Institute, P.O. Box 5607, S-114-86, Stockholm, p. 53.
24. Kleppe, P. J. and Landmark, P., *Proceedings of the 1983 International Symposium on Corrosion in the Pulp and Paper Industry*, Swedish Corrosion Institute, P.O. Box 5607, S-114-86, Stockholm, p. 56.
25. Nienow, A. W., Wisdom, D. J., and Middleton, J. C., *Proceedings of the Second European Conference on Mixing*, Inst. Chem. Eng., Cambridge, U.K., 1977, p. F1.
26. Nishikawa, M., Nakamura, M., Yagi, H., and Hashimoto, K., *J. Chem. Eng. Japan* 14: 219(1981).
27. Tatterson, G. B., *Fluid Mixing and Gas Dispersion in Agitated Tanks*, McGraw-Hill, New York, 1991, p. 510.
28. Froment, G. F. and Bischoff, K. B., *Chemical Reactor Analysis and Design*, 2nd edn., John Wiley & Sons, 1990, Ch. 14.
29. Zweittering, T. N., *Chem. Eng. Sci.* 8: 224(1958).
30. Oldshue, J. Y., *Fluid Mixing Technology*, McGraw-Hill, New York, 1983.
31. Katz, G., *CPPA 1994 80th Annual Meeting Proceedings*, CPPA, Montreal, p. B99.
32. Blain, T. J. and Holton, H. H., *Pulp Paper Can.* 86(6): T124(1983).
33. Homer, G., Epiney, M., and Johnson, S., *TAPPI 1996 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 81.