

Pilot-plant experience with ozone in TCF bleaching of eucalypt pulp

Alfredo Mokfienski and Braz J. Demuner

ABSTRACT: *A commercial mill producing totally-chlorine-free (TCF) and elemental-chlorine-free (ECF) kraft pulp from eucalypts sought to add an ozone stage to its bleach line. TCF bleach sequences with ozone stages were tested at two pilot plants using oxygen-delignified pulp from the mill. Brightness exceeding 89% ISO was obtained with lower chemical consumption than the mill's commercial ECF and TCF processes. However, the tensile strength, bulk, porosity, and opacity of the ozone-treated pulps were lower than the ECF and TCF pulps bleached without ozone treatment. The ozone charge and the pulp consistency during ozone bleaching greatly affect chemical consumption and product quality.*

KEYWORDS: *Bibliographies, chlorine free bleaching, eucalypts, evaluation, kraft pulps, multistage process, ozone, ozone bleaching, pilot plants, test methods.*

Market demand and environmental pressures are forcing the pulp and paper industry to develop technological alternatives to conventional chlorine-based bleaching processes. Research efforts have focused on improving effluent characteristics while maintaining or improving product quality. Many mills are now bleaching pulp using totally chlorine-free (TCF) and elemental-chlorine-free (ECF) sequences.

The Aracruz pulp-production complex (Barra do Riacho, ES, Bra-

zil) began producing ECF market pulp in 1988. At the same time, the mill initiated a research program to develop a TCF bleach sequence for eucalypt pulp (1). The mill was able to begin producing TCF market pulp in October 1991. By this time, it was clear from the accumulated research experience into TCF bleaching that additional technological development would be required to improve pulp brightness at a competitive cost and with minimum adverse impact on the environment.

Ozone-bleaching technology appeared to be a promising alternative, so the mill undertook fundamental studies of ozone bleaching in the laboratory and in two pilot plants. Details about earlier phases of the mill's efforts to develop TCF pulp-bleaching technology have been published elsewhere (1-3). This article reports the main findings of the pilot-plant tests regarding the use of ozone in TCF bleaching of eucalypt pulp.

TCF bleaching

Mill experience, 1991-94

The Aracruz pulp-production complex currently operates with two eucalypt bleached-kraft pulp mills. The total annual pulp production is over 1,000,000 a.d. (air-dried) metric tons, consisting of standard, ECF, and TCF pulp grades. In 1992, the mill produced approximately 30,000 a.d. metric tons of TCF pulp. This jumped to 100,000 a.d. metric tons in 1993 and is expected to increase again in 1994.

Early TCF production runs utilized the sequence A(EPO)APA, with a target brightness of 80% ISO. In July 1992, the mill began producing TCF pulp with newly installed MCC (modified continuous cooking) and oxygen-delignification processes. By the end of 1992, other process improvements had been installed, including a new bleaching tower, mixing equipment, and process control. The result was a significant in-

Mokfienski, pulp technology specialist, and Demuner, manager of product development, are affiliated with Aracruz Celulose S/A, P.O. Box 1011, CEP 29797-000, Aracruz, ES, Brazil.

Ozone Bleaching

I. Characteristics of oxygen-delignified eucalypt kraft pulp samples from the Aracruz mill

Pulp characteristics	No acid treatment	With acid treatment
Kappa number	10.0	9.1
Initial viscosity, dm ³ /kg	947	920
Initial brightness, % ISO	52.5	52.8
COD, kg/a.d. metric ton	11.7	3.1

II. Characteristics of the pilot plants

Plant characteristics	Pilot plant A	Pilot plant B
Process	Continuous	Batch
Z-stage consistency, %	45	10
Filtrate circuit	Closed ^a	Open
Utilities (water/steam)	From pulp mill	Specific for pilot plant
Plant capacity ^b	120 kg/h	250 kg/batch

^a Purge of 2.0 m³/a.d. metric ton
^b Moisture-free pulp

III. Comparison of pilot-plant pulps (ozone) with TCF/ECF commercial pulps (no ozone)^a

Bleach sequence	Final brightness, % ISO	Brightness reversion, %	Kappa number after Z stage	Final viscosity, dm ³ /kg	Chemical charge, kg/ a.d. metric ton				O ₃ consumption, %	Efficiency, kappa-no. reduction per kg O ₃
					H ₂ O ₂	NaOH	O ₃	ClO ₂ ^b		
Plant A ^c										
AZPP	83.1	2.7	2.3	600	27.5	22.0	6.0	...	>90	1.3
AZP	83.9	2.1	1.2	487	15.5	10.0	8.0	...	>90	1.1
A(EPO)AZP	86.2	3.1	2.8	508	26.5	41.0	4.5	...	>90	...
Plant B ^d										
AZ(EPO)P	86.2	2.2	1.8	551	25.0	35.0	6.6	...	>90	1.2
AZP ^e	89.5	2.1	0.9	610	10.0	15.0	6.9	...	>90	1.2
Commercial pulp ^f										
TCF (Nov. 1992) ^g	85.3	6.0	...	694	39.0	...	...	...	...	...
TCF (Jan. 1994) ^h	87.2	2.0	...	762	55.0	...	...	...	...	...
ECF (1993) ^h	89.8	2.0	...	830	...	...	...	50.0	...	...

^a Oxygen-delignified eucalypt pulp
^b As active Cl₂
^c High consistency Z stage, closed filtrate circuit
^d Medium-consistency Z stage, open filtrate circuit, ozone applied in two stages
^e Pulp treated with acid at the mill
^f Countercurrent pulp washing
^g Never-dried pulp; same pulp as used in pilot plants
^h Once-dried pulp; average value

crease in pulp brightness (from 80% ISO to 85% ISO), an increase in daily production (from 500 a.d. metric tons to 600 a.d. metric tons), a small reduction in pulp-production variable cost, and a significant improvement in the characteristics of the mill effluent (2, 3).

At this stage, the mill directed its TCF research efforts toward pending problems related to increasing and stabilizing pulp brightness, increasing production capacity, and

reducing costs. The alternatives considered at that time included application of enzymes, improvement of the acid pulp treatment, and application of ozone as a bleaching stage. The mill decided to focus on ozone bleaching and began carrying out pilot-plant tests. Meanwhile, the existing TCF bleaching process was further optimized, resulting in an additional increase in pulp brightness (from 85% ISO to 87% ISO) and greater brightness stability (bright-

ness reversion down from 6 points to 2 points after 1 hour at 105°C), with no significant difference in pulp properties. Further optimization has produced incremental improvements in brightness, brightness stability, and productivity.

Pilot-plant trials with ozone

The mill's experience in 1992 indicated that the current technology based on oxygen and hydrogen per-

oxide alone could not produce TCF market pulp with the required brightness at a competitive cost. At that time, the current state of knowledge about ozone technology had been summarized in two literature reviews (4, 5). There were only two reports on mill experience, namely Lenzing (medium-consistency Z stage) and Union Camp (high-consistency Z stage) (6, 7). The literature covering work in pilot plants was meager (8), even though there were several pilot plants engaged in active research of ozone bleaching (9). Most of the investigative work has been directed toward improving TCF bleaching of softwoods and birch from the northern hemisphere. Application of ozone for bleaching of eucalypt pulp has been the subject of only a few studies (10–14). Indeed, the current list of industrial installations with TCF bleaching does not include a mill using eucalypt pulp (15).

Ozone-bleaching of eucalypt pulp was unmapped territory. The important unknowns included Z-stage consistency, ozone charge, position of the Z stage in a TCF sequence, effect of acid washing on ozone performance, and effect of ozone on pulp strength. These process issues required further investigation, along with other difficulties related to ozone generation, the mixing of gases with pulp, and the handling of the residual gas mixture. Given the extent of these unknowns, there was a clear need to conduct pilot-plant tests with eucalypt kraft pulp.

The primary objective of the pilot-plant tests was to evaluate the effectiveness of ozone bleaching in improving the brightness of TCF-bleached pulp and reducing production costs. The principal process variables were Z-stage consistency and ozone charge. Results from the pilot-plant tests were compared with commercial TCF and ECF pulps from the Aracruz mill.

Experimental

The ozone-based TCF bleach sequences that were tested in the two pilot plants are listed in Fig. 1, along with a description of the pulps.

Pulp samples

Two commercial pulp samples (oxygen-delignified eucalypt kraft) were collected from the Aracruz mill for use in the pilot-plant tests. One sample was collected without acid treatment after the oxygen-delignification stage. The other sample was collected after being treated in an acid stage following oxygen delignification. Characteristics of the two pulp samples are listed in Table I.

Pilot plants

Two pilot plants were chosen to conduct the tests; Plant A (ASAM pilot plant in Baienfurt, Germany) and Plant B (pilot plant at Centre Technique du Papier in Grenoble, France). Characteristics of the pilot plants are outlined in Table II.

Plant A. The pulp shipped to Plant A was oxygen-delignified without acid treatment at the mill. The required amount of pulp was slushed in a large pulper and transferred to the pulp-bleaching area. The plant operated continuously 24 hours per day throughout the duration of the test at a flow of approximately 120 kg of moisture-free pulp per hour. The filtrate circuit operated on countercurrent mode, with a small filtrate purge of 2.0 m³/a.d. metric ton in the acid stage. Three bleach sequences were tested: AZPP, AZP, and A(EPO)AZP. The Z stage was carried out at high consistency on all three sequences. The "A" in these sequences refers to treatment with sulfuric acid at the pilot plant.

Plant B. Two pulps were shipped to Plant B. Both were oxygen-delignified, with one pulp receiving acid treatment at the mill and the other receiving no acid treatment. The pulp was slushed in a pulper and

transferred to the pulp-bleaching area. Plant B operated in a batch mode, with approximately 250 kg of moisture-free pulp required per batch of pulp bleaching. The pulp and filtrate samples were collected during the pulp-dewatering operation. The acid-treated pulp was bleached in an AZP sequence. The pulp without acid treatment was bleached in an AZ(EPO)P sequence. In both cases, the Z stage was carried out at medium consistency.

Acid treatment

Acid treatment and/or a chelation stage is normally required in TCF pulp bleaching to remove transition metals from the circuit. In the acid treatment (A-stage) at Aracruz mill, the pulp is normally treated with acids to pH 2 at 4.0% consistency for 30 min and then washed. The pulp without a mill acid treatment was acid-treated at the site of the pilot plants with sulfuric acid. The pulp previously treated in an acid stage was slushed and acidified to pH 3, the typical pH for ozone bleaching.

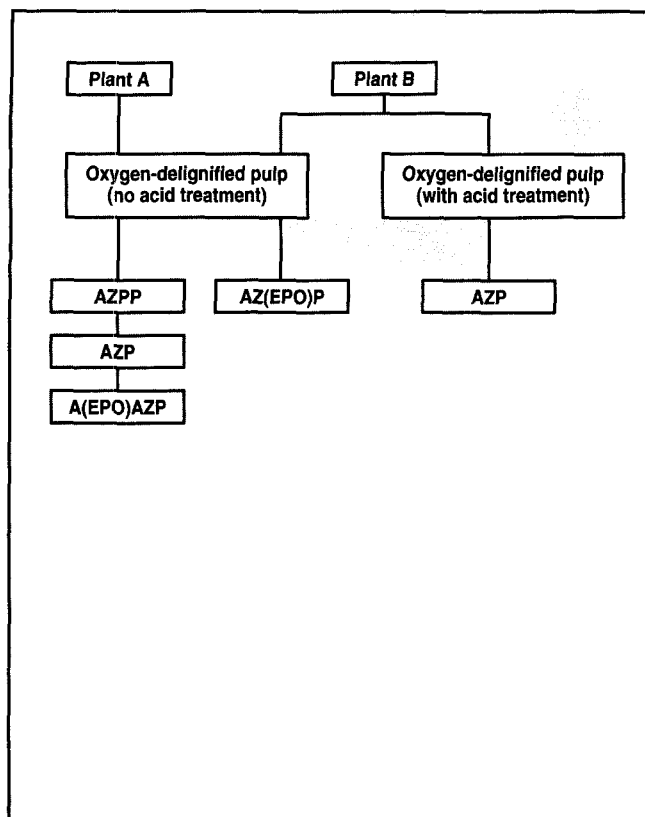
Ozone application

In both plants, ozone was generated at 6.0% concentration w/w (weight per weight). At Plant A (high-consistency Z stage), the ozone-oxygen gas mixture was injected into the pulp with a small positive pressure and concurrently to the downward pulp flow after the fluffer and ahead of the high-density Z stage. At Plant B (medium-consistency Z stage), the ozone charge was applied with a dynamic mixer. However, because of its capacity limitation, it was necessary to split the ozone application into two sequential pulp passes.

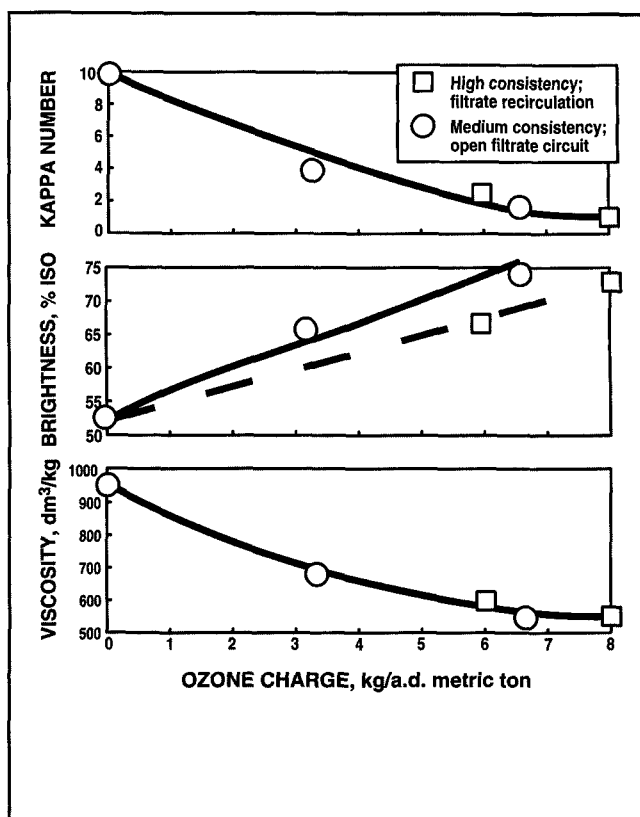
Pilot-plant results—pulp brightness and chemical consumption

Table III shows the performance of the ozone-based TCF bleach sequences that were tested in the pilot

1. Pulps and bleach sequences tested at the two pilot plants



2. Kappa number, brightness, and viscosity of pulp after Z stage as functions of ozone charge at two levels of pulp consistency



plants and compares these results with commercial pulps from the Aracruz mill. The different bleach sequences produced different results with respect to pulp brightness and chemical consumption.

Plant A—high-consistency Z stage

The AZPP sequence was initially tested, but the two consecutive P stages without an intermediate lignin-activation stage did not produce a satisfactory increase in pulp brightness, as described in the literature (16, 17). On the other hand, the AZP sequence at a higher ozone charge yielded pulp of 83.9% ISO brightness. The AZP sequence also showed a significant reduction in the consumptions of hydrogen peroxide and sodium hydroxide. However, the final pulp brightness produced with this sequence was still low, indicat-

IV. Metal content in the pulp

Metal type	Commercial pulp		Pulp from pilot plant A	Pulp from pilot plant B
	(After O stage)	(After A ₁ stage)	(after A ₁ stage)	^a (after A stage) ^b
Manganese, mg/kg	5.8	0.4	31.2	0.1
Iron, mg/kg	4.7	3.8	16.1	7.6
Copper, mg/kg	0.2	0.3	0.8	0.2

^a Oxygen-delignified pulp with no acid treatment
^b Oxygen-delignified pulp with acid treatment

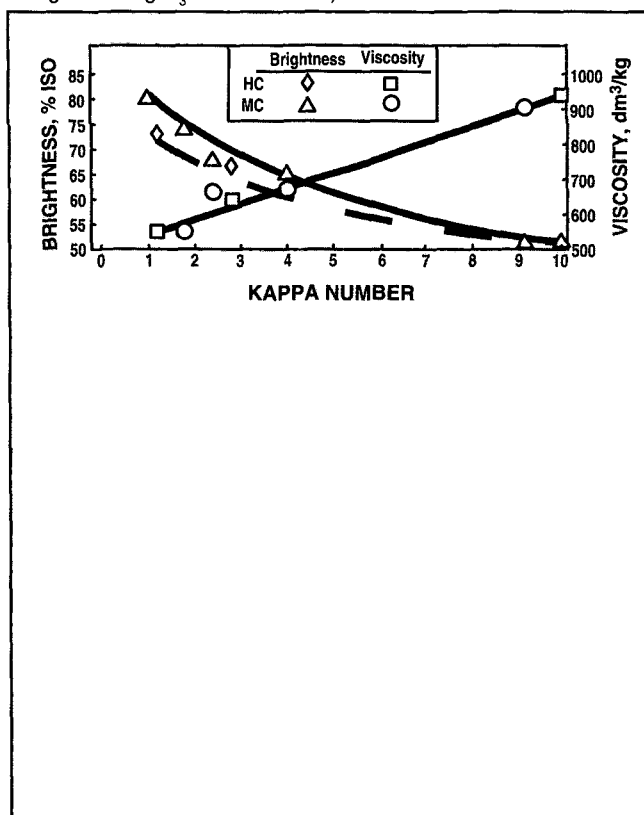
ing the need for further optimization.

As an alternative, an EPO stage was introduced into the bleach sequence before the Z stage, resulting in a five-stage A(EPO)AZP bleach sequence. The Z stage ahead of the final P stage acted as a lignin activator, thus enabling the bleach sequence to produce good-brightness pulp with lower ozone charge at a reasonably low consumption of hy-

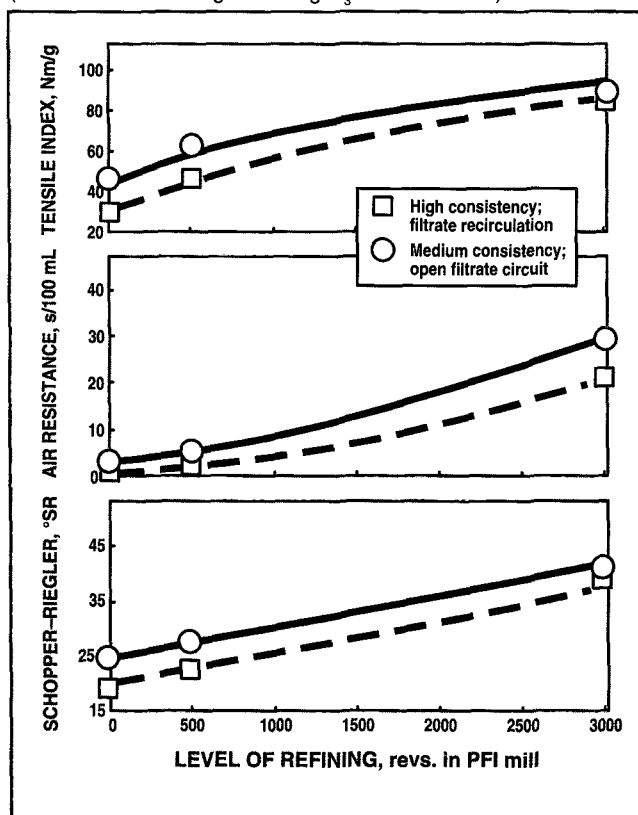
drogen peroxide (17). The final pulp brightness was significantly increased with the use of only 4.5 kg O₂/a.d. metric ton. Similar results were reported in a recent paper covering eucalypt TCF pulp (13).

Up to this phase of the tests at Plant A, it was apparent that higher brightnesses could not be obtained, even at a rather high ozone charge of 8 kg O₂/a.d. metric ton. This difficulty can be attributed to (a) the

3. Brightness and viscosity of pulp after Z stage as functions of kappa number at two levels of pulp consistency (constant ozone charge = 6.0 kg O₃/a.d. metric ton)



4. Tensile index, air resistance, and drainability of pulp after Z stage as functions of degree of beating at two levels of pulp consistency (constant ozone charge = 6.0 kg O₃/a.d. metric ton)



adverse effects of the transition metals in the decomposition of hydrogen peroxide and ozone (6, 8, 11-14, 18-22) as well as (b) the adverse effects of COD on ozone consumption (14, 21). A significant increase (four to six times) of manganese, iron, and copper content in the pulp collected after the acid-treatment stage was noticed, as seen in Table IV. This increase in metal content is due to filtrate recirculation, and the phenomenon has been reported in other papers (14, 23). In the case of Plant A, most of the undesired metals were kept in the process, which made it difficult to obtain high pulp brightness.

On the other hand, the inability to achieve higher brightness cannot be attributed solely to the metal content in the pulp. Other workers have stated that the effect of metal in the decomposition of ozone is small because of the fast reaction of the ozone

with the pulp (14, 21). A recent work (23) stated that the more significant effect of filtrate recirculation is the increase in the COD load to the Z stage.

Plant B—medium-consistency Z stage

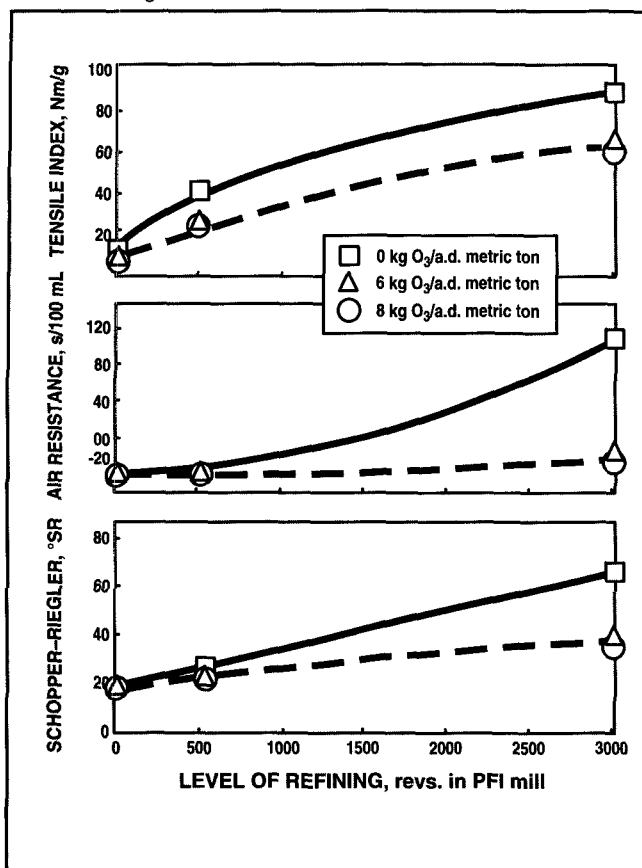
Pulp with no acid pretreatment. The tests in Plant B were facilitated by the experience gained at Plant A and by laboratory tests. The EPO stage was initially introduced in the bleach sequence following the Z stage, resulting in a four-stage AZ(EPO)P bleach sequence. This sequence was evaluated using the same pulp as Plant A—pulp without acid pretreatment at the mill. Table III shows that an ozone charge of 6.6 kg/a.d. metric ton produced a pulp of 86% ISO brightness, with low kappa number and acceptable viscosity.

Pulp with acid pretreatment at the mill. For the pulp previously acid-treated at the mill, the same ozone charge in an AZP bleach sequence produced a higher pulp brightness with much lower charges of hydrogen peroxide and sodium hydroxide, as seen in Table III. The acid-treated pulp also had lower final kappa number and rather high viscosity in comparison with the pulp that received no acid treatment.

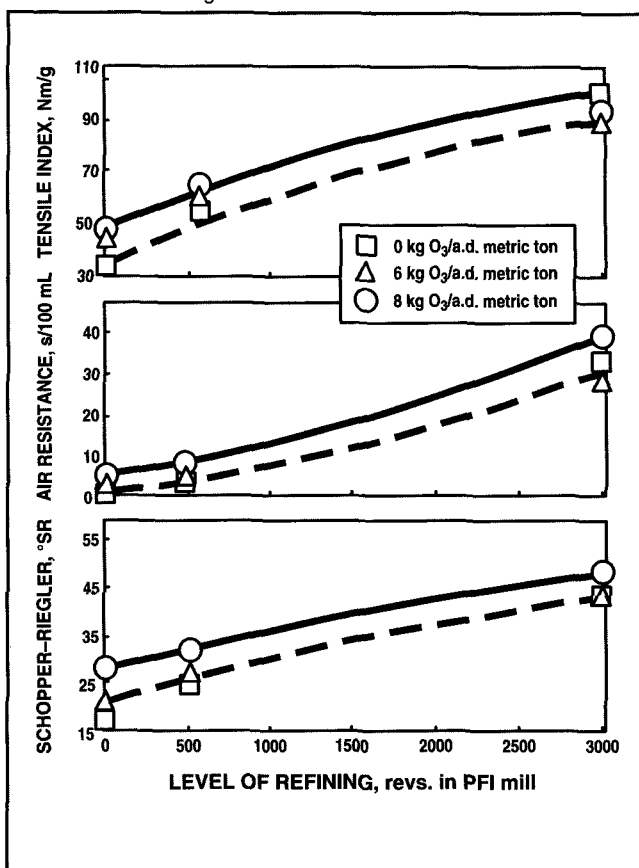
The superior performance of the acid-treated pulp in a TCF bleach sequence can be explained by the efficiency of the acid treatment, which removes transition metals (1, 11, 24) and COD (14, 21). At the Aracruz mill, the acid treatment removed 90% of the manganese ions and over 70% of the pulp's COD content. Additional acidification of the pulp at Plant B, with an open filtrate circuit, resulted in a total manganese removal of approximately 98%

Ozone Bleaching

5. Tensile index, air resistance, and drainability of pulp after high-consistency Z stage as functions of degree of beating at three levels of ozone charge



6. Tensile index, air resistance, and drainability of pulp after medium-consistency Z stage as functions of degree of beating at three levels of ozone charge



(Table IV), which helps explain the high pulp brightness attained with the well-washed, acid-treated pulp.

Effect of Z-stage pulp consistency

The effectiveness of the Z stage was evaluated at two pulp consistencies: medium (10%, Plant B) and high (45%, Plant A).

The fundamental reaction mechanisms of lignin and carbohydrates with ozone are well established at low, medium, and high pulp consistencies (25–30). However, the literature is not unanimous in recommending the Z-stage consistency with the best chemical consumption, brightness, and pulp properties. Nevertheless, there is a clear trend toward application of ozone at medium consistency (15).

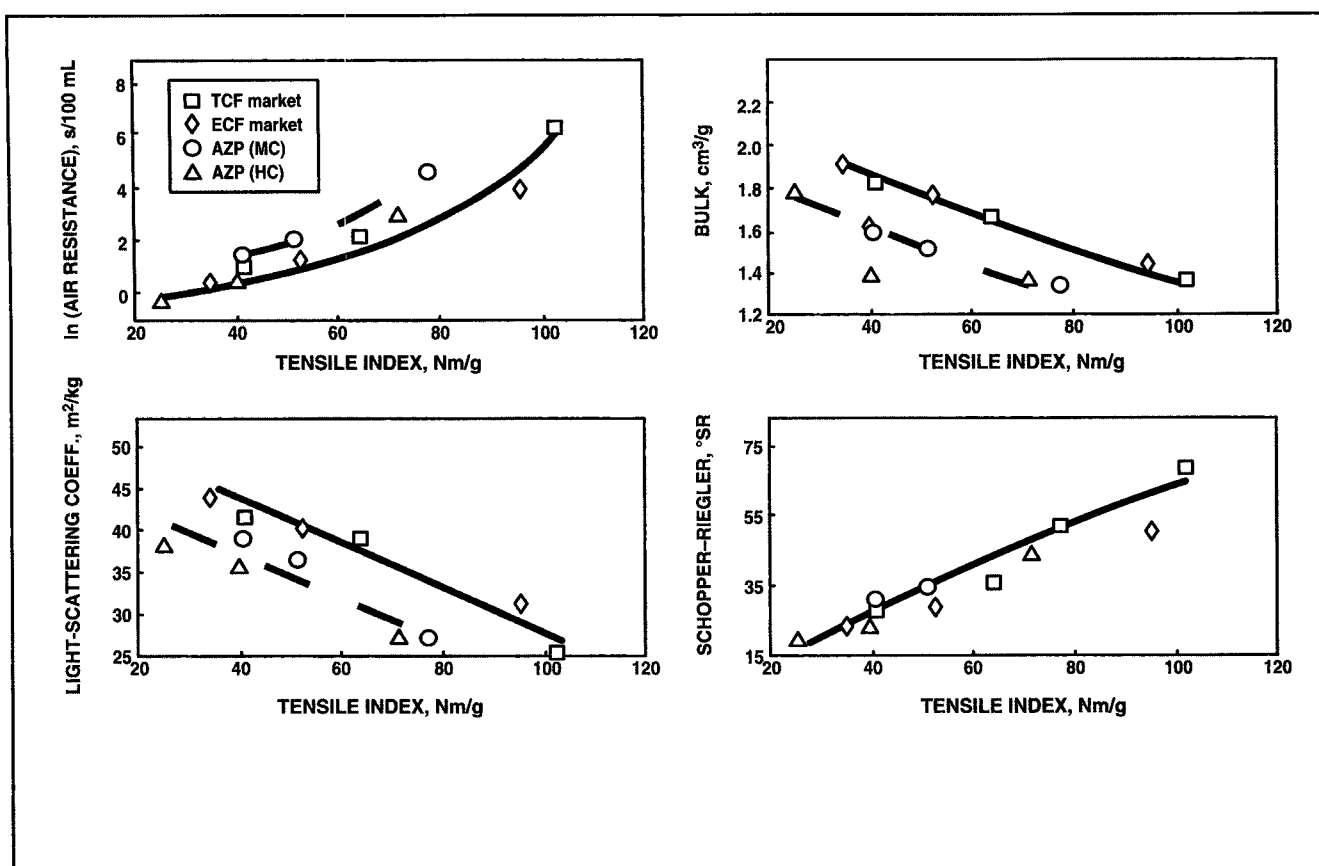
Recent studies (31, 32) indicate that medium-consistency (MC)

ozone bleaching is more selective toward lignin, thus producing a pulp of higher viscosity and strength than pulp bleached in a high-consistency Z stage. On the other hand, several studies indicate that more than 90% of the ozone charge is consumed by the pulp in high consistency (8, 24, 31–34) vs. only 60–90% consumption in medium consistency. Thus ozone treatment of pulp at high consistency would be expected to produce a higher delignification at the Z stage. However, it has been observed that at the same ozone consumption, both medium- and high-consistency ozone bleaching have presented similar results in terms of kappa reduction (8, 22, 33), final brightness, and viscosity levels (33).

In the tests conducted with eucalypt pulp, Z-stage ozone consumptions were found to be 90–100% of

the initial charge at high-consistency and 90–95% at medium consistency, as seen in Table III. A recent study shows an ozone consumption of 95% at an ozone concentration of 11% w/w, while consumption can vary from 96% to 99% at an ozone concentration of 13% w/w for an industrial-scale Z stage at medium consistency (35). With the current ozone generators capable of producing ozone at concentrations of 10–13% w/w, there should be no difference in the ozone consumption between Z stages at medium and high consistencies.

Figure 2 shows the kappa number, brightness, and viscosity of the pilot-plant pulps after the Z stage as functions of ozone charge. The results show that, at a given ozone charge, brightness was higher for the pulps bleached at medium consistency and open filtrate circuit than



at high consistency with filtrate recirculation. However, the consistency of the Z stage had no effect on kappa number or pulp viscosity. Similarly, Fig. 3 shows that, at a given kappa number, brightness was higher for the pulps bleached in a medium-consistency Z stage. The Z-stage consistency had no apparent effect on pulp viscosity.

These results indicate an overall better performance of the Z stage at medium consistency and open filtrate circuit. This is in agreement with the trend toward adoption of TCF bleach sequences with a Z stage at medium consistency (9, 15, 36), a trend that is also promoted by lower investment and installation costs. However, there are several well-known technical difficulties related to medium-consistency ozone bleaching, including chemical/pulp mixing performance, gas-to-pulp ratio on

the reactor, chemical concentration, and pressurization of the gas mixture.

Effect of ozone charge

During the pilot-plant tests, different ozone charges were applied to the pulp at high and medium consistencies. The comparison was carried out using the pulp without acid treatment at the mill. Increasing the ozone charge significantly affected the kappa number, brightness, and pulp viscosity after the Z stage, as seen in Fig. 2.

The kappa-number reduction per kilogram of ozone charged was the same (1.1–1.3 points), regardless of the Z-stage pulp consistency or the state of the filtrate circuit, as seen in Fig. 2. Results from the literature showed reductions of 1.0 unit of kappa number per kilogram of ozone

(mill Z stage, high consistency, closed filtrate circuit, softwood) (37) and 0.7–1.0 units per kilogram of ozone (pilot-plant Z stage, open filtrate circuit) (38). Reductions of 0.6–0.8 units of kappa number were reported for softwood (39, 40) and 1.0 unit for birch (23) in a mill operating a Z stage at medium consistency with an open filtrate circuit.

The larger kappa-number reductions obtained with eucalypt pulp suggest that its residual lignin is more reactive toward ozone than that of softwood and hardwood (birch) pulps.

TCF bleaching with and without ozone

TCF bleaching of eucalypt pulp with ozone demonstrates a high potential for increases in pulp brightness and brightness stability, with significant

Ozone Bleaching

reductions in consumption of hydrogen peroxide (Table III).

Pilot-plant results— pulp quality

Effect of Z-stage pulp consistency

The consistency of the Z stage had a significant effect on pulp properties, as seen in Fig. 4. At the same level of laboratory refining (revolutions in a PFI mill), the pulps bleached in a medium-consistency Z stage had superior properties, confirming results reported elsewhere (31, 32, 41–43). Another possible explanation for this finding is the refining effect of the dynamic mixer that is used during ozone bleaching at medium consistency. The refining effect of the dynamic mixer has been noted previously (44). This refining effect was further enhanced by the need to pass the pulp twice through the Z stage in Plant B.

Effect of ozone charge

The ozone charge in the Z stage also had a significant effect on pulp properties, although the effect depended on the consistency of the pulp.

High consistency. The results in Fig. 5 show that at a given level of refining, the pulps bleached in a high-consistency Z stage had lower tensile strength, air resistance, and Schopper–Riegler drainability than the pulps that were not treated with ozone. These results indicate a strong action of the ozone on the pulp fibers, thus reducing the fiber strength and its inherent bonding capacity.

While these results are in accordance with other works (41, 42, 45, 46), they contradict reports that ozone-bleached pulp have similar (17, 37, 47–50) and even higher strength (51–53) than pulps bleached with CEDED or OD(EO)PD sequences. Conversely, there was no significant difference in properties for pulps treated with ozone charges of 6.0 kg and 8.0 kg/a.d. metric ton, although

pulp properties were slightly lower for the pulps treated at the higher ozone charge.

Medium consistency. The results in Fig. 6 again show that pulps with and without ozone treatment had different properties. However, in the case of medium-consistency ozone treatment, the ozone-treated pulp showed higher levels of tensile strength, air resistance, and Schopper–Riegler drainability. This is the opposite of the results observed at high consistency (Fig. 5). The difference between high consistency and medium consistency can be explained by the refining action of the dynamic mixer at Plant B and by the need to pass the pulp twice through the Z stage. The refining action of the dynamic mixer has been reported elsewhere (44).

TCF bleaching with and without ozone

Figure 7 shows that the mill's TCF and ECF market pulps (without ozone) had comparable levels of porosity, opacity (light scattering coefficient), bulk, and Schopper–Riegler drainability when compared at the same tensile level. However, the ozone-treated TCF pulps from the pilot plants showed different properties than the non-ozone-treated TCF pulp from the mill. The ozone's action imparts to the pulp a more compact structure (lower bulk), lower porosity, and lower opacity when compared with the mill's TCF pulp at the same tensile strength. This indicates that the strength development for pulp with and without ozone bleaching was not obtained through the same combination of beating effects.

The results presented in Fig. 7 suggest that ozone treatment has a more pronounced effect in terms of fiber flexibility than the external fibrillation and fines formation or fiber cutting that occurs during pulp refining. This aspect was confirmed by examining plots of water-reten-

tion value vs. tensile index and air resistance vs. bulk. Both plots revealed a different behavior for the pulp treated with ozone. Conversely, a plot of dynamic drainage time (and Schopper–Riegler) vs. tensile index showed no difference among the four pulps. The strong action of the ozone on the fiber hydrophilicity and also on the fiber flexibility has been studied (53).

Given these findings, it is clear that ozone bleaching has a distinctive effect on fibers and can produce pulps with different properties than those normally produced with ECF and/or TCF bleach sequences without an ozone stage.

Conclusions

Several TCF (totally chlorine free) bleach sequences with ozone stages were evaluated at two pilot plants. Ozone was applied at high consistency in one plant and at medium consistency in the other plant. The oxygen-delignified eucalypt kraft pulp samples used in the trials were obtained from the Aracruz mill in Brazil.

The results showed that the use of ozone in a TCF bleach sequence can increase pulp brightness to better than 89% ISO, reduce brightness reversion, and reduce consumption of hydrogen peroxide. Pulp consistency during the Z stage and the ozone charge greatly affected the physical properties of the pulp.

Optimization of the ozone-bleaching process is still required to achieve the brightness demanded by the market. Nevertheless, the results of the pilot-plant tests with commercial oxygen-delignified eucalypt kraft pulp indicate a great potential to obtain new products with improved brightness at lower production cost. ■

Literature cited

- De Lima, M. M., Manfredi, V., and Claudio Da Silva, E., Jr., *TAPPI 1990 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 799.
- Claudio Da Silva, E., Jr., *TAPPI 1993 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Wackslavowski, A., Peixoto, M. A., De Carvalho Filho, A. C., et al., *26th Pulp and Paper Annual Meeting Proceedings*, ABTCP (Brazilian Pulp and Paper Technical Association), Sao Paulo, Brazil, 1993, p. 25.
- Claudio Da Silva, E., Jr., "The use of ozone to bleach paper pulp," Ph.D. thesis, SUNY, Syracuse, NY, 1979.
- Liebergott, N., Van Lierop, B., and Skothos, A., *Tappi J.* 75(2): 117(1992).
- Peter, W., *TAPPI 1993 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Nutt, W. E., Eachus, S. W., Griggs, B. F., et al., *TAPPI 1992 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1109.
- Funk, E., Szopinski, R., Munro, F., et al., *TAPPI 1992 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1091.
- "Ozone for Pulp Bleaching," Jaakko Poyry AB, Lidingo, Sweden, Sept. 1992.
- Poulin, T. M. and Ferreira, G., *26th Pulp and Paper Annual Meeting Proceedings*, ABTCP (Brazilian Pulp and Paper Technical Association), Sao Paulo, Brazil, 1993, p. 35.
- Sacan, V. M. and Yang, J. L., *26th Pulp and Paper Annual Meeting Proceedings*, ABTCP (Brazilian Pulp and Paper Technical Association), Sao Paulo, Brazil, 1993, p. 1.
- Colodette, J. L., De Oliveira, R. C., Gomide, J. L., et al., *26th Pulp and Paper Annual Meeting Proceedings*, ABTCP (Brazilian Pulp and Paper Technical Association), Sao Paulo, Brazil, 1993, p. 71.
- Kubelka, V., Wizani, W., Neubauer, G., et al., *TAPPI 1994 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Sixta, H., Krotscheck, A. W., and Ruckl, W., *TAPPI 1994 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Albert, R. J., *TAPPI 1994 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Lachenal, D. and Nguyen-Thi, N. B., Internal Report, CR No. 2999, Centre Technique Du Papier, Grenoble, France, 1992, p. 22.
- Colodette, J. L., Ghosh, A. K., Dhasmana, B., *TAPPI 1994 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Devenyns, J., Desprez, F., and Troughton, A. A., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 443.
- Colodette, J. L., Singh, U. P., Ghosh, A. K., et al., *TAPPI 1993 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Bryabt, P. S., Robarge, K., and Edwards, L., *Tappi J.* 76(10): 148(1993).
- Henricson, K. and Pikka, O., *TAPPI 1994 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Szopinski, R. and Stronberg, B., *TAPPI 1993 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Henricson, H., *TAPPI 1994 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Kappel, J., Greeng, M., and Brauer, P., *TAPPI 1993 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Gratzl, J. S., Claus, P., and Recichel, G., *Tappi* 59(11): 86(1976).
- Gierer, J., *Holzforschung* 44(5): 387(1990).
- Jacobson, B., Lindbrad, P. O., and Nilvebrand, N. O., *1991 International Pulp Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta, p. 45.
- Laxen, T., Rynnamen, H., Peltonen, J., et al., *1991 International Pulp Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta, p. 19.
- Lachenal, D. and Muguet, M., *Proceedings of 1991 International Symposium in Wood and Pulping Chemistry*, Vol. 1, TAPPI PRESS, Atlanta, p. 107.
- Gellerstedt, G., *9th Sunds Defibrator Technical Seminar Proceedings*, Williamsburg, VA, 1992, p. 8.
- Hurst, M. M., *TAPPI 1992 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1061.
- Proctor, A. R., *Pulp Paper Can.* 75(6): 1283(1986).
- Greenwood, B. F. and Szopinski, R., *TAPPI 1992 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Oltman, E., Gause, E., Kordsachia, O., et al., *Papier* 46(10): 341(1992).
- Dahllof, H., *TAPPI 1994 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- "Why TCF?" Jaakko Poyry AB, Lidingo, Sweden, October 1993.
- Steffes, F. and Reeve, R., *TAPPI 1994 Non-Chlorine Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta.
- Kappel, J., Bräuer, P., and Kittel, P., *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1173.
- Ebeling, K., *1993 Alfax Ozone Symposium Proceedings*, Alfax AB, Karlstad, Sweden.
- Munro, F., *1993 Alfax Ozone Symposium Proceedings*, Alfax AB, Karlstad, Sweden.
- Lindholm, C. A., *1991 International Pulp and Paper Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta, p. 1.
- Lindholm, C. A., *Paperi Puu* 68(4): 283(1986).
- Lindholm, C. A., *Paperi Puu* 72(2): 145(1989).
- Bennington, C. P. J. and Seth, R. S., in *Fundamentals of Papermaking* (C.F. Baker and V.W. Punton, Eds.), Vol. 1, Mechanical Engineering Publications, London, 1989, p. 87.
- Lindholm, C. A., *Paperi Puu* 69(3): 211(1981).
- Liebergott, N. and Van Lierop, B., *Tappi* 64(6): 95(1981).
- Singh, R. P., *Tappi* 65(2): 45(1982).
- Dillner, B. and Tibbiling, P., *1991 International Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 59.
- Liebergott, N., Van Lierop, B., Garner, B.C., et al., *TAPPI 1987 Environmental Conference Proceedings*, TAPPI PRESS, Atlanta, p. 305.
- Liebergott, N., Van Lierop, B., and Kubes, G. J., *TAPPI 1981 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 157.
- Rothenberg, S., Robinson, D. H., and Johnsonbaugh, D. K., *Tappi* 58(8): 162(1977).
- Djamal, S., Kojima, Y., and Koyama, T., *Japan Tappi* 38(11): 1136(1984).
- Marton, R., Eriksson, K. L., and Granzow, S., Research Report No. 92, ESPRI, Syracuse, NY, 1990, p. 125.

Received for review June 16, 1994.

Accepted July 20, 1994.