

A survey of the use of ozone in bleaching pulps, Part 2

Norman Liebergott, Barbara van Lierop, and Anastasios Skothos

Senior scientist, scientist, and development engineer, Pulp & Paper Research Institute of Canada, 570 St. John's Blvd., Pointe Claire, PQ, Canada H9R 3J9

ABSTRACT *Ozone has been used either alone or with other bleaching agents in a multistage process, primarily to replace delignification stages that use molecular chlorine. The effects of the main variables (consistency, pH, time, temperature, pretreatment of chemicals, and chemical additives) on the properties of hardwood and softwood kraft and kraft-oxygen pulps are reviewed. Results on high-consistency ozone bleaching show that the optimum pH for an ozone stage is between pH 2 and 3. The best ozone consumption on pulp is between 25% and 46% consistency. Raising the temperature to as high as 60°C has little effect on ozone-stage efficiency. An extraction stage after the ozone stage improves the bleachability of the pulp. Furthermore, ozone bleaching is being developed extensively in pilot plants.*

KEYWORDS

Bibliographies
Delignification
High consistency
Kraft pulps
Ozone
Ozone bleaching
Pilot plants
Pulp properties
Variables

Ozone—properties and present uses (continued)

Effect of caustic extraction on kappa number and viscosity

An extraction stage applied to an ozone-treated pulp improves the bleachability of the pulp in the subsequent stages without harming the viscosity.

There are conflicting reports in the literature about the merits of extracting a pulp with an alkali solution after an ozone stage. The general consensus is that an alkali extraction stage decreases the kappa number of the ozone-delignified pulp and is beneficial to the bleaching process (32, 35, 41, 50, 51). Its effect on viscosity and strength, however, is the subject of controversy. Some have proposed (41, 50) that the strong oxidizing activity of ozone promotes the formation of carbonyl and carboxyl groups within the polysaccharide sugar units.

The carbonyl units especially are prone to react under alkaline conditions such as in the extraction stage or even in the cuene viscosity test. This reaction leads to a shortening of the

chain length. Therefore, a true viscosity result measuring the effect of the ozone stage can be obtained only if the carbonyl group is reduced to its original state; otherwise, falsely low viscosities are obtained.

Some authors advocate a borohydride treatment after an ozone stage prior to measuring viscosity (41, 50). We contend that the pulp will be subject to some alkali treatment within the sequence. Therefore, strength is the best parameter to use to measure the effect of the full bleaching sequence containing an ozone stage, instead of inducing a high viscosity reading through a borohydride treatment. Borohydride in an E stage counteracted the alkali decomposition of carbohydrates (3, 52), but its high price limits the industrial use.

Table VI shows the benefits of applying an alkali extraction stage after an ozone treatment on kraft and kraft-oxygen pulps. Extraction of ozonated and washed pulp with dilute aqueous NaOH solution lowered the kappa number by 0.6-3.7 units without affecting the viscosity. (The hard-

wood kraft-oxygen pulp was lowered by 0.6 units, and the softwood kraft pulp was reduced by 3.7 units.)

Table VII shows the effects on later bleaching with a chlorine dioxide stage. After OZD, the brightness of an eastern Canadian softwood pulp was 77.9% ISO; after OZED, it reached 89.2%. Similar advantages of an extraction stage were obtained using the OZEP sequence as compared to the OZP sequence (Table VIII). The extraction stage decreased the kappa number from 6.8 to 5.8, and the brightness after the next P stage increased from 77% to 85% ISO. The viscosity was not affected by including the P stage.

Applying an extraction stage to an unwashed Z-stage pulp was a better option than washing the pulp between the ozone and extraction stage (Table IX). Therefore, O(ZE) was more advantageous than OZE according to the kappa number test. Macas *et al.* (53) also reported that the washing between the Z and E stages could be eliminated without penalty.

VI. Effect of caustic extraction on kappa number and viscosity of ozone-treated pulps

	Kappa no.		Viscosity, mPa·s	
	Kraft	Kraft-oxygen	Kraft	Kraft-oxygen
Softwood				
Initial	29.4	17.7	32.9	23.2
Z stage	20.8	8.2	19.9	18.2
ZE stage	17.1	6.7	24.6	19.6
Hardwood				
Initial	14.5	11.1	17.7	18.6
Z stage	6.9	3.9	18.2	12.8
ZE stage	5.7	3.3	19.6	13.5

Z stage: 1% O₃, 53 s, 40°C, 35% cons., pH 2.2.
 E stage: 1% and 1.5% NaOH, 1 h, 60°C, 10% cons.
 Pulp washed between Z and E stages.

VII. Comparison of OZD and OZED

	Canadian softwood	
	Western	Eastern
Kappa number		
Brownstock	33.3	24.1
Oxygen stage	19.0	12.8
Brightness, % ISO		
OZD	69.1	77.9
OZED	83.4	89.2

Z stage: 0.5–0.75% O₃.
 D stage: 1.0% ClO₂.

XII. Toxicity of Z and ZE effluents (softwood kraft pulp)

Stage	Test species	LC ₅₀ , %
Z	<i>Oncorhynchus mykiss</i> Trout, 96-h LC ₅₀	> 100
Z	<i>Daphnia pulex</i> 48-h LC ₅₀	96
ZE	<i>Oncorhynchus mykiss</i> Trout, 96-h LC ₅₀	> 100
ZE	<i>Daphnia pulex</i> 48-h LC ₅₀	96

IX. Peroxide-ozone treatment of kraft-oxygen pulp (kappa no. 18.2, viscosity of 22.4 mPa·s)

Z stage O ₃ , %	P stage H ₂ O ₂ , %	Kappa no. after:			Viscosity mPa·s
		OZ	OZE	O(ZE)	
0.5	...	6.6	5.5	5.2	18.2
		O(PZ)	O(PZE)	O(PZE)	
0.5	0.5	6.0	4.8	3.4	17.6
	1.0	6.2	5.4	2.9	15.0

Z stage: 35% consistency, 30°C, pH 2.2.
 E stage: 1.0% NaOH in ZE. 1.5% NaOH in (ZE).
 Stages in parentheses indicate no washing between stages.

Oxygen vs. ozone delignification of softwood and hardwood pulps

Both ozone and oxygen treatments decreased the kappa number of a softwood pulp by approximately 40%, with similar effects on viscosity.

Both ozone and oxygen are bulk removers of lignin. Which one should be applied first in the sequence has been the subject of much discussion. Least strength loss and economics will determine which combination is suitable in a commercial operation.

Hartler claimed that the selectivity in ozone delignification is better than oxygen delignification (41). However, the price of ozone prohibits any prolonged delignification in a Z stage. Along with others (51, 54), Hartler favored the OZ combination because less ozone is required than in the ZO combination to achieve comparable kappa numbers. Because ozone is a poor bleaching agent of bark and

X. Comparison between oxygen and ozone delignification

	Softwood kraft		Kraft-oxygen	
	O	ZE	O	ZE
Charge, % on pulp				
O ₂	1.7	...	1.9	...
O ₃	...	1.0	...	1.0
NaOH	3.2	1.5*	2.3	1.0*
Mg ⁺⁺	0.06	...	0.06	...
Time, min	30	1	30	1
Temperature, °C	100	40	100	40
Consistency, %	30	35	30	36
Pressure, atm	6	1	6	1
Kappa number				
Initial	29.4	29.4	14.5	14.5
After O or ZE	17.7	17.1	7.6	5.7
Viscosity, mPa·s				
Initial	32.9	32.9	17.6	17.6
After O or ZE	23.2	24.6	9.9	11.4

* In E stage.

VIII. Comparing OZP, OZEP, and ZOP

Sequence	Stage	Kappa no.	Brightness, % ISO	Viscosity, mPa·s
OZP	O	15.1	39.0	29.7
	Z	6.8	47.9	23.4
	P	...	76.8	21.6
OZEP	O	15.1	39.0	29.7
	Z	6.8	47.9	23.4
	E	5.8	57.9	24.8
	P	...	85.1	22.8
ZOP	Z	15.0	43.0	32.1
	O	6.4	55.9	23.9
	P	...	77.1	22.0

Z-stage: 0.5% O₃ in OZ. 1.0% O₃ in ZO.
P-stage: 2.5% H₂O₂.

XI. Effluent loadings of oxygen and ozone-treated pulps

Pulp	Stage	Effluent load, kg/ton		
		BOD	COD	Color
Softwood	O	15.6	68.0	117.3
	Z	4.9	18.4	15.6
	E	10.3	27.6	27.2
	ZE total	15.2	46.0	42.8
Hardwood	O	13.6	54.3	75.2
	Z	4.0	14.5	12.2
	E	8.1	21.1	18.5
	ZE total	12.1	35.6	30.7

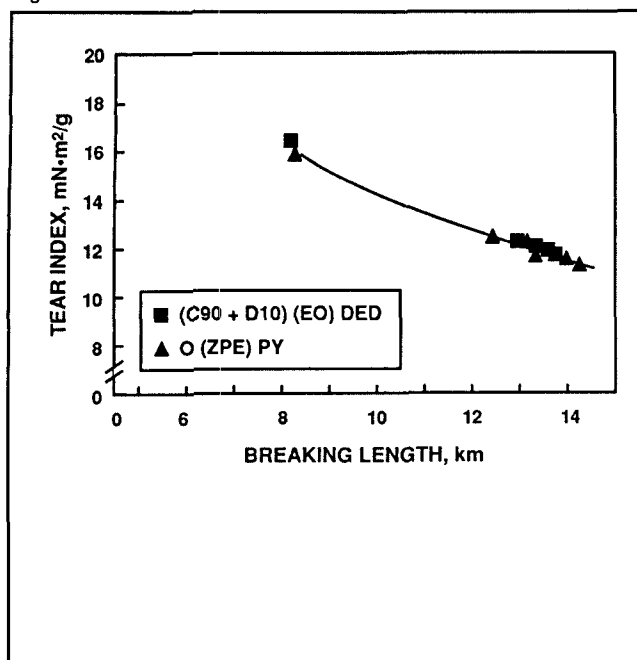
Effluent samples collected after dilution to 1% consistency.

XIII. Pilot plants for ozone bleaching

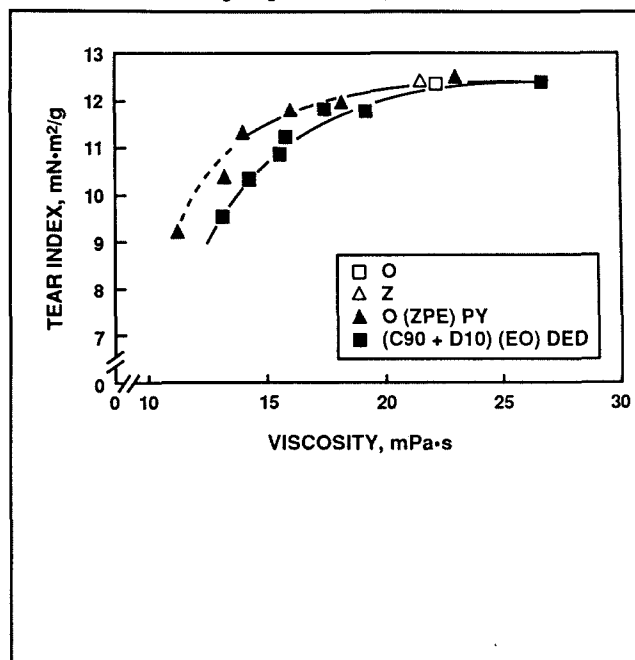
Startup year	Location		Capacity, tons/day	Consistency	Sequence	Pulp type
1971	Paprican	Pointe Claire, Que.	10	high	Z, (PZ)	Mechanical
1973	Scott Paper	Muskegon, MI	15	high	Z	Hardwood kraft
1973	Paprican	Pointe Claire, Que.	10	high	Z	Sulfite, kraft
1975	CTP	Grenoble, France	0.5	high	Z	Mechanical
1976	Myrens Verksted	Holmen-Hellefos, Norway	5	high	Z	Mechanical, sulfite
1982	Weyerhaeuser	Longview, WA	20	low	OZD OZDED	Softwood kraft
1982	PWA	Stockstadt, Germany	3	high	Z	Sulfite
ca. 1988	Union Camp	Eastover, SC	25	high	OZEDD	Kraft
ca. 1989	Waagner-Biro AG	Graz, Austria	1	low	OZP	Sulfite, kraft, nonwood fiber
1990	Kraftanlagen Heidelberg	Baienfurt, Germany	5	high	OZEP	Mg bisulfite
1990	Lenzing AG	Lenzing, Austria	100	medium	(EOP)ZP	Hardwood, dissolving
1991	ÖZF	Gratkorn, Austria	15	low, high	Any sequence	Kraft and sulfite
1991	E.B. Eddy Forest Products Ltd.	Espanola, Ont.	5	Low, medium, high	(O)Z...	Softwood kraft, hardwood kraft
1991	Paprican	Pointe Claire, Que.	5	medium	OZEP, OZED O(pZE)P	All types
1991	CTP	Grenoble, France	3	medium, high	...	All types
1992	Lenzing AG*	Lenzing, Austria	400	medium	(EOP)ZP	Hardwood, dissolving
1992	Union Camp*	Franklin, VA	1000	high	OZ(EO)D OZEP	Kraft, integrated

* Commercial installation.

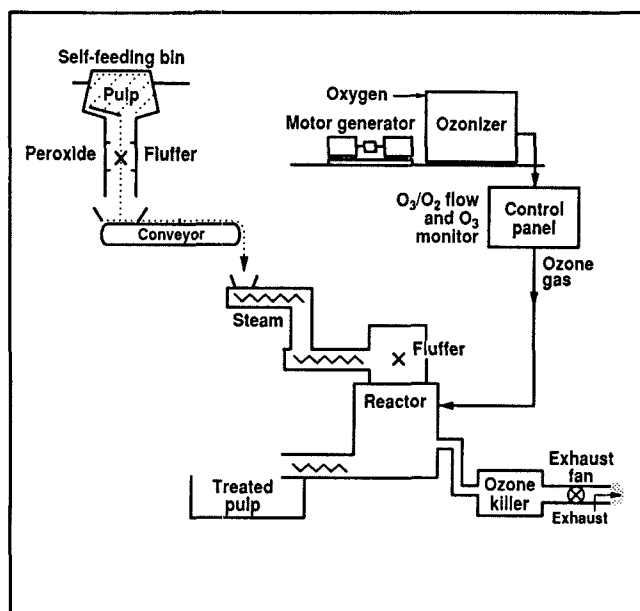
9. Curves for tear strength vs. breaking length for a conventionally bleached pulp and an O(ZPE)Y-bleached pulp at 88-90% ISO brightness



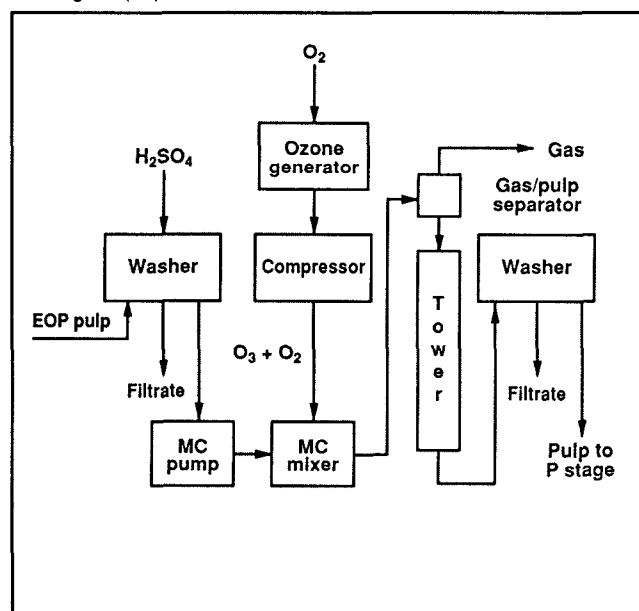
10. The viscosity reading of an O(PZE)PY bleached pulp is lower at given tear value than its (C90+D10)(EO)DED bleached counterpart. (Tear index at a breaking length of 13 km.)



11. Diagram of Paprican's 1973 pilot plant for ozone bleaching (75)



12. Block diagram of medium-consistency ozone bleaching at Lenzing AG (37)



shive particles (46, 54a), applying oxygen before an ozone stage assists in their removal. Also, OZ tends to give consistently favorable results, which is important for commercial application.

The results in Table X show that both oxygen and ozone were capable of delignifying a softwood and a hardwood kraft pulp to about the

same extent, as measured by the kappa number and the viscosity. ODED and ZEDED bleaching gave comparable brightness and strength results (55).

Comparing the effluent loadings from an oxygen stage on the softwood and hardwood kraft pulps and those from an ozone stage and subsequent extraction, the color loadings of the

ZE effluents were approximately 60% lower than those of the O-stage effluents (Table XI). COD loadings of the ZE effluents were appreciably lower than those of the O-stage effluents, but no difference was found in the BOD loadings. Wartiovaara (56) claimed that depending on the parameter in question, the pollution load is 40-90% lower with a ZEDED sequence than

with a (DC)EDED sequence if the initial ZE filtrate can be recycled to the brown stock washing.

Strength properties of ozone-treated pulps

The curve for tear strength vs. breaking length in Fig. 9 shows that the strength properties were not affected when an ozone stage was included in the sequence. The viscosity reading, however, was lower at a given tear value (Fig. 10). Others have also reported that pulps treated with ozone in a sequence did not show lower strength despite the lower viscosity readings (5, 45, 46, 48, 50, 51, 57). Lindholm (44) favored low-consistency ozone delignification for better strength retention than achieved under high-consistency conditions.

If an ozone stage is not carried out under forcing conditions, delignification is acceptable, and strength properties are not impaired (16, 33, 42, 46). A detailed evaluation of ozone-containing sequences applied to conventionally cooked pulp and to pulp cooked according to the modified continuous cooking (MCC) process indicated that caution should be used in making casual comparisons of pulp viscosities among different pulps and in making observations about the relationships between the pulp viscosities and pulp strengths (53).

A pilot plant study indicated no loss of strength properties when ozone was applied to oxygen-delignified kraft and sulfite pulps (58). It has been concluded that the results of low viscosity observed on ozone-treated pulps with the same strength properties as conventionally bleached pulps may be attributable to the viscosity test itself responding to the alkali sensitivity introduced by ozone on cellulose (5).

Toxicity of ozone effluents

Ozone effluents are reported to be essentially nontoxic to rainbow trout (59). Liebergott previously reported that Z and ZE effluents were toxic to *Daphnia pulex* (60). More recent work has indicated that ozone effluents are not toxic to *Daphnia* and to trout (*Oncorhynchus mykiss*) (Table XII).

Further research is required on this subject to evaluate whether an ozone bleaching stage produces by-products

in the effluent that may be problematic in biological systems.

Inorganic and organic additives as ozone pretreatments

Some organic additives—methanol, ureamethanol, DMS, and DMSO—help to retain pulp viscosity in varying degrees during ozone delignification. Inorganic compounds that are effective cellulose protectors in oxygen bleaching offered no protection during ozone delignification.

A considerable amount of research has been devoted to finding an additive or a pretreatment that would protect the cellulose and make the ozone react more preferentially with the lignin component in the fiber. As mentioned, Table I (part 1) presents a list of chemicals used as pretreatments and as additives during ozonization. None could be identified as preventing outright degradation of cellulose while promoting the removal of a large portion of the lignin.

Since the work by Osawa (13) on the ozonization of kraft pulp fibers suspended in pure nitromethane, methyl acetate, and mixtures of these solvents with water, others have published results on other organic and inorganic compounds (see Table I, part 1). Reportedly, the addition of small amounts of metal salts such as iron, copper, and nickel increased cellulose degradation (62). Other compounds used as an effective cellulose protector in oxygen bleaching (magnesium and iodine compounds) failed to protect the cellulose during ozone delignification (63). The addition of methanol (80–100% on pulp) showed some promise (63), but the quantities are too high for commercial application.

Replacing the water with organic solvents seems to prevent viscosity loss somewhat (3, 30, 63, 64). Jacobsen *et al.* (3) assumed that because cellulose reacts with ozone more readily when some lignin is present than it does in "lignin-free" pulps, the residual lignin acts not only as a radical scavenger but also as a radical initiator, which is responsible for the major attack on cellulose. Replacing the water during an ozone stage with a radical scavenger such as methanol water suppresses the radical reactions with cellulose. Lindholm (65) recycled spent liquors from an ozone stage as a pulp pretreatment prior to the ozone stage and found that the dissolved

lignin fragments act as carbohydrate protectors in low-consistency ozone bleaching.

Ozone works best at pH levels of 1–3. Some have considered this pH optimum to result from acid treatment removing the heavy metal ions in the pulp. Heavy metals may decompose the ozone, leaving a portion of it unavailable to react with the lignin (54). The application of a chelant such as DTPA before the Z stage, however, was shown to be best at pH 3 rather than pH 8, suggesting that acid sequestering is best for metal ion removal (48). DTPA chelation at pH 3 caused the Z stage to perform slightly better than sulfuric acid treatment alone.

There is some controversy over the type of acid treatment that is best used before an ozone stage. Some report that an organic acid such as acetic acid is just as effective as sulfuric acid (30, 32, 48). In contradiction to this, Mbachu found that acetic and formic acid pretreatments use less ozone to reach a given kappa number than does a sulfuric acid-treated pulp (28). Oxalic acid (32), acidified DMSO (32, 48), and NO₂ (30) improved the ozone treatment slightly. An acidic peroxide treatment at pH 2–3 just prior to ozone application also improved the efficiency of an ozone delignification stage (Table XI).

The problem of finding a cheap, effective commercial inhibitor of carbohydrate depolymerization during ozone delignification is still to be solved.

Using a sequence with an ozone stage to bleach chemical pulps

A sulfite pulp can be bleached to 90% ISO brightness using an OZP type of sequence, with the exact conditions of the sequence depending on the nature of the furnish. A kraft pulp can be bleached to a brightness of about 83% using an OZEP sequence and to 90% using an OZED sequence.

Ozone gives a substantially better delignification result on sulfite pulp than on a kraft pulp because of the different natures of the two pulps (37, 57). An OZP sequence applied to an Mg-bisulfite pulp at kappa no. 30 resulted in a brightness of 88%, with the pulp having good strength properties despite the viscosity loss (57). A kraft pulp, however, requires a more elaborate sequence to reach a 90%

brightness without a strength penalty.

In some studies, researchers concentrated on applying a multistage ozone treatment to boost the efficiency of ozone applications (29, 53, 54, 66-68). Allison's ZPZP sequence applied to an oxygen-delignified soda-AQ pulp bleached the pulp to a brightness of 85% using 0.65% O_3 , whereas the less-efficient ZEP sequence required 1.07% total O_3 (29). Also noted in Allison's study was that an interstage washing after the Z stage was not required, provided that additional alkali was used in the extraction or peroxide stage.

In the same light, another report described two or more ozone stages with an intermediate alkaline extraction giving a brightness approximately 10 units higher than that obtained after a single stage with the same quantity of ozone (46, 54). Kobayashi also claimed that, to obtain a similar brightness, less ozone was required in a two-stage sequence than in a single-stage treatment (68). Macas *et al.* showed that a TOO(ZE)P(ZE)P sequence, where T is a chelation step, bleached a pulp of low kappa number (kappa number 18.3 on brownstock, kappa number 6.5 after TOO) to a brightness of 91% (53). Their TOO-(ZE)PP sequence reached 85% brightness using 0.21% O_3 on pulp at 1% consistency.

Ozone and peroxide were unable to bleach a pulp above about 85% brightness (51). Consequently, to achieve a brightness of greater than 90% after ozone treatment (single or multistage), combinations of peroxide stages (25, 53, 66, 67), sodium hydrosulfite (51), peracetic acid (66), hypochlorite (54) and chlorine dioxide (3, 16, 33, 36, 40, 44, 46) must be used. Ozone is best for application in the early stage of a bleaching sequence (3, 33).

Ozone can replace the chlorination stage in pulp bleaching, as in a ZEDED sequence (54, 69) or an OZED or OZDED sequence (3, 16, 40, 44, 54, 70). Lindholm obtained a better brightness with an OZD sequence than with an OZED sequence using a low-consistency ozone stage (44).

An O(DZ)(EOP)D(ED) (40) or an O(DZ)ED (36) sequence bleached a pulp to 89-90% brightness, with the sequential DZ stage offering good selectivity and low AOX formation in

the effluent. Wigren (17) was the first to publish, in 1967, on the advantages of placing chlorine-based compounds before the ozone stage. Granum (70) showed that resin removal from sulfite pulps was superior after a (DC)ZEH sequence. In Tsai's work (71), the DZED sequence enhanced the removal of AOX formed during the first D stage.

Yield loss resulting from an ozone-containing sequence has been found to be comparable to the conventional bleaching sequences (16, 55). Others have reported that ozone contributes to some yield loss (54), especially when the pH is increased (72), but this loss may have been caused by forcing the conditions in the ozone stage.

Some authors reported that brightness stability was superior to that of conventionally bleached pulps (33). Others (66, 72, 73) found that the increased brightness reversion attributed to the use of ozone in a sequence could be prevented by either combining peroxide with ozone (72, 73) or by using peroxide or peracetic acid at the end of the sequence (66).

Ozone studies in pilot plants

Pilot-scale studies provide a means of verifying laboratory work. Pilot plants for ozone bleaching of the past twenty years are listed in Table XIII. Installations of ozone brightening of mechanical pulps are also included.

Ozone pilot plants in the 1970s and 1980s

In the 1970s, ozone bleaching and brightening pilot installations were reported (27, 74-78). Ozone brightening of mechanical pulp was demonstrated at Paprican's first pilot plant in 1971. The work was done with the Paprizon reactor, a high-consistency reactor designed at Paprican (75). In 1973, an ozone bleaching pilot plant (high consistency) was installed at Scott's S.D. Warren mill in Muskegon, Mich. (27, 76). The ozone reactor was designed by Ingersoll-Rand.

Subsequent pilot-scale work at Paprican was performed with an Ingersoll-Rand ozone reactor similar to the one used at Muskegon. Figure 11 shows the scheme of the second Paprican high-consistency ozone bleaching pilot plant, located at Pointe Claire, Quebec. It was single stage, and it had a capacity of 10 tons/

day. Trials were held with chemical pulps.

In the early 1980s, low-consistency (0.5%) ozone bleaching work was carried out at the Weyerhaeuser pilot installation at Longview, Wash. In Europe, a high-consistency ozone bleaching pilot plant was installed at the Papierwerke Waldhof-Aschaffenburg (PWA) Mg-sulfite mill in Stockstadt, Germany (79). Work in Austria on low-consistency ozone bleaching was also reported (58).

Ozone pilot plants in the 1990s

More recently, the impetus for commercialization of ozone bleaching technology has been the heightened environmental awareness, and the pressure to eliminate the formation of chlorinated organic compounds in the bleach plant. As a result, there has been a resurgence of ozone bleaching work, particularly at the pilot plant scale. In North America, an industrial high-consistency ozone stage will start up in late 1992 at Union Camp, Franklin, VA.

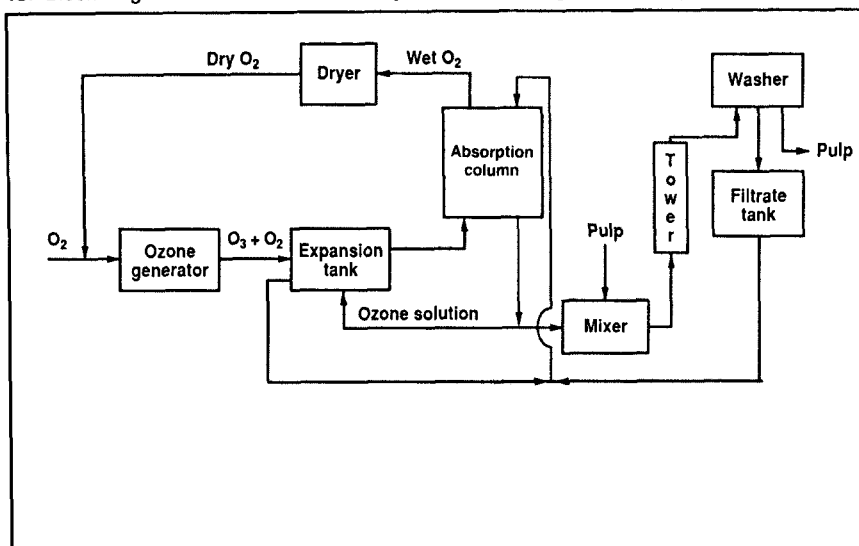
As part of their ASAM pilot plant, Kraftanlagen Heidelberg has installed a 5-ton/day, continuous, OZEP bleach plant with some counter-current recycling of bleaching filtrate (80). The Z stage is done at high consistency.

Medium-consistency ozone bleaching was started up at a pilot production facility (100 tons/day) at Lenzing AG, Lenzing, Austria, in August 1990 (37). An ozone stage replaced the hypochlorite stage in an (EOP)HP sequence, thus converting to (EOP)ZP. Lenzing AG produces hardwood dissolving pulp by the acid magnesium bisulfite process.

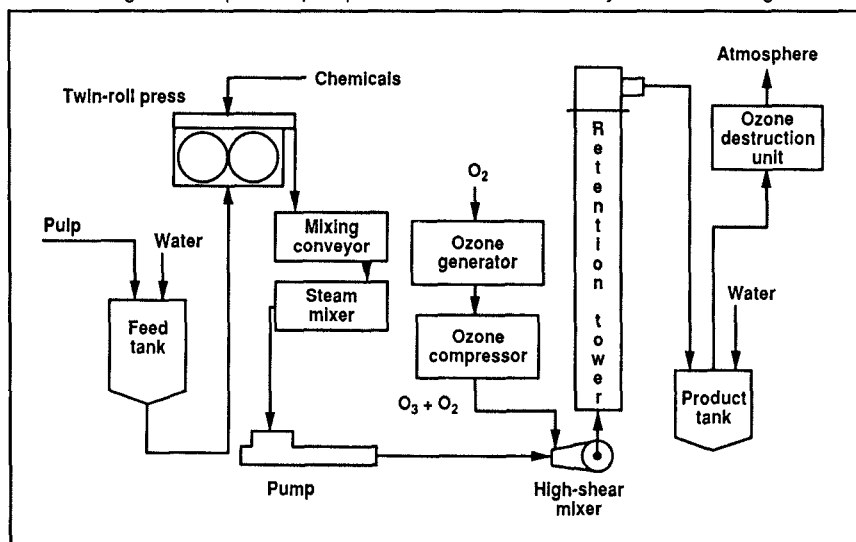
Figure 12 is a block diagram of the Z stage at Lenzing. The ozone-oxygen gas is compressed and added to the pulp at the medium-consistency mixer. The pressure in the mixer is 6.5 bar. The phase ratio, or the ratio of gas volume to pulp suspension volume, is 0.43. To reduce the pulp kappa number from 1.75 to 1.0, 1.76 kg/a.d.ton of O_3 is added to the pulp. Lenzing AG is planning to implement medium-consistency ozone bleaching at 400 tons/day.

To overcome the problem of purifying the excess oxygen in the off-gas from a Z stage, Voest-Alpine Industrieanlagenbau Ges. m.b.H. (VAI) has proposed a process by which ozone is

13. Block diagram of VAI's low-consistency, ozone-bleaching process (81)



14. Flow diagram of Paprican's pilot plant for medium-consistency ozone bleaching



dissolved in water (81). **Figure 13** depicts a block diagram of the process. Bleaching filtrate is recycled to an absorption column under a high pressure, 7 bar, where the ozone is dissolved in water. This way, the wet oxygen from the absorption column can be dried and recycled back to the ozone generator.

The ozone concentration in the gas is increased by recycling a portion of the aqueous ozone solution back to an expansion tank. The ozone gas evolves from solution and increases the concentration of the gas going into the absorption column. The aqueous ozone solution is added to medium-consistency pulp under pressure. Depending on the concentration of

ozone in solution and the desired ozone charge on pulp, the pulp consistency will be between 1% and 5.5%.

One of the major factors that must be considered is the temperature of the filtrate recycled to the absorption column. As temperature increases, ozone solubility decreases.

The VAI process has been installed at the ÖZF pilot plant in Gratkorn, Austria. The facility is a 15-ton/day, multistage pilot bleach plant with full recycling of bleaching filtrate.

Future pilot plants

At E. B. Eddy, Espanola, ON, a 5-ton/day pilot plant will be installed. Low-, medium-, and high-consistency ozone bleaching will be investigated.

A medium-consistency pilot bleach plant will be used to study ozone bleaching at Paprican. Work will be done primarily with softwood kraft pulp, followed by work with other types of pulp. **Figure 14** shows the scheme of the pilot plant. A pilot plant was to start up at CTP, Grenoble, France, in 1991, for the study of medium- and high-consistency ozone bleaching.

Concluding remarks

Published research work from the laboratory and pilot plants shows that ozone is an effective delignification and bleaching agent for kraft pulp. The use of ozone in combination with other bleaching agents such as oxygen, peroxides, and chlorine dioxide will make it possible to obtain a fully bleached pulp of 88-90% brightness. Commercial equipment is now available to conduct gas-phase reactions on high-consistency pulp. □

Literature cited

(Continued from Part 1.)

50. Gupta, M. K. and Eckert, R. C., 1984 Oxygen Delignification Symposium Preprints, TAPPI PRESS, Atlanta, p. 133.
51. Liebergott, N., van Lierop, B., Garner, B. C., and Kubes, G. J., Tappi J. 67(8): 76(1984).
52. Kordsachia, O., Reipschlater, B., and Patt, R., Paperi Puu 72(1): 44(1990).
53. Macas, T. S., Jiang, J. E., Becker, E. S., and Greenwood, B. F., 1991 International Pulp Bleaching Conference Proceedings, SPCI, Stockholm, p. 67.
54. Soteland, N., Pulp Paper Can. 75(4): T153(1974).
- 54a. Germgard, U. and Sjogren, B., Svensk Papperstid. 88(15): R127(1985).
55. Liebergott, N., van Lierop, B., and Kubes, G. J., Ozone: Sci. and Eng. 4: 109(1982).
56. Blomberg, L. and Wartiovaara, I., 22nd EUCEPA Conference, Florence, Italy, Oct. 6-10, 1986, vol. 1, p. 5.
57. Soteland, N. and Carlberg, G., Paperi Puu 69(10): 832(1987).
58. Prutsch, W., Meissl, S., Loquenz, H., and Hruscka, A., 1989 International Symposium on Wood and Pulp Chemistry, TAPPI PRESS, Atlanta, p. 115.
59. Soteland, N. and Kringstad, K., Norsk Skogind. 22(2): 46(1968).
60. Liebergott, N. and van Lierop, B., 1978 Seminar on Oxygen/Ozone/Peroxide Pulp Bleaching, TAPPI, Atlanta, p. 90.
61. Goring, D. A. I., Pulp Paper Mag. Can. 68(8): T372(1967).

62. Kamishima, H., Fujii, T., and Akamatsu, I., *Japan Tappi* 31(9): 226(1976).
63. Kamishima, H., Fujii, T., and Akamatsu, I., *Japan Tappi* 31(10): 669(1977).
64. Kamishima, H., Fujii, T., Akamatsu, I., and Nakayama, S., *J. Japan Wood Res.* 28(6): 370(1982).
65. Lindholm, C.-A., *Paperi Puu* 72(3): 254(1990).
66. Rothenberg, S., Robinson, D. H., and Johnsonbaugh, D. K., *Tappi J.* 58(8): 182(1975).
67. Singh, R. P., *Can. pat.* 970,111 (July 1, 1975).
68. Kobayashi, T., Hosokawa, J., Kubo, T., Kimura, Y., *Japan Tappi* 30(6): 330(1976).
69. Liebergott, N. and van Lierop, B., *Tappi J.* 64(6): 96(1981).
70. Granum, F., Hasvold, K., Loras, V., and Soteland, N., *J. Pulp Paper Sci.* 10(2): J25(1984).
71. Tsai, T. Y., *U.S. pat.* 4,959,124. Sept. 25, 1990.
72. Hosokawa, J., Kobayashi, T., Kubo, T., and Kimura, Y., *J. Japan Wood Res. Soc.* 22(6): 683(1976).
73. Hosokawa, J., Kobayashi, T., Kubo, T., and Kimura, Y., *Japan Tappi* 38(8): 450(1976).
74. Eckert, R. C., *U.S. pat.* 4,119,486 (Oct. 10, 1978).
75. Clayton, D. W., Liebergott, N., and Pye, I. T., *Environment Canada, Project Report 2-2, Progress Report to March 31, 1972.*
76. Perkins, J. K. and Schleinkofer, R. W., 1981 Annual Meeting Proceeding, TAPPI PRESS, Atlanta, p. 263.
77. Abadie-Maumert, F. A., *Papeterie* 99(1): 8(1977).
78. de Choudens, C., Lombardo, G., and Monzie, P., *ATIP Rev.* 32(9): 350(Nov. 1978).
79. Patt, R., Wang, D. L.-K., Kordsachia, O., and Welkener, U., 1984 Oxygen Delignification Symp. Notes, TAPPI PRESS, Atlanta, p. 33.
80. Kraftanlagen Heidelberg Technical Bulletin 2362/2, Oe/4.90/Br, Kraftanlagen Heidelberg.
81. Schwarzl, K., Pulp bleaching using ozone, paper presented at the 1991 Workshop on Emerging Pulping and Chlorine-free Bleaching Technologies, North Carolina State University, Raleigh, N.C.

Received for review Aug. 19, 1991.

Accepted Sept. 5, 1991.

Presented at the TAPPI 1991 Pulping Conference.