A survey of the use of ozone in bleaching pulps, Part 1

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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

The worldwide concern over environmental control has motivated a search for new processes that will eliminate the problem of pollution at the source. Examples are new pulping and bleaching processes that employ chemicals not used in conventional bleaching stages. One solution lies in developing stages based on bleaching agents that contain oxygen or ozone. Spent liquors from these bleaching stages can be combusted in a recovery furnace rather than being released to the environment.

Oxygen delignification is now well established commercially in pulp bleaching technology. Its use is limited to partial lignin removal under alkali conditions that darken the pulp instead of bleaching it. Further bleaching must be done to remove the residual lignin and whiten the pulp without damaging the carbohydrates. If complete lignin removal is accomplished by oxygen, the pulp strength suffers because of the unacceptable destruction of the cellulose under the conditions applied. The conditions used in oxygen delignification to prevent cellulose degradation are well defined.

Ozone has been known as a bleaching agent for cellulosic material since 1913 (*1, 2*). Systematic studies of the effects of using it in pulp bleaching have been conducted within recent years on laboratory and pilot plant scales. Ozone is a strong oxidizing agent that reacts readily with almost any organic material, including lignocellulosic material. Ozone reactions are thought to be selective toward lignin. However, the radicals formed from reactions between ozone and lignin or from the decomposition of ozone in water promote the unwanted attack of ozone on carbohydrates (*3*), which may cause an unacceptable decline in strength properties. This drawback limits the commercial use of ozone in pulp bleaching.

To find out what can be done to favor ozone-lignin reactions, many researchers have focused on the reaction mechanisms of ozone and lignocellulose (*4–13*). Ozone is an indiscriminate oxidizer of wood pulp, and the purpose of many studies is to identify conditions of ozone-pulp reactions that minimize the ozone-carbohydrate reactions. Since the work of Brabender in 1949 (*14*), many reports and patents on ozone bleaching have been published.

Presented in two parts, this survey on the state of ozone bleaching is intended as an industry update on the results of ozone research and pilot plant studies. In next month's issue, Part 2 will pick up where Part 1 leaves off.

Ozone—properties and present uses

Ozone (O_3) is an unstable, toxic, bluish gas with a molecular weight of 48. It becomes a dark blue, unstable liquid at -111.9°C and freezes at -192.5°C. Ozone is more soluble in water than is oxygen, especially as temperature decreases, and it has a higher solubility in some organic solvents such as glacial acetic acid and carbon tetrachloride.

Of all the elements and ions, ozone has the second greatest electronegative oxidation potential, -2.07 electron volts, which is only slightly exceeded by that of fluorine at -2.10 electron volts. This high oxidation potential has made ozone a good bactericide and algicide in the purification of air and

water. Ozone is also used commercially in various chemical oxidation processes, such as in the bleaching of textiles, waxes, and starch. Its uses are limited, however. Ozone must be used in the gaseous state, and ozone generators produce a low concentration of ozone in oxygen or air.

For most uses, ozone is produced from air or oxygen by silent arc discharge generators, which can safely produce up to 10% by weight of ozone but are most efficient at 4-8%. Ozone yield is a function of the oxygen purity of parent gas, oxygen temperature, pressure, flow, peak voltage, frequency, capacity of discharge gap, and capacity of dielectric. Ozone is toxic in small amounts, but its odor can be detected at just 0.01-0.015 ppm. The accepted maximum allowable concentration for a daily 8-h exposure is 0.1 ppm.

Ozone as a chemical pulp bleaching agent

Ozone has been used as a single-stage bleaching agent or in a multistage bleaching process that would include treatment with other bleaching agents such as oxygen, peroxides, chlorine dioxide, and hypochlorite. The fundamental bleaching variables that affect the use of ozone have already been studied. These variables include: (1) the type of pulp (hardwood or softwood), (2) the pulping process used to produce the pulp, (3) pretreatment of the pulp prior to ozonization, (4) sequential treatment of ozone and other bleaching chemicals, (5) pulp consistency, (6) ozone concentration and charge, (7) temperature, (8) time, and (9) pH.

The results of these studies, although consistent in some areas, are sometimes conflicting. In some instances, the discrepancies can be traced to the use of different pulp samples and different techniques and equipment, such as contacting devices for pulp and ozone.

The conditions reported in the relevant literature are:

- Pulping process: sulfite, kraft and soda, soda-AQ, ASAM (alkaline sulfite-AQ-methanol)
- Kappa number: 10-55 for unbleached chemicals pulps, 5-20 for oxygen-treated kraft pulp
- Consistency: 0.1-95%, either in the form of a slurry or stock (0.1-20%), fluffed or shredded pulp (20-90%), or pulp sheets (20-95% consistency)
- pH: 1 to 12
- Bleaching time: 1 s to 6 h
- Temperature: 2°C to 100°C
- Ozone concentration: 0.1-10% by wt. (The ozone-oxygen mixture may be dry or saturated with moisture at ambient temperature.)
- Ozone charge: 0.1% to 20% on o.d. pulp
- Sequential application with other bleaching chemicals: chlorine, chlorine dioxide, peroxide.

I. Chemicals added to pulp before and in combination with an ozone stage

Chemical	*Refs.*	*Chemical*	*Refs.*
	Organic		
Acetone	14, 46	*p*-Phenylenediamine	63
Acetic acid	28, 30, 32, 48, 63, 64	Pyrogallol	63
Formic acid	28	Glucose	63
Galacturonic acid	63	Dextrin	63
Sulfamic acid	63	Starch	63
Peracetic acid		Lecithin	63
Oxalic acid	32, 62, 64	Urea	62, 63
Methyl acetate	12	Lignin	5, 8, 63
Ethylene acetate		CMC	63
Sodium acetate	63		
		EDTA/DTPA	42, 48, 54, 63
Acetic anhydride	63	DMSO	5, 32, 48, 62, 63
Nitromethane	13	DMF	62, 63
Diazomethane		DABCO	5
		Formamide	63
Methanol	3, 63, 65	Hydroquinone	63
Ethanol	64	*p*-benzoquinone	63
Butadiene			
n-Butanal		Triethanolamine	62-64
Methylethyl ketone	63	Monoethanolamine	
L-cystine		Trioxane	5
Thioglycolic acid		Polyethylene glycol	5
Acrylonitrile			
Ethylene oxide			
Pyridine	63		
Methyl cellosolve	63		
	Inorganic		
Sodium carbonate	5	Chlorine	17, 70
Sodium hydroxide	all pH studies	Hypochlorite	17
		Hypochlorous acid	17
Sodium formate	5	Hydrochloric acid	17
Metal borohydrides	18, 63	Chlorine dioxide	36, 40, 70, 71
Hydrogen peroxide		Oxygen	
Sulfur dioxide	30, 32, 48, 62	Magnesium compound	63
		Iodine compounds	63
Sulfuric acid	28, 30, 32, 48, 63, and most pH studies	Hexadecyl, -nonyl-, or trimethyl NH_4Br	74
		NO_2	30
		Additional compounds*	63

*$FeSO_4$, $CoCl_2$, $Mn(NO_3)_2$, NaCl, $(NH_4)_2SO_4$, KH_2PO_4, $Na_2B_4O_7$, $CuSO_4$, $ZnCl_2$, $MnSO_4$, Na_2SO_4, $Al_2(SO_4)_3$, NH_4NO_3, Na_2SiO_3, NH_2NH_2, NH_2OH-HCl, DPPH

Refer to Part 2 for citations 54, 62-64, 70, 71, 74.

Table I presents a list of chemicals applied to pulp as treatments before an ozone stage and as additives during the ozone treatment to limit the reactions to lignin to prevent viscosity loss.

Effects of the reaction variables

An understanding of the effects of reaction variables on pulp properties is critical to assess the commercial viability of a new process and to establish the limits within which the process must operate. Included in this report (Parts 1 and 2), along with a review of the pertinent literature, are

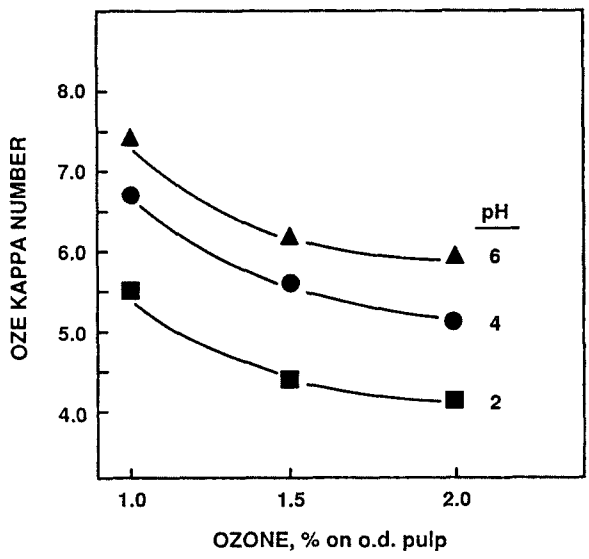
II. The effects of decreasing pH and of ozone charge (1.0%, 1.5%, and 2.0% on pulp in the Z-stage) on pulp properties after the ZE stage

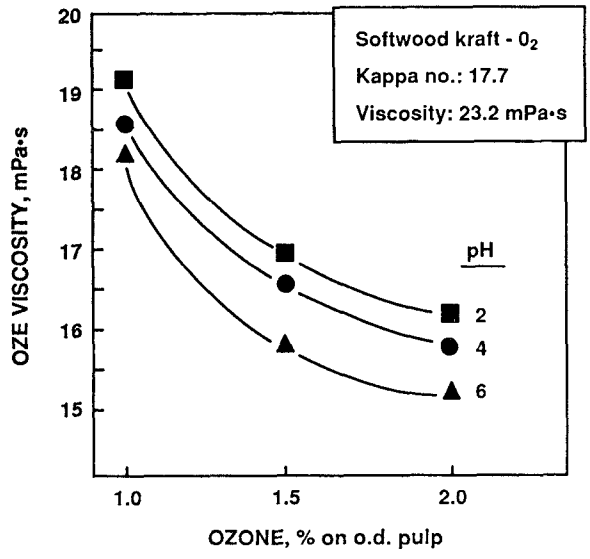
O_3 added, %	Ozone consumed, % on pulp			Kappa number			Viscosity, mPa•s		
	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
Final pH				Softwood kraft[a]					
5.8	0.99	1.48	1.99	16.4	13.6	10.8	22.6	19.9	17.2
4.3	0.99	1.48	1.90	15.1	12.7	10.5	23.3	20.4	17.6
2.1	0.98	1.44	1.91	14.3	12.1	9.9	24.1	21.1	18.0
				Hardwood kraft[b]					
5.7	0.99	1.49	1.97	5.1	4.0	3.2	10.8	8.8	8.1
4.0	0.98	1.46	1.93	4.8	3.7	2.9	11.2	9.0	8.1
2.1	0.98	1.45	1.88	4.5	3.5	2.6	11.3	9.4	8.4
				Softwood kraft-oxygen[c]					
5.7	0.99	1.46	1.93	7.4	6.2	5.9	18.2	15.9	15.2
4.1	0.98	1.44	1.89	6.7	5.6	5.1	18.6	16.6	15.8
2.2	0.95	1.41	1.88	5.5	4.4	4.1	19.2	17.0	16.2
				Hardwood kraft-oxygen[d]					
5.8	0.99	1.49	1.96	3.4	3.0	2.6	11.9	9.9	9.3
4.2	0.98	1.46	1.85	3.2	2.7	2.1	12.5	10.3	9.6
2.1	0.93	1.38	1.81	2.9	2.3	1.8	12.9	10.9	9.9

[a]Kappa no. 29.4, viscosity = 32.9 mPa•s.
[b]Kappa no. 14.5, viscosity = 17.6 mPa•s.
[c]Kappa no. 17.7, viscosity = 23.2 mPa•s.
[d]Kappa no. 11.1, viscosity = 18.6 mPa•s.

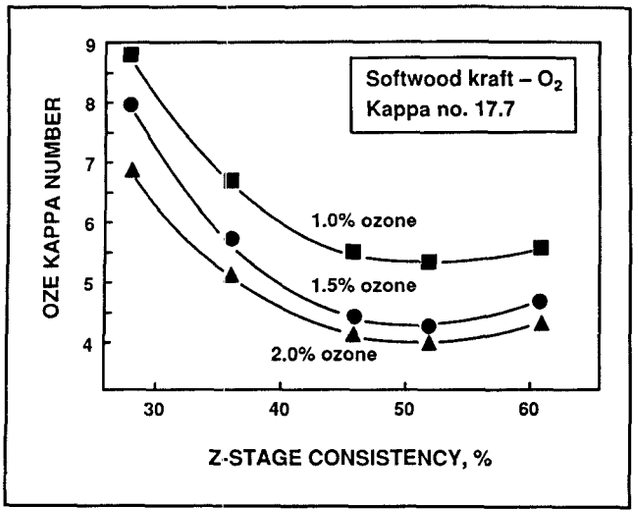
Z stage: 4% wt O_3/wt O_2 + O_3, 53-106 s, 40°C, pH 2.2, 46% consistency.
E stage: 1-1.5%, NaOH, 1 h, 60°C, End pH 10.8-11.3, 10% consistency.

1. Effect of ozone charge in Z stage on kappa number and viscosity after OZE applied to a softwood kraft-oxygen pulp. (Z stage: 53-106 s, 40°C, 45% consistency. E stage: 1-1.5% NaOH, 1 h, 60°C, 10% consistency. Viscosity measured at 0.5% cupriethylenediamine solution.)

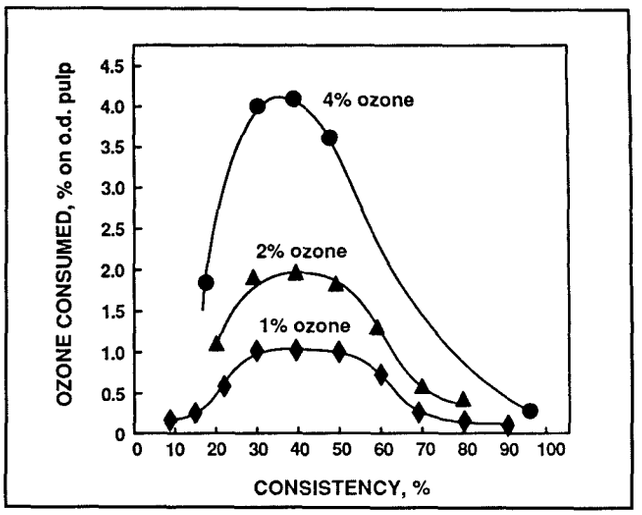




2. The kappa number after OZE decreases as the consistency of the Z stage is increased from 28% to 62%



4. Effect of consistency on ozone consumption (4% charge data from Brabender (*14*), sulfite pulp)



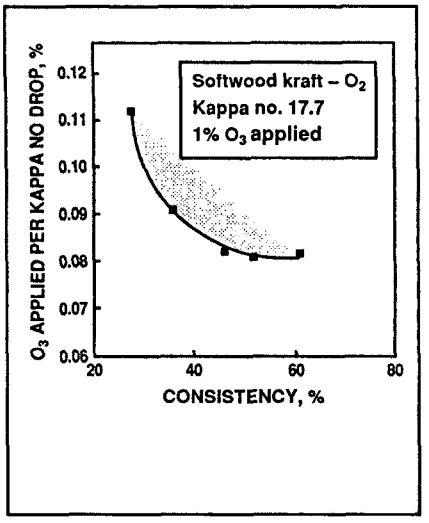
III. The effects of pulp consistency (c_s) and ozone charge (1.0%, 1.5%, and 2.0% on pulp in the Z-stage) on pulp properties after ZE stage

O_3 added, %	Ozone consumed, % on pulp			Kappa number			Viscosity, mPa•s		
	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
				Softwood kraft[a]					
30	0.93	1.40	1.85	21.4	19.0	18.0	25.1	21.6	18.5
36	0.93	1.44	1.90	17.1	15.1	12.8	24.6	21.2	18.4
45	0.98	1.44	1.91	14.3	12.1	9.9	24.1	21.1	18.0
53	0.96	1.42	1.89	13.6	11.9	9.5	23.9	20.2	17.9
60	0.78	1.33	1.81	15.0	13.0	11.8	22.0	18.7	17.5
				Hardwood kraft[b]					
30	0.91	1.32	1.71	9.0	7.4	6.6	11.5	9.6	8.3
36	0.93	1.35	1.82	5.7	4.8	3.6	11.4	9.6	8.5
45	0.93	1.38	1.81	4.5	3.5	2.6	11.3	9.4	8.4
53	0.94	1.38	1.89	4.3	3.4	2.2	11.2	9.3	8.3
60	0.82	1.22	1.76	4.7	3.7	2.5	10.5	9.0	8.1
				Softwood kraft-oxygen[c]					
28	0.86	1.28	1.43	8.8	8.0	6.9	19.7	17.8	16.6
36	0.95	1.39	1.86	6.7	5.8	5.1	19.6	17.2	16.5
46	0.95	1.41	1.88	5.5	4.4	4.1	19.0	17.0	16.2
52	0.93	1.38	1.84	5.3	4.2	3.9	18.4	16.4	15.5
61	0.84	1.29	1.45	5.5	4.6	4.2	17.6	16.0	14.8
				Hardwood kraft-oxygen[d]					
25	0.83	1.22	1.43	4.4	3.6	3.2	14.2	17.5	10.4
35	0.91	1.39	1.85	3.3	2.6	2.1	13.5	11.2	10.2
45	0.93	1.38	1.81	2.8	2.2	1.7	12.9	10.9	9.9
52	0.89	1.28	1.79	2.7	2.2	1.5	11.8	10.0	9.1
60	0.82	1.21	1.42	2.9	2.5	1.8	10.5	8.5	8.0

[a]Kappa no. = 29.4, viscosity = 32.9 mPa•s.
[b]Kappa no. = 14.5, viscosity = 17.6 mPa•s.
[c]Kappa no. = 17.7, viscosity = 23.2 mPa•s.
[d]Kappa no. = 11.1, viscosity = 18.6 mPa•s.

Z stage: 4% wt O_3/wt O_3 + O_2, 53-106 s, 40°C, pH 2.2.
E stage: 1-1.5% NaOH, 1 h, 60°C, pH 10.8-11.3, 10% consistency.

3. As the consistency is increased from 28% to 62%, there is a decrease in the ozone charge per kappa drop.



results obtained on softwood and hardwood kraft pulps, with and without an oxygen delignification stage.

Effect of pH

Acidification of a pulp to a pH of about 2 before the ozone stage produces the lowest kappa number and highest viscosity.

The effects of pH during ozonization on pulp brightness, kappa number, and strength properties has been the subject of numerous papers and patents. Several authors have included the entire pH range of 1-12 (*2, 10, 15, 16*) in their discussions. Others have isolated narrow ranges of pH 2-4 (*3, 17-20*), pH 4-6 (*14, 20-23*), pH 6-7.5 (*23, 24*), or pH 7.5-10.5 (*25, 26*). Generally, the best efficiency of ozone delignification is achieved at a pH of about 2-3 (*3, 10, 16, 27-31*), the extend depending on pulp consistency (*31*).

Lindholm (*32*) showed that the type of acid (sulfuric, acetic, oxalic acid, and SO_2 water) used to decrease the pH of the pulp to about 3 prior to a low-consistency ozone stage did not affect the effectiveness of lignin removal. At a pH of less than 2, however, oxalic acid enhanced lignin removal better than did sulfuric acid pretreatment at low-consistency ozone conditions; this effect was less pronounced at high consistency. An acetic or formic acid treatment was reported to lead to a lower kappa number after high-consistency ozone bleaching at pH 2 than a sulfuric acid treatment (*28*). In recent work, Jacobsen (*3*) showed that low-lignin pulps (at kappa no. 3) had a more irregular dependence on reaction pH during the ozone treatment than did pulps of high residual lignin.

In 1965, the extent of delignification of kraft and kraft-oxygen pulps by ozone treatment was reported to increase slightly with decreasing reaction pH below pH 6 (**Fig. 1, Table II**) (*20*). The lowest kappa number and highest viscosity and brightness were obtained at a pH of about 2. Strong acidity did not contribute to substantial losses of viscosity. At pH 2 and at an O_3 charge of 1%, the kappa numbers were 2.7-6.8% lower, and the viscosities were slightly higher than those observed at about pH 4 on the four pulps.

Effect of pulp consistency

At consistencies ranging from 35% to 55%, 98% of a 1-2% ozone charge was consumed by the pulp in a 1-min reaction. The kappa numbers were 1.6-7 units lower at consistencies between 45% and 53% than they were at 30% consistency.

Various researchers (*1, 2, 15, 33, 24*) have reported that the optimum ozone consumption, which may lead to maximum pulp brightness and maximum kappa number reduction, was obtained in a consistency range of 30-40%. Mixing technology has improved over the past years to make it possible to improve the ozone-pulp contact in the liquid phase at low consistency (*34*) and particularly in the fluidized state at medium consistency. Most ozone delignification comparisons, however, are still limited to low and high consistencies.

Lindholm published extensively on this topic (*35*), and his conclusion corroborated by others (*36*) was that selectivity of bleaching was better at low consistency than at high consistency, particularly when bleaching to low kappa numbers. He did concede that at low consistency 10% more ozone was consumed than at high consistency. Sixta compared ozone bleaching at 1%, 10%, and 36% consistency on a sulfite pulp (*37*). An ozone charge ranging from 1.6% to 1.8% on pulp decreased the kappa number to 0.9, but the kappa number before the Z stage was as low as 2.

We found that in the pulp consistency range of 25-60% the kappa number decreased as the consistency was increased from 25% to 53% (**Fig. 2, Table III**). A further decrease was not observed at consistencies above 52%. The higher the consistency, the less ozone required per unit of kappa number drop (**Fig. 3**).

The viscosities of the softwood and hardwood kraft pulps did not appear to be affected by the changes in consistency. The softwood kraft-oxygen pulp suffered some loss in viscosity as the consistencies were increased above 46%, and the viscosity of hardwood kraft-oxygen pulp tended to decrease progressively as the consistency was increased from 25% to 60%.

Medium-consistency treatment is more adaptable in current mill practice. However, because of the low concentration of ozone in oxygen (the carrier gas), a large volume of gas must be mixed with the pulp suspension. The phase ratio of gas volume to pulp suspension volume is too high to be handled effectively by the high-intensity mixers. One approach to solve this drawback is to compress the ozone-oxygen gas—i.e., reduce the phase ratio of gas-to-pulp suspension and apply the ozone gas to the pulp in pulses (*38-40*).

Almost total consumption of the ozone applied is necessary for successful commercial operation of ozone delignification. We adapted results of previous work to compare the consumption of ozone possible at various consistencies and at various ozone charges. **Figure 4** shows that at an ozone charge of 1.5%, 2.0%, and 4.0%, maximum ozone consumption was obtained at consistencies of 30-50%. The amount of ozone consumed by the pulp decreased considerably at consistencies above 50% and below 22%.

At the time of our research, high-intensity mixers and high ozone concentrations were not available for the medium-consistency tests. A systematic comparison of the amount of ozone required to reach equivalent kappa numbers under low-, medium- and high-consistency optimum conditions using suitable mixing equipment is still lacking.

Effect of ozone charge

Increasing the charge of ozone from 1% to 2% decreases the kappa number at the expense of viscosity. Brightness increases with ozone charge.

IV. The effects of ozone charge (1.0% and 2.0%) applied at pH2 and a consistency of 36% on kappa number and viscosity

	Kraft		*Kraft-oxygen*	
Ozone added	*1.0%*	*2.0%*	*1.0%*	*2.0%*
Softwood				
Kappa number				
Initial	29.4	29.4	17.7	17.7
After ZE	17.1	12.8	6.7	5.1
Decrease				
Kappa units	12.3	16.6	11.0	12.6
Percent	41.8	56.5	62.1	71.2
Viscosity, mPa•s				
Initial	32.9	32.9	23.2	23.2
After ZE	24.6	18.4	19.6	16.5
Hardwood				
Kappa number				
Initial	14.5	14.5	11.1	11.1
After ZE	5.7	3.6	3.3	2.1
Decrease				
Kappa units	8.8	10.9	7.8	9.0
Percent	60.7	75.2	70.3	81.1
Viscosity, mPa•s				
Initial	17.6	17.6	18.6	18.6
After ZE	11.4	8.5	13.5	10.2

Z stage: 53-106 s, 40°C, pH 2.2

E stage: 1-1.5% NaOH, 1 h, 60°C, 10% consistency.

V. Ozone concentrations, gas flow rates, and reaction times for a softwood kraft-oxygen pulp (kappa no. 13.8)

Ozone			
Flow rate, L/min	2.0	2.0	1.1
Concentration, % by wt. O_3/wt. $O_2 + O_3$	1.9	3.9	5.8
Added, % on pulp	0.5	0.5	0.5
Consumed, % on pulp	0.46	0.46	0.48
Reaction time, min	1.5	0.7	0.9
Consistency, %	40	40	40
After ZE			
Kappa no.	6.2	6.1	5.9
Viscosity, mPa•s	15.7	15.4	15.3

Z stage = H_2SO_4 pretreatment to pH 2.0.

E stage: 1.5% NaOH, 1 h, 70°C, 10% consistency.

Because ozone attacks all constituents of wood pulp, high degrees of delignification are not obtainable without a loss in viscosity (*41-46*). The experiments reported at medium consistency also showed this trend (*38*).

An increase in ozone charge from 1% to 2% decreased the kappa number of all four pulps studied under the various conditions with some loss of viscosity (Tables II and III, Fig. 1). **Table IV** summarizes the effects of ozone charge on extracted kappa number and viscosity at an ozone stage carried out at a consistency of 36% and a reaction pH of 2. Without the availability of a cellulose protector, approximately 1% ozone charge is the maximum that can be applied to a kraft pulp before excessive fibre degradation sets in, according to general agreement in the literature (*3, 16, 32, 35, 41-43, 46*).

The effect of ozone charge on kappa number and brightness after ZE is shown in **Fig. 5**. As indicated by others (*20, 32, 45, 46*), kappa number decreases and pulp brightness increases with increasing ozone charge. **Figure 6** shows data that were plotted to express a relationship between a decrease in kappa number and an increase in brightness for ozonated and extracted pulps (*20*). The increase in brightness of softwood pulps is a quantitative measure of lignin degradation, which was corroborated by others (*45, 46*). The values for two hardwood pulps fit on a separate line above that of the softwood pulps, but the slopes of both curves are similar.

A plot of kappa number after the ZE stages and total lignin in the pulp also shows a straight-line fit (**Fig. 7**), indicating that the kappa number is indicative of the residual lignin in the pulp. A correlation of the brightness measurement on the extraction washer (after ozonization) and the kappa number of the pulp may provide a rapid analytical method for controlling the bleaching sequence.

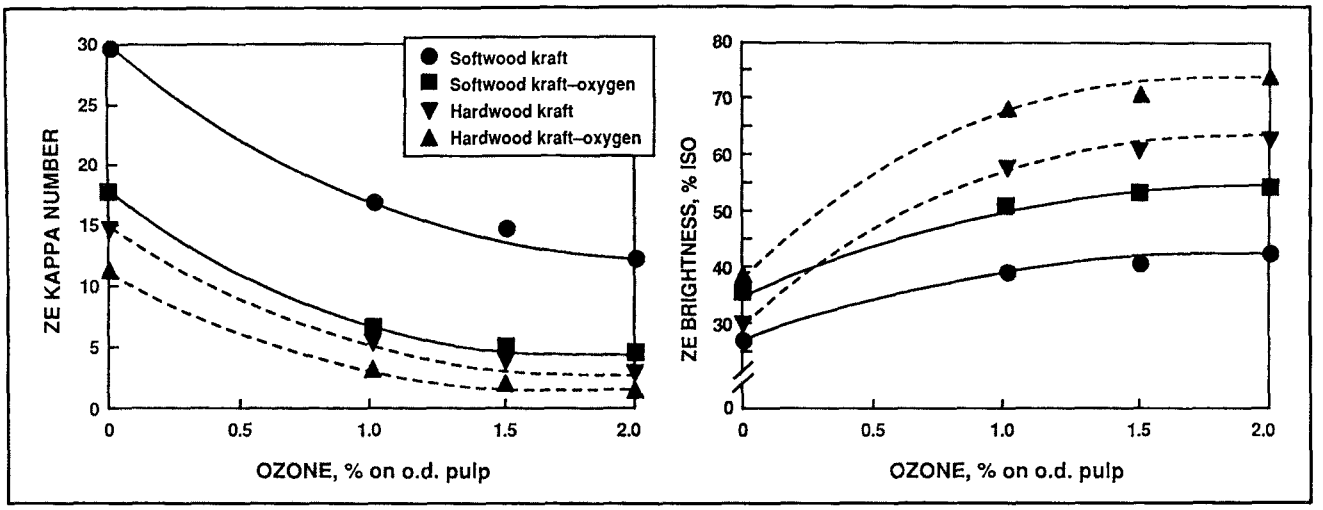
Effect of ozone concentration, gas flow rate, and reaction time

Increasing the ozone concentration from 2.1% to 6% wt. O_3/wt. O_2 on a specified quantity of pulp reduces the reaction time, but it does not affect the kappa number nor the viscosity.

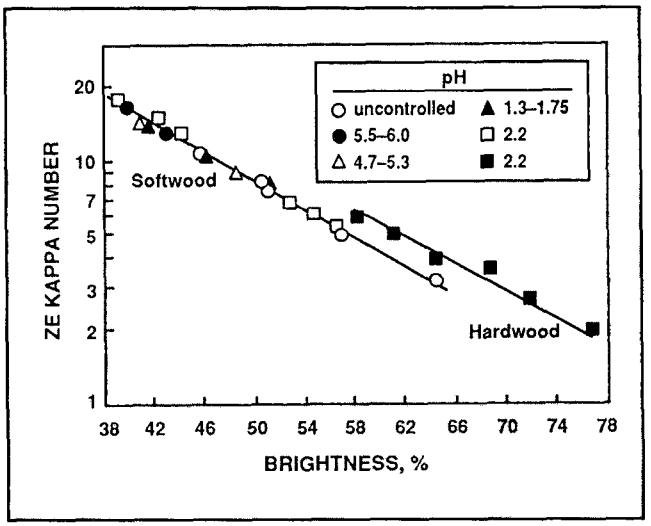
In most articles, the concentration of ozone used to delignify the pulp was generally 1.5-3.5% wt. O_3/wt. O_2, although some articles mentioned the use of ozone concentrations as low as 0.1% (*14, 16, 24*) and as high as 9% (*42*). Hartler's comparison between 2% and 9% ozone concentration showed that the higher concentration decreased the kappa numbers by 1-2 units (*42*).

Table V compares ozone concentration of 2%, 4%, and 6% wt. O_3/wt. O_2. The kappa numbers after OZE were similar regardless of the O_3 flow rate (0.05-0.1 g/min) or the concentration of ozone in oxygen (2% or 6%). Singh (*27*) and Kobayashi (*47*) also demonstrated that increasing the ozone concentration in oxygen gas to 3.5% had no effect on bleaching performance. An advantage of higher ozone concentration is the shorter reaction time. However, the costs for energy required to produce high concentrations of ozone must be considered.

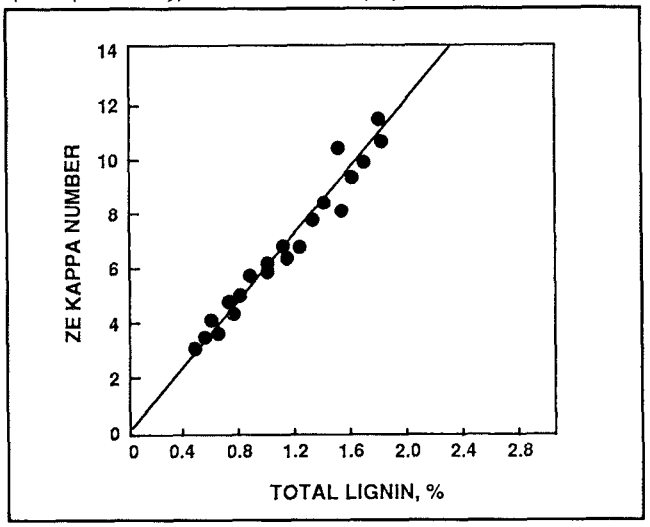
5. Effect of ozone charge in the Z stage on kappa number and brightness after ZE applied to a softwood and hardwood kraft pulp with and without oxygen delignification



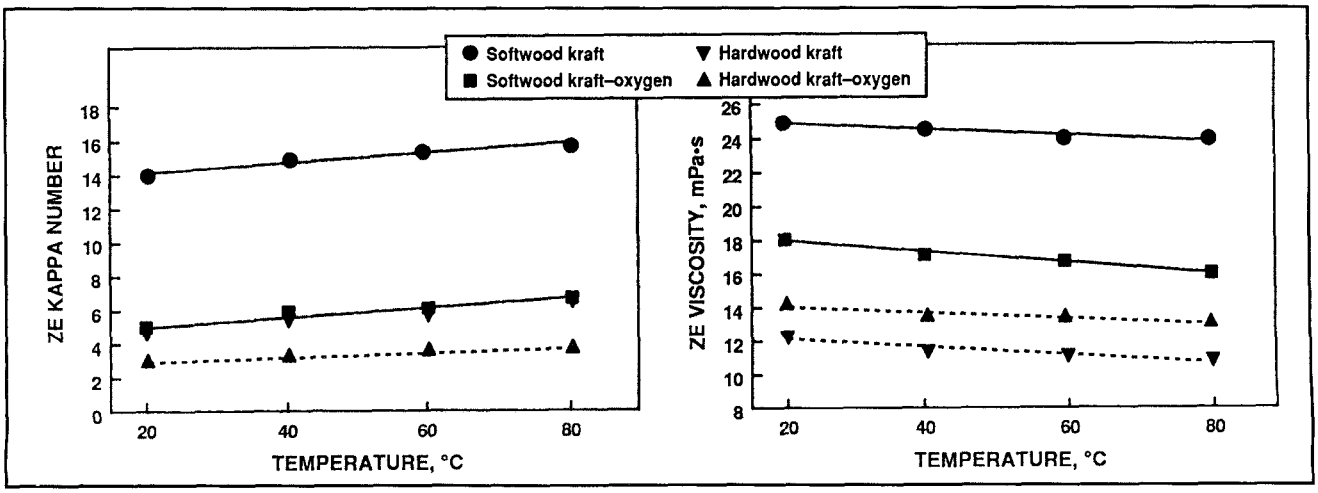
6. Log kappa number vs. brightness of ZE-treated pulps



7. Relationship between kappa number and total lignin including Klason lignin and acid-soluble lignin (determined by ultraviolet spectrophotometry) of ZE-treated kraft pulps



8. Effect of temperature on kappa number and viscosity after ZE applied to a softwood and hardwood kraft pulp with and without oxygen delignification



Effect of temperature on kappa number and viscosity reduction

Increasing the temperature of the Z stage from 20°C to 80°C increased the kappa number by 1-2 units and decreased the viscosity by 1-2 mPa·s.

To understand the effect of temperature on reduction of kappa number and viscosity, we maintained the temperature at four levels (20°C, 40°C, 60°C, and 80°C) with all other ozonization conditions held constant. The results are presented in **Fig. 8**. Increasing the temperature of the Z stage had a marginal effect on kappa number and viscosity after ZE or OZE. For example, the kappa number of the softwood kraft pulp was 14 at 20°C, while at 80°C, it rose to 15.9. This trend was attributed to ozone decomposition (*48*), which must be considered at the industrial scale if a hot pulp from a previous stage is entering the ozone stage. More promising results were claimed at temperatures at or below 0°C (*46, 47, 49*). One report on medium consistency showed a marginal increase in viscosity with increasing reaction temperature (*38*).

Note that ozonization of a kraft pulp can be conducted at different temperatures (20-60°C) without serious effects on kappa number and viscosity. (To be continued in Part 2.)□

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