Delignification and bleaching of chemical pulps with ozone: a literature review

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ABSTRACT *As the pulp and paper industry searches for alternatives to chlorine-based bleaching agents, increasing attention is being focused on the use of oxygen-based agents (oxygen, hydrogen peroxide, and ozone). Not only do these chemicals produce no chlorinated organic materials in the bleaching effluent, but the effluent is also free from corrosive components and can be completely recycled to the mill chemical recovery system. Ozone can play a key role in the development of such closed bleaching processes. Liebergott and van Lierop reviewed ozone bleaching work done up to 1978. This review covers much of the work and includes research done since that time.*

KEYWORDS
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Increasing research and development efforts are being directed toward the use of ozone as a delignification and bleaching agent. Because ozone has good delignifying and brightening abilities but does not produce chlorinated organic materials, it is an attractive candidate for replacement of chlorine-based bleaching agents. In addition, ozone produces an effluent free from corrosive components, so all the effluent from an ozone stage can be recycled to the chemical recovery system. Ozone can thus be a valuable part of a closed bleaching process.

In searching for the best way of using ozone in chemical pulp delignification and bleaching, it is useful to examine the literature for details of previous applications. Liebergott and van Lierop (*1*) published a thorough review in 1978, which detailed the effects of pulp consistency, pH, time, and temperature on the ozonation of hardwood and softwood kraft and kraft-oxygen pulps. The current review covers much of this same work and includes research done since that time. The following categories are covered: studies on ozone bleaching according to pulp type, the effect of main reaction variables, studies on carbohydrate-preserving additives and pretreatments, studies of bleaching sequences containing ozone, and pilot plant studies.

Background

The action of ozone on cellulose-based textile fibers such as cotton and linen was studied as early as 1868 (*2*, *3*), leading to the investigation of ozone as a bleaching agent for such fibers. In 1889, Brin and Brin (*4*) patented a method for bleaching "fibrous substances," including those used in the making of paper, which involved exposing the fibers to a mixture of chlorine and ozone gases. In 1912, it was shown that ozone would preferentially attack the lignin portion of a material such as jute, although the cellulose was also affected (*5*). A patent granted to Mourlaque in 1929 (*6*) describes a process and apparatus for making paper by saturating pieces of "vegetable matter" with water and exposing them to a pressurized atmosphere of ozone gas. In 1934, Campbell and Rolleston (*7*) patented a process for bleaching pulp by sequential treatment with chlorine and ozone. Brabender *et al.* (*8*) studied some of the variables involved in ozonation and in 1949 patented a method for bleaching pulp with a consistency of 25–55% and pH 4–7.

Ozone bleaching by pulp type

Kraft, kraft-oxygen, and kraft-AQ pulps

In 1963, Osawa *et al.* (*9*) found it possible to pulp whole wood in the form of meal, shavings, chips, or blocks, at room temperature with ozone. Osawa and Schuerch (*10*) ozonated kraft pulps at high and low consistency and found that the rate-determining step in either case was the dissolution of ozone gas in the thin-layer or bulk liquid phase.

A number of studies have shown that although ozone is quite capable of delignifying, bleaching and brightening kraft pulps, it tends to degrade

the carbohydrate fraction more than other agents. Procter (*11*) applied ozone gas to high-kappa-number pulps and found that, although some strength properties were improved, there was significant reduction in tear strength, viscosity, and yield. Soteland (*12*) found that eucalypt kraft pulp could be fully bleached using only oxygen, ozone, and peroxide, but the resulting strength properties were inferior to conventionally bleached pulps. Kamishima *et al.* (*13*) showed that hardwood kraft pulps brightened more easily than softwood pulps at the same ozone consumption, but both pulps suffered substantial viscosity loss and were weaker than the unbleached pulps. In a study of kraft bleaching by Soteland (*14*), application of 2% ozone produced full final brightness, but viscosity was reduced significantly. Tensile strength was comparable to conventionally bleached pulps, but tear strength was lower.

Allison (*15*) found that kraft and kraft-AQ pulps bleached with ozone-based sequences (ZEP and ZPZP) had lower viscosity, tear strength, and burst strength compared to conventional pulps. Yield improvements from pulping with anthraquinone were preserved after full bleaching. Liebergott and van Lierop (*16*) treated softwood and hardwood kraft and kraft-AQ pulps with a ZDED sequence. The softwood pulps had somewhat lower strength properties than pulps bleached with a CEDED sequence, but the hardwood pulp properties were similar. For all pulps, the ZDED sequence required less chlorine dioxide than the CEDED sequence, and the yield increases normally seen with addition of anthraquinone were maintained after bleaching. Carlberg *et al.* (*17*) showed that sulfate pulps delignified with ozone resulted in fully bleached pulps with lower viscosity than conventional pulps. Germgard and Sjogren (*18-20*) found that substitution of ozone for chlorine or chlorine dioxide in the prebleaching of regular and modified-cooked, oxygen-delignified pulps resulted in inferior strength properties and a higher level of shives.

Patt *et al.* (*21*) showed that kraft pulp prebleached with ozone, nitrogen dioxide, or a combination of the two agents had lower strength properties than standard pulps, although the pulps were still acceptable for industrial processing. Larsson and Samuelson (*22*) found that the substitution of ozone for chlorine dioxide in the sequence D(EO)D following a nitrogen dioxide treatment resulted in substantial viscosity losses. Lachenal *et al.* (*23*) showed that although an ozone stage followed by alkaline treatment with optional peroxide could remove up to 50% of the unbleached pulp lignin, the delignification was not as selective as a conventional CE sequence.

Other studies have demonstrated that ozone can be used in combination with various other agents to obtain desired brightness levels with acceptable strength properties. Several studies have shown that the inclusion of an oxygen stage prior to an ozone stage gives superior results to single-stage ozonation (*24-27*). Secrist and Singh (*28*) found that hardwood kraft pulps could be bleached satisfactorily with ozone, and an ozone stage could replace chlorination and extraction if a chlorine dioxide stage followed. Singh (*29*) demonstrated that hardwood kraft pulps could be bleached to high brightness with good pulp quality, especially with ZEP or ZED sequences. Djamal *et al.* (*30, 31*) bleached red luan kraft pulp with ozone and peroxide and obtained better strength properties than those of pulp bleached with CEDED. Douglas-fir kraft pulp bleached with oxygen, ozone, and chlorine dioxide by Gupta and Eckert (*32*) had 80-90% of the strength properties of a CEDED pulp. Rothenberg *et al.* (*33*) used oxygen and ozone to produce bleached pine kraft pulps with strength comparable to conventional bleaching. When optimum conditions were employed in the ozone stage following an oxygen stage, pulps studied by Richard and Robert (*34*) had comparable or better strength properties than conventional pulps. Kobayashi *et al.* (*35*) bleached pulp sheets with ozone under optimum conditions and noted that viscosity loss was suppressed. Rutkowski and Sjopinski (*36*) found that multistage bleaching with ozone, followed by chlorine dioxide, resulted in pulps with good yield, high brightness, and good mechanical properties. Good overall bleaching selectivity was obtained by Hartler *et al.* (*37*) with a sequence consisting of modified cooking, ozone (or mild ozonation followed by oxygen), and chlorine dioxide. Soteland and Carlberg (*38*) substituted ozone for chlorine in bleaching and found that strength properties could be maintained. Low-consistency bleaching of kraft pulp with concentrated ozone solution was shown by Fujii *et al.* (*39*) to be a suitable alternative to chlorine-based sequences. Patt *et al.* (*40*) found that prebleaching pulps with a combination of nitrogen dioxide and ozone allowed easy further bleaching to high brightness while maintaining good strength. Liebergott *et al.* (*41*) developed two bleaching sequences using oxygen, ozone, sodium hydroxide, hydrogen peroxide, and sodium hydrosulfite which produced high-brightness pulps with the same strength properties as a CEDED sequence. The sequence OZEP was shown by du Plooy and Male (*42*) to bleach eucalyptus kraft pulp to the same brightness and strength as an ODED sequence.

Sulfite pulps

In general, sulfite and bisulfite pulps were found to respond well to ozone delignification and bleaching. Soteland (*12*) established that sulfite pulps responded more favorably to ozone treatment than kraft pulps, and the strength properties of sulfite pulps were not seriously reduced when ozone and oxygen were used as bleaching agents. Oxygen/ozone bleaching resulted in pulps almost free of extractives. Patt *et al.* (*21*) attributed the better response of sulfite pulp to ozone to the lower lignin content of the unbleached pulp. Pilot plant testing confirmed that sulfite pulps could be easily bleached with ozone. Rutkowski and Sjopinski (*43*) found that ozone readily delignified sulfite pulps and reduced extractives content considerably. These effects increased with increasing ozone concentration, consistency and pH. Mechanical properties of the pulps were reduced significantly, but lack of data at comparable freeness allowed no conclusions to be drawn concerning the effect of ozone on pulp strength. Soteland (*14*) found that application of 2-2.5% ozone in two stages resulted in a fully bleached sulfite pulp (90% ISO brightness) with low viscosity but acceptable strength properties. Sulfite-oxygen pulps treated with less than 0.5% ozone were bleached to 90% brightness with better strength and significantly

lower extractives than pulp bleached with a CEHH sequence.

Christensen and Soteland (*44*) bleached spruce, pine, and beech sulfite pulps to 85–86% ISO brightness with oxygen and ozone, and the strength properties of the bleached pulps were similar to those from OCH and CEH sequences. A final peroxide stage allowed bleaching to 90+% brightness. Christensen and Soteland (*45*) also produced sulfite pulps from different bases and found that all could be bleached with oxygen and ozone while maintaining favorable strength. Oxygen and ozone reduced pulp resin contents. A study by Allison (*46*) on sodium bisulfite pulps showed that pulping yield affected how the unbleached pulp responded to oxygen-based bleaching agents such as ozone, with lower-yield pulps responding more favorably. Three-stage oxygen- and chlorine-based sequences both produced 86% maximum brightness and 49% overall yield, but the chlorine-based sequence produced somewhat stronger pulps with lower brightness stability.

Carlberg *et al.* (*17*) found that sulfite pulps delignified with oxygen/ozone had fully bleached viscosities comparable to conventional sequences. Granum and Hasvold (*47*) found that bleaching sequences starting with oxygen or ozone and followed by chlorine dioxide produced good pulp qualities and minimum effluent problems. Industrial-scale testing by Buinitskaya *et al.* (*48*) showed that ozone delignification of sulfite pulps followed by two-stage peroxide bleaching produced acceptable quality, although the ozone stage did decrease pulp strength. In pilot testing by Norden and Simonson (*49*), sulfite pulps treated with ozone could be bleached to 90% ISO brightness with an HD or (EO)HD sequence. Wang and Patt (*50*) bleached ozone-delignified spruce and beech sulfite pulps in three stages with hypochlorite and chlorine dioxide, with higher yield, higher breaking length, and lower tear strength than conventional sequences. Lindqvist and Marklund (*51*) showed that two-stage sodium sulfite pulp could be bleached to very low kappa numbers with ozone and fully bleached with acceptable strength properties.

Soteland (*52*) bleached sulfite pulps with combinations of oxygen, ozone, chlorine dioxide, and peroxide. When chlorine dioxide was used for final bleaching, both strength and viscosity were acceptable, while final bleaching with only peroxide led to low viscosity and acceptable strength. Patt *et al.* (*40*) found that combining ozone and nitrogen dioxide in the first bleaching stage allowed sulfite pulp to be easily bleached to 90% ISO brightness with good physical properties. Kremlyakova and Ermolinskii (*53*) showed that application of ozone to bisulfite pulp can reduce the amount of chlorine required in the first bleaching stage. Similarly, Soteland and Carlberg (*38*) replaced chlorine with ozone in the first bleaching stage and obtained pulps with lower viscosity but similar strength properties. Pilot studies by Loquenz (*54*) showed that 90% brightness could be achieved on sulfite pulp with an OZP sequence. Farkasova *et al.* (*55*) used an OZPD sequence to produce sulfite pulps with greater than 90% brightness.

A study by du Plooy and Male (*42*) showed that eucalyptus pulps produced from the SAS/AQ (semi-alkaline sulfite/anthraquinone) process can be bleached to 85% brightness with an OZEP sequence, with strength properties comparable to an ODED sequence.

Soda, soda-AQ and oxygen pulps

Miura (*56*) treated cold-soda pulp with ozone gas and discovered that the reactivity of lignin was greater than that of holocellulose. The treatment did not improve strength properties of the pulp. Liebergott and van Lierop (*16*) treated hardwood and softwood soda-AQ pulps with a ZDED sequence and found that, compared to pulps bleached with a CEDED sequence, the ozone-treated pulps required less chlorine dioxide and had similar strength properties in the case of hardwoods and somewhat lower strength properties in the case of softwoods. For both hardwoods and softwoods, the yield increases normally associated with anthraquinone addition were preserved after bleaching. Allison (*15, 57*) bleached oxygen-delignified, soda-AQ pulps with various combinations of ozone and peroxide and found that the resulting pulps had lower viscosity, tear strength, and burst strength compared to conventionally bleached pulps, but had higher brightness stability. The yield advantages of AQ-additive pulping were maintained after full bleaching. In another study, Allison (*58*) found that soda-AQ pulps could have strength properties like those of conventionally bleached kraft pulps if pulping was terminated at high kappa number and followed by an OD/CED sequence. When an OZEP sequence was used instead, the resulting pulp had strength properties at least 25% lower than those of the conventional pulp.

Rothenberg *et al.* (*59*) found that oxygen pulping of hardwoods, followed by ozone bleaching, resulted in a pulp with better strength properties than kraft pulps bleached conventionally. Oxygen pulps were more responsive to ozone bleaching than kraft.

Solvent pulps

Takagi and Kayama (*60*) bleached oak alkali-dioxane pulps with ozone and obtained reasonable pulp properties if optimum conditions were used and ozone consumption was kept under 3%. After final bleaching with peroxide, the pulps had better brightness stability and inferior strength properties compared to CEDED-bleached kraft pulps. Djamal *et al.* (*30, 31*) bleached alkali-methanol and cresol-water pulps with ozone. For the alkali-methanol pulps, strength properties of the ozone-bleached pulp were lower than those for either kraft or alkali-methanol pulps bleached with a CEDED sequence. Strength properties for a cresol-water pulp bleached with ozone were substantially lower than for a kraft-CEDED pulp. Patt and Kordsachia (*61–63*) found that the low residual lignin content of alkaline sulfite-anthraquinone-methanol (ASAM) pulps made them very responsive to ozone bleaching. Small losses of tear strength in the ozone stage could be tolerated because of the higher strength properties of unbleached ASAM pulps. Full bleaching with oxygen, ozone, borohydride, peroxide and dithionite yielded pulps with no significant strength difference compared to conventionally bleached ASAM pulp. Nimz *et al.* (*64*) showed how ozone bleaching could be applied to acetosolv pulps for pollution-free production of bleached pulp.

Effect of reaction variables

Consistency

A 1949 patent by Brabender *et al.* (*8*) claims that optimum ozonation occurs in the 25-55% consistency range. Osawa and Schuerch (*10*) found that the rate of ozonation was highest when the fiber was saturated with water (high consistency, no free water), and the rate decreased as the consistency of the pulp increased. The rate-limiting step was the dissolution of ozone gas in the liquid phase. Secrist and Singh (*28*) found that maximum ozone consumption occurred at 40% consistency. Other investigations (*11, 13, 34, 50, 65-67*) have confirmed that ozone delignifies most efficiently at high consistency (40-55%). However, there is some question as to how sensitive the reaction is to consistency changes within this range. Rutkowski and Sjopinski (*43*), for example, found that delignification rate increased when consistency was raised from 25% to 35%. However, Norden and Simonson (*49*) recorded no significant change in delignification rate when consistency was varied between 35% and 45% at the pilot scale. Liebergott and van Lierop (*1*) found that a 1-2% ozone charge could be consumed in a 1-min reaction within a 25-55% consistency range. Kappa number did decrease with increasing consistency from 28% to 46%, after which the effect leveled off. Kraft pulps did not lose viscosity as the consistency was increased, but kraft-oxygen pulps did suffer some viscosity loss.

A number of studies (*22, 68-72*) have shown that, while requiring higher ozone application and/or more reaction time, low-consistency ozonation tends to preserve yield, viscosity, and strength better than high-consistency ozonation. In addition, Lindholm (*73*) has observed that ozonation at high consistency may be quite heterogenous, causing severe degradation to some parts of fibers while not affecting other parts. Low-consistency ozonation thus has the potential of having a more uniform reaction, resulting in better pulp properties. Hosokawa *et al.*(*74*), in bleaching pulp sheets with ozone, found that thicker sheets tended to bleach more on the outside than the inside, causing non-uniformity in the final product.

Laxen *et al.*(*75*) found that if the ozone concentration in the gas phase were high enough, medium-consistency ozonation could be carried out in a high-shear mixer with results comparable to low-consistency ozonation.

pH

In a 1949 patent, Brabender *et al.* (*8*) established that ozonation was optimal in an acidic pH range between 4 and 7. Liebergott (*76*) found that the extent of kraft pulp delignification with ozone increased slightly with decreasing pH below 6, and the lowest kappa number and highest viscosity were obtained at a pH of about 2. Hosokawa *et al.* (*74*) found that pulp brightness, yield, and viscosity decreased as the pH increased, while overall ozone consumption increased. This effect was attributed to variation in oxidation potentials, rate of self-decomposition of ozone, and differences in reactivity of carbohydrates with ozone. Rutkowski and Sjopinski (*43, 77*) found that the delignification effect of ozone and the bleachability of pulp increased with increasing pH, but the pulp strength properties decreased. Several studies (*29, 36, 49, 50, 60, 67, 78*) have established that the optimal pH range (for efficient use of applied ozone with minimal effect on carbohydrates) is 2-3, with beneficial effects increasing with decreasing pH. Work by Lindholm (*69-71*) suggests that acidification to low pH, either directly or as an acid prewash, does not affect viscosity development. Instead, acidification serves to enhance lignin removal, and this effect is increased if the acidification is carried out as a prewash.

Temperature

Kobayashi *et al.*(*79*) found that decreasing temperature in the range 0-30°C reduced ozone consumption and viscosity loss but increased the ratio of brightness increase to ozone consumed. Further work (*80*) showed that this effect also occurred in multistage ozonation. Liebergott and van Lierop (*1*) found that increasing ozonation temperature from 20°C to 80°C increased pulp kappa number and decreased viscosity. Kamishima *et al.* (*67*) found that bleaching rate decreased with decreasing temperature. Dou *et al.* (*66*) and Allison (*78*) attributed the improved ozone bleaching at lower temperatures to decreased decomposition of the ozone. Kremlyakova and Ermolinskii (*53*) examined ozonation in the 0-50°C range and found that delignification rate decreased and the rate of carbohydrate degradation increased as the temperature increased. Wang and Patt (*50*) recommended that the ozone reaction temperature should exceed room temperature only under conditions of intense mixing and short reaction times. Chandra and Gratzl (*26*) found that the second (residual) phase delignification rate of kraft-oxygen pulps decreased with increasing temperature. Ozone consumption increased at the same time, indicating a higher rate of ozone decay. Pilot plant trials by Singh (*29*) indicated that ozonation temperatures higher than 100°C could result in significant pulp degradation.

Ozone application

Data from Soteland (*12*) show a plateau in the brightness development curve at 1.5-2.5% applied ozone (on ovendry pulp). Liebergott and van Lierop (*1*) found that increasing the ozone charge increased pulp brightness while decreasing kappa number and viscosity. The rate of viscosity loss was greater than delignification. Richard and Robert (*34*) established that up to 1% ozone could be applied to pulp before strength properties were affected. Allison (*57*) showed that pulp viscosity decreased with increasing ozone dosage. Singh (*29*) showed that application of more than 0.9% ozone (on ovendry pulp) to hardwood kraft pulps resulted in no additional brightness improvement per unit kappa number decrease, while viscosity decreased significantly. Optimum application amount was established at 0.9-1.0%. Pilot plant work by Patt *et al.* (*21*) showed that selectivity of ozonation was superior at low ozone charges. Rutkowski and Sjopinski (*36*) found that application of more than 1.5% ozone did not reduce kappa number or increase brightness significantly, but did reduce pulp yield considerably. Soteland (*14*) found that unbleached pulps with high kappa numbers experienced serious degradation due to the large amount of ozone which had to be applied. Installation of an oxygen stage before ozonation was suggested as a way to solve this problem. Plonka *et al.* (*81*) showed that application of

I. Studies of bleach sequences using ozone

Authors	Ref. no.	Sequences studied, (pulping)—bleaching
Singh	29	(Kraft)—ZED
Larsson & Samuelson	22	(Kraft)—NOZEoD
Norden & Simonson	49	(Sulfite)—HD, EoDH
Rutkowski & Sjopinski	36	(Kraft)—ZEDED
Liebergott & van Lierop	16	(Kraft, Kraft-AQ, Soda-AQ)—ZDED
Granum & Hasvold	47	(Sulfite)—D/CZEHD, DZEHD, ZEHD, OZE
Soteland & Carlberg	38	(Sulfite)—ZDH, ZDP, ZHP, ZPH, OZD, OZP (Kraft)—ZDPD, OZDPD
Lindqvist & Marklund	51	(Sulfite)—EZEHD
Allison	46	(Bisulfite)—ZEP
du Plooy & Male	42	(Kraft, SAS/AQ)—OZEP
Kordsachia & Patt	62	(ASAM)—ZERP, OZP
Gupta & Eckert	32	(Kraft)—OZ, OZE, OZD, OZED
Blomberg & Wartiovaara	100	(Kraft)—ZEDED
Liebergott *et al.*	41	(Kraft)—OZEPY, $ZO_{zw}PY$
Christensen & Soteland	45	(Sulfite)—OZE, OZP
Kordsachia & Patt	63	(ASAM)—$OZE_RP(Y)$
Buinitskaya *et al.*	48	(Kraft, Sulfite)—ZPP
Kassebi & Gratzl	65	(Kraft)—OPZEP, OPZED
Fujii *et al.*	97	(Kraft)—OZP
Lachenal & Bokstrom	98	(Kraft)—AZE, NZE
Patt *et al.*	40	(Kraft)—NE/PDED, N/ZE/PDED (Sulfite)—NE/PHDH, N/ZE/PHDH
Loquenz	54	(Sulfite)—OZP
Farkasova *et al.*	55	(Sulfite)—OZPD
Allison	58	(Soda-AQ)—ZEP
Allison	15	(Kraft, Kraft-AQ, Soda-AQ)—ZEP, ZPZP
Liebergott *et al.*	101	(Kraft)—ZDED
Loras & Soteland	102	(Sulfite)—OZP
Dou *et al.*	103	(Kraft)—ZP, PZ, OZP
Lachenal *et al.*	23	(Kraft)—ZE, ZEp
Ow & Singh	24	(Kraft)—OZEP, OZEPD
Wang & Patt	50	(Sulfite)—ZHDH
Christensen & Soteland	44	(Sulfite)—OZE, OZP
Allison	57	(Soda-AQ-O)—ZP, ZEP, ZEZEP, ZEZP, ZPZP
Patt *et al.*	21	(Kraft)—ZEDED, ZE/PDED, N/ZE/PDED (Sulfite)—ZHDH, ZE/PDED, N/ZE/PDED, ZE/PHDH, N/ZE/PHD
Hartler *et al.*	37	(Mod. Kraft)—ZD, ZOD
Rothenberg *et al.*	59	(Kraft)—ZEZ (Oxygen)—ZEZ, ZP, ZA
Kobayashi *et al.*	82	(Kraft)-ZZZ
Soteland	12	(Kraft)—OZH, OZP (Bisulfite)—ZH, ZP
Richard & Robert	34	(Kraft)—OZEZ
Soteland	14	(Kraft)—OZ, OZPZP
Rutkowski & Sjopinski	77	(Kraft)—ZEDED
Rutkowski & Sjopinski	104	(Kraft)—OZEDED, OZEOZDED
Djamal	31	(Kraft)—ZP (Alkali-Methanol)—ZP
Rothenberg *et al.*	33	(Kraft, Kraft-AQ)—ZEZ (Soda-AQ)—ZEZ, ZEZEZ, ZEZEZP
Takagi	60	(Alkali-Dioxane)—ZP

Key:

A - peracetic acid
ASAM - Alkaline sulfite-anthraquinone-methanol pulping
AQ - anthraquinone
C - chlorine
D - chlorine dioxide
E - alkaline extraction
Eo - oxygen-reinforced extraction
Ep - peroxide-reinforced extraction
E_R - reducing agent added to extraction
H - hypochlorite
N - nitrogen dioxide
O - oxygen delignification
O_{zw} - oxygen-stage pulp washed with ozone stage effluent
P - hydrogen peroxide
R - sodium borohydride
Y - sodium dithionite
Z - ozone

more than 1.0% ozone on pulp caused a decrease in the decolorization efficiency.

Ozone concentration

Kobayashi *et al.* (*79*) found that increasing ozone concentration in the carrier gas from 1% to 3% had no effect on the properties of pulp bleached at high consistency. Similarly, Liebergott and van Lierop (*1*) increased ozone concentration from 2.1% to 4% with no effect on delignification, although pulp viscosity was marginally higher when the higher concentration was used. Singh (*29*) also found no effect on delignification or brightness when ozone concentration was increased. Pilot trials by Norden and Simonson (*49*) showed that ozone concentration had no effect on delignification. In a study by Kassebi and Gratzl (*65*) on high-consistency ozonation of kraft and kraft-oxygen pulps, reducing the ozone concentration from 1.9% to 0.3% at a given ozone charge on pulp caused an increase in pulp viscosity. Delignification rate was unaffected by the concentration change.

Number of stages

In the bleaching of oxygen pulps, Rothenberg *et al.* (*59*) found that application of ozone in two stages (separated by washing) instead of one reduced the amount of ozone required. The difference was attributed to the presence of degraded lignin products, which consume ozone, in the single stage. Kobayashi *et al.* (*35, 80, 82, 83*) compared single-stage and three-stage ozonation of kraft pulps and found that the multistage process required only 2.6% ozone, while the single stage required 4.7%. Viscosity loss was less in the multistage process. The effects were attributed to the removal of oxidation products, ashes, and resins by washing. Strength properties of pulps bleached with multiple stage were superior to those of pulps from a single stage. Mbachu and Manley (*84*) found that a two-stage ozone bleaching process with an intermediate wash was more effective than a single stage with respect to delignification efficiency. However, viscosities of pulps from the two-stage process were lower. Rothenberg *et al.*(*33*) showed that high-quality pulps could be obtained from soda-AQ-oxygen pulps by multistage ozone

bleaching. Allison (*57*) found that for bleach sequences employing two ozone stages, overall efficiency was improved if more of the total ozone charge (about 65%) was apportioned to the first stage. Dou *et al.* (*66*) confirmed that ozone bleaching of kraft pulps was more efficient in multiple stages.

Washing/extraction after ozonation

Liebergott and van Lierop (*1*) extracted ozonated pulps with dilute caustic and found that the treatment reduced pulp kappa number and increased viscosity. Christensen and Soteland (*44*) discovered that following the ozone stage with an alkali wash improved bleaching efficiency. A study by Allison (*57*) showed that for an ozone stage followed by extraction, omission of interstage washing did not affect bleachability of the extracted pulp, provided additional alkali was added in the extraction. For an ozone stage followed by a peroxide stage, omission of interstage washing not only increased peroxide-stage alkali requirements, but it also reduced brightness after the peroxide stage because of consumption of peroxide by ozonation products. Patt *et al.* (*21*) found that inclusion of an extraction stage after ozonation of pine kraft pulps reduced the amount of ozone required and enhanced brightness development. However, it also caused a substantial yield loss. Addition of peroxide to the extraction stage increased the beneficial effects of the extraction while reducing yield loss. Rutkowski and Sjopinski (*36*) found that extraction of ozonated kraft pulp affected the pulp properties only slightly, but it caused an increase in pulp brightness in final bleaching stages. Hartler *et al.* (*37*) found that omission of an extraction stage after ozonation increased bleaching selectivity. However, more ozone was required to reach a given kappa number, and more chlorine dioxide was required to reach final brightness.

Carbohydrate-preserving additives and pretreatments

Liebergott and van Lierop (*1*) offer a comprehensive review of additive studies up to 1978.

Osawa and Schuerch (*10*) studied the effect of nitromethane, an organic solvent which preferentially wets lignin, on ozonation selectivity. They found that although the solvent did not increase the selectivity of the lignin attack, it did increase the rate of attack markedly. Kamishima *et al.* (*85, 86*) examined the effect of magnesium compounds, iodine compounds, triethanolamine, metal salts, urea-methanol, methanol, DMF and DMSO on ozonation selectivity. Mbachu and Manley (*84*) found that pulps pretreated with acetic or formic acids consumed substantially less ozone to reach a given kappa number than pulps pretreated with water or sulfuric acid. Kassebi and Gratzl (*65*) examined the effect of sulfuric and acetic acids, DMSO, dimethyl sulfone, and 2-propanol on kraft pulp properties in ozonation. Kamishima *et al.* (*87-92*) studied the effect of 27 organic acids and methanol as potential carbohydrate protectors for unbleached kraft pulp during ozonation. Various other investigations (*25, 36, 68, 71, 78, 93-99*) have examined the suitability of a wide variety of organic and inorganic substances as pretreatments and additives for viscosity and strength preservation during ozone bleaching, with varying degrees of success.

Bleaching sequences containing ozone

A large number of studies have examined the use of ozone in combination with other bleaching agents. **Table I** is a summary of those studies.

Pilot plant studies

Singh (*29*) reported on the operation of a 15-ton/day pilot plant which confirmed that high-brightness, high-quality bleached hardwood kraft pulps could be produced using ozone at high consistency. Buinitskaya *et al.* (*48*) used ozone and peroxide to bleach sulfite and kraft pulp on the industrial scale. With a ZPP sequence, it was possible to produce a sulfite pulp with acceptable strength, but kraft pulp suffered strength loss. Patt *et al.* (*21*) reported on a pilot scale, high-consistency ozone stage, which was successful in delignifying sulfite pulps to kappa numbers 4-8. Norden and Simonson (*49*) reported that beech sulfite pulps were successfully delignified in a pilot high-consistency ozone stage, confirming earlier laboratory results about ozone consumption at a given kappa number. Lindqvist and Marklund (*51*) also reported that pilot high-consistency ozonation of sulfite pulps confirmed laboratory data on kappa number and viscosity decrease. Loquenz (*54*) and Prutsch *et al.*(*105*) described results from a pilot-scale OZP process for sulfite pulps. Pulp kappa number was between 5 and 10 out of the ozone stage, and bleaching with peroxide allowed a final brightness of 90%.

Patent review

A list of patents involving ozone bleaching of chemical pulps is available from the authors.□

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