Developing an ozone bleaching process

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ABSTRACT: Ozone bleaching has been studied for years, but no commercial system for kraft pulp has ever been built. For more than a decade, Union Camp worked on developing a successful ozone bleaching technology with satisfactory pulp properties, much lower bleaching chemical costs than for currently used bleaching sequences, and with large environmental emission improvements. A 900-a.d. metric ton/day OZED bleach plant started up at the company's Franklin, VA, mill in the third quarter of 1992.

KEYWORDS: Bleach plants, construction, costs, development, effluents, kraft pulps, ozone bleaching, Pinus, pulp properties, sequences, utilization, Virginia.

CEDED operation

Union Camp Corp. for many years had standardized on the CEDED bleaching sequence for its bleaching of southern U.S. mixed hardwood (primarily gum and oak) and southern U.S. pine (principally loblolly) pulps, which it uses to produce bleached uncoated freesheet papers and bleached coated and uncoated board grades. Many enhancements over the years had made this a reliable and cost effective process. These included such things as a fail-safe gaseous chlorine delivery system (*1*), a number of firsts in chlorine dioxide manufacture, computer control systems on all bleach lines, and, in some cases, for minimum water use, complete counter-current use of each stage's filtrate so that clean water for washing was only required in two places: the final brownstock washer before the bleach plant and the final dioxide stage in the bleach plant (**Fig. 1**).

With this process, we have been able to take brownstock that would be typical of the production from most southeastern U.S. mills (**Table I**) and produce pulps of good brightness, good fiber properties, and low dirt levels while maintaining reasonable environmental emissions and bleaching costs.

Brightness ceilings for the CEDED sequence as we run it are about 90–92 GE brightness for both pine and hardwood. Because we have been an integrated user of all our own pulp until very recently, we have chosen to operate, generally, in the 83–85 GE brightness range out of our bleach plants. At these relatively low brightness levels, one is usually on the verge of dirt problems, but our CEDED process has kept us consistently below 4 ppm on the TAPPI equivalent black area in dirt for both pine and hardwood. Strength properties are generally excellent. **Table II** contains average properties as we analyze them.

Typical chemical usages for the CEDED bleaching are shown in **Table III**.

Environmentally, this bleaching sequence performed well, as shown in **Table IV**. Still, we recognized that this process was a major source of mill environmental emissions because all of the bleach plant dissolved organics and all of the inorganic bleaching chemicals wind up sewered due to contamination by the chloride ion. Even in an integrated pulp and paper mill, the bleach plant may contribute 50+% of the effluent volume, 35+% of the BOD_5, 60% of the color, and most of the chlorinated organics in the total effluent (*2*). As a result, we initiated aggressive research aimed at developing an improved process from an environmental standpoint. The recent discovery of dioxin in trace quantities resulting from the use of gaseous chlorine has made this a wise decision.

O(DC)ED operation

Our company was quick to recognize the environmental possibilities from the oxygen delignification technology introduced in South Africa and Europe in the '70s. We moved rapidly to install one of the first systems in the United States utilizing oxygen delig-

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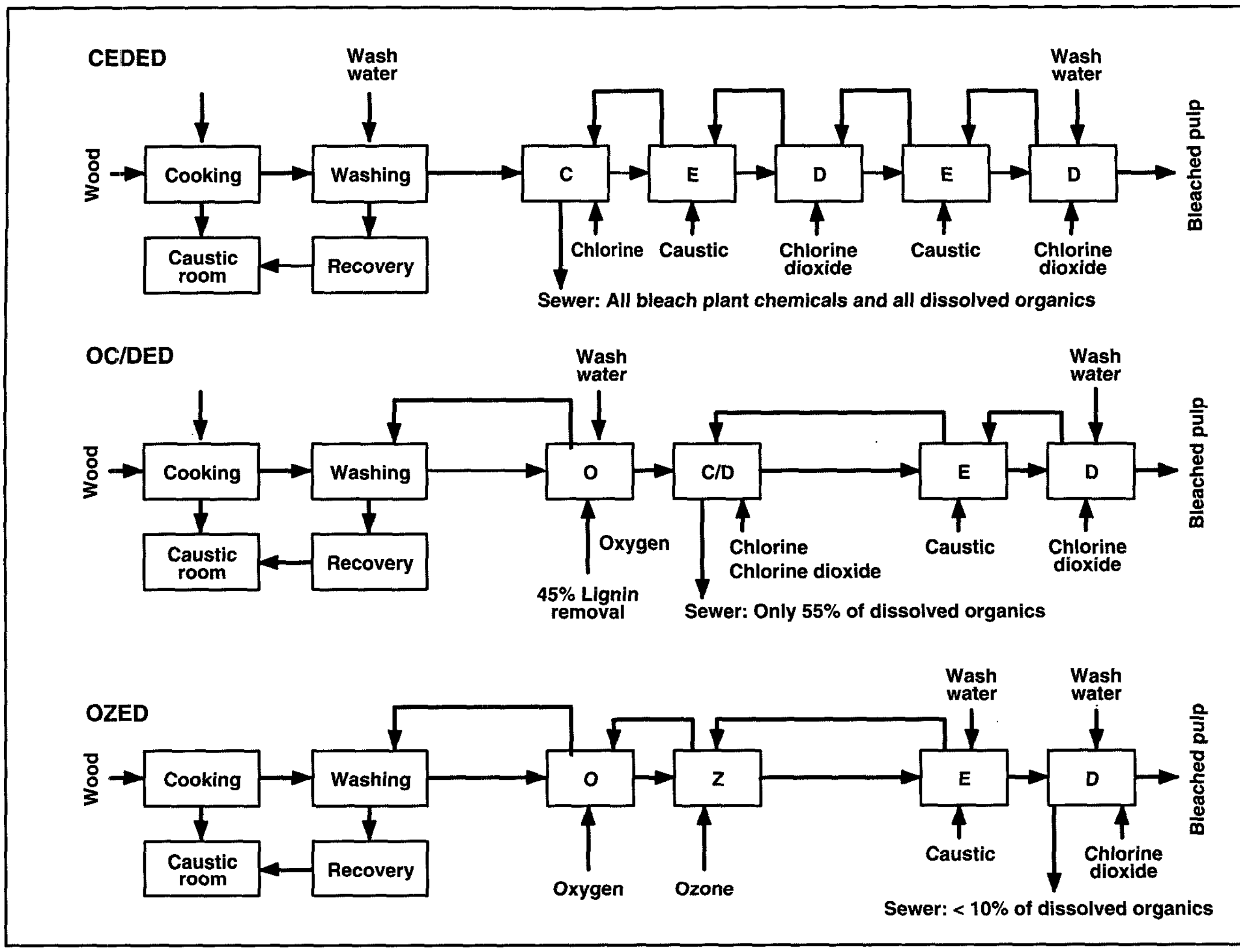
1. Simplified sequence schematics



I. Typical brownstock characteristics

	Pine	*Hardwood*
Screened kappa no.	30–31	16.5
TAPPI viscosity, cp	22–23	28–30
Rejects after screening, *%	0.016	0.047

*10 cut flat screen

II. Typical fiber properties produced by CEDED bleaching

	Pine	*Hardwood*
Breaking length, km	7.5	5.9
Zero span breaking length, km	13.8	14.2
Burst, m^3/cm^3	53	39
Tear, dm^3	111	87
TAPPI viscosity, cp	17	14
Bulk, cm^3/g	1.63	1.65
TAPPI opacity, 577 nm	74	78
TAPPI scattering coefficient, 577 nm	260	354

83-GE brightness pulp, Valley beater refined to 350 mL CSF. Nonstandard handsheet method used of acid sized pulp, fines retained, semirestrained drying to simulate paper machine conditions.

III. Typical chemical usage for CEDED bleaching to produse 83 GE brightness

	Pine	*Hardwood*
Chlorine, %	7.11	2.06
Caustic ($E_1 + E_2 + D$ buffer), %	5.89	1.95
Chlorine dioxide ($D_1 + D_2$), %	2.17	0.83

IV. Typical environmental emissions from CEDED bleaching for 83 GE brightness

	Pine	*Hardwood*
Total organic halides, kg/a.d. metric ton		
Pulp	0.28	0.20
Effluent	6.50	3.00
Chloroform, kg/a.d. metric ton	0.18	0.18
BOD_5, kg/a.d. metric ton	16.00	8.00
COD, kg/a.d. metric ton	65.50	23.00
Color, kg/a.d. metric ton (Chloroplatinate test)	185	55
Volume of effluent		
m^3/a.d. metric ton	55.40	55.40
gal/a.d. ton	13,300	13,300

V. Typical fiber properties produced with O(DC)ED bleaching

	Pine	*Hardwood*
Breaking length, km	7.2	5.8
Zero span breaking length, km	12.4	13.3
Burst, m^3/cm^3	62	41
Tear, dm^3	119	87
TAPPI viscosity, cp	13	13
Bulk, cm^3/g	1.64	1.72
TAPPI opacity, 577 nm	70	79
TAPPI scattering coefficient, 577 nm	242	366

83-GE brightness pulp, Valley beater refined to 350 mL CSF. Nonstandard handsheet method used of acid sized pulp, fines retained, semirestrained drying to simulate paper machine conditions

VI. Typical chemical usage for O(DC)ED bleaching to produce 83 GE brightness

	Pine	*Hardwood*
Oxygen, %	2.50	1.55
Magnesium sulfate, %	0.25	. . .
Oxidized white liquor as NaOH, %	2.11*	1.16*
Chlorine, %	3.34	1.39
Caustic (E + D buffer), %	2.39	0.99
Chlorine dioxide ($D_1 + D_2$), %	1.21	0.51

*All but 0.19% recovered.

VII. Typical environmental emissions from O(DC)ED bleaching to produce 83 GE brightness

	Pine	*Hardwood*
Total organic halides, kg/a.d. metric ton		
Pulp	0.12	0.13
Effluent	3.00	2.00
Chloroform, kg/a.d. metric ton	0.08	0.10
BOD_5, kg/a.d. metric ton	6.50	4.50
COD, kg/a.d. metric ton	22.50	13.00
Color, kg/a.d. metric ton (Chloroplatinate test)	41.50	12.00
Volume of effluent,		
m^3/a.d. metric ton	14.20	14.20
gal/a.d. ton	3400	3400

35% substitution used for DC stage. O-stage filtrate recovered.

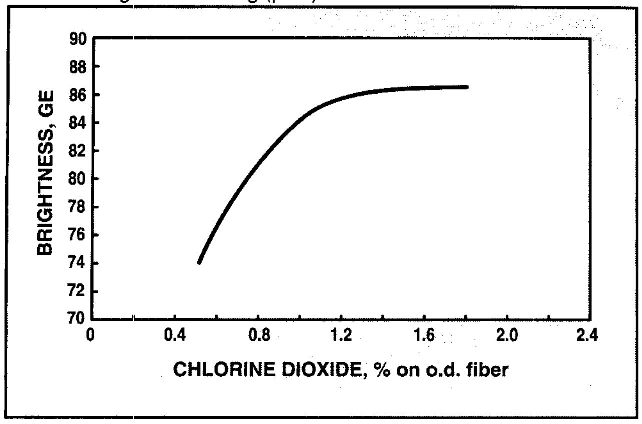
nification, with full recovery of oxygen filtrate, where the inorganics are recovered for reuse and the organics incinerated for fuel. Our first system utilizing an O(DC)ED bleaching sequence (Fig. 1) started up in early 1981 (*3*). We now have three such systems.

Unlike most of the rest of the industry, we have continued to install high-consistency oxygen delignification systems exclusively because they can be operated at much higher levels of delignification before strength loss occurs than can medium-consistency oxygen systems. Typically, we can achieve about 45–50% delignification and see no final strength loss. This advance delignification allows us to eliminate the final ED stages but at a somewhat lower brightness ceiling of 87.5 GE for pine and 89 GE for hardwood. Recently, we have found that we can elevate this brightness ceiling to greater than 90-GE brightness by augmenting the E stage with oxygen and running elevated D-stage temperatures.

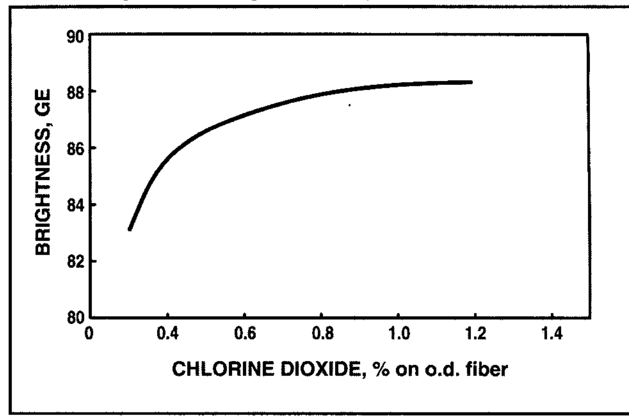
Dirt levels remain excellent, again with less than 4 ppm equivalent black area on both pine and hardwood. Pulp properties are not affected, as can be seen by comparing **Table V** to Table II. One exception is viscosity, which is depressed substantially by the oxygen stage. Since viscosity is not a functional end-use parameter but a surrogate test for strength, this is not a problem once people understand that oxygen pulps have a different viscosity-to-strength correlation than do CEDED pulps.

Chemical usage for O(DC)ED bleaching is low (typical numbers are shown in **Table VI**), leading to quite low bleaching costs when compared to the CEDED process. Based on fairly

2. OZED brightness ceiling (pine)



3. OZED brightness ceiling (hardwood)



typical U.S. raw material bleaching costs, as shown in the **Appendix**, the relative bleaching costs compared to CEDED would be about 40% lower for pine and 25% lower for hardwood pulps.

Environmentally, emissions are substantially reduced by use of the O(DC)ED bleaching approach, as shown in **Table VII.**

OZED bleaching

While a significant improvement over CEDED, the O(DC)ED bleach plant is still a substantial emitter of pollution. We resolved to solve these problems by eliminating the chlorine stage, thereby allowing closeup and recovery of most of the bleach plant effluent. After examining many alternatives, we began to converge on the use of ozone. Ozone had been studied for years by others due to its promise of being a nonchlorine-containing compound that is a powerful lignin dissolver and produces effluent that has the potential to be recycled. A recent National Council for Air and Stream Improvement literature survey lists some 105 literature articles and 55 patents granted on ozone (*4*).

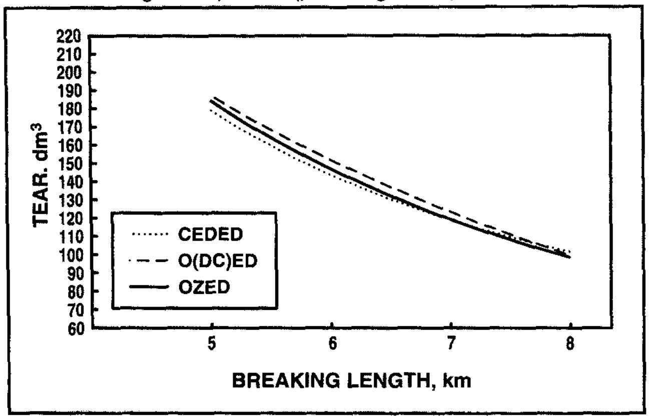
Years ago, Rudra Singh strongly advocated the use of ozone based on his research at Scott Paper (*5*). Still, no one had commercialized an ozone bleaching system, and virtually all bleaching researchers had closed their research into ozone and proceeded in other directions. For example, at the TAPPI 1989 Pulping Conference (*6*), out of 16 papers presented on bleaching there was not even a mention of ozone work; and, at the Bleach Plant Operations Seminar that year, only Axegård forecasted that ozone combined with chlorine dioxide was likely to be employed in the future (*7*). The apparent reasons for this lack of continuing interest were (a) poor selectivity of ozone, which produced inferior-strength pulp when adequate amounts of ozone were used to do significant bleaching, (b) nonuniform bleaching that resulted from the highly reactive ozone, and (c) the high cost of the ozone required.

Through about 10 years of research, our R&D began to solve these problems. Developments in extending the level of delignification before the ozone stage (like modified continuous cooking, rapid displacement heating, Superbatch, and kraft/anthraquinone in extended cooking or a modified oxygen delignification process developed by Union Camp, or both) have reduced the amount of work that must be done in the ozone stage, which is a key to implementation of this technology. We will not attempt to detail our enhanced oxygen delignification development here because it was the subject of a paper at the recent CPPA Annual Meeting (*8*).

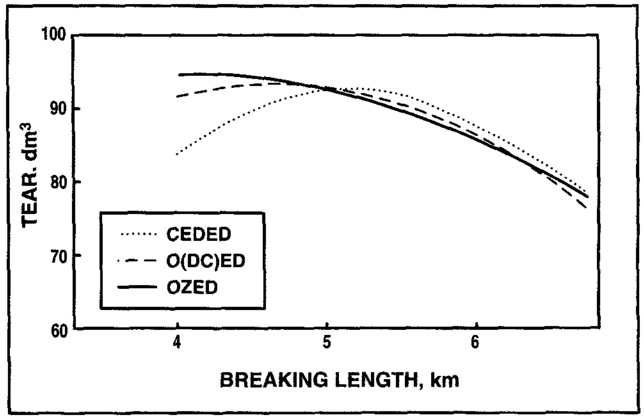
Through the thorough investigation of dozens of ozone utilization variables such as pulp consistency, pH, temperature, time, heavy metal interactions, methods of control, gas recovery and recycling technology, and mass transfer and reaction kinetics, we have been able to optimize and control ozone treatment to maximize benefits and reduce undesirable effects. One of the most critical decisions was the selection of the pulp consistency for ozone reaction. We have chosen to operate in the ultra-high-consistency region (above 35%). There is a great deal of sentiment within our industry these days that the optimum technology for ozone treatment will be in the medium-consistency area. The thinking is that ozone will follow a similar development as oxygen delignification, which began with high consistency and then went almost exclusively to medium consistency because of perceived lower capital costs. We believe this is not likely to happen for ozone, as we believe it should not have happened for oxygen delignification, because there are some major reasons that high consistency will be superior:

1. The medium-consistency technology is faced with a gas volume to liquid volume ratio limit beyond which one is unable to sustain the intimate contact of the two phases (*9, 10*). Thus, unless one is interested in applying only a few tenths of a percent ozone into the fiber, multiple application and reaction steps must be installed. Multiple stages will quickly nullify the potential capital cost advantages of medium consistency.

4. OZED strength comparison (pine, brightness)



5. OZED strength comparison (hardwood 83 GE)



VIII. Typical fiber properties produced with OZED bleaching

	Pine	*Hardwood*
Breaking length, km	7.0	5.7
Zero span breaking length, km	12.5	13.7
Burst, m^3/cm^3	59	39
Tear, dm^3	124	85
TAPPI viscosity, cp	11	12
Bulk, cm^3/g	1.66	1.71
TAPPI opacity, 577 nm	72	79
TAPPI scattering coefficient, 577 nm	254	368

83-GE brightness pulp, Valley beater refined to 350 mL CSF. Nonstandard handsheet method used of acid sized pulp, fines retained, semirestrained drying to simulate paper machine conditions.

IX. Typical chemical usage for OZED bleaching to produce 83 GE brightness

	Pine	*Hardwood*
	OZ(EO)D[a]	*OZED*
Oxygen (O + EO stage), %	3.33	1.55
Magnesium sulfate (O stage), %	0.25	...
Oxidized white liquor (O + E stages) as NaOH, %	4.00[b]	2.56[b]
Ozone, %	0.72[c]	0.4[c]
Sulfuric acid, %	1.25	1.25
Chelant, %	0.11	0.11
Caustic (D buffer), %	0.22	0.05
Chlorine dioxide, %	0.65	0.28

[a]Oxygen augmentation of extraction stage is cost effective for pine.
[b]All but 0.78% recovered.
[c]Includes amount consumed by water and carryover/carryback solids into stage.

One approach for overcoming this barrier is to go to increased pressure of the ozone gas. Pressures exceeding 14.5 kPa (100 psi) are being attempted. This approach increases capital costs and creates increased safety problems in handling toxic gases. Our high-consistency process operates at very near atmospheric pressure.

Another approach has been to go to increased ozone concentration. Generation of ozone at higher concentration does require extra electrical energy, and thus operating and capital costs are increased. In addition, as one edges closer to the concentration point where ozone and oxygen mixtures reach an autoexplosion point (claimed by various researchers to be as low as 14% ozone) safety concerns increase. Our high-consistency system operates at conventional ozone concentrations that have been produced for years.

2. The water layer that surrounds each fiber at medium consistency is a well established diffusion resistance barrier for ozone passage (*11*). Overcoming this with intense mixing for a long enough time for diffusion to occur is very difficult to achieve. Achievement of complete ozone consumption is very difficult. Sensitivity to incoming consistency variations is also a problem.

3. The extra water volume that is carried into the ozone reaction (three to six times as much for medium consistency versus high) creates major problems. The extra water and solids in the water consume ozone. The amount of chemical required for pH adjustment and heavy metal treatment are increased. Complete recovery of the filtrate, which is so desirable from a BOD and color aspect, is much more complicated.

This is not to say that medium-consistency ozonation may not have a place for low addition, polishing steps, but it is unlikely to satisfactorily compete with high-consistency ozonation for bulk delignification treatments.

By 1987, we reached the point where we believed we had developed a satisfactory ozone bleaching process. To verify this and to develop the scale-up information necessary to design a commercial plant, we decided to install a 25-ton/day, US$ 6.5-million pilot plant. This plant was installed at our Eastover, SC, mill where mill-produced oxygen-delignified pine and hardwood feed stocks were continuously available.

The pilot plant consisted of a complete ozone stage (including ozone generation), reactor off-gas reclaim, cleanup, and recycle. Since we had adequate experience at performing finishing bleaching steps like extraction or chlorine dioxide in the lab, we thought it unnecessary to include such steps in the pilot plant.

This plant now has been operated routinely for over four years and has been invaluable in assuring our success. For example, in the larger scale, we ran into the well known phenomena of nonuniform bleaching associated with high-consistency ozonation. The original packed-bed ozone reactor we had installed proved to be completely unsatisfactory and was removed. We went back to first principles and designed a new type of reactor that, after numerous evolutionary steps, has completely solved the nonuniformity problems. Probably more than any other single factor, this unique design is the secret of our success. Again, we will not attempt to elaborate on the design of the reactor in this paper since a presentation was made on this topic at the recent CPPA Annual Meeting (*12*).

Finally, by early 1990, we had reached the point where we knew we could build a successful, commercial-sized system utilizing ozone bleaching. Since we needed to replace two old 455-a.d. metric tons/day, CEDED pine bleach lines at our Franklin, VA, mill because of age and maintenance problems and to assure compliance with new state dioxin stream standards, we seized the opportunity to move into a dramatically improved position with respect to virtually all environmental emissions from bleaching. We chose to install a new bleach line using our ozone technology to completely eliminate any use of gaseous chlorine and to sharply reduce our use of chlorine dioxide.

The commercial facility that we built and started up is a 900-a.d. metric tons/day bleach plant using an OZED bleaching sequence (Fig. 1). It is a line dedicated to bleaching southern kraft pine pulp. Target brightness will be about 83–85 GE. Capital costs for the bleach line, exclusive of other mill changes such as a new hot stock screening system, were just under US$ 90 million.

Projected results from our new OZED bleaching sequence for both pine and hardwood are as follows. Brightness ceiling curves are shown in **Figs. 2 and 3**. Higher ceiling brightnesses can, of course, be obtained with additional stages or by augmenting existing stages with oxygen or peroxide. Dirt levels will be below 4 ppm equivalent black area for both pine and hardwood. To check the rela-

X. Typical environmental emissions from OZED bleaching to produce 83 GE brightness

	Pine	*Hardwood*
Total organic halides, kg/a.d. metric ton		
Pulp	0.04	0.03
Effluent	0.075	0.06
Chloroform, kg/a.d. metric ton	0.0015	0.0015
BOD_5, kg/a.d. metric ton	2.0	1.0
COD, kg/a.d. metric ton	6.0	2.0
Color, kg/a.d. metric ton (Chloroplatinate test)	1.5	0.5
Volume of effluent		
m^3/a.d. metric ton	7.5	7.5
gal/a.d. ton	1800	1800

All but D-stage filtrates are recycled.

XI. Reduction in environmental emissions from OZED to produce 83 GE brightness

	Pine		*Hardwood*	
	Compared to CEDED	*Compared to O(DC)ED*	*Compared to CEDED*	*Compared to O(DC)ED*
Total organic halides, %				
Pulp	86	67	85	77
Effluent	99	98	98	97
Chloroform, %	99	98	99	98
BOD_5, %	88	69	88	77
COD, %	91	73	91	85
Color, %	99+	96	99+	96
Volume of effluent, %	86	47	86	47

XII. Results of strength tests on different woods

	GE brightness	Tear obtained at a given tensile — Tear, dm³: Conventional sequence [a]	OZED sequence	At tensile, km [b]
Scandinavian birch	89	75	75	6.0
Southern mixed hardwood	88	87	85	6.0
Brazilian eucalyptus	89	88	86	6.0
Scandinavian spruce/pine	89	145	135	7.5
Canadian hemlock/ Douglas-fir	88	154	161	7.5
Southern pine	88	108	111	7.5

[a]The conventional sequence was a version of CEDED except for birch (where an oxygen and 100% dioxide substitution was used) and spruce/pine (where oxygen was also used). For both the conventional and OZED sequences, variations like EO or a second D stage were used to optimize efficiencies.
[b]Evaluation point was changed between softwoods and hardwoods to keep within the usable freeness of 300–400 CSF.

XIII. OZED reduction in bleaching chemical costs for 90 GE brightness

	Conventional bleaching		100% Substitution	
	Reference sequence	Reduction, %	Reference sequence	Reduction, %
Birch	O(DC)EDED	42	ODEDED	47
Southern hardwood	CEDED	20	DEDED	52
Eucalyptus	CEDED	16	DEDED	46
Spruce/pine	O(DC)EDED	35	ODEDED	32
Hemlock/Douglas-fir	CEDED	38	DEDED	61
Southern pine	CEDED	55	DEDED	68

Based on raw material cost appendix

XIV. OZED reduction in bleach plant effluent for 90 GE brightness

	Compared to reference sequence	Percent reduction with OZED: Color	BOD_5	TOX	COD
Birch	ODEDED	88	76	71	58
Southern hardwood	CEDED	99	88	98	91
Southern hardwood	$O(D_{30}C)ED$	96	78	97	90
Eucalyptus	CEDED	98	87	97	88
Spruce/pine	$O(D_{70}C)EDED$	98	...	97	85
Hemlock/Douglas-fir	CEDED	96	91	84	92
Southern pine	CEDED	99	88	99	91
Southern pine	$O(D_{30}C)ED$	96	69	98	73

tive dirt removal efficiency of the OZED sequence versus the CEDED and O(DC)ED sequence, we introduced (spiked) extra dirt into the brownstock feed so that the fully bleached product's dirt levels were at a high enough dirt test range to be accurate tests. These tests showed equivalent removal for all three sequences.

Measured pulp property tests are shown in **Table VIII**. Comparison to Tables II and V shows no significant differences except in viscosity, where, similar to the phenomena for oxygen, ozone pulp is depressed in viscosity without being lower in strength. Another standard way to look at the relative strengths is to compare the tear and tensile curves over an entire freeness range. **Figures 4 and 5** show this comparison for pine and hardwood. Our conclusion is that there are no significant differences.

With our process, we are able to achieve very low bleaching chemical dosages. **Table IX** shows typical numbers. As these numbers suggest, bleaching chemical cost, including ozone manufacture, is very competitive with the CEDED and O(DC)ED sequences. In fact, using the raw material costs in the Appendix, we calculate relative OZED bleaching costs to be 52% lower for pine and 17% lower for hardwood.

Perhaps a more practical comparison in today's environment is to compare OZED to DEDED and ODED bleaching cost, predicting that, due to dioxin and total chlorinated organic considerations, the only viable way to operate CEDED and O(DC)ED systems in the future will be as 100% substitution of chlorine with dioxide. We estimate that total chlorine dioxide use in the DEDED process would be 5.64% for pine and 1.83% for hardwood. Total use for the ODED process would be 3.10% for pine and 1.29% for hardwood.

Based on these estimates of chlorine dioxide usage for 100% substitution and using DEDED costs as the base, we calculate relative bleaching costs for pine to be 44% lower for ODED and 68% lower for OZED. Relative costs for hardwood would be 27% lower for ODED and 43% lower for OZED.

The gap between OZED and standard sequence chemical costs widens even more as one goes to higher brightnesses.

Environmental emissions projected for the OZED sequence are astoundingly low, due to the projected recycle and recovery of virtually all of the O-, Z-, and E-stage effluents. **Table X** contains these projections. In percent reduction from the conventional CEDED and $O(D_{30}C)ED$ sequences, the numbers are even more dramatic (**Table XI**).

One might question that our continued use of a chlorine dioxide stage might introduce the possibility of producing a small amount of dioxin from the chlorine contamination present in commercial chlorine dioxide solutions. We have checked this carefully, using the most sensitive dioxin testing currently available, for both a relatively "dirty" chlorine dioxide (R-3 generated) and a "clean" chlorine dioxide (R-8 generated). In neither case did we detect dioxin, in either the pulp or the D-stage filtrate. Even when we pushed up the brightness by using additional chlorine dioxide, detection limits were about .16 ppt for the pulp testing and about 4 ppg for the filtrate.

Appendix

Raw material costs used for bleaching cost comparisons

Chlorine	US$ 168.30/metric ton US$ 153.00/ton	
Chlorine dioxide	US$ 0.70/kg US$ 0.32/lb	Includes by-product saltcake credit
Oxygen	US$ 58.30/metric ton US$ 53.00/ton	
Magnesium sulfate	US$ 533.50/metric ton US$ 485.00/ton	
Caustic co-purchased with chlorine on ECU basis	US$ 236.50/metric ton US$ 215.00/ton	Used for CEDED requirements and used for half of O(DC)ED requirements
Caustic purchased independent of chlorine	US$ 374/metric ton US$ 340/ton	Used for OZED requirements and used for half of O(DC)ED requirements
Cost of preparing oxidized white liquor	US$ 31.90/metric ton US$ 29.00/ton as NaOH	
Sulfuric acid cost	US$ 74.80/metric ton US$ 68.00/ton	
Chelant	US$ 1.29/kg US$ 0.51/lb	
Ozone	US$ 0.64/kg US$ 0.29/lb	Based on power costs of 36-MW/h and Union Camp's design of a recirculating ozone generation system

Total chlorine compound free bleaching

One issue that has become clear since the time that we decided to proceed with the OZED installation is that some parts of the world are going to demand total chlorine compound free bleaching (TCF) in order to be 100% free of any chlorinated organics. We have performed considerable testing on combinations of our oxygen and ozone technology with peroxide stages and are convinced that we can make acceptable TCF pulp. Bleaching costs are considerably higher [in the range of original CEDED and O(DC)ED costs but probably considerably below other TCF bleaching approaches], but it can be done. Additional environmental benefits are, of course, marginal.

Considerations for other applications

After Union Camp made the public announcement about its ozone bleaching development, we were flooded with inquiries from other paper companies about allowing them to examine and possibly use our technology. After some deliberation, we decided to offer our process to the industry via an agreement with Sunds Defibrator, in which they supply the process and the equipment to the industry with our assistance. After one year of dialogue with potential users, we now have developed considerable additional knowledge about two areas that we had not previously addressed: Will our process achieve market pulp brightness, and will it work on other wood species? Our test results are affirmative to both questions. To illustrate this, we have summarized some of our results in **Tables XII–XIV**. Table XII illustrates that satisfactory strengths were obtained at high brightness on a variety of woods. Table XIII illustrates that bleaching chemical costs were invariably lower. Environmental results also were always quite good, as Table XIV shows.

Capital costs

All of the positive benefits of the OZED process are not obtained without cost. The capital cost of an ozone-based bleach plant will be more than the current state-of-the-art bleaching sequence: O(DC)ED. Our experience indicates at this point that the bleach plant capital costs may be about 25% more. On the other hand, particularly for a new fiber line installation, there may be substantial off-sets in capital costs outside the bleach plant itself because of the OZED process. If a new chlorine dioxide plant is required, the OZED process may reduce new chlorine dioxide capital costs substantially. Capital savings in chlorine handling, effluent treatment, fresh water supply, etc. may also result. In some cases, the potential capital savings outside the bleach plant may completely offset the increased capital cost of the bleach plant itself.

There is one other significant point we'd like to make. Realizing the full benefits of the OZED process is predicated upon adequate recovery boiler capacity to accommodate the approximately 7% additional solids load that occurs from recovering the O, Z, and E filtrates. If one is already operating an oxygen bleach plant and recovering its filtrate, then the increase in recovery boiler solids load is only about 3% for the Z and E recovery. Of course, the recovered solids have a significant fuel value which should be realized by recycling.

Conclusions

We came to the following conclusions:

1. High-consistency ozone treatment can be satisfactorily used to completely replace a chlorine stage in kraft pulp bleaching. This is true even up to market pulp brightness levels and seems to be applicable for all wood species.
2. Pulp properties for the OZED bleaching sequence are as good as with conventional sequences like CEDED or O(DC)ED.
3. Bleaching chemical costs will be lower for OZED bleaching (as we plan to employ it) than for conventional CEDED or O(DC)ED bleaching. Bleaching costs will be much lower than 100% substitution versions of the conventional sequences.
4. Major environmental improvements are achieved by the use of OZED bleaching, not only in chlorinated organic emissions but also in aspects like color and BOD. ■

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Received for review July 21, 1992.

Accepted Oct. 14, 1992.

Presented at the TAPPI 1992 Pulping Conference.