NONSULFUR PULPING

A sulfur-free, chlorine-free alternative to kraft pulping

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ABSTRACT

A surfactant-based digester additive (DrewKPA-300) has helped to decrease the active alkali charge in the soda–AQ pulping of mixed hardwoods. Cooking time and temperature were moderately reduced, the anthraquinone charge was reduced by 1.36 kg per digester, and about 47 kg of caustic could be saved per ton of o.d. pulp. The pulp could be bleached to over 88% ISO brightness by short-sequence bleaching. Laboratory studies revealed that soda–AQ pulping can be extended to kappa numbers as low as 13.0 with the additive.

Application:

Soda–AQ pulping provides an attractive alternative to kraft pulping. Soda–AQ pulp can be bleached at a low cost without cholorine.

SODA PULPING IS A PULPING process that does not use sulfur. The release of malodorous reduced sulfur compounds to the atmosphere is the greatest disadvantage of kraft pulping, which is the dominant pulping process today. To ease the odor problem, kraft mills must install and operate expensive systems to control these noncondensable gases.

The soda pulping process, with or without anthraquinone (AQ), does not release any reduced sulfur compounds to the atmosphere. However, the soda process is carried out at an *H*-factor (cooking time and temperature) and chemical charge that exceed the conditions a kraft process would require to reach the same kappa number. Longer, hotter cooks with greater amounts of chemicals produce pulps that are weaker than kraft pulping produces at equal delignification. The pulp yield also suffers.

If the *H*-factor and chemical charge could be reduced without changing the brownstock kappa number, soda pulps and soda–AQ pulps would gain in strength and yield. In mill trials, we studied two surfactant-based digester additives, DrewKPA-200™ and DrewKPA-300™.* Our objective was to determine how effective these additives would be in reducing the active alkali charge. In subsequent laboratory trials, we studied the possibility of extending soda–AQ pulping with the digester additive.

*DrewKPA-200 and DrewKPA-300 are trademarks of Ashland Chemical, Drew Pulp and Paper Division, Boonton, NJ.

MILL DESCRIPTION

The Kingsport mill of the Mead Fine Paper Divsion was pulping hardwood by the soda process until 1976, when it switched to soda–AQ pulping. Before a drum debarker was installed in May 1993, the mill was pulping chips from wood that had bark in it. With impurities in the chips, the mill had to pulp to low permanganate numbers to minimize the dirt and shives. It was necessary to apply a high *H*-factor (approx. 1100), active alkali (16.9% as Na_2O), and anthraquinone (0.0692% AQ on o.d. chips) to cook to permanganate numbers of 11.5–12.0 (kappa nos. 17.0–18.0).

After the debarker was installed, the mill was able to increase the chips loading to the digesters and was able to decrease the active alkali, *H*-factor, and anthraquinone. Still, the soda–AQ process required aggressive cooking conditions to pulp to a target permanganate number of 12.0.

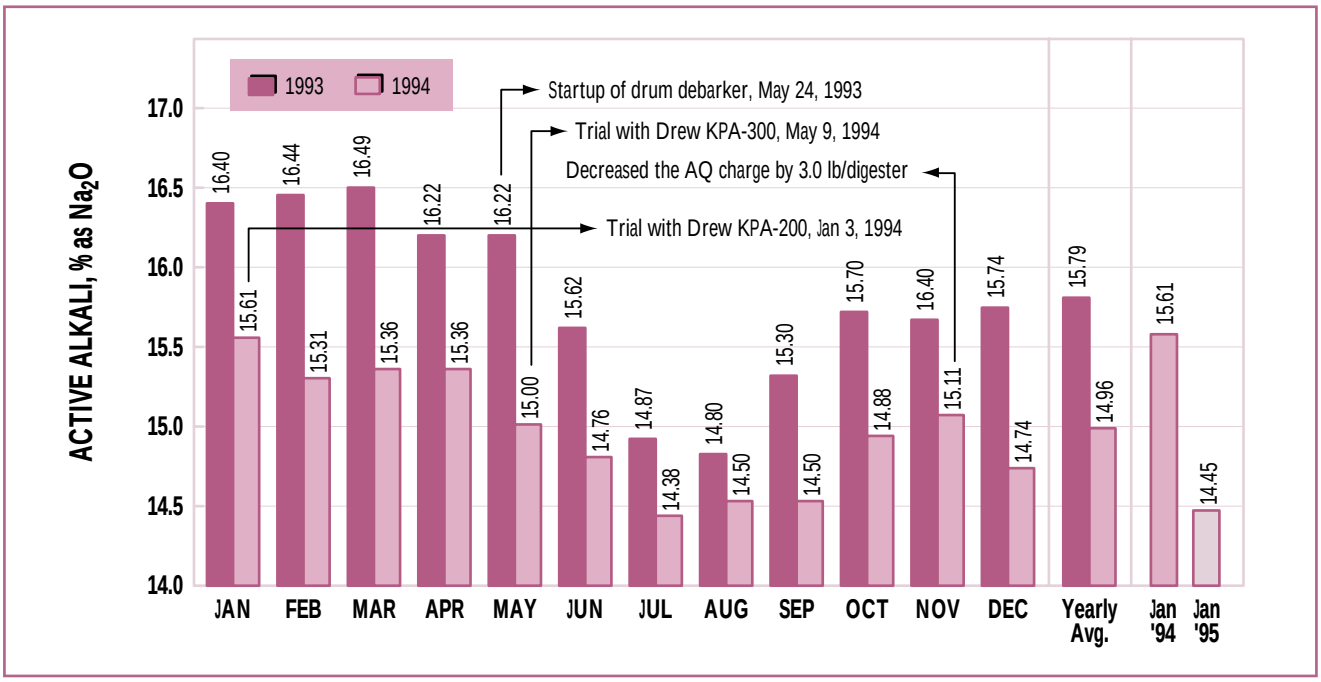
The bleach plant was converted to CED bleaching from a CEHP sequence after the startup of a chlorine dioxide generator in 1986. This conversion retired one washing stage and two retention towers. The washer and the retention towers can be incorporated into future modifications of the bleach plant.

Currently, the bleach plant operates at 50% chlorine dioxide substitution at the first stage. The plant began using hydrogen peroxide to reinforce the extraction stage (EOP) in August 1993. The purpose was to decrease the chlorine dioxide charge at the final D stage and still reach a pulp brightness of 86.0% ISO. In October 1993, the mill started post-peroxide bleaching to increase the pulp brightness to 86.5% ISO, but this process was discontinued in February 1994.

The salt cake from the chlorine dioxide generator has no use as a makeup in the recovery of soda spent liquor and is sewered after being neutralized with alkali or (EOP)-stage filtrate. To switch to 100% ClO_2 substitution at the first stage, the ClO_2 capacity would have to be increased. Any increase in chlorine dioxide capacity would increase the salt cake production proportionally, and its disposal would pose problems. This drawback is a good reason to explore ClO_2-generation technologies that produce little salt cake *(1)*.

BACKGROUND

According to the pulping kinetics, the concentration of NaOH has to be low at the beginning of the cook to decrease the random, endwise cleav-



1. The active alkali charge to the digesters changed with the use of digester additive.

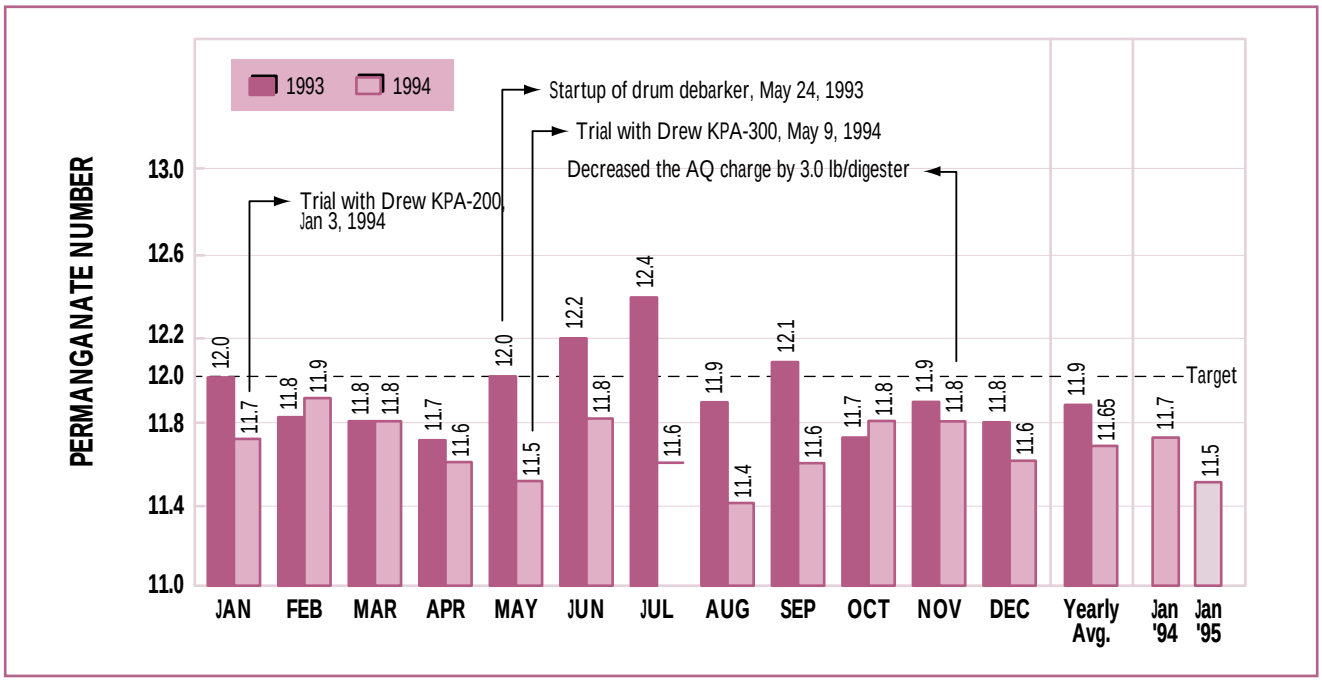
age of the cellulose chain while maintaining the rate of delignification. Such a condition is easier to meet in kraft pulping than in soda pulping. In kraft pulping, the NaOH concentration can be decreased by controlling the ratio of NaOH to Na_2S during the initial, bulk phase of pulping. This technique is called "liquor profiling." In soda pulping, liquor profiling is not possible because the only active ingredient is sodium hydroxide.

The only way to decrease the molar concentration of NaOH in soda pulping is to decrease the active alkali charge while keeping the liquor-to-wood ratio constant. Any strategy to decrease the active alkali charge to the digesters needs to be carefully evaluated. An uncontrolled decrease in active alkali would increase the pulp kappa number and the amount of screened material, or rejects. Any decrease in active alkali charge is likely to decrease the residual active alkali in black liquor, whereas a certain amount of residual active alkali is essential in the black liquor if the evaporators are to operate trouble-free.

An increase in brownstock yield leads to an increase in the bleached pulp production. Mild cooking conditions, like a low *H*-factor and a low active alkali charge, will increase the brownstock yield. However, mild cooking conditions do not lead to high kappa numbers. The pulp at a lower kappa number will consume greater amounts of bleaching chemicals, and the net effect is to shrink the bleached pulp yield. Also, changes in pulping and bleaching conditions should not cause the effluent characteristics to vary, because such deviations make it difficult to meet the effluent guidelines.

Over the past two decades, many digester additives have been studied to see if they could increase the pulp yield, decrease chemical consumption, decrease screenings (rejects), and improve brownstock washing *(2, 3)*. Pulping is a topochemical reaction *(4)*, and the diffusion of chemicals into wood chips plays an important role in the uniformity of the pulp *(5)*. Better penetration of the cooking liquor into the wood increases the rate of delignification and minimizes the nonuniformity of chip pulping. By improving the effectiveness of cooking chemicals, we can accelerate delignification even with less use of chemicals. The penetration of chemicals is more important in the soda and soda–AQ pulping processes than in the kraft process.

Compared to kraft pulp, soda–AQ pulp is difficult to bleach. At the equivalent brownstock kappa number, soda–AQ pulp demands more ClO_2 at the first stage to reach a given permanganate number (K number) in the extraction stage than kraft pulp requires *(6)*. The short sequence bleaching in itself demands more chemical application than five-stage bleaching demands *(7)*. To reach the target pulp brightness, a pulp with a lower K number after extraction requires less chlorine dioxide charge at the final D



2. The brownstock permanganate number changed with the use of digester additive.

stage. A low extraction-stage K number can be obtained from soda–AQ pulp only with high chemical charges in the first two stages.

However, high chemical usage in the first two stages would result in a high discharge of adsorbable organic halogens (AOX). The generation of AOX stems from the chemical use at the bleach plant, and the first two stages account for about 70% of the AOX released from the bleach plant *(8)*. As everyone knows, mills are under pressure to decrease the amount of AOX discharged into receiving streams.

In earlier work, our research group studied the gaseous chlorine dioxide delignification of conventional softwood kraft pulps in comparison to liquid-phase chlorine dioxide delignification. Gaseous ClO_2 delignification produced the same kappa number after delignification and extraction as did the liquid-phase ClO_2 delignification, but at less chlorine dioxide applied in the first stage *(8–10)*. The chlorine dioxide demand was less because of the ease of chemical diffusion and the ease of mass transfer of the reactants to the bulk solution *(8–10)*.

With pulp washing eliminated between the first D stage and the EO stage, conventional kraft pulps were bleached by a D(EO)DED sequence to 88–90% ISO brightness with an AOX discharge of about 0.3 kg/a.d ton of pulp *(8, 9)*. Because it is a high-consistency delignification, gas-phase delignification generates about 20–30% less effluent. The elimination of pulp washing between the first D stage and the EO stage decreases the effluent volume by another 20–30% *(10)*.

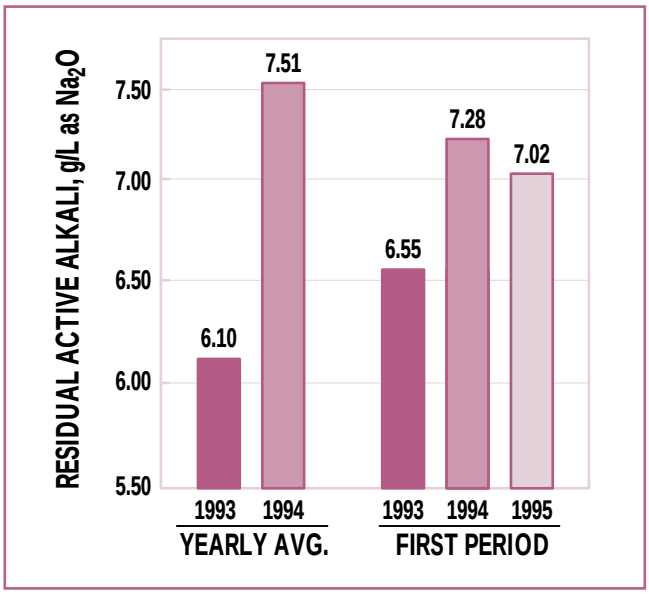
RESULTS AND DISCUSSION

Mill trials with digester additives

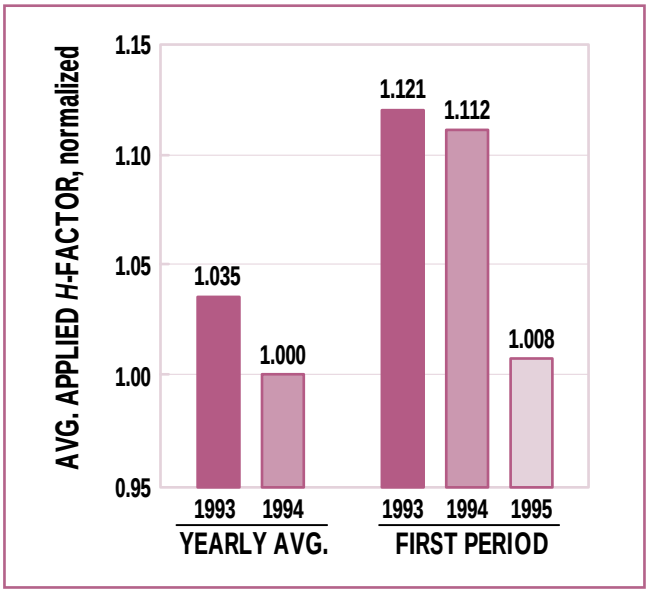
Under ideal pulping conditions, the alkaline cooking liquor uniformly penetrates the wood chips in all directions. Conditions are never ideal, but the ongoing cooking conditions establish a baseline for attaining a target kappa number. If additives are used, the NaOH charge to the digesters can be decreased. This decrease in chemical charge produces milder cooking conditions, but the additive promotes uniform penetration of cooking liquor. These modifications to the cook should increase yield and strength without changing the brownstock kappa number.

The digester additives tried in the mill were blends of two nonionic surfactants, DrewKPA-200 and DrewKPA-300. The first trial started in January 1994, with DrewKPA-200. The reduction in active alkali charge was chosen as the parameter by which to judge the success of the program because the active alkali charge is easy to measure and control. A decrease of about 4.0% in the use of active alkali was deemed satisfactory and would be considered to justify continuing the use of the additive.

It was suggested that the additive be diluted with the black liquor before being fed to the digesters to maximize the benefit *(11)*. Since the black liquor is fed by the force of gravity to our digesters, the black



3. The residual active alkali in the black liquor increased with the use of digester additive.



4. H-factor application decreased as a result of using the digester additive.

liquor stream does not afford us a practical point of addition. Instead, the additive was fed through the white liquor pump.

The first trial was hampered by cold weather. The weather caused a number of operational problems, including a change in viscosity in the additive, which was stored outside. The second trial started in February and ran through April. These two trials showed that the digester additive could allow a savings of about 3.8% in active alkali.

The third trial was made with a new product, DrewKPA-300, which was formulated to be fed with the white liquor *(11)*. Comparative values for the years 1993 and 1994 are presented in Figs. 1–3 for the active alkali, the kappa number of the brownstock, and the residual active alkali in the black liquor. This additive was effective, as reflected in the strong decrease in active alkali during the trial period of May through September 1994.

Active alkali (Na_2O) and caustic (NaOH) dropped when the mill began to use the additive. The additive charge was optimized at 0.025% (on o.d. chips). On average, the use of caustic was decreased by about 47 kg per ton of bleached pulp. With the decrease in the active alkali and caustic, we expected an increase in permanganate number, but the brownstock permanganate number remained below 12.0 (Fig. 2). When the permanganate number of the brownstock had remained below 12.0 for 11 consecutive months, the anthraquinone charge was decreased by 3.0 lb per digester (approx. 1.36 kg per digester) to about 33.0 lb per digester (0.0635% on o.d. chips).

The *H*-factor was decreased by about 35 points after the additive was introduced, as Fig. 4 indicates. As a result, the average number of digester blows per day increased by 1.1 in 1994. The savings obtained from the decrease in *H*-factor are calculated to be US$ 0.52 per ton of bleached pulp. Compared to the bleached pulp yield of 44.65% in 1993, the bleached pulp yield averaged 46.38% in 1994. From 11.61 bleached tons per digester in 1993, the yield went to 12.05 bleached tons per digester in 1994.

Despite the decreases in active alkali charge and caustic use, the residual active alkali in the spent liquor remained high. The residual active alkali (as Na_2O) in the weak black liquor averaged about 7.5 g/L for the 11-month period in 1994, as opposed to the 1993 average of 6.3 g/L (Fig. 3). For our evaporators to run trouble-free, the residual active alkali in weak black liquor should be maintained between 6.0 g/L and 6.5 g/L. The residual active alkali was higher than we needed, indicating that the active alkali charge and caustic charge to the digester could be decreased even further.

In August 1993, the brightness target of the pulp sent to the paper machines was moved up to 86.0% ISO. To achieve this final brightness, the EO stage was reinforced with hydrogen peroxide. In October 1993, the final pulp brightness target was raised to 86.5% ISO. To reach this objective, the bleach plant personnel switched to post-peroxide bleaching in high-density storage.

	1	2	3	4	5	6	7	8	9	10
Additive, % on o.d. chips	…	…	…	…	…	0.025	0.025	0.025	0.025	0.025
AQ, % on o.d. chips	…	…	0.06	0.06	0.06	0.06	0.06	0.06	…	…
Active alkali, % as Na_2O	19	20	20	19	18	19	17	19	19	20
Liquor/wood ratio	3.65	3.65	3.65	3.65	3.65	3.65	3.65	3.65	3.65	3.65
Time to temp., min	90	90	90	90	90	90	90	90	90	90
Time at temp., min	53	129	129	53	30	53	30	129	53	129
Max. digester temp., °C	168	168	168	168	168	168	168	168	168	168
H-factor	1007	1998	1998	1007	707	1007	707	1998	1007	1998
K number (40 mL)	13.7	10.1	8.2	10.8	12.3	9.4	13.0	8.0	13.8	9.0
Kappa number	20.8	13.8	11.6	14.9	18.1	13.0	19.8	11.0	20.8	12.8
Yield										
Screened yield, %	47.98	46.13	47.45	48.72	49.20	48.65	49.33	47.79	48.27	46.36
Screenings, %	0.85	0.16	0.08	0.68	1.11	0.85	1.88	0.21	0.66	0.25
Total yield, %	48.83	46.29	47.53	49.40	50.31	49.50	51.21	48.00	48.93	46.61
Black liquor pH	13.0	12.9	13.0	13.0	13.0	12.0	12.9	13.0	13.0	13.0
Residual active alkali, g/L as Na_2O	16.8	15.4	15.8	17.0	16.8	16.0	13.0	13.2	17.2	17.0

I. Results of ten laboratory cooks in the study of extended delignification of soda-AQ pulps with the use of digester additive

After the digester additive was introduced, the personnel observed an increase in the final brightness. The brightness averaged 87.1% ISO for the month of February 1994. With the brightness higher than the target value, the post-peroxide bleaching was discontinued. Even then, the final brightness remained high, posting above 87.5% ISO, as Fig. 5 illustrates. The bleach plant personnel decreased the hydrogen peroxide charge to the EOP stage by 2 lb per ton of bleached pulp (about 0.91 kg/ton). This decrease represented an annual savings of 140 tons of hydrogen peroxide.

Despite these changes, the pulp brightness remained above 87.5% ISO, representing a gain of 1.5 points over the 1993 average of 86.0% ISO. The additive has not only helped in the penetration of the cooking chemicals but has also opened up the pulp to make it respond more favorably to the bleaching chemicals. The mill personnel estimated the net savings to be about US$ 19.50 per ton of bleached pulp after paying for the additive.

Extended delignification: laboratory results

Success in the mill prompted us to study the possibility of using the digester additive to extend soda–AQ pulping. In the laboratory cooks, unlike the cooks in the mill trials, black liquor was not used to adjust the liquor-to-wood ratio. To compensate, we used a high *H*-factor and a high charge of active alkali.

The results from the laboratory cooks showed that it is possible to extend the soda–AQ pulping to kappa no. 11.0 with the help of the digester additive DrewKPA-300. Results for Cooks 1–10 are presented in Table I. Comparing Cook 4 with Cook 6, we see that the digester additive lowered the pulp kappa number by 1.9 points under identical cooking conditions, a decrease of about 13%. The total yields from the cooks were the same, which shows that the additive did not cause a loss in yield in promoting delignification.

If the *H*-factor is doubled in the soda–AQ pulping with additive, from 1007 in Cook 6 to 1998 in Cook 8, the kappa number can be lowered to 11.0. This decrease in kappa number is a decrease of about 26.0% over soda–AQ pulping and a decrease of about 15.0% over the soda–AQ pulping with additive (Cook 6). However, the increase in *H*-factor resulted in a yield loss of about 3.0% over the yields of Cooks 4 and 6. (On a pulp basis, the yield is 48.00% for Cook 8, 49.40% for Cook 4, and 49.50% for Cook 6.)

The use of digester additive alone without the catalytic influence of anthraquinone required the mill to double the *H*-factor and use more active alkali (Cook 10) to extend the pulping to kappa no. 13.0. This pulp is equivalent to the pulp obtained from soda–AQ pulping with the use of additive at *H*-factor 1007 (Cook 6). The doubling of the *H*-factor and the additional active alkali resulted in a sharp yield loss over Cook 6 (approx. 4.71% on pulp basis, screened yield).

The laboratory cooks established that the soda–AQ pulping of hardwood can be extended to very low kappa numbers with the help of the

	COOK 3		COOK 4		COOK 5		COOK 6		COOK 8		KRAFT
	Well washed	High solids	Well washed	High solids	Well washed	High solids	Well washed	High solids	Well washed	High solids	High solids
Additive, 0.025%	…	…	…	…	…	…	Yes	Yes	Yes	Yes	…
Caustic, % as NaOH	2.5	2.5	2.5	2.5	3.0	3.0	2.5	2.5	2.5	2.5	4.0
Time at temp., min	129	129	53	53	30	30	53	53	129	129	53
O_2 reaction time, min	45	45	45	45	50	50	45	45	45	45	60
Kappa no.											
Incoming	11.6	11.6	14.9	14.9	18.1	18.1	13.0	13.0	11.0	11.0	24.0
Outgoing	5.0	5.0	8.2	10.5	10.5	13.5	5.2	5.8	5.5	6.0	14.0
Decrease, %	57.9	34.5	45.0	29.5	42.0	25.4	60.0	55.4	50.0	45.5	41.7
Screened yield, %											
Without O_2	47.5	47.5	48.7	48.7	49.2	49.2	48.7	48.7	47.8	47.8	49.4
With O_2	46.9	47.2	48.2	48.6	48.4	49.0	48.4	48.6	47.0	47.3	48.7
Shrinkage unit	0.6	0.3	0.5	0.1	0.8	0.2	0.3	0.1	0.8	0.5	0.7
Yield, %	98.7	99.4	99.0	99.8	99.6	99.4	99.8	98.3	98.3	99.0	98.6

The pulp consistency was 12.0% for all pulps. The oxygen stage temperature was 110°C in all cooks.

II. Laboratory cooks showing the effects of oxygen delignification of soda–AQ, soda–AQ with additive, and kraft pulps

digester additive. However, to preserve the pulp yield, it is beneficial to end the pulping at a kappa number of 13.0, then use oxygen delignification to lower the kappa number. Oxygen delignification is one way to decrease the kappa number of the pulp entering the bleach plant without the need for as much kappa factor application to bleach to the target pulp brightness. Retrofitting a bleach plant with oxygen delignification is an expensive proposition, however. Conventional pulp, if it can be delignified with low kappa factor and yet be bleached to 88–89% ISO brightness, is the best low-cost approach to pulp bleaching with low AOX discharge.

Oxygen delignification of extended soda–AQ pulps

In the laboratory, we carried out oxygen treatments of extended-delignification soda–AQ pulps and soda–AQ pulps with additive to evaluate the possibility of reducing the kappa number further. A decrease in kappa number of at least 25% to as much as 60% is possible by medium-consistency oxygen delignification with very little reduction in the pulp yield. Results of these experiments are given in Table II.

The use of the additive was not a factor in the oxygen treatment. The decrease in pulp kappa number depends on the incoming kappa number of the pulp. The other factor that determines the extent of oxygen delignification is the black liquor solids carryover with the incoming pulp. Between the well-washed pulp and the pulp with high carryover, the delignification favors the well-washed pulp. In proportion to the decrease in kappa number, the pulp shrinkage was also greater for the well-washed pulp. However, compared to the reduction in kappa number, the yield decrease was insignificant.

Laboratory bleaching of soda–AQ pulps

Table III lists the results from the D(EOP)DP bleaching of conventional soda–AQ, soda–AQ with additive, and kraft pulps, with and without oxygen delignification. The soda–AQ pulp and the soda–AQ pulp with oxygen delignification bleached poorly. The highest pulp brightness obtained, even with the post peroxide bleaching, was only 84% ISO. Both the soda–AQ pulp with additive and the soda–AQ pulp with additive and oxygen delignification (kappa no. 13.0 and 5.2, respectively) responded well and bleached to 86.5% ISO brightness. With post peroxide bleaching, these same pulps were bleached to 89.0% ISO brightness.

In the extended soda–AQ and soda–AQ pulps with oxygen delignification, there may not be enough available free phenolic propane units in the lignin macromolecules to make these molecules respond favorably to chlorine dioxide delignification and bleaching. Hardwoods have fewer free phenolic propane units than softwoods have. Removing them in bulk by pulping and oxygen delignification leaves few of these units for chlorine dioxide to react with and remove. This deficiency in reactive free phenolics

	SODA–AQ		SODA–AQ WITH ADDITIVE		KRAFT	
	No O_2	*With O_2*	*No O_2*	*With O_2*	*No O_2*	*With O_2*
Incoming kappa no.	18.1	10.5	13.0	5.2	24.0	14.0
First D Stage						
Applied kappa factor	0.3	0.3	0.3	0.3	0.3	0.3
Active Cl_2, % as Cl_2	4.9	2.8	3.5	1.4	6.5	3.8
Active Cl_2, % as ClO_2	1.9	1.1	1.3	0.5	2.5	1.4
Temp., °C	50	50	50	50	50	50
Time, min	30	30	30	30	30	30
Consistency, %	2.0	2.0	2.0	2.0	2.0	2.0
ClO_2 consumed, %	1.8	1.0	1.3	0.5	2.3	1.3
EOP Stage						
%NaOH	2.5	1.5	1.5	1.5	3.5	2.5
%H_2O_2	0.2	0.2	0.2	0.2	0.2	0.2
Temp., °C	75	75	75	75	75	75
Time, min	45	30	35	30	60	45
Consistency, %	12	12.0	12.0	12.0	12.0	12.0
O_2 pressure, kPa	400	400	400	400	400	400
DE K number	2.3	1.3	1.2	0.8	3.2	1.2
Final D stage						
%ClO_2	1.4	1.1	1.2	1.0	1.4	1.2
%NaOH	0.5	0.4	0.5	0.3	0.5	0.5
Temp., °C	75	75	75	75	75	75
Time, min	300	300	300	300	300	300
Consistency, %	12	12	12	12	12	12
pH out	3.8	3.5	3.7	3.9	4.2	3.5
%ClO_2 consumed	1.3	1.1	1.2	0.9	1.3	1.1
% Yield	96.3	97.2	97.3	98.9	98.6	99.0
Viscosity,[a] mPa·s	16.5	15.0	18.6	17.8	32.0	24.0
Brightness, %ISO	82.8	83.2	86.2	86.6	86.3	86.8
Reverted,[b] %ISO	80.4	80.2	84.7	84.7	84.2	84.3
Post-Peroxide Stage						
%H_2O_2	0.2	0.2	0.2	0.2	0.2	0.2
Temp., °C	45	45	45	45	45	45
Time, min	600	600	600	600	600	600
Consistency, %	12	12	12	12	12	12
Brightness, %ISO	83.2	84.0	88.2	88.8	87.6	87.8
Reverted,[b] %ISO	80.7	80.6	85.9	85.7	85.6	85.3
Bleach Plant Effluent						
Total AOX, kg/a.d. ton	1.3	0.9	1.0	0.7	1.4	1.1

[a]Measured in 0.5*M* CED. [b]Reverted brightness after thermal aging at 105°C for 2 h.

III. Laboratory results of D(EOP)DP bleaching of soda–AQ, soda–AQ with additive, and kraft, with and without oxygen delignification

	Pulp I	Pulp II
Kappa no.	18.1	20.5
First-stage pH	5.00	5.00
ClO_2 applied in the first stage, %[b]	0.62	0.94
Kappa no. of extracted pulp	5.00	5.50
Viscosity, mPa·s (0.5*M* CED)	19.8	18.2
AOX, kg/a.d. metric ton	0.223	0.197
COD, kg/a.d metric ton	33.50	20.60
BOD, kg/a.d. metric ton	9.20	8.90

[a]Gas-phase chlorine dioxide delignification by Olin's 01 process.
[b]As ClO_2, % on o.d. pulp.

IV. Analysis of combined effluents from the 01[a] and E(OP) stages for soda–AQ hardwood pulps bleached by the 01 E(OP)DE(P)D sequence

	CIE color values			Final brightness, %ISO
	L*	a*	b*	
Pulp I				
01E(OP)DE(P)D	97.6	– 0.93	4.3	89.0
01(EOP)D	96.4	– 1.30	6.4	83.3
Pulp II				
01E(OP)DE(P)D	97.8	0.00	4.1	89.9
(reverted)	96.6	0.21	4.1	87.1
01(EOP)D	95.6	–1.09	8.7	78.5

Target brightness = 88–90% ISO.

V. L*a*b* and final brightness values for the pulps of Table IV

KEYWORDS
Additives, alkaline pulping, angiosperms, anthraquinone, bibliographies, bleaching, chemical pulping, chemical treatment, chlorine dioxide, chlorine free bleaching, hardwoods, ketones, nonsulfur pulping, oxides, plants, quinones, soda pulping, surfactants.

may be the reason these pulps have such a poor brightness gain.

Gaseous ClO_2 delignification and bleaching of soda–AQ pulps

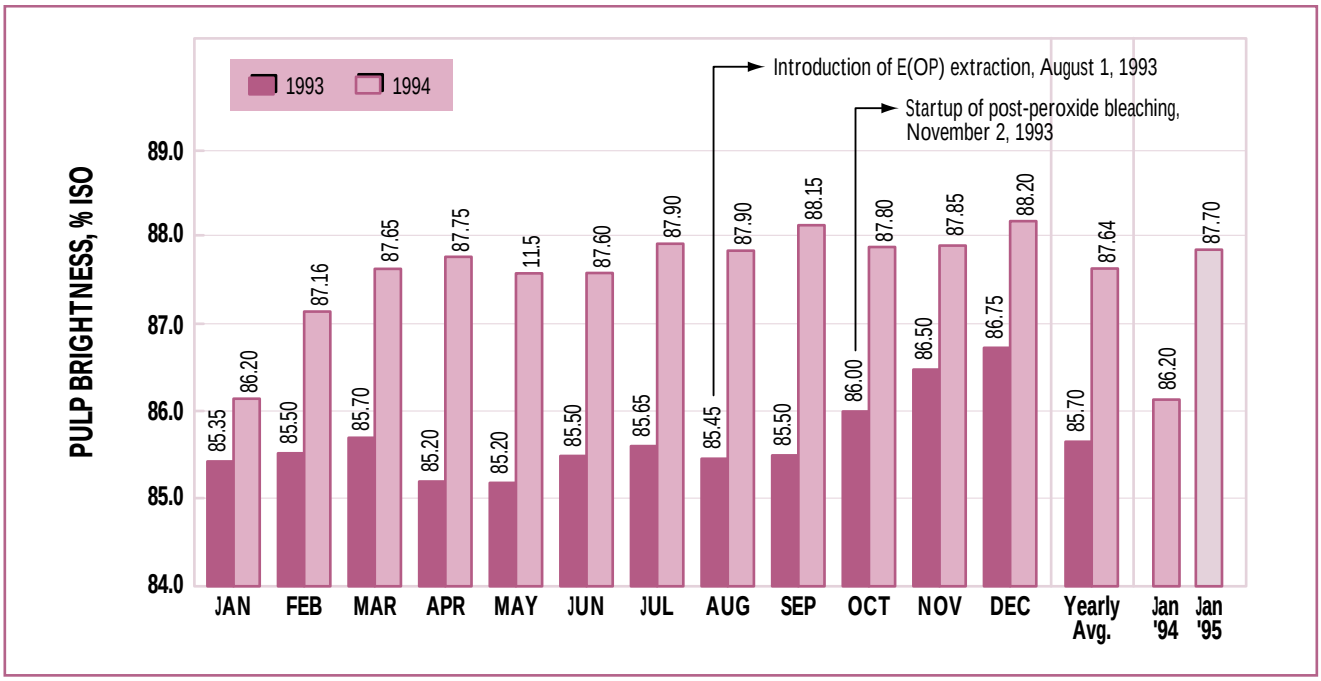
Gaseous chlorine dioxide delignification has been shown to bleach conventional softwood kraft pulps of kappa nos. 30–32 to 88–89% ISO brightness with as little as 0.1 kappa factor application at the first stage *(8, 9, 12, 13)*. Although we have collected a considerable database for the gaseous chlorine dioxide delignification of kraft pulps *(12, 13)*, no such data are available for the soda or soda–AQ pulps.

Two soda–AQ pulps with additive were obtained from the mill. These pulps, at kappa nos. 18.1 and 20.5, were delignified in the laboratory with gaseous chlorine dioxide, then alkaline extracted by an E(OP) process. Table IV presents the analysis of the effluents from the first two stages. Washing was eliminated between the oxygen delignification and the E(OP) extraction. The delignified and extracted pulps were bleached by D(EP)D and D sequences. Table V lists the values for brightness, viscosity (measured in 0.5 *M* cupraethylenediamine), and CIE L*a*b* values for the bleached pulps.

The gaseous chlorine dioxide delignification required very little chlorine dioxide in the first stage (less than 1.0% on ClO_2) to reach the DE kappa numbers of 5.0 and 5.5. This treatment represents kappa factor applications of 0.09 and 0.12 for the pulps of kappa nos. 18.1 and 20.5, respectively. The elimination of washing between the gaseous chlorine dioxide delignification and alkaline extraction decreased the discharge of AOX from these two stages by as much as 50% without changing the DE kappa number. Subsequent DED bleaching provided bleached pulps of 87–88% ISO brightness with a viscosity of 20 mPa·s. With secondary effluent treatment in place, the gaseous chlorine dioxide delignification and (EO)DED bleaching of conventional hardwood soda–AQ of kappa no. 20 can result in an AOX discharge of less than 0.3 kg per air-dried ton of pulp.

Elimination of the pulp washing between the D and E(OP) stages would free one washer for pulp washing. This change would allow the mill to convert its bleach plant from CEHP to CED bleaching by using the idled washer and the two idled retention towers. This switch may even allow the mill to swing between hardwood and softwood pulp bleaching, provided softwoods can be pulped by the soda–AQ process to low kappa numbers. Currently, experiments are under way to explore the possibility of soda–AQ pulping of softwoods using the surfactant-based digester additives as pulping aids. If the soda–AQ pulping of softwoods with additive proves viable, then the pulp can be delignified by gaseous chlorine dioxide and bleached by an E(OP)DED sequence to 88–90% ISO brightness with a low AOX discharge from the bleach plant, as established for conventional kraft softwood pulps *(9, 10, 12, 13)*.

One advantage of this gaseous chlorine dioxide delignification is that Olin's O1 process of generating



5. Final pulp brightness improved dramatically in 1994. After a new high brightness of 87.1% ISO with the first use of additive in February 1994, the pulp brightness averaged above 87.5% ISO each month.

the chlorine dioxide does not produce salt cake as a byproduct *(1, 13)*. This advantage is important because the process does not use sodium sulfide in the cooking liquor. In the laboratory, the process has tested successfully, and the next step is the mill trial. Results from the mill trial will allow us to calculate the cost benefit of using this process on a large-scale basis.

CONCLUSIONS

Surfactant-based digester additives reduced the active alkali charge at the digester by about 6%. In conjunction with this decrease, the caustic use at the digester was decreased by about 47 kg/a.d. ton of bleached pulp. Anthraquinone was reduced by 1.36 kg per digester, and the *H*-factor was lowered by 35 points per cook.

The use of digester additive resulted in pulp that responded well to short-sequence bleaching. With the use of digester additive, the bleach plant discontinued post-peroxide bleaching and cut the hydrogen peroxide charge to the EOP stage by 0.91 kg per ton of pulp. In addition, the mill gained an increase in brightness of two percentage points ISO.

Extended delignification at the digesters to kappa no. 13.0 is possible with the use of digester additives. Oxygen delignification of the extended delignified pulps decreased the chemical use at the first stage but hampered the bleaching response of the soda–AQ pulps. The maximum brightness achieved for the oxygen-delignified soda–AQ pulp was 86.5% ISO with post-peroxide bleaching. However, oxygen-delignified soda–AQ pulp with additive reached 86.5% ISO brightness without post-peroxide bleaching and 89.0% ISO brightness with post-peroxide bleaching. Total AOX discharges of less than 0.7 kg/a.d. ton of pulp are possible with the D(EOP)D bleaching of oxygen-delignified soda–AQ pulp with additive.

Gaseous chlorine dioxide delignification followed by (EOP)D or (EOP)D(EP)D bleaching can produce fully bleached pulp (88–89% ISO) with a viscosity of 20 mPa·s. The gaseous chlorine dioxide delignification followed by either three-stage or five-stage bleaching provided soda–AQ pulps of 88–89% ISO brightness with a viscosity of 18–20 mPa·s. The AOX discharge from the bleach plant was less than 0.5 kg/a.d ton of pulp. Based on the results presented here, we suggest that, with the adaptation of elemental-chlorine-free bleaching, soda–AQ pulping can provide a sulfur-free pulping alternative and a chlorine-free bleaching alternative to kraft pulp.

EXPERIMENTAL PROCEDURES

The extended pulping and bleaching of screened mixed hardwoods is described elsewhere *(14)*. The gaseous chlorine dioxide delignification and the bleaching of hardwood pulps were carried out as described by Parthasarathy and Rudie *(9)* and

by Mendiratta *et al. (13)*. The AOX, pulp viscosity, pulp brightness, and CIE L*a*b* were measured by following standard procedures. TJ

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