Low-chlorine bleaching with nitrosylsulfuric acid pretreatment

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ABSTRACT *Three different types of bleached pulp were prepared for the evaluation of physical properties: brownstock, oxygen-delignified pulp, and oxygen-delignified pulp pretreated with nitrosylsulfuric acid (NSA) as a liquid nitrosating agent. Each type of pulp was bleached by a three-stage (C+D)(EO)D sequence and by a five-stage (C+D)(EO)DED bleaching. The bleached pulps were beaten in a PFI mill beater. Kraft pulps pretreated with NSA showed an improvement in delignification, with good viscosity protection in the succeeding alkaline oxygen stage. The fully bleached pulp with NSA pretreatment exhibited physical properties comparable to the pulp without NSA pretreatment. However, NSA-pretreated pulp required not only less active chlorine charge in the C+D stage but also less caustic charge in the EO stage. The effluents from the C+D and EO stages exhibited lower AOX content with NSA pretreatment.*

KEYWORDS
Bleaching
Chlorine
Delignification
Effluents
Pulping

The environmental problems involved with the presence of chlorinated organic compounds in the bleaching mill have recently become important issues. The formation of chlorinated organic compounds is generally a function of the consumption of elemental chlorine. These chlorinated organic compounds are difficult to destroy or remove from the environment. Recent research efforts have focused on how to eliminate the use of chlorine and chlorine-based products.

The common methods of reducing the chlorine demand of the pulp are (a) through the use of extended delignification processes with delignification improvements in pulping processes or with an alkaline oxygen-delignification stage before bleaching and (b) by replacing chlorine partially or fully with other chemicals (*1–4*). One of the obstacles of oxygen delignification is the severe loss of viscosity associated with the high level of delignification (*5*). However, recent developments in the area of pretreatment of brownstock with NO_2 prior to alkaline oxygen delignification have made it possible to increase delignification while maintaining acceptable pulp viscosity.

Available literature concerning the use of nitrogen oxides for kraft pulp delignification is fairly extensive. Clarke replaced chlorine with nitrogen dioxide in the bleaching of cellulose pulps and found that a severe cellulose degradation occurred in the nitrogen-dioxide-treated pulp (*6*). In the past decade, Samuelson and coworkers (*7–14*) have described the use and the practicality of nitrogen dioxide as a pretreatment chemical for alkaline oxygen delignification under various conditions. Samuelson's system, named "PRENOX," has reached the pilot plant scale and is proceeding toward the commercial demonstration stage (*15, 16*).

The pretreatment of kraft pulp using the nitrosylsulfuric acid (NSA) as a liquid-phase nitrosating agent has already been conducted in laboratory research (*17*). Our purpose in this study was to examine the effects of NSA-pretreated kraft pulp on pulp

qualities and on environmental aspects related to AOX reduction. Three different types of bleached pulp were prepared: brownstock, oxygen-delignified pulp, and oxygen-delignified pulp with NSA pretreatment. Each type of pulp was bleached by the three-stage (C+D)(EO)D sequence and by the five-stage (C+D)(EO)DED sequence.

Experimental procedures

NSA pretreatment and oxygen delignification

Figure 1 is a diagram of the high-shear mixer used to carry out alkaline oxygen pretreatment with liquid-phase nitrosation/nitration. The pulp was a southern pine kraft brownstock. Nitrosylsulfuric acid was injected into the reactor under oxygen pressure at 40 psig through a perforated baffle.

The commercial NSA contains 40% NSA, 52.2% H_2SO_4, and 7.8% H_2O (DuPont Co., Wilmington, Del.). The acid pretreatment stage with NSA has been specified as the "A" stage here. The experimental conditions for the A stage and the oxygen stage are listed in **Table I.** The oxygen bleaching was conducted in the high-shear mixer as well.

After the alkaline oxygen stage, the kappa number and viscosity of the pulp were determined. The pulp selectivity is expressed as:

$$Sel = (v_0 - v_f)/(kappa_0 - kappa_f) \quad (1)$$

where

Sel = selectivity

v_0 = initial viscosity

v_f = final viscosity

$kappa_0$ = initial kappa no.

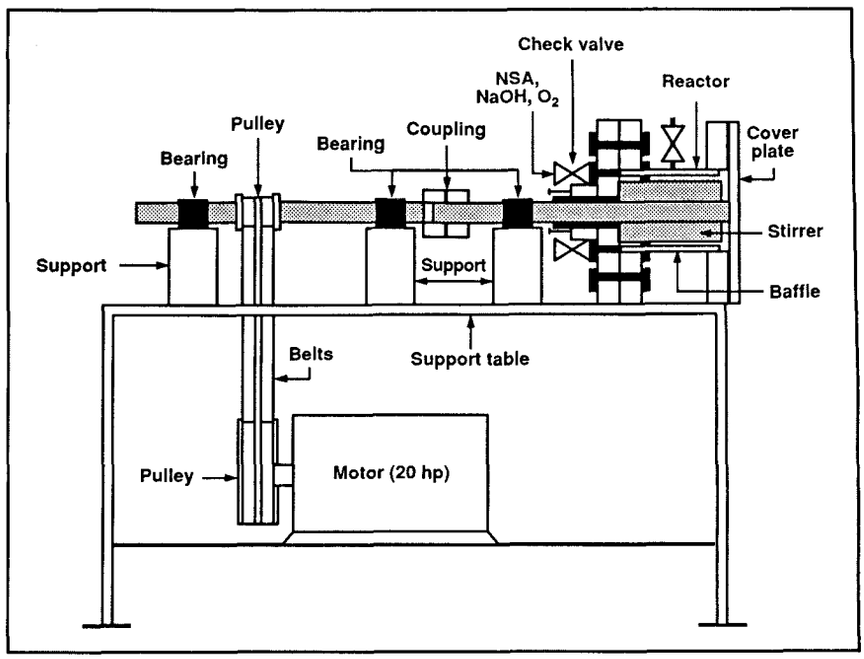
$kappa_f$ = final kappa no.

The selectivity is the combination of two pulp properties: lower selectivity is equivalent to higher viscosity at a given kappa number.

Bleaching

Three types of pulp were bleached in the three-stage (C + D)(EO)D and the five-stage (C + D)(EO)DED sequence with a 10% ClO_2 substitution in the C + D stage. All the bleaching conditions are listed in Table I. Chlorine and chlorine dioxide were used in aqueous solutions.

1. Diagram of the high-shear mixer



I. Conditions for prebleaching and for bleaching

Stage	Consistency, %	Time, min	Temp., °C	Other conditions
S	11	20	30	90 psig. 3% NaOH, 0.2% Mg^{++}
O	11	60	95	...
C+D	3.5	30	30	0.22 chlorine multiple 10% ClO_2 substitution
EO	11	60	70	20 psig O_2 for 20 min 0.6 caustic charge factor
D	10	180	70	...
E	11	60	70	2% NaOH on brownstock 1% NaOH on O_2 pulp 1% NaOH on NSA and O_2 pulp
D	10	180	70	1.2% ClO_2 on brownstock 0.6% ClO_2 on O_2 pulp 0.6% ClO_2 on NSA and O_2 pulp

The bleached pulps were washed with distilled water after each stage. The washing filtrates were measured for the amount of AOX. A Dohrmann DX-20 total organic halide analyzer was used for AOX analysis.

Handsheet preparation and analytical methods

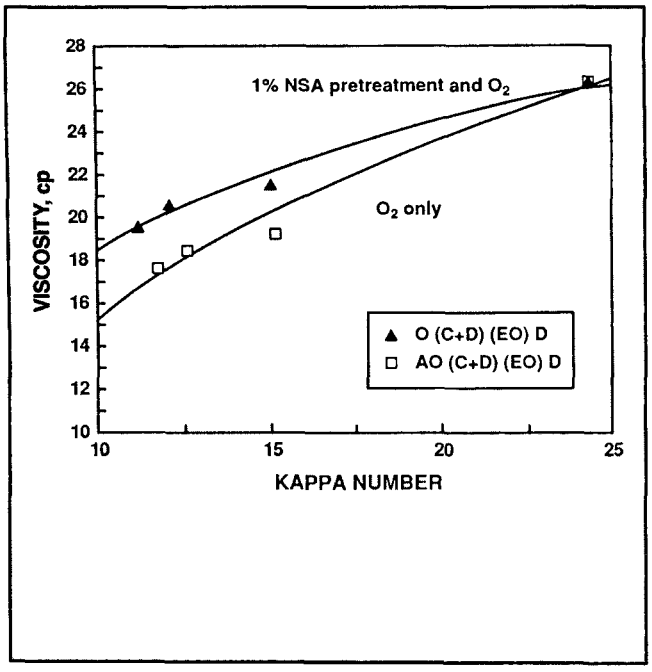
Handsheets were prepared according to TAPPI T 205 om-88 and were tested for physical properties according to TAPPI T 220 om-88 and some specific references. Brightness values were recorded on a G.E. brightness tester. The EPA method 9020 is adopted for the AOX instrument operation.

Results and discussions

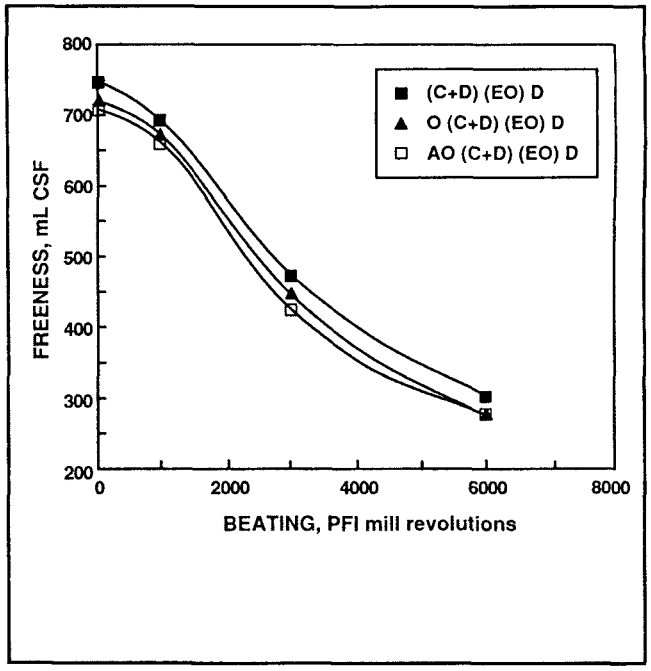
Delignification and selectivity

NSA-pretreated pulp followed by an alkaline oxygen stage exhibited a lower kappa number and better selectivity than the pulp subjected to an alkaline oxygen delignification only.

2. The oxygen-delignified pulp pretreated with NSA exhibited a higher viscosity at the same kappa number than the oxygen-delignified pulp without NSA.



4. All three pulps exhibit the same general trends in freeness reduction with increased beating.



II. Pulp selectivity after oxygen bleaching

Stage	*Kappa number*	*Viscosity, cp*	*Selectivity*	*Chlorine charge, %*	*Caustic charge, %*
Brownstock 1	24.4	26.2	...	...	...
1% NSA and O_2 (2% NaOH)	15.1	21.5	0.51	...	...
1% NSA and O_2 (4% NaOH)	12.1	20.5	0.46	...	...
1% NSA and O_2 (7% NaOH)	11.2	19.5	0.51	...	...
O_2 (2% NaOH)	15.2	19.2	0.76	...	...
O_2 (4% NaOH)	12.6	18.4	0.66	...	...
O_2 (7% NaOH)	11.8	17.6	0.68	...	...
Brownstock 2	16.1	26	...	3.54	2.12
2% NSA and O_2 (3% NaOH)	5.7	17.2	0.85	1.25	0.75
O_2 (3% NaOH)	7.8	17.8	0.99	1.72	1.03

Brownstock 2 is used for the bleaching experiment.

III. Brightness after bleaching

Stage	*Brightness, % G.E.*
3 stages	
(C+D) (EO)D	79.0
O(C+D) (EO)D	85.8
AO(C+D) (EO)D	85.2
5 stages	
(C+D) (EO)DED	87.2
O(C+D) (EO)DED	89.8
AO(C+D) (EO)DED	90.2

The results are presented in **Table II** and **Fig. 2.**

(In the table, Brownstock 1 and Brownstock 2 are two different batches. Brownstock 1 was used for the NSA and oxygen pretreatment experiments to establish the selectivity curves shown in Fig. 2. Brownstock 2 was used for the 3-stage and 5-stage bleaching.)

Electrophilic substitution of nitrosonium ion (NO^+) at the ortho and para positions of the phenolic ring has been proven (*18, 19*). Because lignin contains substantial amounts of phenolics, an activated lignin structure may be formed as a result of the lignin-nitrosating and -nitrating reaction. The presence of activated lignin phenolics is believed to make the lignin more susceptible in the succeeding alkaline oxidation process; meanwhile, the structure protects the cellulose fraction of the pulp from free radical degradation. Therefore, the resulting oxygen-bleached pulp with NSA pretreatment reveals a better selectivity than the one without NSA pretreatment.

Chlorine and caustic consumption

Chlorine consumption in the first bleaching stage (C+D) was determined by the kappa number of the pulp entering this C+D stage. A chlorine multiple of 0.22 was used. Compared to the O(C+D)(EO)D sequence, the AO(C+D)(EO)D sequence allows a reduction in chlorine charge

in the C+D stage of approximately 26%, while maintaining similar handsheet properties.

The amount of caustic used in the first extraction stage (EO) was determined by active chlorine charge in the first C+D stage. A caustic multiple of 0.6 was used in the EO stage. Compared to the O(C+D)(EO)D bleaching sequence, an approximately 27% savings in caustic in the EO stage can be obtained for the AO(C+D)(EO)D bleaching sequence.

Brightness

The pulp brightness was determined after the full bleaching sequence. The brightness data are shown in **Table III**. In the three-stage bleaching, the (AO)(C+D)(EO)D and the O(C+D)(EO)D pulps have similar brightnesses, which are about 6 units higher than that of the (C+D)(EO)D pulp. Nevertheless, in regard to chemical consumption in the C+D and EO stages, the O(C+D)(EO)D sequence consumes 50% and the (AO)(C+D)(EO)D sequence consumes 35% of the amount consumed in the (C+D)(EO)D sequence.

The range of brightness for the three-stage bleaching is from 79% to 86% G.E. The range of brightness for the five-stage bleaching is from 87% to 90% G.E. brightness.

AOX reduction

The amount of AOX formed during bleaching was linearly proportional to the amount of elemental chlorine in Cl_2 and ClO_2. The AOX results are shown in **Fig. 3**. The effluent from the bleaching stages with an NSA pretreatment stage exhibited a lower AOX content than the effluent from stages without NSA pretreatment.

Pulp quality

The oxygen-delignified pulp with NSA pretreatment, the alkaline oxygen-delignified pulp, and the brownstock pulp were bleached in the three-stage sequence with a 10% ClO_2 substitution in the C+D stage. To reach a higher brightness, all three types of pulp are subjected to the five-stage bleaching as well. The bleached pulps were beaten in a PFI mill to four different freeness levels ranging from the unbeaten pulp freeness to 200 mL CSF. Canadian Standard Freeness was determined, and handsheets were made.

Freeness. Figure 4 shows the responses of three types of pulp to beating in a PFI mill. As the pulps are subjected to more stages in the bleaching sequence, the beating responses become more sensitive. At a given value of freeness, both the AO(C+D)(EO)D and the O(C+D)(EO)D pulps required less beating than did the (C+D)(EO)D pulp. However, the beating curve generated from the AO(C+D)(EO)D pulp is similar to that of the O(C+D)(EO)D pulp. All three types of bleached pulp were beaten at the same rate. The general trends of freeness reduction with the increased beating are similar for all three.

Strength. **Figure 5** presents the tear index, tensile index, burst index, and folding endurance properties as a function of freeness for the three-stage bleaching sequence. There is almost no strength difference between the AO(C+D)(EO)D pulp and the O(C+D)(EO)D pulp. In general, the (C+D)(EO)D pulp exhibits a slightly better tensile index but a lower tear index than the AO(C+D)(EO)D and O(C+D)(EO)D pulps.

Figure 6 shows the curves for tear index vs. tensile index. For the three-stage bleaching sequence, all three types of pulp show similar tear indexes at any specific tensile index.

3. AOX in the bleaching effluent

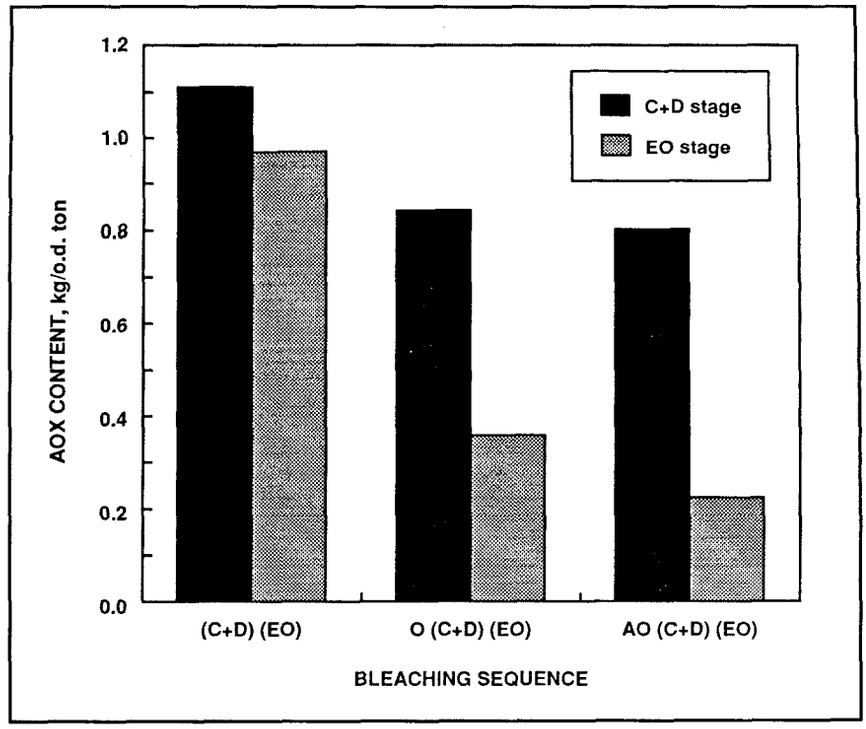


Figure 7 shows tensile index as a function of freeness for the five-stage bleaching sequence. All three types exhibit similar trends and levels of tensile strength with beating. Compared to three-stage bleaching, the tensile indexes for the three types of pulp are getting closer because of the different amounts of chemical consumption in the last two bleaching stages.

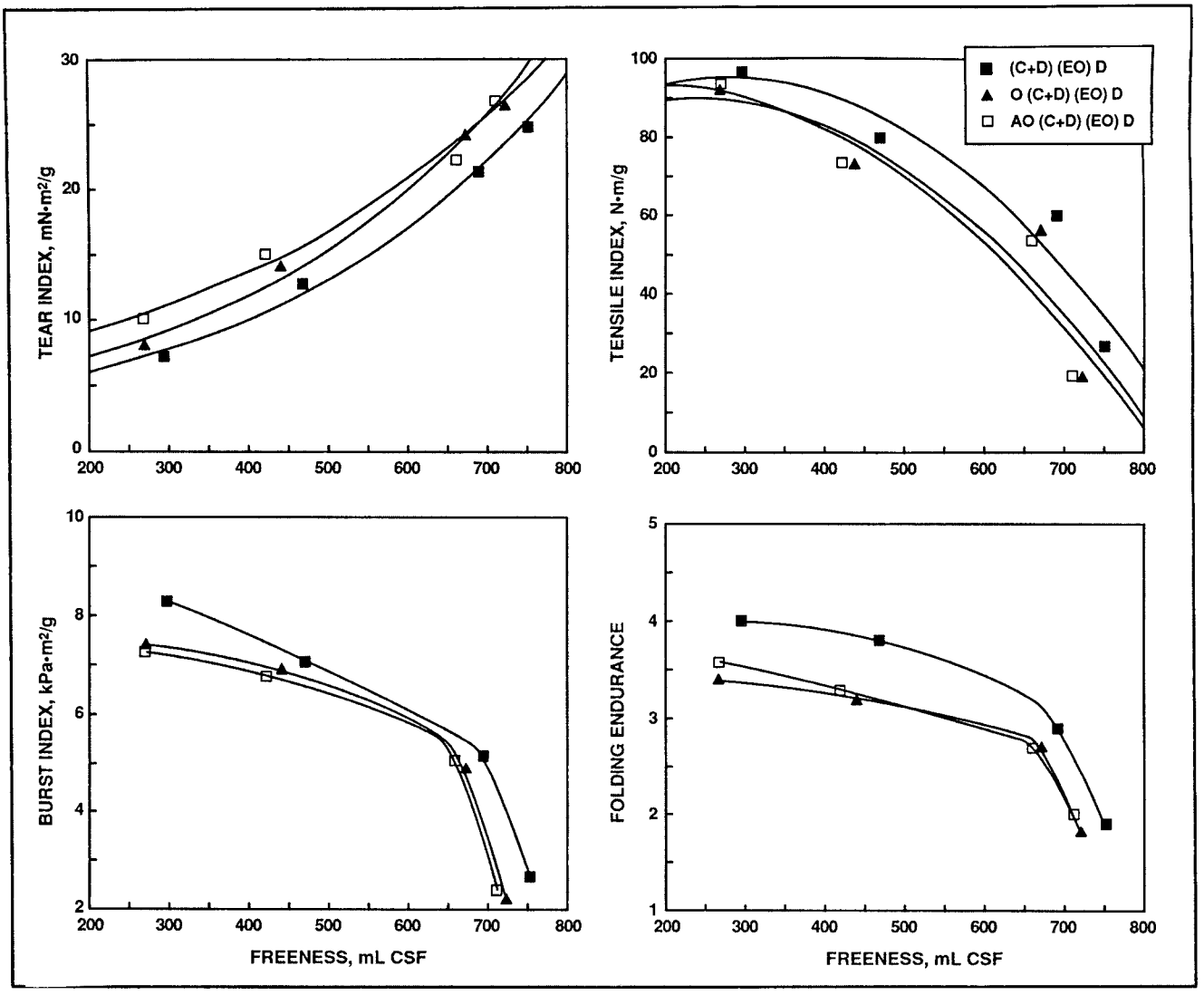
The curve of tear index vs. tensile index is shown in the plot on the right in Fig. 6 for the five-stage bleaching. The result is almost identical with that obtained from the three-stage bleaching.

These strength results represent only the preliminary work. Each bleaching stage should be optimized to obtain the best performance in pulp properties because the NSA pretreatment is likely to cause some structural modification of the pulp.

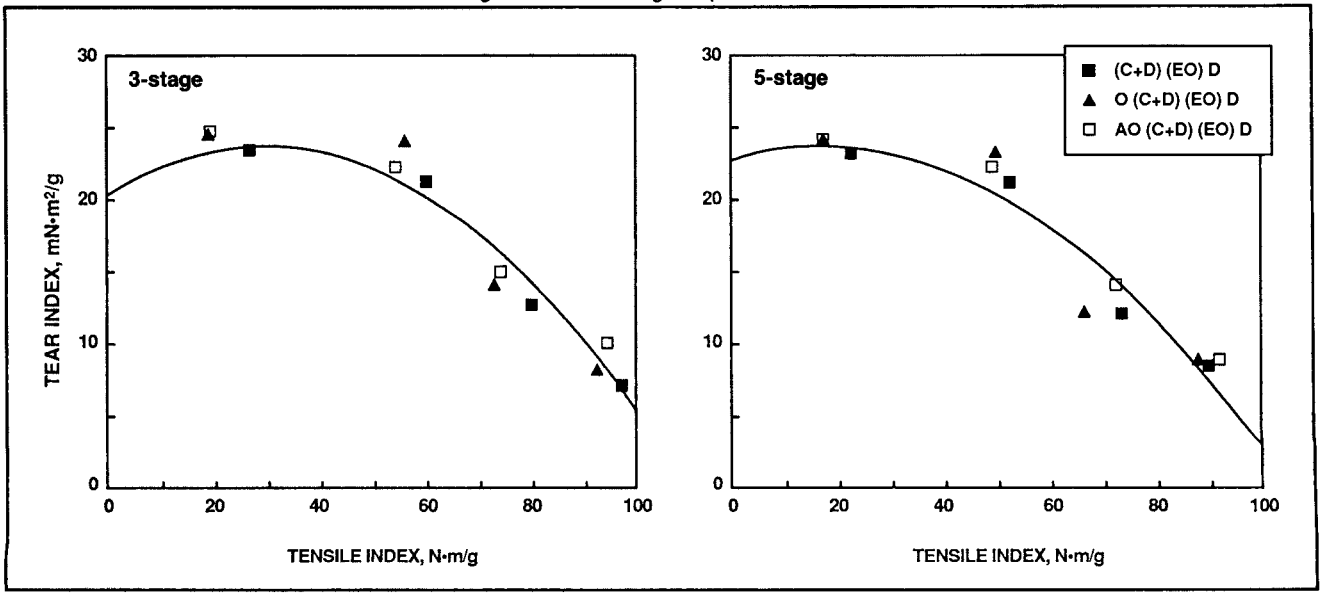
Conclusions

A study of the effects of NSA-pretreated kraft pulp on pulp qualities and on environmental aspects related to AOX reduction has been performed. Based on this study, the following conclusions have been drawn:

5. Freeness vs. tear index, tensile strength, burst index, and folding endurance for the three-stage sequence. There is little difference in strength between the AO(C+D)(EO)D and O(C+D)(EO)D pulps.

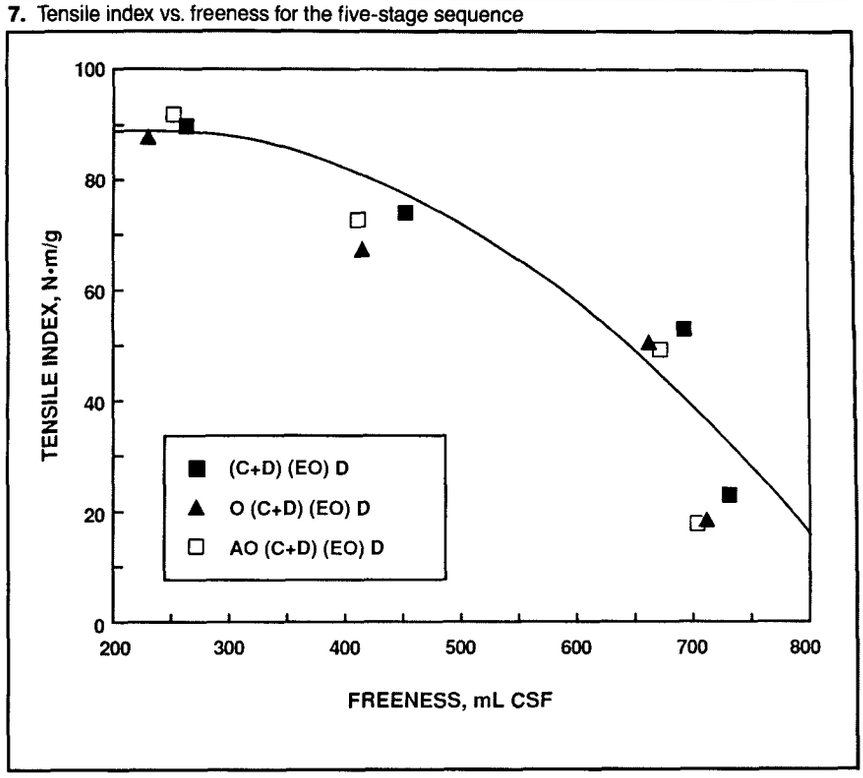


6. Tear index vs. tensile index for both the three-stage and the five-stage sequences



1. The oxygen-delignified pulp with NSA pretreatment has a better selectivity than the oxygen-delignified pulp without NSA pretreatment.
2. During the bleaching sequence, the AO(C+D)(EO)D pulp requires less chlorine and caustic than either the (C+D)(EO)D pulp or the O(C+D)(EO)D pulp, though similar handsheet brightness is achieved.
3. Starting with a conventional bleaching process, the NSA pretreatment substantially lowers the amount of AOX released into bleaching effluent stream.
4. The fully bleached pulp with NSA pretreatment exhibits physical properties comparable to those without NSA pretreatment.□

7. Tensile index vs. freeness for the five-stage sequence



Literature cited

1. Heimburger, S. A., Blevins, D. S., Bostwick, J. H., and Donnini, G. P., Tappi J. 71(10): 51(1988).
2. Backlund, E. A., 1984 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 1.
3. Tench, L. and Harper, S., Tappi J. 70(11): 55(1987).
4. Pryke, D., Tappi J. 72(10): 147(1989).
5. Enz, S. M. and Emmerling, F. A., 1987 International Oxygen Delignification Conference Proceedings, TAPPI PRESS, Atlanta, p. 13.
6. Clarke, G. L., Paper Trade J., Tappi Sec. 118(8): 62(1944).
7. Samuelson, O., U.S. pat. 4,406,735 (1983).
8. Samuelson, O., U.S. pat. 4,439,271 (1984).
9. Samuelson, O., U.S. pat. 4,445,969 (1984).
10. Samuelson, O., U.S. pat. 4,602,982 (1986).
11. Samuelson, O. and Ojteg, U., J. Pulp Paper Sci. 13(5): J150(1987).
12. Samuelson, O. and Ojteg, U., Cellulose Chem. Technology 21(2): 129(1987).
13. Samuelson, O., 1987 International Oxygen Delignification Conference, TAPPI PRESS, Atlanta, p. 45.
14. Rasmusson, D. and Samuelson, O., Nordic Pulp Paper Res. J. 3: 138(1989).
15. Samuelson, O., Lindstrom, L.-A., and Marklund, A., 1986 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 49.
16. Brannland, R., Lindstrom, L.-A., and Norden, S., 1989 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 195.
17. D'Souza, R., Hsieh, J. S., and Jayawant, M. D., 1989 Pulping Conference Proceedings, TAPPI PRESS, Atlanta, p. 203.
18. Blackall, E. L., Hughes, E. D., and Ingold, C. K., J. Chem. Soc. Part I (Jan.): 28(1952).
19. Williams, D. L. H., Nitrosation, Cambridge University Press, 1988, p. 30.

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