



*Institute of Paper Science and Technology
Atlanta, Georgia*

IPST Technical Paper Series Number 708

Comparison of Oxidative Alkaline Extraction Reaction's Impact
on Pulp Properties and the Environment

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March 1998

Submitted to
1998 International Pulp Bleaching Conference
Helsinki, Finland
June 1–5, 1998

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ABSTRACT

Environmental concerns around kraft bleaching operations are prompting many mills to switch to 100% chlorine dioxide use in the initial delignification stage and to increase the effectiveness of the subsequent alkaline extraction stage with oxidant reinforcement of oxygen and/or hydrogen peroxide. Although extensive research has been performed on chlorine dioxide, less attention has been directed towards the subsequent alkaline extraction stage. This paper explores the effect of oxidant reinforcement in the first alkaline extraction stage after a ClO₂ delignification stage. Five types of alkaline extraction stages were examined, including E, E+O, E+P, E+O+P, and an E stage done under argon after all dissolved and atmospheric oxygen had been removed. The findings from these studies indicate that oxygen reinforcement's main benefits are in delignification while hydrogen peroxide reinforcement facilitates the destruction of chromophores. The oxidative reinforcements were also beneficial in lowering the AOX levels in the effluents of the combined ClO₂ stage and alkaline extraction stage.

INTRODUCTION

Recently proposed environmental regulations will limit the amounts of chlorine dioxide that can be employed for bleaching kraft pulps. One solution for enhancing the delignification of kraft pulps will be to reinforce the first alkaline extraction stage with an oxidant. Numerous researchers have already documented the improved delignification performance of an (E+O), (E+P), or an (E+O+P) stage versus an E-stage after a D delignification stage (1, 2, 3, 4, 5, 6, 7, 8, 9)

OBJECTIVES

This study will directly compare the effects of oxygen and hydrogen peroxide on lignin content, cellulose degradation, and brightness. Isolated lignin from the various stages were spectrally examined to provide additional information on chromophore destruction.

EXPERIMENTAL

Pulps

A kraft pulp was obtained from a single Loblolly Pine (*Pinus taeda*) approximately 30 years in age and free from disease. The wood was debarked, chipped, screened, and conventionally cooked in a MK digester. The brownstock was screened, washed, and then subjected to a typical D delignification stage (0.20 kappa factor) in a Quantum reactor at 10% consistency for 45 minutes at 45°C. The bleached pulp was then filtered, washed with water, and characterized for kappa number, Klason lignin percentage, and pulp viscosity.

Chemicals and Reagents

All chemicals used in this research were purchased from Aldrich, VWR, and Isotec. Except for the p-dioxane, which was purified by distilling in the presence of NaBH₄ prior to use, all chemicals were used without further purification. Filtered Nanopure de-ionized (DI) water was used in all instances when water was required. Chlorine dioxide was prepared by reducing NaClO₃ by acidification in the presence of oxalic acid. Chlorine dioxide was generated by reducing sodium chlorate with oxalic acid. The small amount of chlorine that was generated in this process was removed by reducing it with equal molar amounts of sodium chlorite to form chlorine dioxide and chloride.

Alkaline Extraction

The D delignified pulp was added to a continuously stirred pressure reactor, and the consistency was adjusted to 10%. The pulp was then warmed to 70°C; bleaching chemicals were added; and the mixture was stirred for 75 minutes. Table I summarizes the chemicals and charges employed during the alkaline extraction stage. Upon completion of the extraction, the pulp was removed from the reactor, filtered, and thoroughly washed. The alkaline extracted pulps were characterized in terms of kappa number, Klason lignin percentage, and pulp viscosity.

D1 Bleaching

The alkaline extracted pulps were then bleached using a 0.75% charge of ClO₂ at 10% consistency in plastic bags immersed in a water bath at 70°C for 3 hours. The pulps were thoroughly kneaded every half hour, and upon completion the bleached pulps were filtered and washed. The pulps were characterized for Klason lignin, pulp viscosity, and ISO brightness on TAPPI Standard prepared handsheets.

Table I. Alkaline Extraction Conditions.

Bleach Stage	Bleaching Conditions Employed ^a
E	2.0% charge of NaOH, performed under atmospheric pressure.
E+O	2.5% charge of NaOH, 60 psig initially, then decreased by 12 psig/5 minutes, final 50 minutes were performed at atmospheric pressure.
E+P	2.5% NaOH and 0.5% charge of hydrogen peroxide.
E+O+P	2.5% charge of NaOH, 0.5% charge of hydrogen peroxide, 60 psig initially, then decreased by 12 psig/5 minutes, final 50 minutes were performed at atmospheric pressure.
E+Ar	All oxygen was removed from the pulp, and chemicals via a freeze-thaw cycle. 2.0% charge of NaOH was used, and the reactor was slightly pressured with argon (10 psig) to prevent the introduction of O ₂ into the reactor.

^aNote: The charge of NaOH employed was selected to ensure that a terminal pH > 10.5

E2 and D2 Bleaching

A portion of the D1 pulps were treated with a 1.0% charge of NaOH at 10% consistency for 60 minutes at 70°C. These pulps were well washed and bleached in a D2 stage. The ClO₂ charges were varied (0.2% - 0.8%) and were added with a small amount of NaOH (25% of the ClO₂ added) for pH adjustment.

Pulp Characterization

The lignin content was measured using a 1/4 kappa test and a modified Klason lignin test method (10, 11). Modification to the Klason lignin method involved the use of an autoclave to speed up the sulfuric acid hydrolyzation of the carbohydrates in the pulp. The remaining lignin was filtered, dried, and weighed to give an acid-insoluble weight percentage (12). Three Klason lignin and kappa number determinations were performed for each bleach sequence except for the D1 stage, which had a lignin content too low to perform kappa numbers. Carbohydrate degradation was measured indirectly by solvating the pulps in cupriethylenediamine and measuring these solutions' viscosity with a capillary viscometer (13). Handsheets were prepared from the D1 pulp at a basis weight of 150 g/m² using a standard test procedure (14), and then used to measure ISO brightness.

Visible Spectrum of Lignin

Isolated lignin was measured out and dissolved in a known quantity of 9:1 para-dioxane:water solution. The absorbance values were measured using a 1-cm quartz cell using a Shimadzu UV160U spectrophotometer. A second cell containing the para-dioxane:water solution was used to correct for the solution's absorbance.

AOX Testing

Filtrate samples from the stages were collected and stored in glass containers with no air space at 4°C. The samples were mixed at an equal volume ratio since all stages were performed at 10% consistency. The combined filtrates were allowed to mix for 1 hour before acidifying to a pH of < 2 with concentrated HNO₃. The filtrates were tested for AOX by Savannah Laboratories using AOX-EPA Method 1650 rev. B (15). Total organic carbon measurements of the filtrates were also measured to normalize the AOX to the amount of lignin in the effluent. Normalized AOX was expressed in terms of chlorine atoms/100 carbon atoms.

RESULTS AND DISCUSSION

The first comparison that can be made between the various alkaline extraction stages is on the amount of delignification. Kappa numbers were performed on the first alkaline extraction stages and Klason lignin (acid insoluble weight %) were determined for the first alkaline extraction stage and following D1 stage. The results shown in Figure 1 depict the residual lignin content decreasing with increasing oxidant in the first alkaline extraction stage. The differences between the different oxidant reinforcement levels are diminished after the D1 stages. Comparing the oxygen and peroxide reinforcement stages, it appears that oxygen is better at delignifying than hydrogen peroxide. A combination of the two gives the most delignification. This is expected since this represents the most oxidant reinforcement

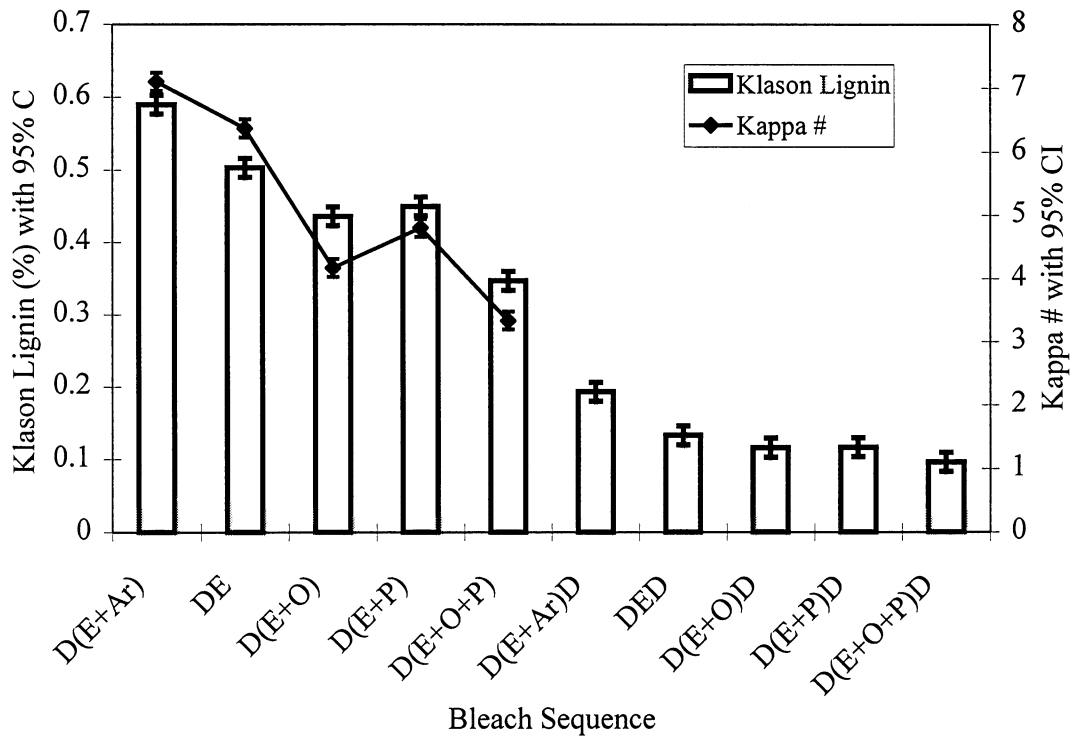


Figure 1. Lignin Content of Bleached Pulps with 95% Confidence Interval. The kappa numbers for the brownstock and D_0 stages were 30.4 and 14.6 respectively, while Klason lignin for the brownstock and D_0 stages were 3.6 and 2.5 respectively.

Cellulose degradation was also measured by means of CED viscosity for the various pulps. The CED viscosity decreased slightly with each bleaching stage. A comparison of the different alkaline extraction stages, revealed that oxygen reinforcement appeared to degrade the cellulose more than the hydrogen peroxide. Figure 2 also contains ISO brightness data from TAPPI standard handsheets made from the D1 stage pulps. The data depicts an increase in brightness with increasing oxidant especially with hydrogen peroxide reinforcement in the E1 stage, which brightened the pulp significantly better than oxygen reinforcement.

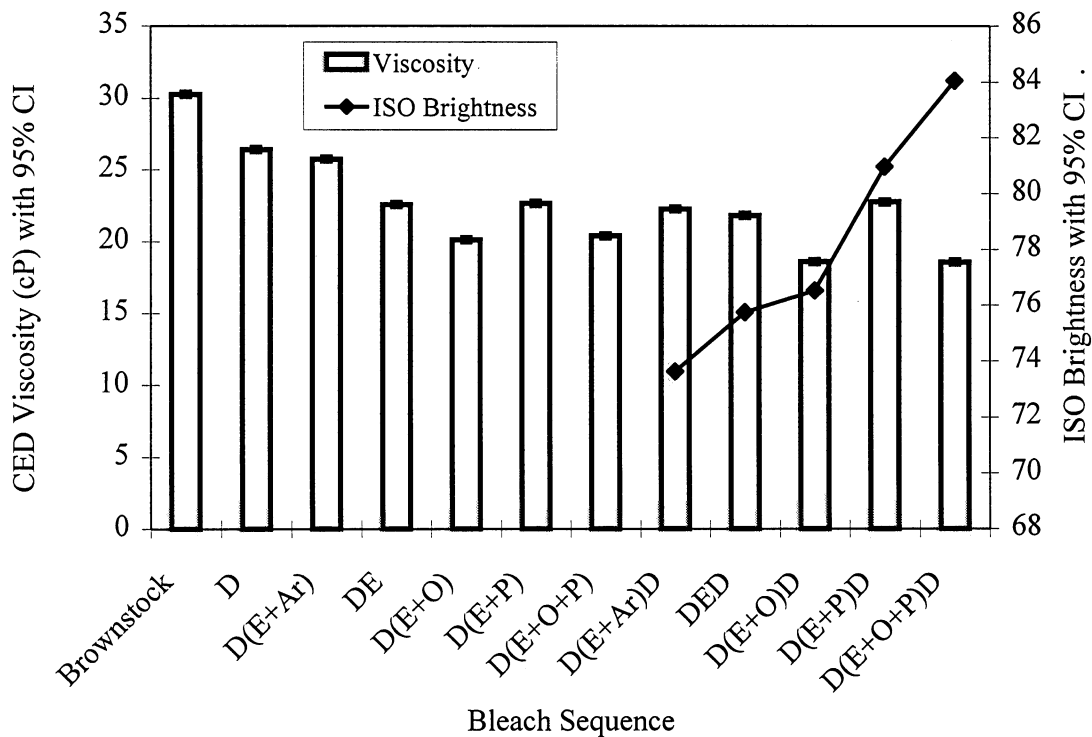


Figure 2. CED Viscosity Data of the First Three Bleach Stages and ISO Brightness of the D1 Stage with 95% Confidence Interval.

It was desired to know whether or not the oxidative alkaline extraction brightness increases measured in the D1 stage could be carried through to the final D2 stage. Using earlier described conditions, brightness ceiling data were generated for the pulps with the 5 different alkaline extraction conditions and are shown in Figure 3. The figures shows oxygen reinforcement, which did help delignification, did not substantial increase the brightness ceiling. Conversely, hydrogen peroxide, which delignified less than oxygen reinforcement, gave substantial increases in the brightness ceiling. This data suggests that hydrogen peroxide was able to react with chromophore structures in the pulp that oxygen and chlorine dioxide cannot.

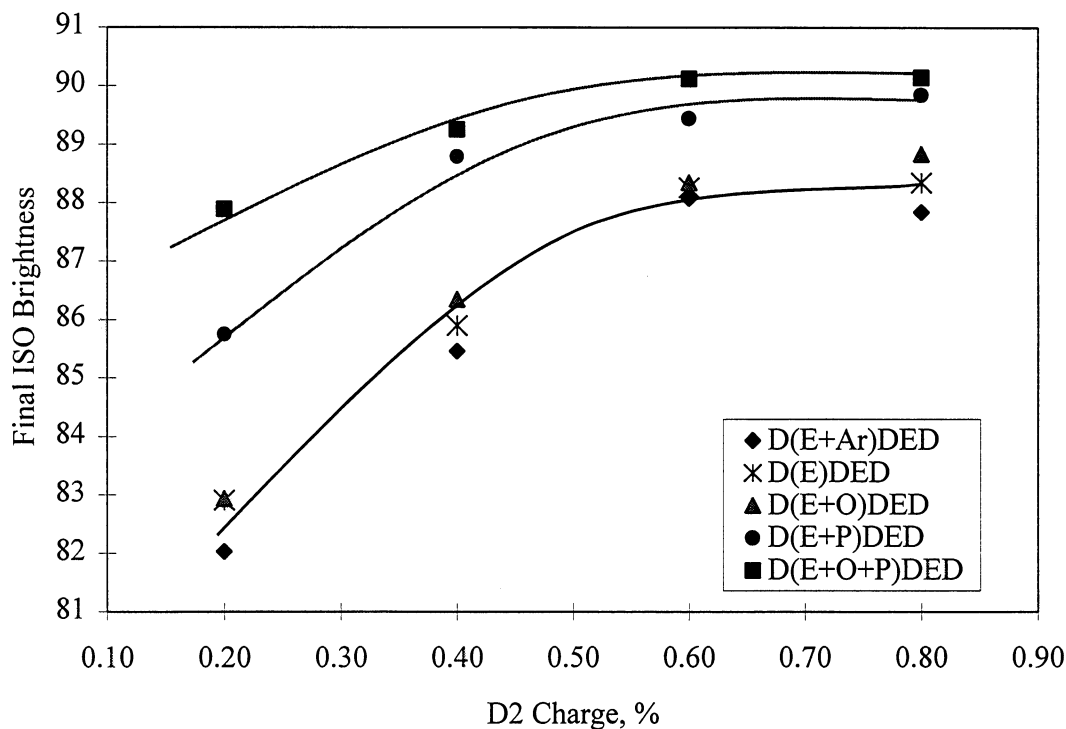


Figure 3. Brightness Ceiling Data Comparing the Different Alkaline Extraction Conditions. (The curves for the data are freehand curves, used only to help visualize the relationship.)

The brightness data suggests that lignin alteration in the alkaline extraction stage had a profound affect on the final brightness ceilings. This led us to measure the visible spectrum of isolated lignins from various bleaching stages. The lignins were isolated using published procedures (16, 17, 18). Both residual and effluent isolated lignin were suspended in a 9:1 p-dioxane:water solution. The absorbance of the suspension was measured and corrected for the concentration. Subtracting the brownstock residual lignin's absorbance, difference spectra were obtained and are shown in Figures 4 and 5 for the residual and effluent lignins, respectively.

Inspection of this data reveals the lignins will increase in color from the initial D stage and will increase again with the alkaline extraction without oxidant reinforcement. Adding pressurized oxygen gave a slight decrease to the lignin's light absorbance, but not as dramatically as hydrogen peroxide reinforcement, which significantly decreases the color of the lignin. The same trends of lower color with added oxidant and hydrogen peroxide are seen in both the residual lignin and effluent lignin spectra. The data also shows that the effluent lignins have less color than the residual lignins. This is possibly due to these lignins being less condensed, which is expected as this lignin was removed from the fiber. Isolation procedures may have also affected the color difference between the two types of lignin.

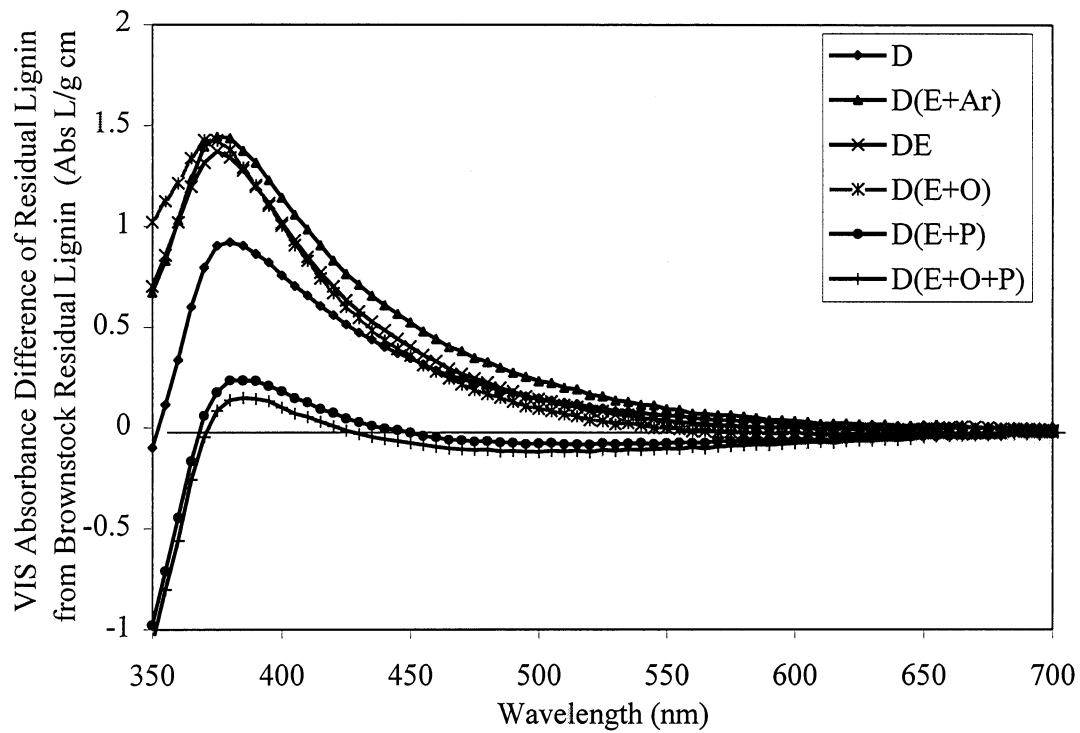


Figure 4. Difference Absorbance Spectrums of Residual Lignins.

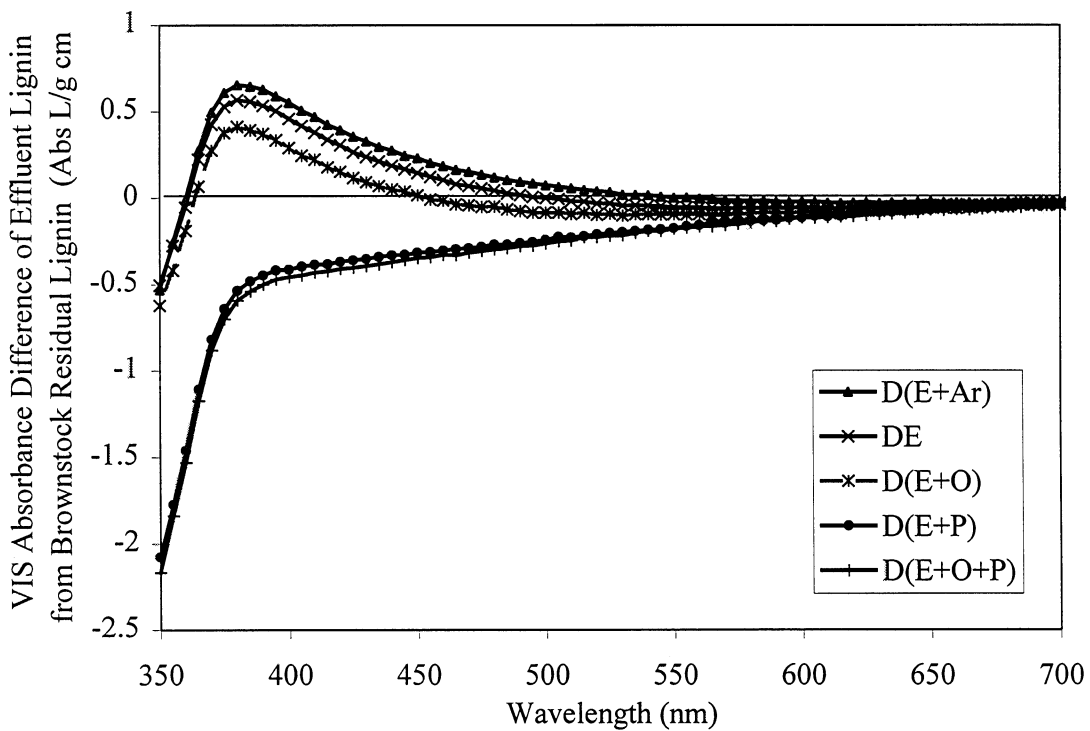


Figure 5. Difference Absorbance Spectrums of Effluent Lignins.

Quantification of the amount of color was possible by integrating under the original visible spectra. These integration values were normalized to the brownstock residual lignin to give a ratio of color absorbance to the brownstock lignin. A percentage of 100% would indicate that the lignin has the same amount of color, whereas a lower value means it has less color. The calculations of color change were plotted and are shown in figure 6. The data clearly show the ability of hydrogen peroxide to significantly decrease the color of lignin. Alkaline extraction without oxidant was shown to increase the color of the lignin. This observation could be attributed to alkali darkening reactions of condensing quinone structures.

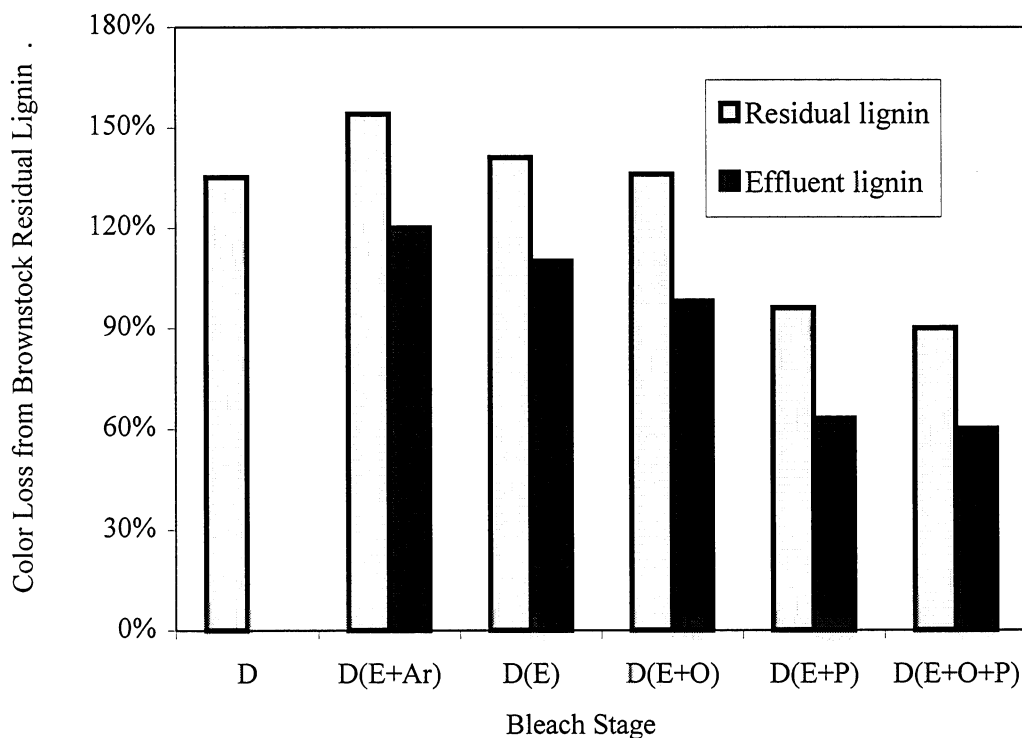


Figure 6. Color Change of Bleached Lignins from Brownstock Residual Lignin.

Alkaline extraction oxidative reinforcement conditions were found to affect delignification and brightening of the pulp. Also of interest is the oxidative alkaline extraction's effect on AOX destruction. Effluents from the initial D stage and various E1 stages were collected and stored at 4°C. The effluents were combined and allowed to mix for 1 hour and then acidified to a pH <2 with concentrated nitric acid. AOX measurements on the combined samples were plotted and are shown in Figure 7. The data depicts a trend for reduced AOX with increased oxidant reinforcement although the effect is small.

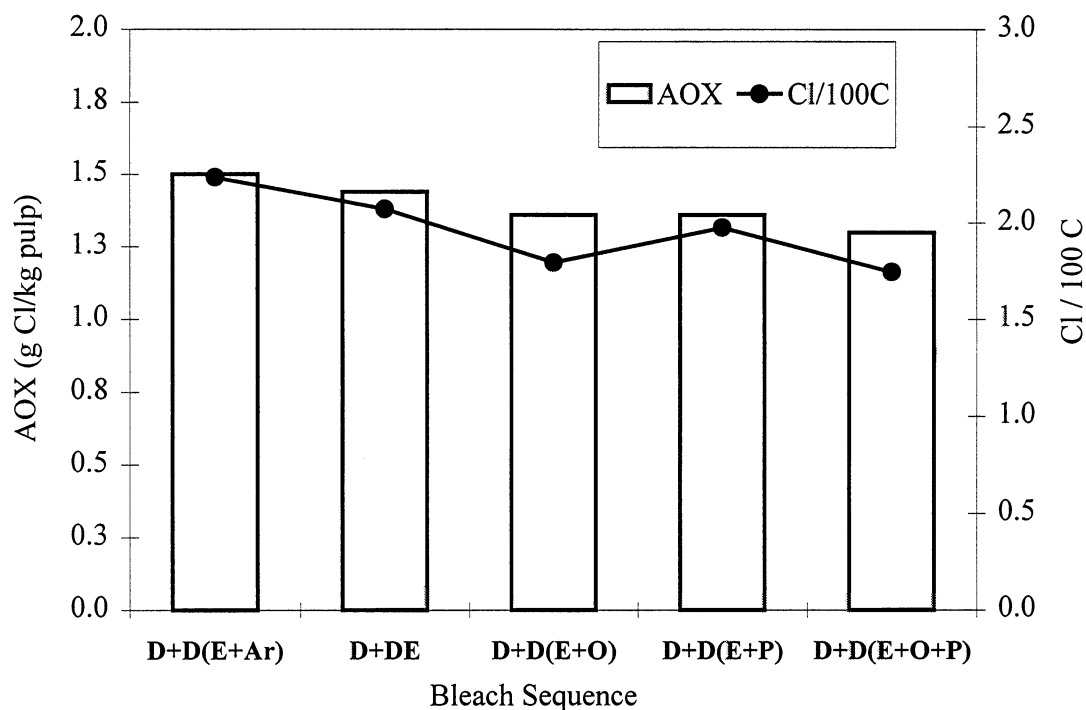


Figure 7. AOX and Cl/100 C for Combined Bleach Effluents.

The absolute values of the combined effluent are high enough to indicate that little destruction of D stage effluent AOX occurred during its mixing with the E stage effluent. It is believed that the low temperature needed to preserve the AOX in the effluent was too low to allow significant amounts of base catalyzed chlorine elimination. Additional work is needed to properly simulate the bleach plant's mixing of acid and alkaline bleach stage effluents.

CONCLUSIONS

Oxidative alkaline extraction can contribute significantly to delignification and brightening. Oxygen reinforcement appears to delignify better than hydrogen peroxide. Hydrogen peroxide reinforcement causes less cellulose degradation and is able to substantially increase the brightness ceiling. A combination of hydrogen peroxide and oxygen provides substantial delignification and chromophore destruction. The destruction of chromophores by oxidative alkaline extraction can be measured on the isolated lignins by visible spectroscopy. The changes in lignin color correlates well with the brightness ceiling of the pulp.

ACKNOWLEDGEMENTS

The authors wish to thank Drs. T.J. McDonough and D.R. Dimmel for valuable discussions and constructive suggestions, and the Institute of Paper Science and Technology and its Member Companies for supporting this research. The authors would like to specifically thank Union Camp Corporation for the donation of the Loblolly Pine log, and Potlatch Corporation for the kraft cook of the chips. Portions of this work were used by T.M.R. as partial fulfillment of the requirements for the Ph.D. degree at IPST.

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