

# Dechlorination and decolorization of high-molecular-weight chlorolignin from bleach plant effluents by an oxidation process

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**ABSTRACT** *The total organic chlorine and color of the high-molecular-weight chlorolignin from spent alkali extraction-stage effluent were effectively removed by an oxygen oxidation process. Under laboratory conditions, oxygen pressure, temperature, and alkali charge were not the limiting factors for either dechlorination or decolorization. Mass transfer may be important, however, especially during the initial 30 min of the process. Under the best conditions, about 70–80% of the total organic chlorine with an initial value of 2200 mg/L and 60–70% of the color with an initial value of 220,000 pcu were removed in less than 1 h. The high-molecular-weight chlorolignins were degraded to a lower molecular weight. A process combining ultrafiltration, oxidation, and biological treatment could be an effective, economical option to remove the TOCl and color from the spent alkali extraction effluent.*

## KEYWORDS

Chemical  
analysis  
Chlorine  
Bleaching  
Effluents  
Environmental  
control  
Lignin

During the chlorination of pulp in the bleach plant, chlorolignin is formed as a major constituent of the organic fraction in the spent effluent. Most of the chlorolignins have high molecular weights ( $> 1000$ ) (1), although some chlorolignins of low molecular weight are also formed. Much of the chlorolignin is contained in the effluent of the first alkaline extraction stage. As a result, the effluent has a high color and total organic chlorine content as well as a high biological oxygen demand (BOD) and chemical oxygen demand (COD).

The impact of BOD and COD on the environment is well known. Color retards sunlight transmission in water and is aesthetically displeasing. The low-molecular-weight chlorolignins are already known to be toxic, mutagenic, and bioaccumulative (2, 3) because they are able to penetrate cell membranes, while the high-

molecular-weight chlorolignins are likely to be biologically inactive because they have difficulty in penetrating the cell membranes of target organisms. They cannot be removed by conventional primary and secondary treatment. However, long-term, slow biodegradation of high-molecular-weight chlorolignin may cause environmental problems.

Future effluent regulations may require the pulp and paper industry to substantially reduce nonconventional pollutants such as color and total organic chlorine (TOCl). TOCl and color can be reduced by (a) process modification within the mill or (b) external treatment. In-plant modification can range from simple, inexpensive measures such as improved pulp washing (brownstock) to complex technological changes such as modified pulping for extended delignification, oxygen bleaching, or

high chlorine dioxide substitution in the chlorination stage.

While in-plant changes should be considered as a first preference, effluent treatment will still be required in many cases. A variety of effluent treatment schemes have been studied, including chemical precipitation or flocculation (4, 5), ultrafiltration (6, 7), activated sludge or aerated lagoon treatment (8, 9), the MyCoR process (mycelial color removal) (10–12). However, none of these have been applied commonly as an effective way to remove TOCl and color in bleach plants because of economic or technological drawbacks.

One possible solution for the removal of color and TOCl is the oxidation of the effluent by oxygen. Oxygen can react with lignin under alkaline conditions (13). Oxygen may also react with chlorolignin and oxidize chromophores. Oxidation has been proven to

be an effective alternative for the destruction of organics in sludges (14, 15), and for detoxification of specific organic substances (16).

The objectives of our research were:

1. To study the treatability of high-molecular-weight chlorolignins in the first E-stage effluent by an oxygen oxidation process
2. To study the factors that affect dechlorination and decolorization by this process.

## Experimental procedures

### Effluent from the first E stage

The E-stage effluent was obtained from a commercial kraft softwood bleach plant using a CEDED sequence. The effluent was ultrafiltered using a Proto-Sep III bench-scale unit (Koch Membrane Systems Inc., Boston) utilizing a spiral-wound membrane with a molecular weight cut-off of 1500. The effluent was concentrated to 10% of its original volume, and the concentrate was stored at 4°C until used.

### Oxidation operation

A volume of 1500 mL of concentrated effluent with or without the addition of 5 g/L NaOH was put in a 1-gal Parr reactor (Moline III). The reactor was equipped with a pressure gauge, a gas inlet, and two thermocouples at the top; effluent samples were taken from the base of the reactor. The reactor was also equipped with a stirrer that could be operated at up to 900 rpm; baffles were used in the reactor to improve mixing.

The temperature was controlled so that the system was isothermal once the selected temperature was reached. When the temperature was within 5°C of the target, we pressurized with oxygen and stirred, since the temperature rises by about 5°C with pressurization. The pressure and stirring speed were maintained constant throughout the reaction period. The term "oxygen pressure," as used in this study, denotes the actual total reaction pressure since we did not monitor the oxygen gas partial pressure separately.

At predetermined times, samples were taken for TOCl, color, and other effluent analyses.

### Determination of TOCl

TOCl was determined by subtracting

the inorganic chloride from the total chlorine (TCI) obtained using the Schoniger combustion flask method (17). The chloride concentration of the sample and original effluent were determined using a chlorine selective electrode (Model 94-17, Orion Research Inc., Boston).

### Determination of color

Color was measured by a spectrophotometer as the absorbance at 465 nm of the sample after filtration through a 0.8- $\mu$ m membrane filter and transformed to platinum-cobalt units (pcu) (18).

### Molecular weight distribution

We analyzed the molecular weight distribution of the chlorolignin using gel permeation chromatography. The gel was Sephadex-75, and the eluant was a mixture of 0.1N NaOH and 0.1N LiCl.

## Results and discussion

The oxidation process relies on conditions of elevated temperature and pressure to oxidize organic substance in aqueous solution. Pressure and temperature are recognized as the most important process parameters (19). Pressure is needed to maintain the effluent in the liquid state and provide a minimum oxygen pressure. At any given temperature, the reactor pressure must be higher than the steam pressure by enough to maintain a slight excess of oxygen pressure.

The excess pressure requirement depends on the mass transfer characteristic of the reaction system. Thus, we studied the effects of pressure and other parameters on the TOCl and color removal.

### Effect of pressure on TOCl and color removal

The effect of the oxygen pressure on TOCl and color removal is shown in Fig. 1. As the pressure was increased from 100 to 150 psi, both the TOCl and color removal remained about the same. This finding was expected. Because the reaction system was gas-liquid, increasing the oxygen pressure at a high temperature and a particular mixing condition may not increase the dissolved oxygen concentration in the first E-stage effluent. As a result, the removal rate for TOCl and color was not increased at the

higher pressure.

During the heating-up period for the first E-stage effluent, even though no mixing took place and oxygen was not supplied, both the TOCl and color could be reduced by about 20%. The heating-up period was approximately 40–60 min. The reduction of TOCl and color during this period may be caused by the dissolved oxygen in the effluent and the nucleophilic substitution of the

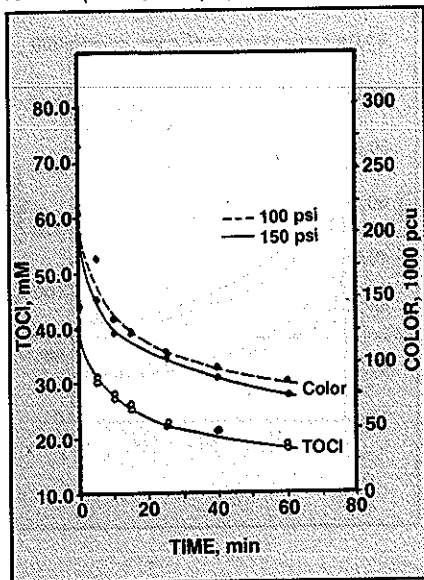
In Fig. 1, the rate of the dechlorination and decolorization was fast in the initial 15 min; then, after 25 min, it became much slower. At the beginning of the oxidation, dechlorination and decolorization take place rapidly because of the high pH and high concentration of TOCl and color in the system. As the reaction proceeds, acids produced from carbohydrates and chlorolignin by oxidation are neutralized by the base. As the concentrations of TOCl, color, and hydrogen ion (pH) drop, the rate of the dechlorination and decolorization decreases. Eventually, after a buffer solution system formed, dechlorination and decolorization leveled off.

### Effect of temperature on TOCl and color removal

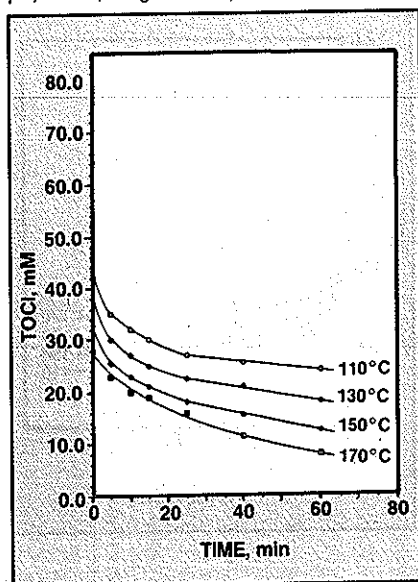
Under a given set of conditions, in a range of 110°C to 170°C an increase of 20°C in temperature resulted in a 10–20% additional removal of TOCl. However, since it takes longer to reach a higher target temperature, the initial value of the TOCl at a high temperature would be lower than at a lower temperature. As shown in Fig. 2, if the initial values of the TOCl were the same for the different temperatures, the differences in TOCl removal efficiencies would be slight. Temperature, therefore, is not a factor controlling the dechlorination.

A similar observation can be made for color removal. As shown in Fig. 3, however, when the temperature was increased to 170°C, color first increased for the initial 5 min and then decreased. The final color, however, was still higher than at 150°C. This difference may indicate that chlorolignin was polymerized at this temperature (170°C) and that the newly-formed high-molecular-weight material was more difficult to degrade. This outcome corresponds to a higher absorbance area in the high-molecular-weight portion of the gas permeation chromatography curve at

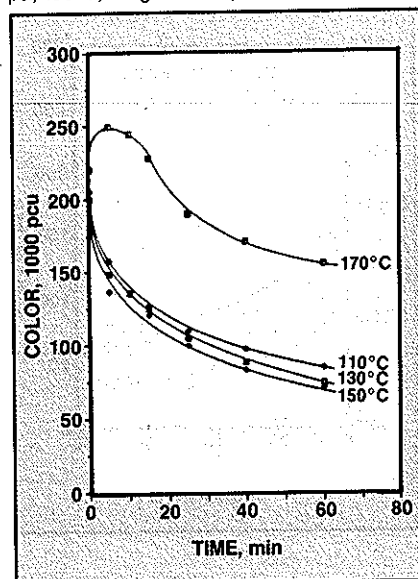
1. The effect of pressure on TOCl and color removal (150°C, 900 rpm)



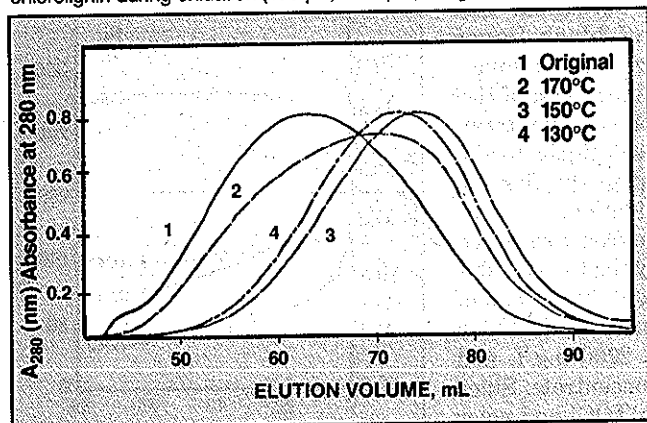
2. TOCl reduction at different temperatures (150 psi, 150°C, 5.0 g/L NaOH)



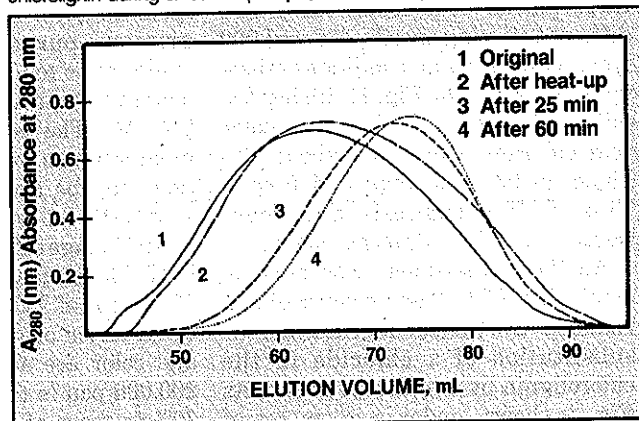
3. Color removal at different temperatures (150 psi, 150°C, 5.0 g/L NaOH)



4. The effect of temperature on the molecular weight distribution of chlorolignin during oxidation (150 psi, 900 rpm, 5.0 g/L NaOH)



5. The effect of temperature on the molecular weight distribution of chlorolignin during oxidation (150 psi, 150°C, 900 rpm, 5.0 g/L NaOH, 60 min)



170°C as compared to the curve at 150°C or 130°C (Fig. 4).

Figure 5 shows the change in the molecular weight distribution during the oxidation. During the heating-up period, some of the high molecular chlorolignins were degraded; this is in agreement with the decrease in TOCl and color in this period. The degradation rate is faster during the initial 25 min. The reason may be attributable to the high pH and high concentration of TOCl and color in the effluent during this period. Thus, degradation, dechlorination, and decolorization take place rapidly only at a high pH and a high concentration of chlorolignin; furthermore, their rates might be different.

#### Effect of alkali charge on the TOCl and color removal

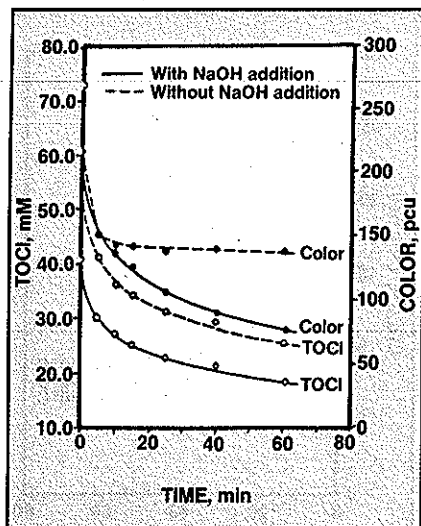
Two experiments were conducted to determine the effects of alkali on TOCl and color removal. The first experiment was conducted using a 5-g/L NaOH charge, and the second was conducted without any NaOH addition. Both experiments were conducted under otherwise the same conditions: 150 psi, 130°C, and 900 rpm.

As Fig. 6 shows, adding 5 g/L NaOH in the effluent gave a much better color removal. For the TOCl, there was only a higher removal efficiency during the heating-up period. The TOCl removal rate in both cases was about the same, although the final TOCl was much lower when 5 g/L of NaOH was added. These

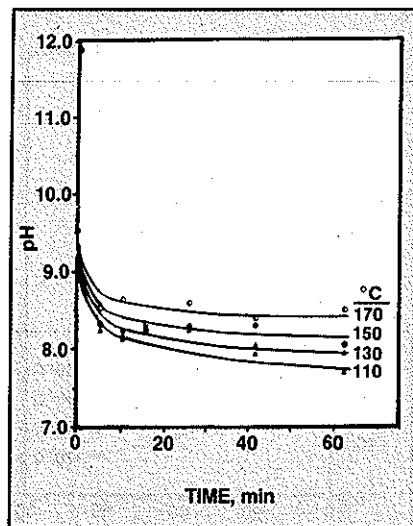
results indicate that the mechanisms of dechlorination and decolorization of the chlorolignin are different. Alkali charge may be more important for decolorization, or, in other words, high pH favors decolorization.

The change of pH during the course of the reaction is presented in Fig. 7. The pH leveled off after 15 min because a buffer system formed, decreasing the TOCl and color removal rates. However, the final pH was higher at a higher temperature. This finding is contrary to what we expected: to determine the reason for it will require further investigation.

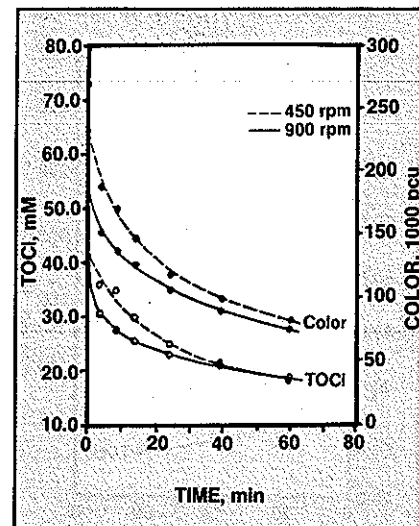
6. The effect of alkaline addition on TOCl and color removal (150 psi, 150°C, 900 rpm)



7. The change in pH during oxidation (150 psi, 150°C, 5.0 g/L NaOH)



8. The effect of stirring speed on TOCl and color removal (150 psi, 150°C)



### Effect of stirring on TOCl and color removal

Increasing the stirring speed can improve the mass transfer efficiency. Experiments were conducted at two different stirring speeds, 450 and 900 rpm, with the same conditions otherwise. As shown in Fig. 8, during the initial 25 min, the TOCl and color removal rates were both about 10% higher at 900 rpm than at 450 rpm. This finding suggests that mass transfer may be a limiting factor.

Another experiment was done to determine if TOCl and color could be reduced by thermodegradation or substitution of a chloride in the chlorolignin by a hydroxyl group. As Fig. 9 shows, under a given set of conditions, the color of the effluent increased about 10% when the reactor was pressurized with nitrogen, while the TOCl hardly decreased, although the pH and temperature were high in the system. This finding suggests that both dechlorination and decolorization could only be achieved by oxidation rather than by thermodegradation or a substitution reaction.

The pressure and temperature for the oxidation process are much lower than they would be for the Zimpro process. In a typical Zimpro process, the reaction temperature is 500°F (260°C) and the pressure is 2000 psi (20). In treating pulp mill black liquors, this process is applied to attain a high degree of oxidation to get maximum chemical and heat recovery (21). For removing TOCl and color from the effluent from the first E stage

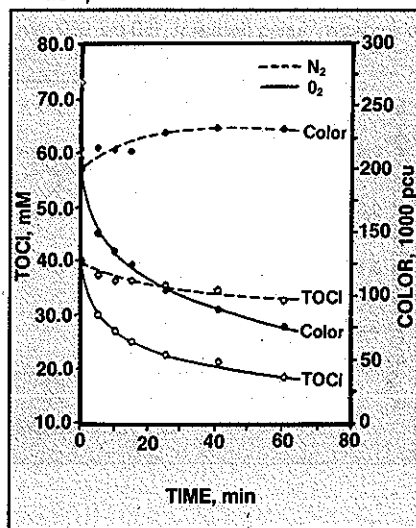
by the oxidation process, only a partial oxidation of the chlorolignin is desired, because of economic considerations.

This oxidation process is different from black liquor oxidation. The primary purpose of black liquor oxidation is to oxidize  $\text{Na}_2\text{S}$  to innocuous salts to prevent the release of  $\text{H}_2\text{S}$  (22, 23). The equipment and treatment systems for black liquor oxidation may be applied to the first E-stage effluent for oxidation.

An E-stage effluent from a softwood kraft bleach plant typically has 300–350 mg/L of TOCl and 22,000 pcu of color. After ultrafiltration, the TOCl and color are about 2200 mg/L and 200,000 pcu in the concentrate. Since 70% or more of both TOCl and color removal can be achieved by oxidation, mixing the oxidized effluent with the ultrafiltration permeate would result in an effluent with an average TOCl of 100–150 mg/L and a color of 7000–8000 pcu.

It may be economical and effective to combine ultrafiltration, oxidation, and a biological treatment system such as the MyCoR process or an aerated lagoon to form a complete treatment system for the effluent from the first E stage. There are two reasons for this. First, ultrafiltration can reduce the volume of the effluent to be treated by oxidation, reducing the capital and operating cost and improving the efficiency of the oxidation process. Second, high-molecular-weight chlorolignin is oxidized and degraded to a lower molecular weight. The ease with which the effluent can be treated by

9. The effect of oxygen on TOCl and color removal (150 psi, 150°C, 900 rpm, and 5.0 g/L NaOH)



a biological treatment system would probably be enhanced, making the process more economically and technologically feasible.

### Summary and conclusions

The oxidation process can effectively remove total organic chlorine and color from the high-molecular-weight chlorolignin in the effluent from the first extraction stage. Under a given set of conditions (150°C, 150 psi, 900 rpm, 40–60 min), about 70–80% of TOCl and 60–70% of color can be removed, with initial values of 2200 mg/L of TOCl and 60–70% of color.

Under the laboratory conditions, both dechlorination and decolorization can only be achieved by oxidation rather than thermodegradation. High-molecular-weight chlorolignin was degraded to a lower molecular weight, suggesting it could improve the efficiency of further biological treatment. The limiting factor affecting the dechlorination and decolorization of the effluent under the laboratory conditions may be the mass transfer, while the effects of the temperature, pressure, alkali charge, and time are not significant.□

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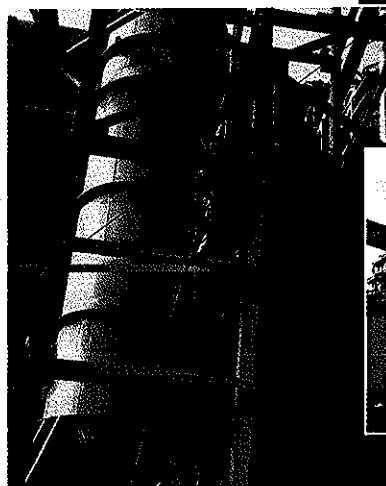
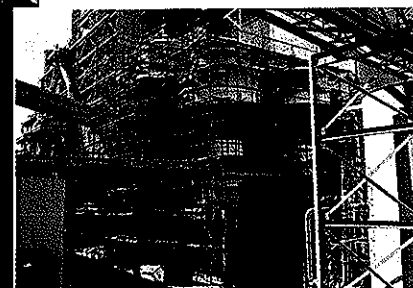
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