

ORIGINAL ARTICLE

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Evaluation of the extent of the oxidation reaction during chlorine bleaching of pulp*

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Abstract A modified method was developed to evaluate how much chlorine is consumed by the oxidation reaction during the chlorine bleaching process. This evaluation is, in principle, based on the sum of chloride produced during the chlorination stage (C-stage) and produced during alkali treatment of both the C-stage effluent and the chlorinated pulp. Results obtained by this method proved that about 50%–75% of chlorine was consumed by the oxidation reaction during chlorine bleaching, depending on the reaction condition of chlorination. Even under a reaction condition that is not favorable to an oxidation reaction (low pH), approximately three electrons were abstracted from one lignin structural unit by chlorine bleaching. This result provides additional evidence for our recent observation that lignin is extensively oxidized during chlorine bleaching even when pure chlorine without any chlorine dioxide substitution was used.

Key words Chlorine bleaching · Alkali extraction · Oxidation · Substitution reaction · Chloride · Ion chromatography

Introduction

Chlorine is an effective bleaching agent, but it brings a serious environmental problem because it inevitably forms chloroorganics during the chlorine bleaching process. Alternative bleaching agents are therefore being developed all over the world. It would be necessary to know in detail how chlorine reacts with residual lignin in kraft pulp to apply its mechanism to the development of new bleaching agents with

an effectiveness comparable to that of chlorine. However, the main reaction responsible for delignification during chlorine bleaching process has yet to be fully understood.

Possible reactions reported in previous studies¹ are summarized in Fig. 1. The chlorine-consuming reactions are divided mainly into two patterns: substitution and oxidation reaction expressed as Eqs. [1] and [2], respectively, in Fig. 1. Although a chlorine substitution reaction is essentially an oxidative reaction, chlorine substitution reactions and oxidative reactions other than substitution reactions have been historically classified into different categories in the field of bleaching chemistry. This classification has provided some fruitful results for the better understanding of chlorine bleaching. This traditional classification was followed in this report to express the types of reaction during chlorine bleaching.

The substitution reaction consumes 1 mol of chlorine to form 1 mol of chloride, whereas the oxidation reaction consumes 1 mol of chlorine to form 2 mol of chloride. Catalytic hydrolysis (Eq. [4]), on the other hand, does not consume any chlorine molecule, although it is assumed to be greatly related to the changes of lignin structure.

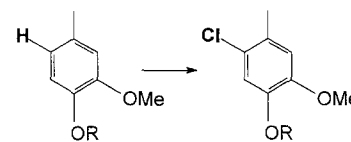
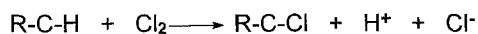
It was once supposed that during chlorine bleaching the substitution reaction contributed more to delignification than oxidation, and that oxidation should be suppressed to maintain the strength of the pulp obtained.² Grangaard³ pointed out that some chlorine consumption by the oxidation reaction also plays an important role in rendering the lignin in kraft pulp soluble when the lignin content in pulp is relatively low. They did not put a strong emphasis on the indispensability of oxidation because they supposed the substitution reaction to be important as well. Tabei and coworkers,⁴ in contrast, suggested that the effect of the oxidation reaction on delignification should be of greater importance. They observed delignification behaviors quantitatively by intentionally varying the proportion of the oxidation and substitution reactions under a given chlorine consumption. They proposed a method to evaluate the amount of chlorine consumed by the oxidation and substitution reactions. As is discussed below (see Results and discussion), their calculation was based on the amount of chloride determined in the

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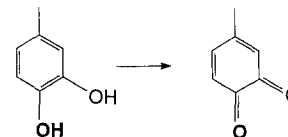
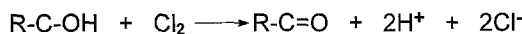
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Fig. 1. Reactions used to express the types of chlorine reaction

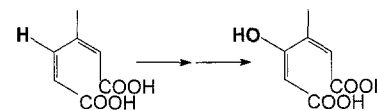
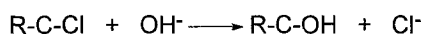
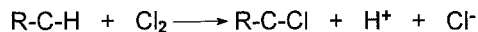
[1] Substitution reaction



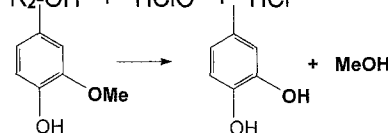
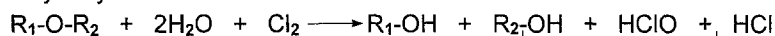
[2] Oxidation reaction 1



[3] Oxidation reaction 2



[4] Catalytic hydrolysis



chlorination stage (C-stage) effluent. The presence of structures carrying unstable organic chlorines⁵ in both the C-stage effluent and the chlorinated pulp were not taken into consideration. Some of the structures with organically bound chlorine produced during the C-stage (seen as Eq. [1]) are susceptible to warm alkali treatment to form chloride (described as Eq. [3]).⁵ If the amount of chloride can be used as a measure of the extent of the oxidation reaction, such chlorides released from organically bound chlorines during alkali treatment should also be taken into account. For example, as is expressed in Eq. [3], the resulting structure carries, in most cases, a hydroxyl group at the position where a hydrogen atom was present before the chlorination reaction. Conversion of a carbon-hydrogen bond to a carbon-oxygen bond is certainly an oxidative reaction. It should be noted here that organically bound chlorines in chlorinated phenols are in most cases quite stable to the warm alkali treatment employed in this experiment.⁶ Therefore, to estimate properly the extent of the oxidation reaction during chlorine delignification, the chloride not only produced during C-stage but also derived from such unstable organic chlorines by a warm alkali treatment must be determined. We have here evaluated the significant role of oxidation reaction in the chlorine bleaching on the basis of a modified calculation method.

Experimental

Chlorination

Unbleached hardwood kraft pulp (kappa number 11.5, 20 g of o.d. pulp) was treated with chlorine water (chlorine mul-

tiple was 0.15, and the pulp consistency was 5%) under two conditions.

Condition 1: treated with chlorine water prepared by the introduction of gaseous chlorine into deionized water without pH adjustment (pH was found to be 2.5 after 1 h of bleaching at room temperature)

Condition 2: treated with pH-adjusted chlorine water prepared by the addition of NaOH to the chlorine water (pH was found to be 4.4 after 2 h of bleaching at room temperature)

Each bleached pulp was separated from the chlorination liquor and washed three times with 300 ml of deionized water. The chloride contained in the chlorination liquor and the three washings was determined according to the procedure described below.

Alkali treatment

The chlorination liquor and the first washing were treated with NaOH at 70°C for 1 h. The NaOH doses were varied so the molar ratio of NaOH to the amount of chloride found in the liquor before alkali treatment ranged from 1 to 10. After the treatment, each sample was cooled and the chloride contained in those solutions determined.

Chlorinated pulp (1g) was also treated with NaOH solution under 70°C for 1 h and the chloride released into suspension determined. NaOH doses employed here were 0.5, 1.0, 2.0, 5.0, and 18% of the weight of chlorinated pulp. After the treatment, each sample was cooled and the chloride contained in those suspensions determined.

Chloride determination

The chloride concentration in the C-stage liquors (before and after alkali treatment) and the chloride released from chlorinated pulps after alkali treatment was determined by ion chromatography (LC-10A series; Shimadzu) with bromide (added as 0.10 mM KBr solution) as an internal standard.⁷ The determination was carried out on an anion-exchange column (Shim-pack IC-A1) with an electrical conductivity detector (CDD-6A; Shimadzu). The eluent was tris(hydroxymethyl)aminomethane buffer (0.42 mM, pH 3.5) containing 0.50 mM phthalic acid. The flow rate was 1.5 ml/min. The temperature of the column and detector was 40°C. The injection volume was 0.020 ml at each operation.

Results and discussion

Calculation of the proportion of oxidation and substitution reaction

The proportion of oxidation and substitution reaction during chlorine bleaching can be calculated based on the amount of chloride produced by the reaction.

$$\begin{aligned} \text{Substitution (\%)} &= (2x - y) \times 100/x \\ \text{Oxidation (\%)} &= 100 - \text{substitution (\%)} \\ &= (y - x) \times 100/x \end{aligned}$$

(where x is the Cl_2 consumed (mol), and y is the Cl^- produced (mol)).

For the value y , the method of Tabei et al.⁴ employs only the chloride determined in the chlorination stage (C-stage) liquor. In contrast, our modified method employs total chloride ions found in C-stage liquor and produced by the alkali treatment of both C-stage liquor and chlorinated pulp. In our study, the amount of Cl_2 consumed in the C-stage was regarded as that of Cl_2 added because no residual chlorine was detected in any C-stage liquors or washings after the reaction by iodometric titration.

Figure 2 shows the amount of chloride determined in the C-stage liquor and the three washings before alkali treatment. Irrespective of the difference between the two conditions employed, almost all the chloride determined without alkali treatment was found in the C-stage liquor and the first washing, and so it can safely be said that chloride existing in C-stage liquor and the first washing practically represents the chloride produced during the C-stage. This amount of chloride is described as a , and it is used to evaluate the proportion of oxidation and substitution reaction according to a calculation method previously proposed by Tabei and coworkers.⁴ The result is compared with that obtained according to our modified method.

After the C-stage liquor and the first washing were treated with warm alkali, chloride was determined again. The effect of the NaOH dose on the amount of chloride found in alkali-treated C-stage liquor is shown in Fig. 3. In both conditions 1 and 2, the chloride amount increased with the increase in the NaOH dose and finally reached a con-

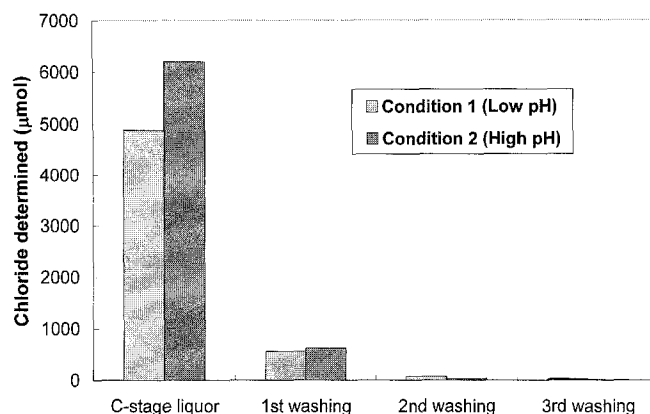


Fig. 2. Chloride determined in C-stage liquor and washings

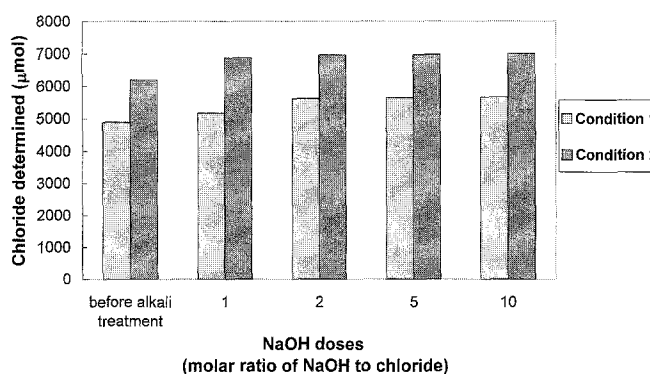


Fig. 3. Increase in chloride in C-stage liquor by 70°C alkali treatment

stant value at a certain NaOH dose. A similar tendency was observed for the first washing prepared under both conditions. The sum of chloride determined in C-stage liquor and the first washing after NaOH treatment (NaOH dose was 10 times the chloride detected before alkali treatment) is defined as b , and it is used in our modified calculation method (discussed later).

Chlorinated pulps were also subjected to a treatment in warm NaOH solution. As can be seen in Fig. 4, the amount of chloride released from the pulp increased with the increase in NaOH dose and finally reached a constant value. A similar tendency was observed for both chlorinated pulps. Chloride measured after warm alkali treatment (NaOH 18% on pulp) is defined as c and is used in our modified calculation method.

The proportion of oxidation and substitution reaction is calculated based on the results (Figs. 2–4) described so far. The results obtained by the Tabei et al. method and by our modified method are compared in Fig. 5. With the former method the evaluation was based only on the amount of chloride produced in the C-stage liquor during chlorination. According to their method, the value a is used as y in the calculation formula described above. The results obtained by this conventional method are expressed as calculation 1

in Fig. 5. On the other hand, the modified method developed in this study employs $b + c$ as the value y in the calculation formula. The results obtained by our modified method are described as calculation 2 in Fig. 5.

Obviously there is a large difference between the results obtained by the two calculation methods, as shown in Fig. 5. The proportion of oxidation during chlorine bleaching should be properly estimated to make the first step toward learning the main reaction responsible for delignification. As mentioned earlier, the substitution reaction consumes 1 mol of chlorine to form 1 mol of chloride, whereas the oxidation reaction consumes 1 mol of chlorine to form 2 mol of chloride. Some organically bound chlorine atoms that are labile to alkali treatment to form chloride are left out of the account according to the conventional method (calculation 1). It is clear that the proportion of the oxidation reaction has been extremely underestimated. The result obtained by our modified method (calculation 2) proved that when 0.15 of chlorine multiple was employed, about 50%–75% of chlorine was consumed by the oxidation reaction during

chlorine bleaching of hardwood kraft pulp, depending on the reaction condition of the chlorination. We can say with fair certainty that oxidation plays a much more important role than has been assumed so far.

On the basis of the amount of chlorine consumed by oxidation reaction (calculation 2, Fig. 5), it is possible to calculate how many electrons were abstracted from one phenylpropane unit of lignin structure. When the equivalent molecular weight of lignin (EMW) is assumed to be 200, it was found that approximately 3.0–4.4 electrons were abstracted from one lignin structural unit during chlorine bleaching of hardwood kraft pulp, depending on the reaction condition of the chlorination (Fig. 6). It should be noted that no fewer than three electrons were abstracted from one lignin unit even under a reaction condition not favorable to the oxidation reaction. Because four-electron abstraction from one aromatic nucleus corresponds to a ring opening reaction, this result provides additional evidence for extensive oxidation during the chlorine bleaching process.⁸

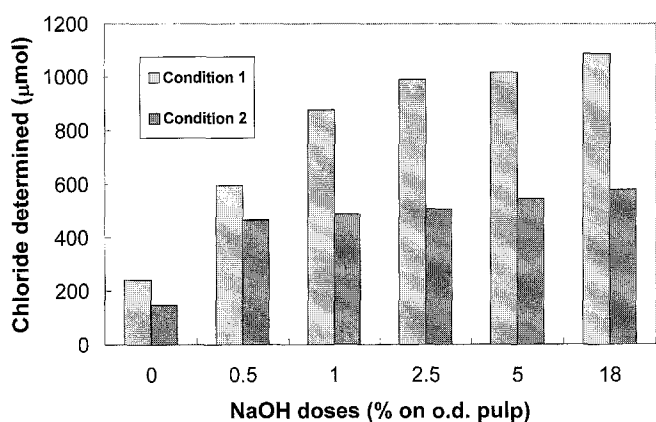


Fig. 4. Liberation of chloride from chlorinated pulp by 70°C alkali treatment

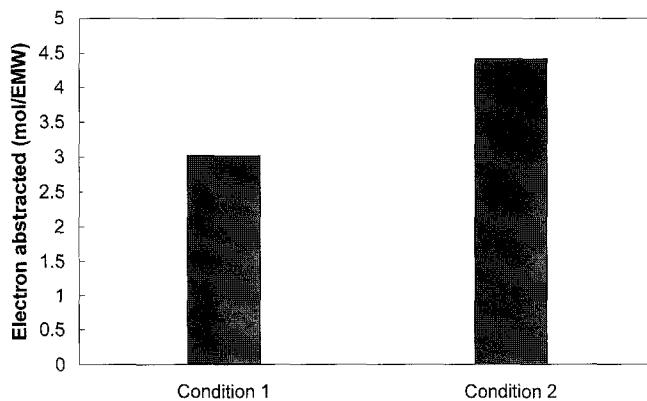
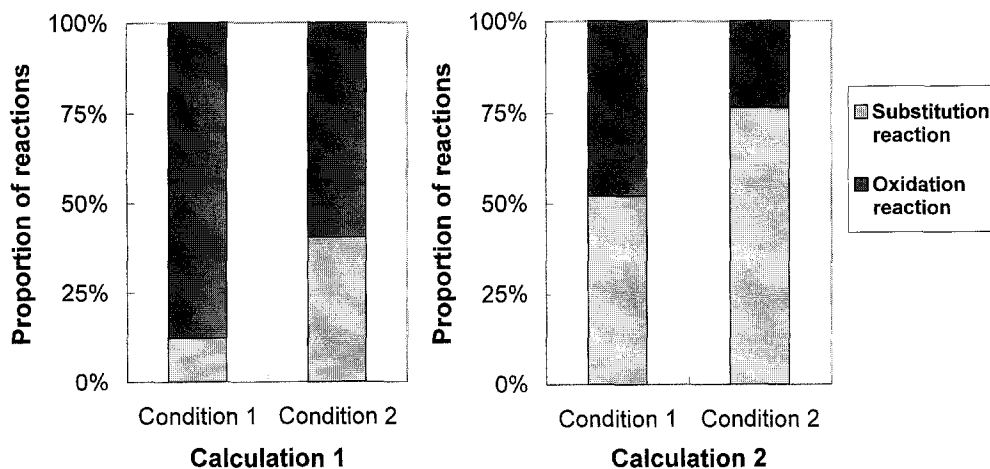


Fig. 6. Extent of oxidation expressed as the number of electrons abstracted from one phenylpropane unit after C- and E-stage. EMW, equivalent molecular weight

Fig. 5. Contribution of chlorine oxidation calculated by two methods



References

1. Rydholm SA (1965) Pulping processes. Wiley-Interscience, New York, pp 916–939
2. Giertz HW (1951) Developments in bleaching processes. *Tappi* 34(5):209–215
3. Grangaard DH (1956) Bleaching. I. The chlorination of pulp. *Tappi* 39(5):270–276
4. Tabei K, Kaneko Y, Akiyama T, Ueno T (1980) Studies on bleaching of pulps. Part 1. The oxidation reaction and the substitution reaction in chlorine treatment (in Japanese). *Jpn Tappi J* 34(9):621–628
5. Shintani H, Matsumoto Y, Ishizu A, Meshitsuka G (1994) Formation characteristics of chloroorganics from hardwood kraft pulp during chlorine bleaching. *Seni Gakkaishi* 50:587–592
6. Migita N, Nakano J, Ishizu A (1955) Studies on lignin. XXIV. On the chlorination of lignin (in Japanese). *Mokuzai Gakkaishi* 1:55–59
7. Shintani H, Matsumoto Y, Meshitsuka G (1996) The unsuitability of AOX as a measure of the organic chlorine content of C-stage effluents. *J Pulp Paper Sci* 22(10):J372–J375
8. Shintani H, Matsumoto Y, Meshitsuka G (1995) Structure of high molecular weight chlorolignin produced by chlorine bleaching. In: *Proceedings of 8th ISWPC (vol II)*, pp 309–314