Installing Ozone Bleaching and Hot Acid Treatment at NPI Mills

Shunichiro Uno* and Takeshi Iimori†

*Researcher, Nippon Paper Industries, Co, Ltd.,
5-21-1 Oji, Kita-ku, Tokyo, Japan
0990186@np-g.com
†Ph.D, Research Manager, Nippon Paper Industries, Co, Ltd.,
0089010@np-g.com

ABSTRACT

Nippon Paper Industries, Co., Ltd. declared conversion of all the bleaching process to ECF, and most of the production had converted by now. To reduce ECF bleaching cost, we found that depending on electricity supply condition of the mill, utilization of ozone bleaching could be very effective. In addition, hot acid treatment of unbleached pulp also seemed to be effective for hardwood. In this study, several conditions for each technology were examined with the pulps from our own mills to reduce bleaching cost and to keep fiber quality acceptable level.

In hot acid treatment study, with mild conditions (temperature lower than 90℃), sufficient reduction in Kappa number and hexenuronic acids content of the pulp were observed, while pulp viscosity was maintained. Moreover, to maintain strength of bleached pulp that subjected both to ozone bleaching and hot acid treatment, recommended Kappa number after ozone bleaching was more than 3.

Based on these findings, two of our mills had installed medium-consistency ozone bleaching facilities and three mills installed hot acid treatment. Especially in Yatsushiro mill, both were installed in one bleaching line (A-ZD-E/P-D sequence), and running successfully.

INTRODUCTION

With rising concern over the environmental issues, most of the Japanese kraft pulp bleaching processes have been converted or converting to ECF. Nippon Paper Industries, Co., Ltd. declared conversion of all the bleaching process to ECF, and most of the production had already been converted by now.

The largest problem we have faced during the conversion was the increased cost for bleaching chemicals, especially, chlorine dioxide. Japanese pulp mills depends on imported chlorate to generate chlorine dioxide and some mills still have old facilities.

To reduce dosage of chlorine dioxide to lower pulp production cost, use of ozone found to be effective, especially for the mills that has ability to supply self-generated electricity to ozone production.

In addition, hot acid treatment of unbleached pulp seemed to be another way to decrease chemical dosage. The treatment can remove hexenuronic acids, which consumes bleaching agents[(1),(2),(3),(4)].

The conditions for ozone bleaching and hot acid treatment had carefully studied by several researchers. The aim of our study is to find practical conditions to reduce bleaching cost and to keep fiber quality with the pulps from our own mills.

Ozone bleaching

Numerous studies about ozone bleaching were already published[(5),(6),(7)]. Moreover, we already presented the part of our results elsewhere, in which we clearly indicated observed strength drop of medium-consistency ozone bleached pulp was caused by the high-intensity mixing under acidic condition of laboratory mixer[(8)]. In Figure 1, fiber strength of conventional bleached pulp (◇), conventional bleached pulp (◆)followed by acidic mixing and ozone bleached pulp (▲) were shown.

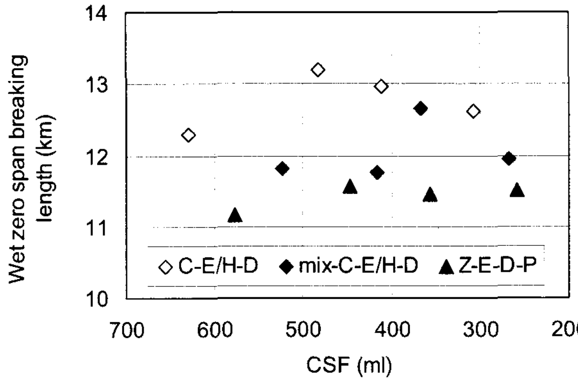

Fig. 1 Fiber strength of bleached pulps

Several studies showed that the strength drop caused by ozone strongly related to the lower Kappa number of ozone-bleached pulp. In our earlier results, ozone dosage was limited to 5-6kg/ADTP for medium-consistency bleaching, so that such relationship could not be observed.

However, before we install hot acid treatment and medium-consistency ozone bleaching at the same bleaching line, strength drop related to lower Kappa number of ozone-bleached pulp needed to be examined.

Hot acid treatment

Hot acid treatment of unbleached pulp thought to be effective to lower chemical cost by removing hexenuronic acids and lowering Kappa number of the pulp. The conditions such as over 90℃ of temperature were seemed too strong to maintain pulp strength or viscosity. Furthermore, such high temperature requires too much steam. Therefore, we decided to investigate the effect of milder condition (temperature blow 90℃).

EXPERIMENTS

Samples

Each sample was prepared from oxygen delignificated, hardwood kraft pulp from each mill. Kappa number or other measured values were shown in each experiment.

Analysis

Hexenuronic acids content were measured by acidic decomposing method[9]. Other pulp analyses were based on ISO standards.

Hot acid treatment

For hot acid treatment, two different experiments were designed. In experiment #1, effect of conditions on pulp viscosity and Kappa number were examined. In experiment #2 the relationship between Kappa number reduction and Hexeuronic acids was investigated. In addition, with Experiment #2, two different samples were subjected for the treatment.

Method of hot acid treatment in this study was same in every experiment. 10% consistency of pulps were adjusted to certain pH and put in plastic bags. Then it kneaded well by hand. Temperature raised and kept by steam autoclave. After certain minutes of treatment, samples were removed from the bag, washed well and subjected to the analysis.

Kappa number was determined for the experiment #1, #2, viscosity for #1, hexenuronic acids content for #2.

Details of conditions were shown in Table 1.

Table 1. Conditions for hot acid treatment

Experiment #1	
Reaction time (min.)	120
Temperature (℃)	80, 85, 90
pH	1.5, 2.3, 3.0, 3.5
Kappa No. of sample	11.3
Viscosity (cP)	24.4
Experiment #2	
Reaction time (min.)	120
Temperature (℃)	75, 80, 83, 85
pH	2.0, 2.3, 3.0
Kappa No. of sample A	7.8
Hexenuronic acids content of sample A (mmol/kg pulp)	52.3
Kappa No. of sample B	8.9
Hexenuronic acids content of sample B (mmol/kg pulp)	55.7

Hot acid treatment plus ozone bleaching

Fully bleached A-Z(E/P)-D pulps were prepared, where A for acid treatment, Z for medium-consistency ozone bleaching, E/P for alkali extraction with hydrogen peroxide bleaching, D for chlorine dioxide bleaching and - for washing. From those bleached pulps, handsheets were made and strength of the sheets was measured.

To observe the effect of lower Kappa number of ozone-bleached pulp, conditions for acid treatment were changed, when ozone dosage was kept constant (5kg/ADTP). CRS laboratory mixer was used for medium-consistency ozone bleaching. Procedure for the acid treatment was shown above. Other bleaching was carried out in plastic bags and water bath.

To compare with ECF pulp, conventional bleached pulp were also prepared, the bleaching sequence was C/D-E/P-D, where C/D for elementary chlorine with chlorine dioxide bleaching. To prevent the effect of laboratory mixer, pulps for conventional bleaching were also subjected to acidic mixing by CRS mixer with no ozone gas addition.

Pulp for these bleaching was oxygen delignificated, Kappa of 10.4, Brightness of 45.9%, and the details of conditions for acidic treatment shown in Table 2. Bleaching results and conditions of ECF and conventional bleaching shown in Appendix.

Table 2. Hot acid treatment for ECF bleaching

ID	Temp(℃)	Time(min.)	pH
A1	85	120	3.0
A2	85	120	3.5
A3	85	20	3.0
A4	85	60	3.0
A5	60	20	3.0
A6	85	120	4.0

RESULTS AND DISCUSSION

Hot acid treatment

Kappa number of acid treated pulps in experiment #1 were shown in Fig. 2. Kappa number of pulps were decreased when the temperature raised to 85℃ from 80℃. In addition, when pH of treatment was lowered, Kappa number was also decreased. Figure 3. shows the viscosity of treated pulps. Significant drop of pulp viscosity was observed when the pH of the treatment was decreased to 2. The pulp treated at 85℃ showed higher viscosity than the one treated at 90℃.

From these findings, it was concluded that the treatment at 85℃ and pH of 3.0 is the most favorable condition to achieve higher Kappa reduction and lower viscosity drop for acid treatment.

In addition, with the pulps treated at temperature of 80℃, significant reduction of Kappa number was still observed (2 to 3 point). In experiment #2, the relationship between reduction of Kappa number and hexenuronic acids content was investigated, including those "mild" conditions (Figure 4). From the results, linear relationship was observed with whole range of conditions, 75 to 85℃ of temperature, 2.0 to 3.0 of pH. It was suggested that the mechanism of Kappa reduction were strongly related to the removal of hexenuronic acids.

Removal of hexenuronic acids were supposed to prevent brightness reversion of bleached pulp[3),(10)]. Thus, the application of acid treatment at lower temperature may have some effect on product quality through partial removal of hexenuronic acids.

Fig.2 Treatment conditions and Kappa number

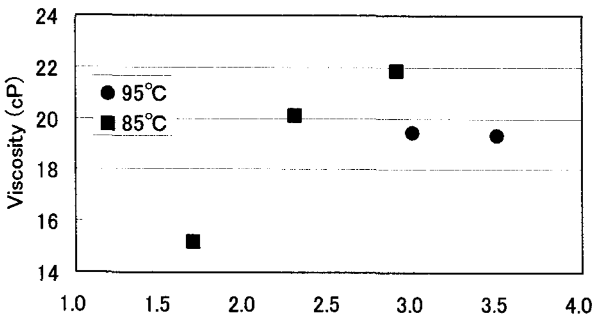

Fig.3 Viscosity of acid treated pulps

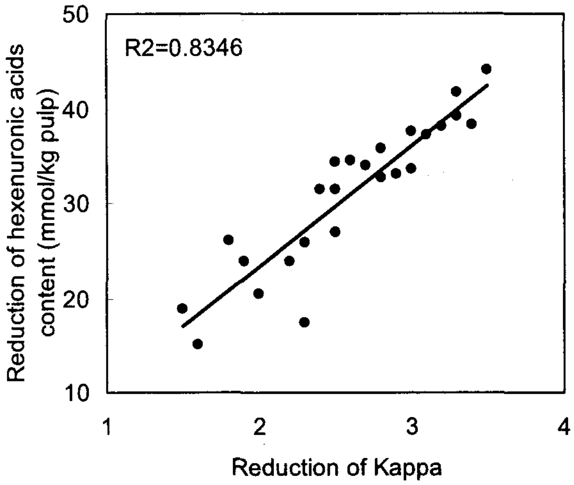

Fig. 4 Relationship between the reduction of Kappa and hexenuronic acids content

Hot acid treatment plus ozone bleaching

Kappa number of acid treated pulps was shown in Table 3. The range of Kappa number after ozone bleaching was 1.8 to 3.8. This was lower than our earlier ozone bleaching study.

In this experiment, the increased Kappa number reduction with lower pH was observed from acid treatment A1,A2 and A6. These results agrees to the result shown in Fig. 2.

With condition A5, small amount of reduction of Kappa number was observed at temperature of 60℃. This may caused by washing during treatment.

Table 3. Result of hot acid treatment for ECF bleaching

ID	Kappa after acid treatment	Kappa reduction	Kappa after A-Z bleacing
A1	5.2	5.2	2.1
A2	5.5	4.9	2.0
A3	9.0	1.4	3.3
A4	7.3	3.1	2.5
A5	9.7	0.7	3.8
A6	6.1	4.3	1.8

*Kappa number of pulp before the treatment was 10.4

Tear index of the fully bleached pulps were shown in Fig. 5. This figure suggests that the strength of fully bleached and beaten (by PFI mill) pulps at CSF of 400mL related to the Kappa number after ozone bleaching. Dotted line shows the strength of conventional bleached pulp after laboratory acidic mixing. Sudden drop of tear index was observed when the Kappa number after ozone bleaching was decreased to 2. However the Kappa was kept over that point, strength of the ECF bleached pulps were same as the conventional bleached pulps.

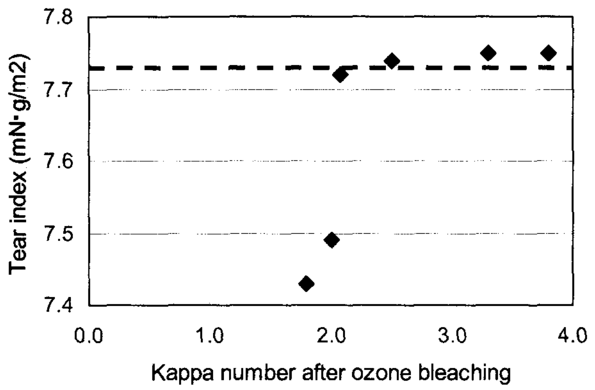

Fig.5 Tear index of A-Z ECF bleached pulp
(Doted line: conventional bleaching)

Other strength values did not show any drop (ex. Fig. 6). However, to keep the quality of products, it seemed better to keep the Kappa number over 3.

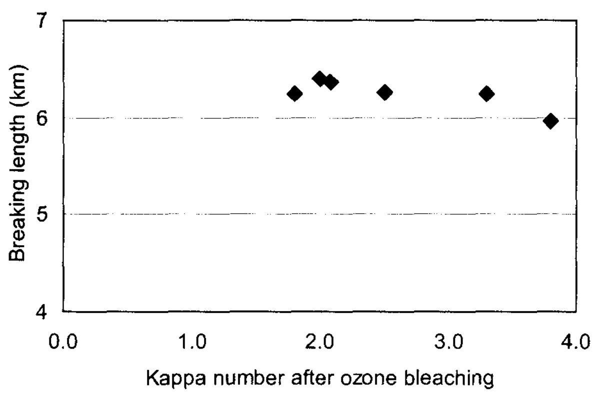

Fig.6 Breaking length of A-Z ECF bleached pulp

One of the major reasons for lower selectivity of ozone bleaching caused by the hydroxyl radicals formed by the reaction between ozone and phenolic hydroxyl groups[(11),(12)] of lignin. During the hot acid treatment, those groups of lignin increase[(13)]. Thus, in A-Z bleaching sequence, increased phenolic hydroxyl groups by hot acid treatment may cause decreased selectivity (lower viscosity or pulp strength for the Kappa number) in ozone bleaching.

However, in this study, selectivity of ozone bleaching seemed similar to other studies.

CONCLUSIONS

Conditions for hot acid treatment of hard wood oxygen delignificated pulp were examined. Sufficient reduction in Kappa number and hexenuronic acids content of the pulp were observed even when the treatment at mild conditions (temperature lower than 90℃), while pulp viscosity was maintained.

Moreover, strength of bleached pulp subjected both to ozone bleaching and hot acid treatment was dropped when Kappa number of ozone bleached pulp decreased to 2. Therefore the recommended Kappa number of ozone bleached pulp was more than 3.

Based on these findings, A-ZD-E/P-D sequence ECF bleaching line was installed at Yatsushiro mill, in 2003. Up to this date, the mill has been successfully producing ECF bleached pulp with this sequence. After Yatsushiro mill, we had installed hot acid treatments at other two mills.

REFERENCES

(1) Li, J. and Gellerstedt, G., The contribution to kappa number from hexenuronic acid groups in pulp xylan, Carbohydrate Research 302:213-218(1997).

(2) Teleman, A., Hausalo, T., Tenkanen, M. and Vuorinen, T., Identification of the acidic degradation products of hexeneuronic acid and characterisation of hexenuronic acid-substituted xylooligosaccharides by NMR spectroscopy, Carbohydrate Research 280:197-208(1996).

(3) Vuorinen, T., Fagerström, P., Buchert, J., Tenkanen, M. and Teleman, A., Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps, Journal of Pulp and Paper Science, 25(5):155-162(1999).

(4) Ikeda, T., Hosoya, S., Tomimura, Y., Magara, K. and Ishihara, M., Contribution of LCC bond cleavage to the kappa number reduction of kraft pulp, Proc. 9th International Symposium on Wood and Pulping Chemistry (ISWPC), J5-1(1997).

(5) Liebergott, N., van Lierop, B. and Skothos, A., The use of Ozone in Bleaching pulps, Proc. TAPPI Pulping Conf., 1-23 (1991).

(6) Magara, K., Takano, I., and Hosoya, S., Ozone Bleaching of Kraft Pulp, Japan TAPPI Journal 51(12):110-118(1997).

(7) Fuhrmann, A., Ozone bleaching parameters - Summary of the effects on the bleaching result, Proc. 13th International Symposium on Wood, Fiber and Pulping Chemistry (ISWFPC), 3D22(2005).

(8) Uno, S., Iimori, T., and Miyanishi, T., A study of the strength of medium-consistency ozone bleached pulp, Proc. 71th Pulp and Paper Research Conference (Japan TAPPI)(2004).
(9) Gellerstedt, G. and Li, J., An HPLC method for the quantitative determination of hexeneuronic acid groups in chemical pulps, Carbohydrate Research 294:41-51(1996).
(10) Jiang, Z., van Lierop, B. and Berry, R., Hexenuronic acid groups in pulping and bleaching chemistry, TAPPI Journal 83(1):167-175(2000).
(11) Jacobson, B., Lindblad, P-O. and Nilvebrant, N-O., Lignin reaction affect the attack of ozone on carbohydrates, Proc. International Pulp Bleaching Conference, SPCI, 45-58(1991).
(12) Magara, K., Ikeda, T., Tomimura, Y. and Hosoya, S., Accelerated degradation of cellulose by lignin during ozonolysis, Mokuzai Gakkaishi,40(10):1152-1154(1994).
(13) Gellerstedt, G. and Lindfors, E-L., Hydrophilic groups in lignin after oxygen bleaching, TAPPI Journal 70(6):119-122(1987).

APPENDIX

Bleaching conditions for ECF bleaching

Bleaching conditions for ECF bleaching were shown in Table 4, and brightness of bleached pulps were in Table 5. Chlorine dioxide dosage at the last bleaching stage were altered within the range of 0.2 to 0.6% to a certain brightness of bleached pulp.

Table 4 Conditions for ECF bleaching

Z	
Consistency of pulp (%)	10
Temperature (℃)	60
Reaction time (min)	10
pH (after bleaching)	3.0
E/P	
Consistency of pulp (%)	10
Temperature (℃)	70
Reaction time (min)	75
Hydrogen peroxide dosage (%)	0.4
pH (after reaction)	10.3–9.7
D	
Consistency of pulp (%)	10
Temperature (℃)	70
Reaction time (min)	150

Table 5 Brightness of ECF bleached pulps

ID	After Z	After D
A1	65.4	87.2
A2	66.0	87.3
A3	63.4	85.2
A4	65.0	87.0
A5	62.3	84.3
A6	67.3	88.1

Bleaching conditions for conventional bleaching

Bleaching conditions for conventional bleaching and brightness of bleached pulp was shown Table 6.

Table 6 Conditions for conventional bleaching

C/D	
Consistency of pulp (%)	10
Temperature (℃)	60
Reaction time (min)	20
ClO2 dosage (%)	0.14
Cl2 dosage (%)	1.5
E/P	
Consistency of pulp (%)	10
Temperature (℃)	70
Reaction time (min)	75
Hydrogen peroxide dosage (%)	0.22
pH (after reaction)	9.7
D	
Consistency of pulp (%)	10
Temperature (℃)	70
Reaction time (min)	150
ClO2 dosage (%)	0.44
Bleached pulp	
Brightness (%)	86.1