Reduction of AOX formation by intrastage washing

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ABSTRACT: It is accepted practice to add chlorine dioxide shortly before chlorine in a pulp chlorination stage. In the present study, by applying ClO_2 at a kappa factor of 0.11 followed by a washing step (called intrastage washing) and then a minor chlorine treatment, a threefold reduction in AOX formation was achieved compared to conventional bleaching; the same degree of delignification as found in a standard $D_{50}C_{50}$ operation was maintained.

In order to facilitate introduction in a commercial bleach plant, we investigated whether chlorine dioxide treatment time before the intrastage washing can be decreased. An optimal time of about 10 min was found when the initial pH of the ClO_2 treatment is reduced to about 2. With these process modifications, and ClO_2 and chlorine charges of 1.20% and 1.53%, respectively, a kraft black spruce pulp with a kappa number of about 30 can be bleached to a kappa number below 4 after caustic extraction, with a total AOX production of less than 1.5 kg/ton for the untreated combined chlorination and extraction effluents.

KEYWORDS: Adsorbable organic halogen, bleaching, chlorine compounds, chlorine dioxide, kappa number, multistage process, washing.

The organochlorine compounds released from the pulp bleaching process are collectively identified as AOX (adsorbable organic halides). The environmental impact of these chlorinated organics has become an increasing concern in recent years. Demonstrated technologies that decrease the formation of organochlorines when producing fully bleached pulp include (a) decreasing the lignin content of pulp entering the bleach plant by extended delignification *(1)* and/or oxygen delignification *(2)*, (b) increasing replacement of chlorine by chlorine dioxide *(3)*, (c) reducing the kappa factor combined with a peroxide-reinforced oxidative extraction stage (E_{op}) *(4)*, and (d) wastewater treatment of the bleach plant effluent *(5)*.

Ni *et al. (6)* show that a charge of 1.20% chlorine dioxide (ClO_2) to a kappa no. 28.7 unbleached kraft pulp (equivalent to a kappa factor of 0.11) results in a decrease to about kappa no. 15 at an AOX content in the effluent of only 0.34 kg/ton pulp. When the pulp suspension is subsequently contacted with chlorine, as is typically done in an industrial DC chlorination stage, it is likely that the dissolved lignin generated during the chlorine dioxide treatment will compete with the residual lignin in the pulp for reaction with the charged chlorine. This not only results in less efficient use of chlorine for delignification, but also in additional AOX formation. Thus, by introducing a washing stage between the consecutive additions of ClO_2 and chlorine (Cl_2), it is expected that the delignification efficiency of chlorine will be increased while the formation of organically bound chlorine will be decreased. The objective of this paper is to explore the possibility of reducing AOX formation by introducing a washing stage between

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I. The effect of intrastage washing on AOX formation

Test	Cl_2 kappa factor	Kappa number C	Kappa number E	Effluent AOX, kg/ton pulp C	Effluent AOX, kg/ton pulp E	NaOH charge, %	Viscosity D/C E, mPa·s	Total AOX D+C+E, kg/ton	Total kappa factor D+C
1	0.053	7.2	3.5	0.92	0.28	2.55	26.1	1.52	0.163
2	0.037	9.0	4.2	0.55	0.21	2.29	26.5	1.08	0.147
3	0.053	11.6	6.0	1.53*	0.48	2.57	-	2.01	0.163
4	0.110	6.7	3.4	4.03*	0.51	3.47	-	4.54	0.220

*AOX of the combined D/C stage

the consecutive additions of chlorine dioxide and chlorine (called intrastage washing).

Results and discussion

Intrastage washing

The intrastage washing experiments consisted of treating a kappa no. 28.7 kraft pulp with a ClO_2 charge of 1.20% on pulp (kappa factor of 0.11) at 45°C and 2% consistency for 45 min. After 45 min, both the ClO_2 and the generated ClO_2^- were completely consumed. The kappa number and organically bound chlorine content of the chlorinated pulp were 15.8 and 0.50 kg/ton pulp, respectively, while the AOX content of the filtrate was 0.32 kg/ton pulp. After being thoroughly washed, the pulp was further treated with different charges of chlorine; chlorination conditions were 45°C, 1% consistency, and 45 min contact time. The kappa number of the chlorine-treated and washed pulp as well as the AOX content of the chlorination filtrate were determined. Subsequently, the pulp was extracted with caustic soda. The NaOH charge was 0.55 times the sum of the active chlorine charges as chlorine dioxide and chlorine added in the two stages. Kappa number after extraction, viscosity of the extracted pulp, and AOX content of the extraction filtrate were measured. The analysis results for two experiments with different chlorine charges are identified in **Table I** as Tests 1 and 2.

II. Organically bound chlorine formation and kappa number after the D stage. Consistency: 2%; temp.: 45°C; time: 45 min; initial pH: 3.0; final pH: 2.5.

Test	Charge, % on pulp Chlorite	Charge, % on pulp ClO_2	Charge, % on pulp Total	Org. chlorine, kg/ton AOX	Org. chlorine, kg/ton D pulp	D Kappa no.
A	0.060	1.140	1.20	0.22	0.35	14.6
B	0.084	1.596	1.68	0.35	0.42	12.0

For comparison, two conventional D/C E bleaching experiments are also included in Table I as Tests 3 and 4. In these tests, pure chlorine water is added 1 min after adding chlorine dioxide to the unbleached pulp without an intrastage washing step. The ClO_2 and Cl_2 charges in Test 3 are 1.20% and 1.52% (on o.d. pulp), respectively. In Test 4, the ClO_2 and Cl_2 charges are 1.20% and 3.16%, respectively. Comparing Test 3 with Test 1 shows that intrastage washing reduces the combined AOX production of the D/C E stages from 2.01 to 1.52 kg/ton, respectively, while the CE kappa numbers are 6.0 and 3.5, respectively. There is less delignification in Test 3 because part of the charged chlorine reacts with the dissolved lignin generated during the chlorine dioxide treatment rather than with the residual lignin in the pulp. Since the CE kappa number of Test 3 is rather high, a fairer evaluation of intrastage washing effectiveness is obtained by comparing Test 1 with Test 4; they have almost the same CE kappa numbers (3.4 and 3.5, respectively). In Test 4, the combined effect of the higher total active chlorine charge and the absence of intrastage washing leads to a combined AOX production of the D/C and E stages of 4.54 kg/ton o.d. pulp, three times larger than that obtained in Test 1. The lower AOX formation with intrastage washing is obviously due to the lower chlorine charge and the removal of dissolved lignin generated as a result of delignification by ClO_2.

Next a series of bleaching experiments with intrastage washing was performed. The objective was to obtain a well delignified semibleached pulp (kappa no. < 4) at a total AOX production (i.e., the sum of D, C, and E effluents) of less than 1.5 kg/ton pulp. Variables were the charges of chlorine dioxide and chlorine. Five percent of the chlorine dioxide in the D stage of the D/C sequence with intrastage washing was substituted with chlorite to further reduce the formation of AOX *(7)*. The results for two different chlorine dioxide charges are given in **Table II.**

III. AOX formation with intrastage washing

Test	Cl_2 charge, %	Kappa number C	Kappa number E	Effluent AOX, kg/ton pulp C	Effluent AOX, kg/ton pulp E	NaOH charge, %	Viscosity D/C E, mPa·s	Total AOX D+C+E, kg/ton	Total kappa factor D+C
A1	1.53	6.6	3.5	0.95	0.27	2.57	28.1	1.44	0.163
A2	1.05	8.1	3.7	0.44	0.17	2.31	27.5	0.83	0.147
B1	1.00	6.4	3.4	0.51	0.21	2.98	26.8	1.07	0.189
B2	0.70	7.6	3.8	0.38	0.13	2.82	26.4	0.86	0.178

IV. The effect of NaOH charge on E kappa number during caustic extraction of the pulp obtained from the intrastage washing technique

NaOH, %	Extracted kappa no.	AOX in E effluent, kg/ton pulp	Final pH
0.586	4.9	0.39	10.1
0.840	4.3	0.40	11.1
1.285	3.9	0.42	11.8
1.800	3.7	0.42	12.0
2.570	3.6	0.25	12.3

The kappa factors for Tests A and B are 0.11 and 0.154, respectively. Some HCl was added to the mixture of chlorine dioxide and chlorite, giving a pH of 2.5 after 45 min of reaction with ClO_2.

The chlorine-dioxide-treated and washed pulp Samples A and B were then subjected to a mixture of chlorine and chlorine dioxide (ClO_2 substitution level of 15%). Subsequently the pulps were extracted with caustic soda using the same standard conditions as used for the experiments shown in Table I. The results are shown in **Table III**, with Tests A1, A2, B1, and B2 performed on the chlorine-dioxide-treated samples listed as A and B, respectively, in Table II.

The results in Table III show that a total AOX production of less than 1.5 kg/o.d. ton pulp can be obtained with the intrastage washing technique after applying 1.20% chlorine dioxide on pulp (corresponding to a kappa factor of 0.11) while at the same time producing a well delignified pulp after caustic extraction. Further increase in the ClO_2 charge, from 1.20% to 1.68%, decreases the AOX production to only about 1 kg/ton at the expense of a slightly higher total kappa factor.

Effect of intrastage washing on caustic extraction

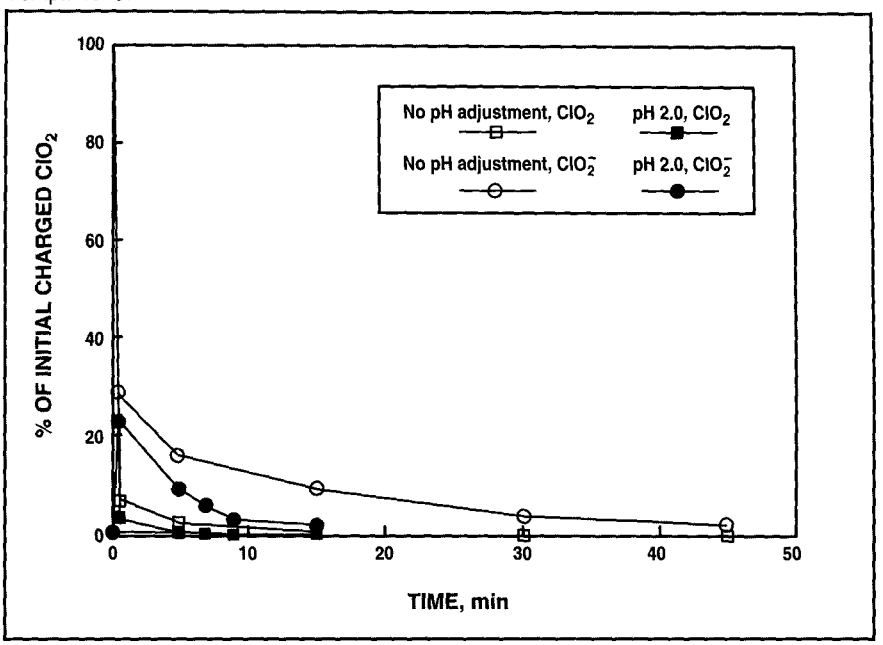
Because the total kappa factor can be reduced significantly below the traditional value of 0.22 with intrastage washing (see Table III), we investigated whether a similar charge reduction can be realized for caustic in the extraction stage. The pulp was prepared using a ClO_2 charge of 1.20% [with an addition of 0.03% H_2O_2 on pulp for AOX reduction *(7)*] for 30 min at 45°C and an initial pH of 3.0. Intrastage washing was then followed by chlorination at a total active chlorine charge of 1.53% (ClO_2 substitution level of 20%) for 30 min at 45°C. In the subsequent extraction stage, the sodium hydroxide charge was varied from 0.586% to 2.57%. The other extraction conditions are 70°C for 1 hour at 10% consistency.

The kappa number after extraction, the AOX content in the extraction (E) filtrate, and the final pH in the extraction stage are shown in **Table IV**. The final pH is higher than 11 when the alkali charge is greater than or equal to 0.84% [i.e., when the alkali charge is equal to 0.55 times the chlorination stage charge of 1.53%, as is recommended for conventional chlorination *(8)*]. A final pH above 11 after 1 hour extraction is generally considered sufficient for efficient alkali extraction. Note also that an alkali charge of 2.57% (0.55 times the combined active chlorine charge of the D and C stages) results in significant dechlorination of the dissolved organically bound chlorine by the excess alkali in the E-stage effluent. More importantly, however, the present results show that, with intrastage washing, an NaOH charge of 1.285% is sufficient to reach an extracted kappa number of less than 4. This caustic charge should be compared to a charge of 3.47%, which is recommended for extraction of the present kappa no. 28.7 pulp after a conventional chlorine bleaching stage (28.7 x 0.22 x 0.55 = 3.47%).

For comparison, two conventional D/C E bleaching experiments were also performed with a caustic charge of 1.285%. In these tests, 1.53% and 3.16% (on pulp) of chlorine, respectively, was added 1 min after mixing the unbleached pulp with pure chlorine dioxide at a charge of 1.20% (on pulp). Then, after washing, both pulps were extracted with caustic

soda at a charge of 1.285% but otherwise at standard extraction conditions. The kappa factors of these two tests were 0.163 and 0.22, respectively. A comparison of the kappa number and final pH after caustic extraction of these two tests with those of the corresponding intrastage washing experiment in **Table V** shows that a caustic charge of 1.285% is insufficient for conventional bleaching. Therefore, by introducing a washing stage between the chlorine dioxide treatment and chlorine addition, a significant caustic savings can be realized in addition to reducing the amount of AOX produced in the bleaching process and decreasing the chlorine requirement. In a commercial bleach plant, because of carryover to the extraction stage, more than 1.285% caustic is probably required in the subsequent caustic extraction stage after applying the intrastage washing technique. However, we expect that large caustic savings could still be achieved in comparison with the normal caustic requirement in conventional bleaching.

1. Development of residual ClO_2^- and ClO_2 during bleaching of kraft pulp at an initial ClO_2 charge of 1.20% with and without pH adjustment. Consistency: 1%; ClO_2 charge: 1.2%; Temp.: 45°C.



V. Comparison of intrastage-washed and conventionally D/C-processed pulp. Chlorine dioxide charge: 1.2%; NaOH charge: 1.285%.

Test	Intrastage washing	Chlorine charge, %	Total kappa factor	Kappa no. after E	Final pH in E
1	No	1.53	0.163	7.3	10.9
2	No	3.16	0.220	4.2	10.8
3	Yes	1.53	0.163	3.9	11.8

Practical implementation of intrastage washing

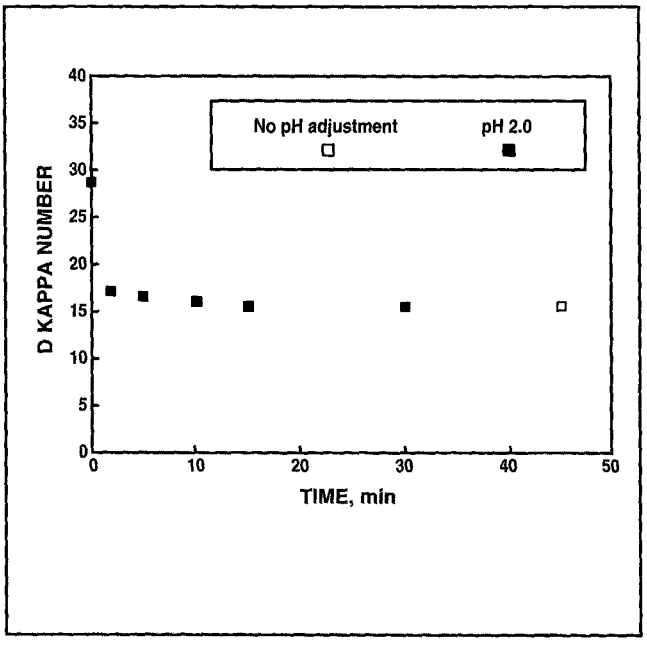
In the previous section, we showed that intrastage washing is beneficial from the AOX reduction and chemical savings standpoints. However, the 45-min duration of the D stage in the intrastage washing experiments requires the addition of another retention tower. In order to facilitate the industrial introduction of intrastage washing, it is of interest to investigate whether the reaction time of the chlorine dioxide treatment before intrastage washing can be decreased so that the ClO_2 treatment can be performed in a retention leg.

At a chlorine dioxide charge of 1.20% on pulp, we found that chlorine dioxide is completely consumed within 2 min *(6)*. This is in agreement with Histed *et al. (9)*, who found that ClO_2 is consumed within 2 min for a kappa factor of 0.19 and a ClO_2 substitution ratio of 50% at 30°C for a similar unbleached kraft pulp. However, a significant amount of residual chlorite still remains. Since chlorite can be converted into chlorine dioxide, an intrastage washing operation at this point would result in a loss of potential delignification. Thus, in order to decrease the D-stage time before intrastage washing, the conversion rate of chlorite to chlorine dioxide must be increased.

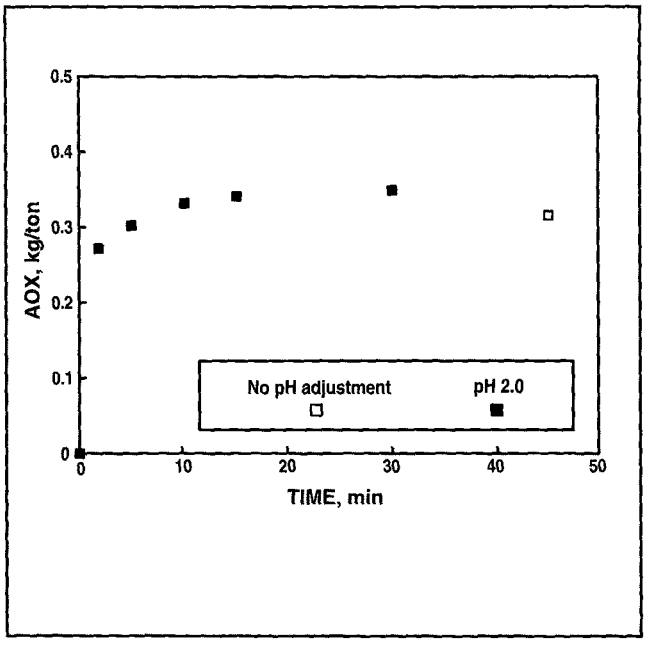
The formation rate of chlorine dioxide from chlorite can be enhanced by increasing the acidity *(10)*. **Figure 1** shows the chlorite and chlorine dioxide concentrations during ClO_2 treatment of the standard kraft pulp without initial pH adjustment and with initial pH adjustment to 2.0 by hydrochloric acid. The chlorite is essentially consumed at about 30 min and 10 min, respectively, with or without initial pH adjustment. This shows that the D-stage time before intrastage washing can be decreased to about 10 min by initial acidification.

The development of the D kappa number and AOX formation during the D stage at an initial pH of 2 are shown in **Figs. 2 and 3,** respectively. Also included are the corresponding values for the same pulp without pH adjustment after 45 min of reaction. These results show that, after 10 min at a pH of 2.0, the D kappa number and AOX formation have approached their respective plateau values, which are also close to the corre-

2. Development of the D kappa number in a D stage at an initial pH of 2. Consistency: 1%; ClO_2 charge: 1.2%; Temp.: 45°C.



3. Development of AOX formation in a D stage at an initial pH of 2. Consistency: 1%; ClO_2 charge: 1.2%; Temp.: 45°C.



sponding values obtained after 45 min without initial pH adjustment. Therefore, the benefits shown in the previous sections can also be obtained by performing the D stage in a retention leg (rather than a new tower), which provides a reaction time of about 10 min before application of intrastage washing. In practice, of course, one should use medium-consistency operation for the D stage rather than the 2% consistency used in the present experiments. The higher concentrations associated with medium-consistency operation will further increase the rate of chlorite consumption and thus the required ClO_2 reaction time in the retention leg.

Conclusions

The AOX formation during a conventional D/C stage can be decreased by decreasing the concentration of dissolved lignin before adding chlorine to the pulp. This can be accomplished by introducing a washing stage between the sequential additions of chlorine dioxide and chlorine. Introducing a washing step between chlorine dioxide treatment and chlorine addition in a conventional D/C bleaching sequence, with a ClO_2 charge corresponding to 50% ClO_2 substitution and a kappa factor of 0.22, reduces AOX formation by a factor of nearly three when compared at the same degree of delignification as in a conventional sequence.

Other advantages of introducing this intrastage washing step are a reduction in the chlorine charge by a factor of about two and significant savings in the caustic requirement of the extraction stage. The chlorine savings are the result of eliminating the further reaction of chlorine with dissolved lignin produced during ClO_2 delignification in a conventional D/C sequence. This also explains the large reduction in AOX formation with the intrastage washing technique. A pulp washer and a retention leg providing 10 min reaction time for the chlorine dioxide treatment are needed for practical implementation of the intrastage washing technique in a conventional D/C E sequence.

Experimental procedures

A kappa no. 28.7 kraft black spruce pulp was bleached with chlorine dioxide in a three-neck round bottom flask. The chlorine dioxide solution was added to 4 grams of pulp, which were well dispersed in deionized water by mechanical stirring. A high ClO_2 concentration was used, so the chlorine dioxide addition could be completed in about 5 seconds. After chlorine dioxide treatment, the pulp was thoroughly washed with a large amount of tap water, washed three times with distilled water in a British handsheet-making machine, and subsequently air dried. Chlorination was performed in the same reactor. First a specified amount of chlorine water was introduced by a pipette into the reactor. The required amount of pulp was then rapidly added to the reaction in the form of a concentrated suspension with a 50-mL open-end syringe. Before addition of the pulp, the chlorine concentration in the reactor was determined, and chlorine water and water were added so the desired chlorine concentration and consis-

tency would be obtained at the start of pulp chlorination. At specified times, a small amount of bleach liquor was removed from the pulp suspension for AOX analysis. The pulp was washed and made into a handsheet for further treatment or analysis.

Alkali extraction was performed at 10% consistency with the required amount of caustic at 70°C. After 1 hour, the extracted pulp was thoroughly washed, and the air-dried handsheets were saved for further analysis.

The AOX content of the filtrates was measured with a Dohrmann DX20 analyzer. The organically bound chlorine content of chlorine-dioxide-treated pulp was determined using the method described in Reference 6. The kappa number and viscosity were determined according to CPPA standard methods.

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