Modified chlorine dioxide delignification of softwood pulps for high brightness and ultra-low AOX

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ABSTRACT

In comparison to liquid-phase chlorine dioxide delignification, the gaseous chlorine dioxide delignification of softwood kraft and extended kraft pulps (kappa nos. 35–12) required only half the kappa factor (KF) to provide a given DE kappa number. The gaseous chlorine dioxide delignification is faster than the liquid-phase delignification and is completed in less than 5 min. The total AOX from D(gas)EDED bleaching of conventional kraft pulp (kappa nos. 30.0–35.0) to 88–90% ISO brightness was less than 1.30 kg/o.d. ton if the pulp was washed after D(gas) delignification but before alkaline extraction. Elimination of pulp washing between D(gas) delignification and alkaline extraction resulted in AOX discharge of about 0.65 kg/o.d. ton and 0.50 kg/o.d. ton for conventional kraft pulp of kappa no. 35, and PS-AQ/O_2 pulp of kappa no. 12.0, respectively. An outfall AOX discharge of less than 0.30 kg/o.d. ton of pulp is possible if the effluent is subjected to secondary treatment. Compared at constant brightness, the final pulp viscosity from gaseous chlorine dioxide delignification and bleaching was equal to liquid-phase chlorine dioxide delignification and bleaching.

ENVIRONMENTAL AND MARKET pressures are forcing many bleach plants to eliminate the use of elemental chlorine in pulp bleaching. An integral part of elemental chlorine-free (ECF) bleaching is the total substitution of chlorine by chlorine dioxide at the first stage (D0 delignification). Research and mill trials have shown a substantial decrease in the discharge of adsorbable organic halides (AOX) when switching to D0 delignification *(1–8)*. The D0 delignification of softwood kraft pulp (kappa no. 30.0) resulted in a final pulp of 88–90% ISO brightness with an AOX discharge of about 1.80 kg/air-dried (a.d.) ton of pulp *(9)*. To achieve additional AOX decrease, it is imperative to bleach low-kappa pulps *(10)*. AOX discharge of less than 1.0 kg/a.d. ton of pulp is possible by the DO delignification and EOP extraction of oxygen-prebleached pulp *(1)*. The advantage of DO delignification is its efficiency in lowering the concentration of lipophilic phenolic compounds, which substantially decrease the toxicity of the effluent *(3, 4, 8, 11–15)*. At a chlorine dioxide substitution of 70% and above at the first stage, the 2,3,7,8-TCDD and 2,3,7,8-TCDF in the effluent become nondeduct *(14, 15)*.

Chlorine dioxide delignification differs from chlorine dioxide bleaching and requires different operating conditions *(1, 2, 6–8)*. Unlike chlorine, chlorine dioxide is not an efficient delignifying chemical. To compensate for this, an increase in chlorine dioxide charge (on an equivalent chlorine basis) is necessary. Therefore, ECF pulp bleaching requires a higher kappa factor (KF) application at the first stage than for chlorination of pulp. Since chlorine dioxide is more expensive than chlorine, an increase in chlorine dioxide use due to high KF demand increases the cost of bleaching pulp to a certain final brightness.

In DO pulp delignification, the formation of chlorate (ClO_3^-) represents a loss in the delignification power of ClO_2 *(16–18)*. Gordon *et al. (19–21)*, who studied the formation of ClO_3^- from ClO_2, found that the reaction between the chlorite ion (ClO_2^-) and hypochlorous acid (HOCl) resulted in stoichiometric amounts of ClO_3^-. Therefore, to improve the delignification efficiency of ClO_2, the conditions that are conducive to the generation of ClO_2^- and HOCl should be avoided to minimize the formation of ClO_3^-.

The diffusion rate of ClO_2 into the fiber and the transportation of the reactants from fiber to the bulk phase is directly proportional to the molar concentration of ClO_2. The molar concentration of ClO_2 increases with pulp consistency. In the DO delignification of conventional hardwood kraft pulp, increasing the pulp consistency from 3.0 to 12.0% increased the delignification rate (as measured by extracted kappa number) by 15% *(22)*. However, for oxygen-delignified pulps, the rate of increase was small *(23)*. Increasing the pulp consistency from 3.0 to 35% resulted in as much as 50% increase in the rate of DO delignification *(24–26)*. It therefore is assumed that in the DO delignification of pulp, high-consistency (35.0%) delignification would require less chlorine dioxide or KF than low-consistency (3.0%) or medium-consistency (12.0%) pulps to provide certain extracted (DE) kappa numbers.

As discussed earlier, the formation of chlorate hinders the delignification efficiency of chlorine dioxide. In the chlorine dioxide delignification of pulp, the formation of ClO_3^- at any given ClO_2 consumption

Trial no.	Initial pulp pH	Washing of pulp between DO and E stage	Reaction time, s	Kappa factor	DE kappa no.	AOX,* kg/a.d. ton of pulp
1	2.0	Yes	41	0.087	6.5	1.145
2	2.0	No	41	0.087	6.5	0.703
3	2.0	Yes	47	0.087	6.6	1.144
4	2.0	No	47	0.087	6.7	0.721
5	2.0	Yes	112	0.173	5.3	1.370
6	2.0	Yes	102	0.173	5.4	1.370
7	2.0	Yes	171	0.260	5.0	1.505
8	2.0	Yes	519	1.040	4.0	2.046
9	5.0	Yes	46	0.088	6.1	1.406
10	5.0	No	46	0.088	6.4	0.749
11	5.0	Yes	91	0.176	5.6	1.262
12	5.0	Yes	152	0.264	5.2	1.478
13	5.0	Yes	564	1.200	4.0	2.010
14	8.0	Yes	34	0.094	7.1	0.794
15	8.0	No	34	0.094	7.8	0.451
16	8.0	Yes	34	0.094	6.4	0.920
17	8.0	No	34	0.094	7.5	0.514
18	8.0	Yes	65	0.188	5.8	1.127
19	8.0	Yes	98	0.281	5.1	1.181
20	8.0	Yes	371	1.130	3.7	1.821

*Total AOX from bleaching pulps to 88-90% ISO brightness by D(gas)ED$_1$E$_2$D$_2$ sequence

I. Gaseous ClO$_2$ delignification of southern pine kraft pulp—Unbleached pulp: kappa no. 29.6

depends on the initial kappa number of the pulp *(27)*. Chlorine dioxide reacts poorly with nonphenolic lignin model compounds *(28)*. The ratio of phenolic to nonphenolic groups in the lignin structure depends on the kappa number of the pulp *(29, 30)*. Germgard *(31)* found that the ClO_2 delignification of partially methylated kraft pulp was slow compared to unmethylated pulp, confirming the findings of Logen *et al. (28)*. These findings suggest that the rate of ClO_2 delignification would be high for high-kappa-number pulps due to the presence of large amounts of phenolic groups in their lignin structure that would facilitate ClO_2 reaction and due to the decreased amount of chlorate formation *(27–30)*.

For an efficient chlorine dioxide pulp delignification, the unbleached pulp should be preacidified *(32)* before the addition of ClO_2. In chlorine–water equilibrium, the concentration of HOCl is maximum from pH 4.5–8.0 *(33)*. High concentrations of HOCl would lead to converting chlorine dioxide to chlorate, thus decreasing the delignification efficiency of chlorine dioxide. Chlorine dioxide oxidation of phenols under neutral pH conditions was studied by Wajon *et al. (34)*. According to them, even in the presence of large amounts of Cl_2, the oxidation of phenols by ClO_2 was the more dominant reaction than either the oxidation by HOCl or substitution by Cl_2. Their finding suggests that in neutral pH, in the presence of ClO_2, only small amounts of Cl_2 would be converting to HOCl, and the conversion of ClO_2 to chlorate should be minimal. Allison and Wrathal concluded that in the ClO_2 delignification of oxygen-delignified pulps, preacidification is not necessary and may slow the delignification rate *(35)*.

The mass transfer and diffusion model described for the ozone bleaching *(36)* is applicable to the gaseous ClO_2 delignification of pulps. The resistance to the transportation of ClO_2 from the bulk to the solid phase (fiber) comes from both the mobile and immobile fluid layers that adjoin the fiber. The thickness of these layers decides the rate of diffusion into the fiber and the transportation of the products from the fiber to the bulk phase. Increasing the pulp consistency decreases the mobile layer thickness. In high-consistency pulp, unlike low-consistency pulp, the thickness of the immobile water layer surrounding the fiber is so small that the fluid transportation should face little resistance. This then implies that the delignification rate under high-con-

Trial no.	Initial pulp kappa no.	Consistency, %	Initial pulp pH	Washing	Kappa factor	AOX, kg/ o.d. ton pulp	DE kappa no.
1	29.6	39.3	2	Yes	0.087	1.145	6.5
2	29.6	39.3	2	No	0.087	0.703	6.5
3	29.6	39.3	2	Yes	0.087	1.144	6.6
4	29.6	39.3	2	No	0.087	0.721	6.7
5	29.6	39.3	2	Yes	0.173	1.370	5.3
6	29.6	39.3	2	Yes	0.173	1.370	5.4
7	29.6	39.3	2	Yes	0.260	1.505	5.0
8	29.6	39.3	2	Yes	1.040	2.046	4.0
9	29.6	38.7	5	Yes	0.088	1.406	6.1
10	29.6	38.7	5	No	0.088	0.749	6.4
11	29.6	38.7	5	Yes	0.176	1.262	5.6
12	29.6	38.7	5	Yes	0.264	1.478	5.2
13	29.6	38.7	5	Yes	1.060	2.010	4.0
14	29.6	36.3	5	Yes	0.094	1.070	7.1
15	29.6	36.3	8	No	0.094	0.690	7.8
16	29.6	36.3	8	Yes	0.094	0.910	6.4
17	29.6	36.3	8	No	0.094	0.660	7.5
18	29.6	36.3	8	Yes	0.188	1.140	5.8
19	29.6	36.3	8	Yes	0.281	1.200	5.1
20	29.6	36.3	8	Yes	1.130	1.910	3.7
21	29.6	36.3	2	Yes	0.150	0.790	7.1
22	29.6	36.3	8	Yes	0.150	0.730	7.1
23	29.6	36.3	8	Yes	0.150	0.800	6.2
24	29.6	36.3	8	Yes	0.150	0.640	6.9
25	29.6	36.3	8	Yes	0.160	0.890	6.2
26	29.6	36.3	8	Yes	0.180	0.940	6.6
27	36.0	36.3	8	Yes	0.150	0.780	7.3
28	36.0	12.0	8	No	0.220	0.760	5.1
29	36.0	12.0	8	No	0.220	0.920	5.2
30	25.0	35.0	8	Yes	0.196	0.970	6.2
31	25.0	35.0	8	Yes	0.243	1.540	4.7
32	25.0	35.0	8	Yes	0.287	1.050	6.3
33	25.0	35.0	8	Yes	0.102	1.630	4.7

*Total AOX from bleaching pulps to 88-90% ISO brightness by D(gas)ED$_1$E$_2$D$_2$ sequence

Regression for AOX

$AOX = 1.10 + 0.5802\ X_1 - (1/X_2)^{0.299} + 0.052\ X_3 + (X_4)^{0.9893}$; $R^2 = 0.88$

where:

Constant (K) = 1.10

Std. error of y estimate = 0.193

Independent variables:

X_1: Washing (Yes = 1.0 and No = 0.0)

X_2: Initial kappa no.

X_3: pH (pH<5.0 = 1.0 and pH>5.0 = 0.0)

X_4: Kappa factor

Relationship between DE kappa no. and AOX

For washing between D0 and E stages (DE = DE kappa no.):

$AOX = 0.95 + 1.0 \exp (2.18 - 0.51\ DE)$; $R^2 = 0.88$

For no washing between D0 and E stages (direct alkaline extraction):

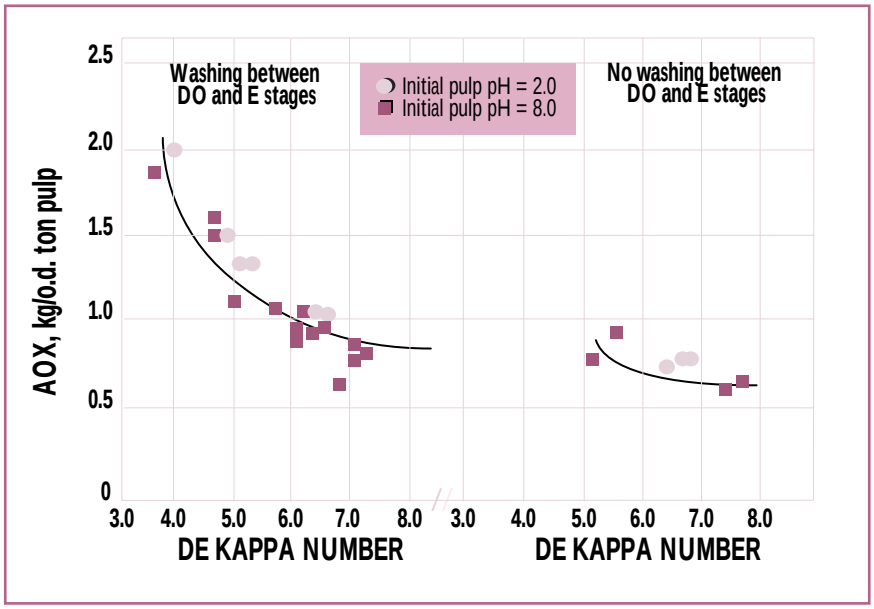
$AOX = 0.48 + 0.45 \exp (1.8 - 0.49\ DE)$; $R^2 = 0.83$

II. Relationship between DE kappa no. and AOX*

sistency conditions should be faster than the low- or medium-consistency conditions.

Cook *(37)* reported a substantial reduction in the bleach plant AOX when the pulp washing between the DO delignification and alkaline extraction is eliminated. Conversion of organic halides to sodium chloride is the reason for such a decrease in AOX *(38)*. Nystrom *et al. (39)*, Bottger *et al. (40)*, and Milosevich and Hill *(41)* observed that the AOX in the DE effluent can be decreased by about 40% by increasing the pH of the chlorination effluent above 11.0.

Based on the above discussion, the gaseous chlorine dioxide delignification would be faster than the liquid-phase chlorine dioxide delignification, and variables such as pulp consistency, molar concentration of ClO_2, and pulp pH have a strong influence on the gaseous ClO_2 delignification of pulp. The AOX formation in the gaseous ClO_2 delignification also is affected by these variables. In comparison to liquid-phase delignification, the high-consistency gaseous ClO_2 delignification should require less ClO_2 for a given extracted (DE) kappa number. It is presumed that conventional kraft pulps can be delignified by gaseous ClO_2 as effectively as extended delignified low-kappa-number pulps. A significant question is whether there would be a substantial difference in AOX concentration from the bleaching of conventional kraft pulps to that of extended delignified pulps.



1. Regression between DE kappa number and AOX—effect of pulp washing

RESULTS AND DISCUSSION

The gaseous ClO_2 delignification of pulps at different initial pulp pH and kappa factors is listed in Table I. At a given KF, the DE kappa number was the same for pulps with an initial pH of 2.0 and 5.0 (Table I). However, the pulp with an initial pH of 8.0 has a higher DE kappa number than either the pH 2.0 or 5.0 pulp. Elimination of pulp washing be-tween gaseous ClO_2 delignification and alkaline extraction resulted in high DE kappa numbers and was significantly high for pulp with an initial pH of 8.0. However, the elimination of pulp washing between DO delignification and alkaline extraction decreased the AOX discharge from the bleach plant by as much as 40%.

Regression model

Table II shows the regression equation for the dependent variables, DE kappa number, and total AOX from the bleach plant. The independent variables are (a) washing and no washing after DO treatment, (b) initial pulp kappa number, (c) KF, and (d) initial pulp pH. Piecewise linear regression was used to estimate the dependent variables *(42)*. The washing and no washing of pulp is a nonparametric variable. To accommodate this in the model, values of 1 for washing and 0 for no washing were assigned. The regression was further simplified by assigning values of 1 for the initial pulp pH ≥5 and 0 for pH ≤5. These two simplifications have somewhat skewed the regression. However, the calculated standard error of the *y* estimate was less than 20% of the regression constant, suggesting that the precision of the estimate was not overly compromised. At the end of the gas-phase delignification, the final pulp pH was measured. Pulp with an initial pH of 5.0 had a final pH between 3.0 and 3.5, and pulps with an initial pH of 2.0 and 8.0 had end pH values of 1.5 and 5.0–5.5, respectively. The de-crease in pH was particularly steep for pulps with a high initial pH. The KF used in the delignification of pulps ranged from 0.1 to 0.3. To evaluate the highest kappa number reduction from DO delignification, experiments were also carried out at very high kappa factors of 1.0 and 1.2.

The model is not applicable for liquid-phase chlorine dioxide delignification and is limited to the interpretation of AOX discharge from the gas-phase delignification. Again, the model is valid only within an operating domain of unbleached kappa numbers from 25.0 to 36.0. From

	LIQUID-PHASE ClO_2 DELIGNIFICATION				GASEOUS ClO_2 DELIGNIFICATION			
	Eastern Canadian kappa factor		Southern pine kappa factor		Eastern Canadian kappa factor		Southern pine kappa factor	
Parameter	**0.20**	**0.30**	**0.20**	**0.30**	**0.16**	**0.20**	**0.16**	**0.20**
Active chlorine, %[b]	7.00	10.50	5.92	8.88	5.60	7.00	4.80	6.00
ClO_2 charge at the D0 delignification, % ClO_2	2.66	3.99	2.25	3.38	2.13	2.66	1.83	2.28
ClO_2 charge at the D_1 and D_2 stages, % ClO_2	1.60	1.45	1.60	1.45	1.60	1.45	1.60	1.45
DE kappa no.	5.10	4.30	5.30	4.70	5.00	4.40	5.60	4.90
Final brightness, % ISO	89.3	90.3	89.0	90.1	88.7	89.1	88.2	88.7
0.5 CED viscosity, mPa·s	26.0	25.8	15.0	14.3	27.3	27.0	17.0	16.5
AOX, kg/o.d. ton of pulp after D0E-stage[c]	1.54	1.80	1.44	1.77	0.84	0.91	0.87	1.03
AOX, kg/o.d. ton of pulp after $D_1E_2D_2$-stages	0.37	0.46	0.36	0.54	0.27	0.29	0.32	0.27
Total AOX, kg/o.d. ton of pulp	1.81	2.26	1.80	2.31	1.11	1.20	1.09	1.30

[a]Well-washed pulps with less than 10 kg/ton of COD carryover
[b]Chemical charges are on an o.d. pulp basis.
[c]Pulps were washed after D0 delignification and before alkali extraction.

III. Gas- and liquid-phase ClO_2 delignification and bleaching of softwood kraft pulps—Unbleached pulp kappa nos.[a]: southern pine=29.6, eastern Canadian=35.0

the regression equation (Table II), the washing and no washing of DO-delignified pulp has a strong influence on the AOX discharge from the bleach plant. The initial kappa number of the pulp and KF have a small but significant impact on the AOX discharge. From this equation, it is estimated that the total AOX from the gas-phase delignification and bleaching of a pulp of kappa no. 30.0 (at 0.2 KF and an initial pulp pH of less than 5.0) would be 1.31 kg/a.d. ton of pulp, if the pulp is washed before alkaline extraction. About 40% of this AOX came from the washing and the extraction of the DO-delignified pulp. The relationship between the AOX and DE kappa number of pulp is exponential (Fig. 1), the AOX becoming asymptotic to the DE kappa number. Elimination of pulp washing between DO delignification and alkaline extraction resulted in about a 30% decrease in AOX to 1.0 kg/oven-dried (o.d.) ton (0.952 kg/a.d. ton) of pulp. Our results agreed with those reported by Cook *(37)*. At a given KF, changing the initial pulp pH has only a small effect on the DE kappa number. However, at a given initial pulp pH, increasing the KF from 0.1 to 1.2 lowered the kappa number by as much as 30% (Tables I and II).

Effect of end pH and kappa factor on gas-phase chlorine dioxide delignification

Basta *et al. (1)* reported that for southern pine kraft pulp of kappa no. 24.0, at KF of 0.17, the lowest DE kappa number obtained was at an end pH of 3.0. The DE kappa number of the pulp from the liquid-phase chlorine dioxide delignification to an end pH of 1.5–3.5 remained constant. However, an increase in the end pH from 3.5 to 5.0 increased the DE kappa number sharply. After gaseous chlorine dioxide delignification, the pulp with an initial pH of 2.0 had a final pH of <1.5. The pulps with the starting pH of 5.0 and 8.0 had end pH values of 3.5 and 5.0, respectively. The estimated DE kappa numbers for the pulp delignified by liquid-phase chlorine dioxide are 7.0 and 8.5, respectively, if the end pH is 3.5 and 5.0 *(1)*. Under similar KF application (KF=0.17) and end pH range (3.5–5.0), the gas-phase delignification of a kappa no. 30 pulp would result in an estimated DE kappa number of 6.0. Compared to liquid-phase delignification and bleaching, the gaseous chlorine dioxide delignification required about 35% less ClO_2 to provide the same DE kappa number and final pulp brightness (Table III). Appropriately, the AOX discharge from the bleach plant also decreased by about 35%. To obtain a pulp brightness of 88–89% ISO, the gas-phase delignification required a lower KF than the liquid-phase delignification. The AOX discharge is also lower than

Pulp [Liquid (L)- or gas (G)-phase delignification]	Pulp kappa no. (initial)	Kappa factor	DE kappa no.	AOX,[a] kg/o.d. ton pulp: Measured	Estimated	Absolute error	Percent error
Kraft (L)	34.8	0.25	5.4	2.58	-	-	-
Kraft (G)	34.8	0.20	5.8	1.23	1.13	0.10	8.13
Kraft (G)	34.8	0.10	6.6	0.99	1.02	-0.03	-3.03
PS/AQ (L)	29.9	0.25	5.6	2.50	-	-	-
PS/AQ (G)	29.9	0.25	5.2	1.44	1.11	0.33	22.92
PS/AQ (G)	29.9	0.20	5.4	1.20	1.07	0.13	10.83
PS/AQ (G)	29.9	0.15	6.1	1.13	1.03	0.10	8.85
Extended PS/AQ (L)	24.8	0.20	5.0	1.58	-	-	-
Extended PS/AQ (G)	24.8	0.10	5.3	0.90	0.91	-0.01	-1.11
PS/AQ+O_2 (L)	15.8	0.20	4.6	1.23	-	-	-
PS/AQ+O_2 (G)	15.8	0.20	4.2	0.86	0.92	-0.06	-6.98
PS/AQ+O_2 (G)	15.8	0.10	4.6	0.63	0.82	-0.19	-30.16
Extended kraft+O_2 (L)	13.4	0.20	4.0	1.08	-	-	-
Extended kraft+O_2 (G)	13.4	0.15	4.0	0.84	0.85	-0.01	-1.19
Extended PS/AQ+O_2 (L)	12.1	0.20	3.6	1.00	-	-	-
Extended PS/AQ+O_2 (G)	12.1	0.15	3.2	0.60	0.83	-0.23	- 38.33
Kraft (G)[b]	34.8	0.10	6.8	0.65	0.51	0.14	21.54
PS/AQ (G)	29.9	0.15	6.1	0.62	0.51	0.11	17.74
PS/AQ+O_2[b]	15.8	0.20	4.5	0.60	0.46	0.14	23.33
Extended kraft+O_2[b]	13.4	0.15	4.4	0.55	0.42	0.13	23.64
Extended PS/AQ+O_2[b]	12.1	0.15	3.6	0.48	0.41	0.07	14.58

[a]Total AOX from bleaching pulp to 89% ISO brightness by $D0E_1D_1E_2D_2$ sequence; AOX is not estimated for liquid-phase D0 delignification and bleaching.
[b]Pulps were extracted directly without washing between D0 delignification and E stages.

Regression for AOX (for gas-phase delignification and bleaching only)
For washing between D0 and E stages (IK = initial kappa no., KF = kappa factor):
$AOX = 0.053 + 0.011\ IK + KF^{0.2303}$; $R^2 = 0.92$

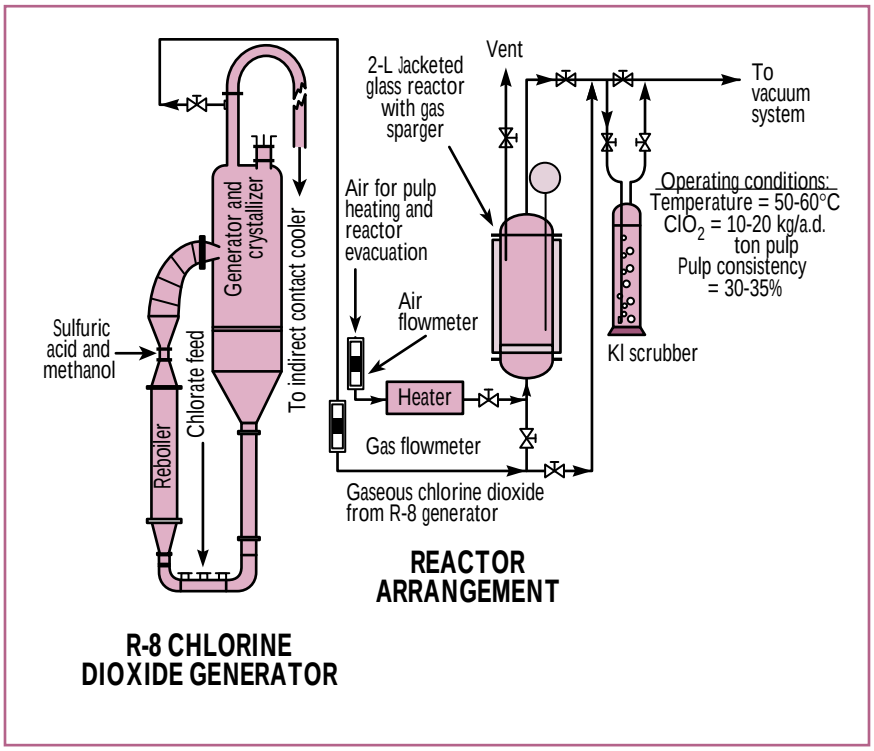
For no washing between D0 and E stages (direct alkaline extraction):
$AOX = 0.0527 + 0.006\ IK + 0.852\ KF^{0.2303}$; $R^2 = 0.92$

IV. Gas- and liquid-phase ClO_2 delignification and bleaching of conventional and extended kraft, polysulfide/AQ (PS/AQ), and polysulfide/AQ+oxygen (PS/AQ+O_2) pulps

that of the liquid-phase chlorine dioxide delignification. The viscosity of bleached pulp (88–90% ISO brightness) from gaseous chlorine dioxide delignification and bleaching of conventional kraft pulp is not different from the liquid-phase chlorine dioxide delignification and bleaching (Table III).

Effect of extended pulping on gas-phase chlorine dioxide delignification

Table IV lists the DO delignification and bleaching of conventional and extended kraft pulps. For PS-AQ/O_2 pulp of kappa no. 12.0, the AOX discharge was less than 0.4 kg/o.d. ton of pulp. At these AOX emissions, the toxicity equivalent factor (TEF) of the effluent should be very low *(3, 4)*. The AOX discharge from the bleaching of conventional kraft pulp was about 1.15 kg/o.d. ton of pulp (if the pulp is washed between chlorine dioxide delignification and extraction stages). By eliminating the interstage washing between chlorine dioxide delignification and alkaline extraction, the AOX discharge can be decreased to about 0.6–0.7 kg/o.d. ton of pulp; this decrease is achieved without compromising the final pulp brightness (Table IV).



2. Experimental setup

Since gaseous chlorine dioxide delignification of pulp demands a low KF to reach a certain DE kappa number (Table IV), the gaseous chlorine dioxide delignification and bleaching of kraft and extended-delignified pulp (PS-AQ/O_2) to a given pulp brightness is less expensive than the liquid-phase delignification and bleaching.

The upper confidence bounds and prediction intervals for the AOX from gaseous chlorine dioxide delignification and bleaching were estimated from appropriate statistical procedures *(42)*. Based on the data listed in Tables III and IV, the 70% upper confidence bound for AOX discharge from the gaseous chlorine dioxide delignification of kappa no. 35 pulp, at 0.3 KF, was 0.79 kg/o.d. ton. The AOX discharge has a range of 0.38–1.43 kg/o.d. ton, depending on the pulp kappa number and the applied kappa factor. The maximum AOX discharge from the gaseous chlorine dioxide delignification and bleaching of conventional kraft pulp (kappa no. 35.0) would not exceed 1.43 kg/o.d. ton even at the maximum applied KF of 0.3. This represents a reduction of about 29% over the AOX reported by Liebergott *et al. (9)* for the liquid-phase DO delignification of conventional softwood pulp (kappa no.≈35). The AOX from the gaseous chlorine dioxide delignification and multistage bleaching should be about 50% lower by eliminating the pulp washing between the DO delignification and alkaline extraction.

EXPERIMENTAL

Southern pine kraft pulp of kappa no. 29.6 and eastern Canadian softwood pulp of kappa no. 35.0 were used in this study. Extended-delignified (kraft-oxygen or PS-AQ/oxygen) pulps used in the study were laboratory pulps. The gaseous ClO_2 delignification of pulps in a fixed bed reactor is depicted in Fig. 2. Gaseous ClO_2 from an R-8 chlorine dioxide generator, captured before the indirect contact cooler and absorber, was used in the experiments. Once the gaseous ClO_2 broke through the pulp bed, the gas flow was turned off, and the bed was evacuated by pumping air through it. The evacuated ClO_2 was scrubbed with potassium iodide (KI) solution and analyzed. From the mass flow rate and the residual concentration of ClO_2, the consumption of ClO_2 by pulp was calculated. The pulp consistency for most of the bleaching was 35%, but it was varied between 20 and 40% for some bleaching experiments. The initial pulp pH ranged from 2.0 to 8.0.

The pulp from gaseous ClO_2 delignification (DO stage) was split into two portions. One portion was extracted with alkali without washing. The other part was washed free of residual ClO_2 before alkaline extraction. The alkali-extracted pulp was bleached by DED sequence to 88–90% ISO brightness. Alkaline extraction and $D_1E_2D_2$ bleaching conditions are listed in Table V. AOX was measured individually for effluents from the DO and E stages and on the combined effluent from the $D_1E_2D_2$ sequences. The unbleached and extracted pulp kappa number, final pulp brightness, and pulp viscosity are measured using standard TAPPI Test Methods.

CONCLUSIONS

Conventional kraft pulp of kappa no. 30–35 can be delignified in the gas phase with 100% chlorine dioxide to 88–90% ISO brightness at a lower chlorine dioxide charge (KF) than that required in liquid-phase delignification. The AOX emission from the bleach plant can be decreased by as much as 30% by gas-phase bleaching compared to liquid-phase bleaching.

Parameter	E stage	D_1 stage	E_2 stage	D_2 stage
Sodium hydroxide, %[b]	3.0	0.2	0.5	0.0
Chlorine dioxide, % as ClO_2[b]	-	1.2	-	0.5
Pulp consistency, %	10.0	12.0	10.0	12.0
Temperature, °C	70.0	70.0	50.0	70.0
Reaction time, min	120	240	30	120
Pulp pH (final)	10.8/11.0	3.5/4.0	9.5/9.8	3.5/4.0

[a]First stage: The liquid-phase ClO_2 pulp delignification was carried out at 10% consistency. The gaseous ClO_2 delignification was carried out at 35% consistency (unless otherwise indicated).
[b]All chemical charges are on an o.d. pulp basis.

V. Bleaching conditions[a]

KEYWORDS
Adsorbable organic halogen, alkali extraction, anthraquinone, bibliographies, bleaching, brightness, chlorine dioxide, delignification, kappa number, kraft pulps, oxygen, polysulfides, softwood pulps, vapor phases, viscosity, washing.

Based on the empirical model, the most important variable that affects the AOX formation in gas-phase bleaching is washing and no washing of pulps between the DO and E stage. Both the initial kappa number and the applied KF have a moderate influence on the AOX generation during gaseous chlorine dioxide pulp delignification.

The elimination of pulp washing between the DO and E stage can decrease the AOX emission from these stages by as much as 50%. AOX emission of less than 1.0 kg/o.d. ton of pulp from the gaseous chlorine dioxide delignification and bleaching of conventional kraft pulp is possible with an applied KF of 0.1 and without washing the pulp after the chlorine delignification and before the alkaline extraction. The gaseous chlorine dioxide delignification of conventional kraft pulp (kappa no. 30–35) at such a low KF did not impede brightness development. Final brightness of 88–89% ISO can still be achieved without an increase in the chemical charge in the final bleaching stages.

Gas-phase delignification and bleaching of extended kraft pulps (kappa no. 12–15) resulted in 88–89% ISO pulp at a total AOX of less than 0.48 kg/o.d. ton of pulp if the pulp is not washed between the DO and E stage. The outfall AOX can be decreased to less than 0.3 kg/o.d. ton of pulp with secondary effluent treatment. This brightness (88–89% ISO) and low AOX (<0.3 kg/o.d. ton pulp) are achieved at half the chemical requirement of the liquid-phase chlorine dioxide delignification. TJ

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The authors wish to acknowledge the management of Mead Central Research for the permission to present this paper. Our thanks are also due to Mead's Business and Communication Papers (Kingsport) Division for allowing us to use the R-8 chlorine dioxide generation facilities. William Blair and Amos Detty are thanked for their skillful measurement of AOX.

Received for review Oct. 12, 1994.
Accepted April 28, 1995.

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