MILL EXPERIENCE WITH CHLORINE DIOXIDE DELIGNIFICATION

Produces good pulp accompanied by an improvement in effluent quality

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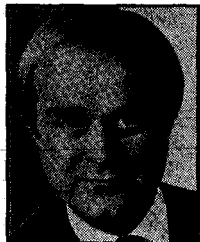
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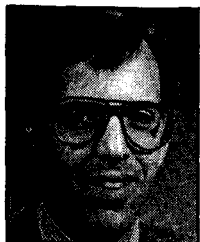
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HOWE SOUND PULP and Paper (HSPP) was formed in April 1988 as an equally-owned joint enterprise between Canfor Corporation and Oji Pulp and Paper of Japan. The thrust behind this alliance was to expand and modernize the existing kraft pulp mill in Port Mellon, B.C. and to diversify into the manufacture of high quality newsprint. The goal was to construct a modern facility which would meet both pulp quality and environmental standards well into the next century.
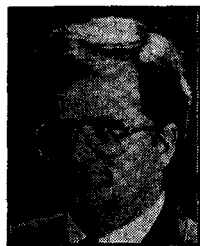
The site at Port Mellon has recently completed a $C1.1 billion expansion and modernization. The project included the construction of a new 585 air dry tonnes/day (adt/d) newsprint and thermomechanical pulp mill and a major modernization of the existing kraft mill. Market kraft pulp produc-
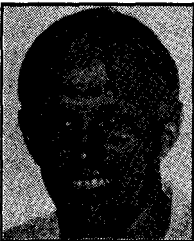
tion increased from 650 to 1200 adt/d.

The kraft mill modernization included:
• A 1400-adt/d Kamyr MCC® digester;
• A two-stage Kamyr atmospheric diffuser;
• Ingersoll-Rand knotters, screens and deckers;
• Kamyr two-stage MC® oxygen delignification;
• A Dorr-Oliver causticizing system;
• A Boledin-Allis lime kiln;
• Five-effect Kamyr falling film evaporators;
• A Babcock and Wilcox recovery boiler;
• A Mitsubishi 62.5-MW turbo generator.

A second Mitsubishi 50-MW turbo generator was commissioned in December 1991 and a new high-pressure Babcock and Wilcox power boiler will
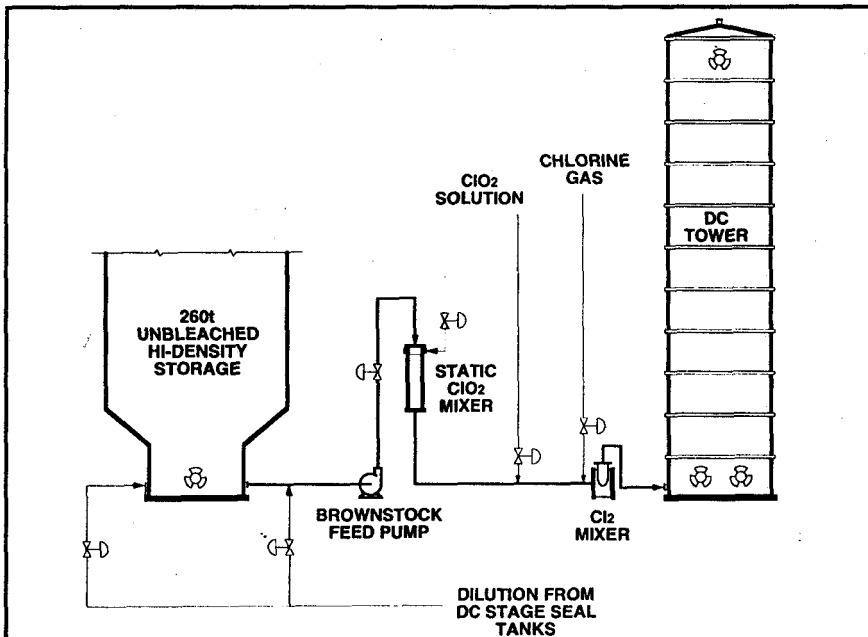

FIG. 1. OVERVIEW OF (D,C+D) STAGE OF NEW BLEACH PLANT.

become operational in September 1992.

Environmental protection systems for air include: dilute and concentrated noncondensible gas collection and incineration, a low-odor recovery boiler, and Flakt electrostatic precipitators to minimize particulate emissions from both the lime kiln and recovery boiler. The new power boiler will also be equipped with a Flakt electrostatic precipitator.

Environmental protection systems for water include a primary effluent clarifier and secondary effluent treatment using an oxygen activated sludge system (UNOX) complete with secondary clarification of the effluent prior to discharge via a submerged diffuser. Of primary importance in the modernization was the incorporation of the best available technology to minimize the formation and discharge of 2378-TCDD/-TCDF and adsorbable organically bound halogen, AOX.

To achieve these goals, in addition to design features such as extended delignification and oxygen delignification, a new 35-t/d R8 chlorine dioxide generator was installed, replacing the existing 12-t/d modified Mathieson generator. The increased chlorine dioxide capacity allows the mill to operate the first stage of bleaching with up to 100% chlorine dioxide substitution. This and the fact that the chlorine dioxide produced has extremely low chlorine content, allow the mill to satisfy customer demands for "molecular-chlorine-gas-free" market pulps.

The purpose of this paper is to report mill experience with increasing chlorine dioxide substitution from 60 to 100% in the first stage of bleaching. Specifically, this paper examines the effect of chlorine dioxide delignification (100% substitution with chlorine dioxide) of oxygen delignified softwood pulps and addresses:
• Bleaching chemical consumption;
• Bleaching cost;
• Pulp quality;
• Effluent quality and treatability.

BLEACH PLANT DESIGN

The pre-expansion, conventional five-stage (C+D)(E+O)DED bleach plant was converted to (D,C+D)(E+O)(DE)D, incorporating two parallel (E+O)(DE) stages between the (D,C+D) and D stages.

The pre-expansion bleaching strategy used 10% chlorine dioxide substitution in the first stage (C+D) at approximately 0.28 Kappa factor. All chlorine dioxide was supplied by a 12-t/d modified Mathieson generator normally operating at 8 to 10 t/d. Chlorine was injected as a chlorine-water dispersion into the pulp and subsequently mixed

TABLE I. MILL EXPERIENCE WITH CHLORINE DIOXIDE DELIGNIFICATION – OPERATING DATA AND PULP QUALITY.

	Pulp Grade 1		Pulp Grade 2	
	60% ClO_2	100% ClO_2	60% ClO_2	100% ClO_2
Dates	Feb. 5-7	Feb. 9-12,22	Feb. 16-20,26	Feb. 13-15
Average bleached pulp production, adt/day	770	827	905	810
Brownstock, O_2 Kappa No.	21.3	20.2	20.0	20.1
Bleaching chemical consumption				
(D,C +D) Stage				
Cl_2 (kg/adt)	19.0	0.0	18.6	0.0
Cl_2 in ClO_2 (kg/adt)	0.3	0.6	0.3	0.6
ClO_2 (kg/adt)	10.9	20.6	10.6	20.9
Active Cl_2 (kg/adt)	47.9	54.8	46.8	55.5
Kappa Factor	0.22	0.27	0.23	0.28
Molecular Cl_2 Multiple	0.09	0.00	0.09	0.0
(E +O) Stage				
NaOH (kg/adt)	26.7	23.2	25.1	19.6
O_2 (kg/adt)	5.3	5.2	5.1	5.2
End pH	10.4	10.5	10.1	10.5
NaOH/Active Cl_2	0.6	0.4	0.5	0.4
NaOH/Molecular Cl_2	1.1	2.0	1.0	1.7
DE Stage				
ClO_2 (kg/adt)	7.3	9.2	8.8	10.7
NaOH (kg/adt)	11.6	14.8	14.8	15.7
NaOH/ClO_2	1.6	1.6	1.7	1.5
Brightness, Elrepho	82.8	80.4	84.4	82.1
D Stage				
ClO_2 (kg/adt)	4.0	3.4	3.4	3.9
Brightness, Elrepho	90.6	88.9	90.1	89.1
Active chlorine consumption				
Cl_2 (kg/adt)	19.0	0.0	18.6	0.0
Cl_2 in ClO_2 (kg/adt)	0.7	1.0	0.7	1.1
ClO_2 as Cl_2 (kg/adt)	58.3	87.3	59.9	93.2
Total Active Cl_2 (kg/adt)	77.9	88.3	79.2	94.3
Sequence Kappa Factor	0.37	0.44	0.40	0.47
Total bleaching chemical consumption				
Cl_2 (kg/adt)	19.0	0.0	18.6	0.0
ClO_2 (kg/adt)	22.2	33.2	22.8	35.5
NaOH (kg/adt)	38.3	38.0	39.9	35.2
O_2 (kg/adt)	5.3	5.2	5.1	5.2
Pulp quality				
Brightness, Elrepho	91.4	88.6	90.5	89.8
Dirt, ppm	3.5	2.5	1.3	1.2
Shives, ppm	0.1	0.0	0.0	0.1
Viscosity, cp	21.7	21.4	21.3	22.3

TABLE II. CONCENTRATIONS OF ORGANICALLY-BOUND CHLORINE IN FULLY BLEACHED PULP PRODUCED USING 60% AND 100% CHLORINE DIOXIDE SUBSTITUTION.

	Cl, g/adt pulp			
Pulp Grade (% ClO_2)	Total organically-bound	Water-extractable, carbon-adsorbable	Extracted by EtOH/toluene	Not extracted by water or EtOH/toluene
1 (60)	322	22	115	185
1 (100)	167	7	<20	140
2 (60)	409	49	170	190
2 (100)	208	18	<25	165

via two static Komax mixers. Chlorination was controlled with a Kajaani optical and residual sensor system. Conventional (E+O) extraction technology, including an upflow preretention tube, was installed in 1984, incorporating a sintered metal oxygen sparger following a Kamyr MC® pump. The final three stages, DED, operated at typical industry conditions. Pulp washing was jump-stage counter-current. Semi- and fully-bleached market pulps were produced.

The new four-stage (D,C+D)(E+O)(DE)D bleaching line was designed to nearly double capacity to 1200 adt/d. Following a common (D,C+D) tower, 3.5% consistency stock is equally split to two washers; an existing Ingersoll-Rand and a new LaValley. Following washing, two parallel (E+O)(DE) stages denoted "A" and "B", extract and bleach the pulp to 82 Elrepho brightness. Bleached stock from the (DE) stages is combined and fully bleached in a new final D tower. The pulp is again washed using two new LaValley washers.

Jump-stage counter-current washing is used. Water usage was decreased from 48 to 30 m³/adt.

(D,C+D) stage: The first stage of bleaching, (D,C+D) was designed for 70% substitution by chlorine dioxide. As shown in Fig. 1, chlorine dioxide solution is added first to a Komax static mixer approximately 40 seconds before a Sunds SMB high shear mixer. The total applied chlorine dioxide is split 85% to the first mixer, with the balance, for viscosity protection, added to the second mixer just before chlorine gas addition.

Following chemical addition, the stock line diameter increases to permit 10 seconds of retention prior to the Kajaani brightness and residual sensors

used to control chemical application. The control system incorporates a brightness sensor at the outlet of the 25-minute (D,C+D) tower which adjusts the tower inlet compensated brightness setpoint. Temperature is typically 45 to 48°C and final pH is 1.8 to 2.0.

Chlorine dioxide delignification: When practising chlorine dioxide delignification, (i.e., without molecular chlorine gas), chlorine dioxide is also split between the two mixers, with 70% to the first mixer. The control strategy is identical. However, setpoints are different. The temperature is increased by approximately 5°C to compensate for the slower chlorine dioxide reactions. The pH is not controlled, increasing slightly to 2.0 to 2.2.

MILL EXPERIENCE

Mill experience with chlorine dioxide delignification: HSPP produces semi- and fully-bleached market softwood kraft pulp from three furnish mixes:
- Grade 1, 50% cedar:50% spruce-pine-fir;
- Grade 2, 100% western hemlock;
- Grade 3, 50% hemlock:50% fir;

Grades 1 and 2 were produced during the current trials.

Normally, 60% chlorine dioxide substitution is used in the first stage. However, to meet increasing customer demand for "molecular-chlorine-gas-free" pulps, increasingly greater amounts of pulp are being produced with only chlorine dioxide in the first stage of the bleach plant.

Results are presented comparing 60% chlorine dioxide substitution to chlorine dioxide delignification. Bleaching chemical consumption and bleach plant operating data were taken from operating log sheets and computer summaries. Data are reported as aver-

age values for at least three consecutive operating days during February 1991. The detailed data summary is found in Table I.

Effluent quality is based on analyses of 24-hour composite samples into the oxygen activated sludge treatment system and out of the secondary clarifiers. Samples were time-shifted to account for system retention time. Three consecutive composites were obtained for each operating condition.

Bleaching chemical consumption: Substitution of a portion of the available chlorine demand of unbleached pulp with chlorine dioxide can significantly improve delignification. For a fixed charge of oxidizing power (equivalent chlorine) the minimum extracted Kappa no. is typically achieved at 30 to 50% substitution [1] when the chlorine dioxide has been applied in advance of chlorine. As chlorine dioxide is further substituted, the extracted Kappa no. increases. Complete replacement with chlorine dioxide results in a higher extracted Kappa no. than would be achieved with "low substitution" (i.e., 10%). This has been shown by a number of researchers [2, 3, 4] for conventionally delignified as well as for oxygen delignified pulps, the effect being more pronounced for the latter pulp. Chlorine dioxide is less reactive with oxygen delignified pulps as both oxygen and chlorine dioxide attack the free phenolic groups in lignin [5]. Laboratory studies have shown that to overcome this inefficiency, either the Kappa factor applied in the first stage or peroxide and/or chlorine dioxide addition in subsequent bleaching stages, must be increased.

The mill experience supports the above discussion. As shown in Fig. 2, the Kappa factor in the first stage of
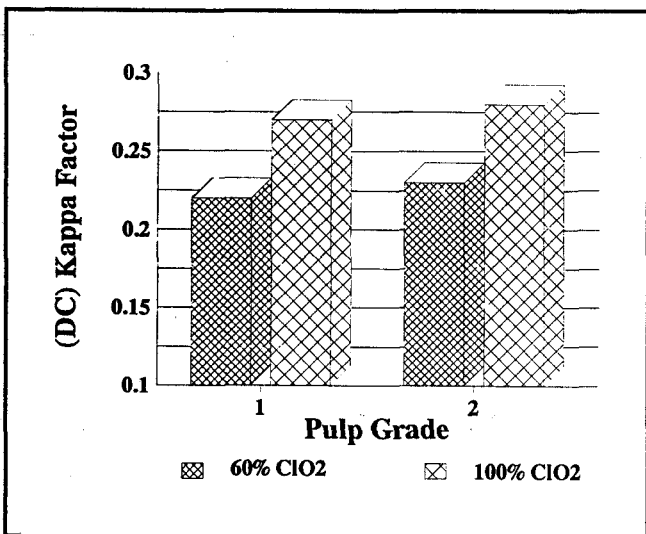

FIG. 2. THE KAPPA FACTOR IN THE FIRST STAGE OF BLEACHING INCREASED BY APPROXIMATELY 20% FROM 0.22 TO 0.28 FOR BOTH PULP GRADES AS SUBSTITUTION WAS INCREASED FROM 60 TO 100%.
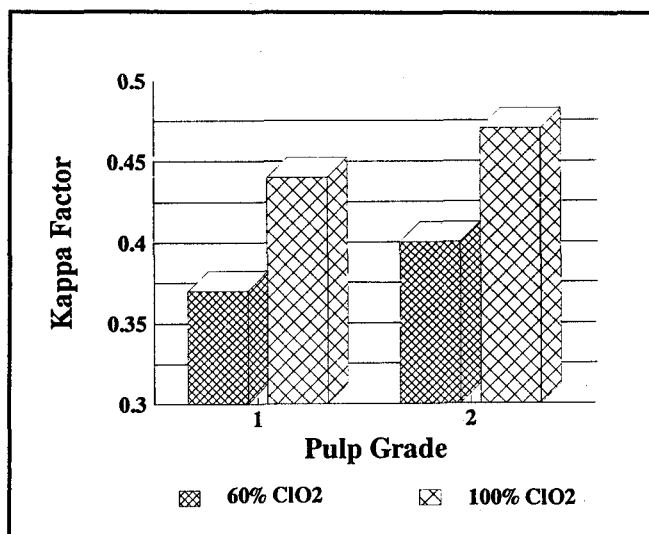

FIG. 3. SIGNIFICANTLY MORE EQUIVALENT CHLORINE IS REQUIRED IN THE ENTIRE SEQUENCE TO BLEACH BROWNSTOCK PULP WITH THE SAME UNBLEACHED KAPPA NO. TO SAME FINAL BRIGHTNESS.

bleaching increased by approximately 20% from 0.22 to 0.28 for both pulp grades as substitution was increased from 60 to 100%. The extracted Kappa no. is not routinely measured. Mill spot checks during other periods showed, however, that the extracted Kappa no. typically increases 1 to 2 units with chlorine dioxide delignification. It is clear that a similar increase in extracted Kappa no. occurred during this period, since increased chlorine dioxide was required in the (DE) stage to reach a lower (DE) brightness, Table I.

In the (E+O) stage, 25 to 30% less sodium hydroxide was required, Table I. This is expected as less acid in the associated filtrate, and less Cl in pulp requiring hydrolysis, are produced with chlorine dioxide delignification. Chlorine dioxide application in the final D stage was similar in all cases.

Bleaching cost: Bleaching cost increases with chlorine dioxide delignification for two reasons. Chlorine dioxide delignification (100% chlorine dioxide) is less efficient than bleaching with 60% chlorine dioxide substitution. Significantly more equivalent chlorine is required in the entire sequence to bleach brownstock pulp with the same unbleached Kappa no. to the same final brightness. This inefficiency is shown graphically in Fig. 3.

The second factor contributing to increased bleaching cost is the replacement of chlorine with more expensive chlorine dioxide. As shown graphically in Fig. 4, bleaching cost increases approximately 20% comparing chlorine dioxide delignification to 60% chlorine dioxide substitution.

Pulp quality: While average final pulp brightness was 2.8 points lower for the

cedar-spruce-fir grade (Pulp Grade 1), comparing chlorine dioxide delignification to 60% chlorine dioxide substitution, no appreciable difference in brightness for the two levels of substitution was observed for the hemlock grade (Pulp Grade 2). All other pulp quality parameters (dirt, shives and viscosity) were unchanged as shown in Table I.

Pulp strength was maintained. However, reaching the same freeness required approximately 5 to 10% more revolutions in the PFI mill comparing chlorine dioxide delignification to 60% chlorine dioxide substitution. This may result in increased refining energy requirements for papermakers.

Pulp samples were analyzed for organically-bound chlorine in pulp according to the method described by Reeve [7]. The results are shown in
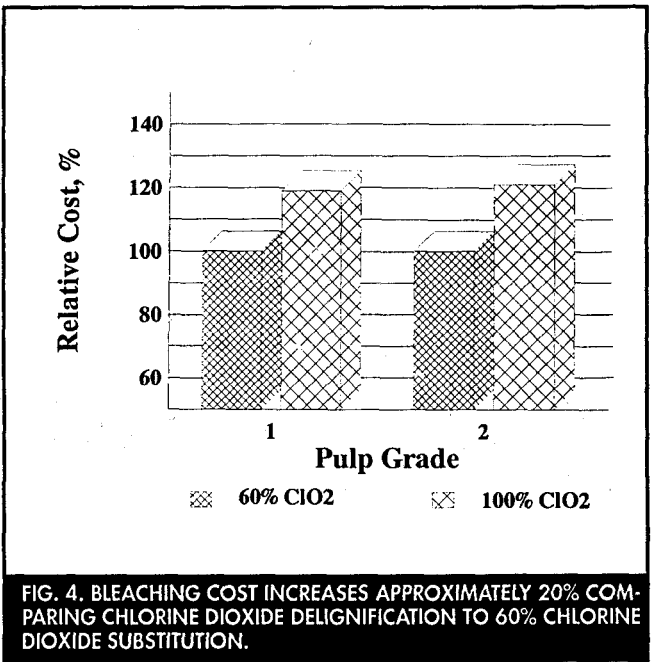

FIG. 4. BLEACHING COST INCREASES APPROXIMATELY 20% COMPARING CHLORINE DIOXIDE DELIGNIFICATION TO 60% CHLORINE DIOXIDE SUBSTITUTION.
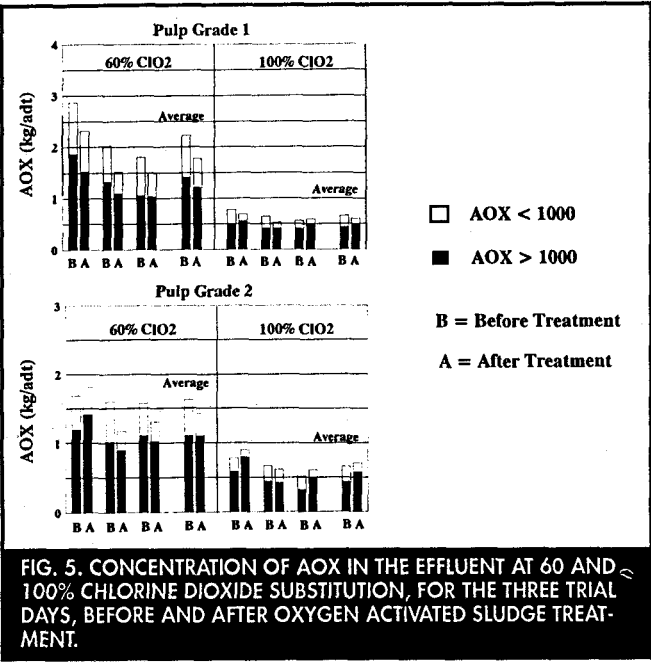

FIG. 5. CONCENTRATION OF AOX IN THE EFFLUENT AT 60 AND 100% CHLORINE DIOXIDE SUBSTITUTION, FOR THE THREE TRIAL DAYS, BEFORE AND AFTER OXYGEN ACTIVATED SLUDGE TREATMENT.

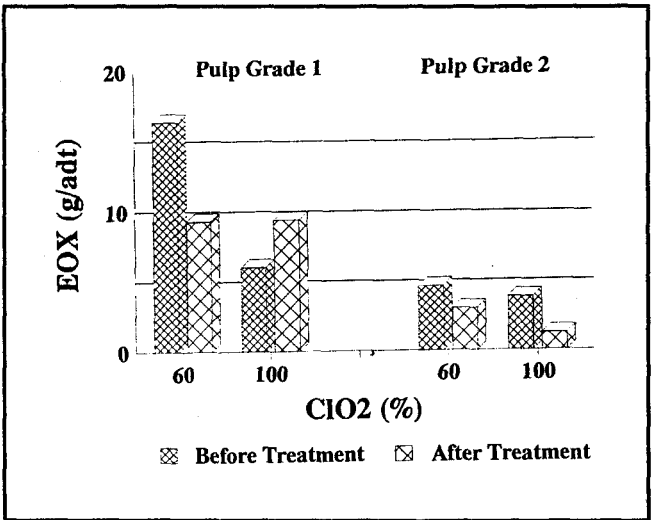FIG. 6. AVERAGE CONCENTRATIONS OF EOX IN THE EFFLUENT AT 60 AND 100% CHLORINE DIOXIDE SUBSTITUTION, BEFORE AND AFTER OXYGEN ACTIVATED SLUDGE TREATMENT.
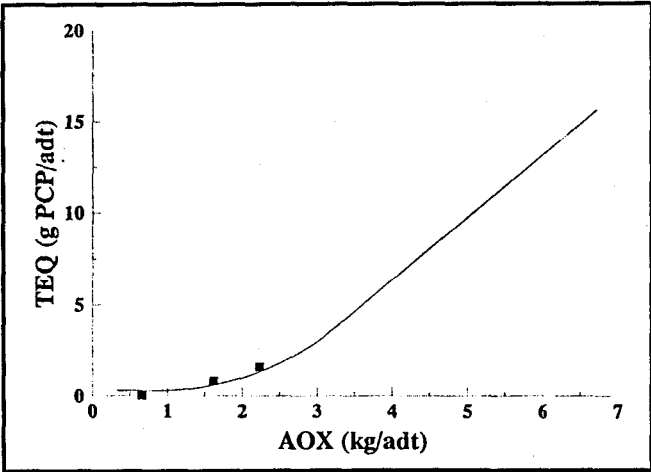

FIG. 7. LABORATORY (CURVE) [14] AND MILL (SQUARES) DATA SHOWING THE RELATIONSHIP BETWEEN AOX AND PENTACHLOROPHENOL-BASED TEQS, WHEN PROCESS MODIFICATIONS INVOLVING CHANGES BASED ON KAPPA FACTOR AND CHLORINE DIOXIDE SUBSTITUTION ARE BEING MADE.

Table II. For both pulp grades, the water extractable organically-bound halogen (termed AOX) obtained at 60 and 100% chlorine dioxide substitution were typical of fully-bleached softwood pulp [7]. The organically-bound chlorine extractable by ethanol/toluene, for both pulp grades at 60% chlorine dioxide substitution, was also characteristic of fully-bleached softwood pulp [7]. However, for both pulp grades, the increase in chlorine dioxide substitution to 100% resulted in a significant decrease in the ethanol/toluene extractable organically-bound chlorine.

EFFLUENT QUALITY

Formation of chlorinated organic compounds: Of the elemental chlorine used during bleaching, about 90% is converted to inorganic chloride ion and only about 10% becomes bound to the organic material removed from the pulp [8-12]. This organically-bound chlorine is commonly measured as AOX. Its inadequacies as a relevant indicator of environmental impact are well known [13-14]. Nonetheless, an understanding of the response of the

TABLE III. ACUTE TOXICITY DATA (RAINBOW TROUT) AND COLOR OF EFFLUENTS PRODUCED AT 60% AND 100% CHLORINE DIOXIDE SUBSTITUTION BEFORE AND AFTER TREATMENT USING AN OXYGEN ACTIVATED SLUDGE SYSTEM.

Pulp Grade	1	1	2	2
ClO_2, %	60	100	60	100
Treatment system:				
Inlet LC_{50}, %	23	26	22	22
Outlet LC_{50}, %	100	100	100	100
Effluent color kg/adt (outlet)	106	73	129	85

TABLE IV. THE AVERAGE CONCENTRATIONS (EXPRESSED IN TERMS OF PULP PRODUCTION) OF CHLORINATED PHENOLIC COMPOUNDS IN EFFLUENTS PRODUCED AT 60% AND 100% CHLORINE DIOXIDE SUBSTITUTION, BEFORE BIOLOGICAL TREATMENT.

	Pulp Grade 1, g/adt			Pulp Grade 2, g/adt		
	60% ClO_2	100% ClO_2	Decrease % ++	60% ClO_2	100% ClO_2	Decrease % ++
Phenols						
2,4-dichlorophenol	0.49	0.10	80	0.36	0.08	79
2,4,6-trichlorophenol	0.36	ND	100	0.21	ND	100
2,3,4,6-tetrachlorophenol	0.09	ND	+	0.06	ND	+
pentachlorophenol	0.05	ND	+	ND	ND	*
Phenol sub total	1.00	0.10	88	0.63	0.08	87
TEQ sub total	0.17	0.01	94	0.10	ND	95
Guaiacols						
4,6-dichloroguaiacol	0.04	0.88	—	0.17	0.23	—
3,4-dichloroguaiacol	0.88	0.38	56	0.84	0.10	88
4,5-dichloroguaiacol	2.60	0.11	96	0.58	0.09	84
3,4,6-trichloroguaiacol	0.05	ND	+	ND	ND	*
3,4,5-trichloroguaiacol	0.02	ND	+	ND	ND	*
4,5,6-trichloroguaiacol	0.50	ND	100	0.28	ND	100
tetrachloroguaiacol	0.28	ND	100	0.11	ND	+
Guaiacol sub total	4.36	1.37	88	1.98	0.42	89
TEQ sub total	0.47	0.10	92	0.20	0.03	94
Catechols						
4,5-dichlorocatechol	4.99	0.13	97	3.51	0.06	98
3,4,5-trichlorocatechol	2.47	ND	100	1.09	ND	100
tetrachlorocatechol	0.43	ND	100	0.15	ND	100
Catechol sub total	7.89	0.13	98	4.75	0.06	99
TEQ sub total	1.02	0.01	99	0.52	ND	100
Vanillins						
6-chlorovanillin	0.29	0.25	14	1.69	0.22	87
5,6-dichlorovanillin	0.29	0.02	94	0.58	ND	100
Vanillin sub total	0.58	0.26	54	2.27	0.22	90
TEQ sub total	0.03	0.01	78	0.09	0.01	93
CPC total	13.83	1.86	93	9.63	0.77	94
TEQ total	1.69	0.12	96	0.92	0.04	98

++ Calculation based on data where a numerical value could be assigned to the % decrease in inlet CPC levels.
+ Increased ClO_2 substitution appears to decrease CPC formation.
— Increased ClO_2 substitution appears to increase CPC formation.
* Increased ClO_2 substitution appears to have no effect on CPC formation.
ND = less than 0.06 g/adt; figures cited in table may be lower because they represent averages.
TEQ = toxicity equivalent based on pentachloro phenol.
CPC = chlorinated phenolic compound.

AOX parameter to process change is imperative, since its discharge is being regulated in several regions of Canada.

The low molecular weight AOX (AOX < 1000 Daltons; reported to range from 25 to 50% of AOX in untreated effluents [15-18]) is of somewhat greater potential environmental significance, in that it has the ability to penetrate cell membranes and contains the relatively lipophilic EOX (extractable organically-bound halogen; about 1 to 3% of AOX [19]). A small fraction of this EOX (0.1% of AOX) has the pro-pensity to bioaccumulate in the fatty tissue of higher organisms and contains compounds such as the polychlorinated aromatics which are considered to be potentially the most toxic and persistent in the receiving environment. Chlorinated phenolic compounds (CPCs) may form a significant portion of this latter category, and for this reason it is instructive to monitor changes in their formation when mill process modifications are being made.

Effect of increased chlorine dioxide substitution: *Acute toxicity and effluent color:* Table III shows that increasing chlorine dioxide substitution from 60 to 100% did not have a significant effect on the rainbow trout acute toxicity of the whole mill effluent, prior to secondary treatment. It is possible that the bleach plant effluent toxicity was decreased but the effect was not large enough to overcome contributions from other mill effluent streams. Concentrations of resin and fatty acids, before biotreatment, measured by the gas chromatographic method of Voss et al. [20] were low, ranging from 0.02 to 0.05 kg/adt (0.26 to 0.90 mg/L).

Effluent color was expected to decrease as chlorine dioxide substitution was increased from 60 to 100% [3]. As shown in Table III, effluent color, measured at the outlet of the treatment system, was decreased by approximately 30 to 35%.

AOX and EOX: It is well known that decreasing applied molecular chlorine by increasing chlorine dioxide substitution decreases the formation of chlorinated organic compounds [3, 5, 21-24]. Many predictive equations have been developed to estimate AOX formation from various bleaching sequences. Such equations take the following form when chlorine and chlorine dioxide are expressed in kg/adt:

AOX, kg/adt =

TABLE V. THE REMOVAL OF CHLORINATED PHENOLIC COMPOUNDS BY AN OXYGEN ACTIVATED SLUDGE TREATMENT SYSTEM.

	Pulp grade 1				Pulp grade 2		
	60% ClO$_2$		100% ClO$_2$		60% ClO$_2$		100% ClO$_2$
	Removal, %		Removal, %		Removal, %		Removal
	Range	Avg.	Range	Avg.	Range	Avg.	
Phenols							
2,4-dichlorophenol	-88 →0	-38		—	-160 → -100	-137	—
2,4,6-trichlorophenol	50 →83	67		•		+	•
2,3,4,6-tetrachlorophenol		+		•		+	•
pentachlorophenol		•		•		•	•
Phenol sub total	-29 →21	-2			-160 → -100	-137	
TEQ sub total	0 →49	18			-160 → -100	-137	
Guaiacols							
4,6-dichloroguaiacol		—	5 →67	42		+	+
3,4-dichloroguaiacol	40 →59	52	-25 →25	-7	83 →100	89	+
4,5-dichloroguaiacol	-33 →94	38	•	•	22 →50	34	•
3,4,6-trichloroguaiacol		•		•		•	•
3,4,5-trichloroguaiacol		•		—		•	•
4,5,6-trichloroguaiacol	-11 →25	5		—	-25 →40	13	•
tetrachloroguaiacol		67		•		+	•
Guaiacol sub total	-6 →81	40	-6 →54	27	52 →67	58	
TEQ sub total	11-73	39	-3 →54	28	46 →52	48	
Catechols							
4,5-dichlorocatechol	6 →46	29	-150 → -100	-125	21 →53	36	—
3,4,5-trichlorocatechol	60 →65	62		—	57 →71	63	—
tetrachlorocatechol	61 →70	65		—		+	—
Catechol sub total	31 →50	42	-150 → -100	-125	31 →57	43	
TEQ sub total	48 →53	51	-150 → -100	-125	41 →61	49	
Vanillins							
6-chlorovanillin	-167 →16	-75	40 →71	56	76 →84	79	+
5,6-dichlorovanillin	75 →80	78		•	88 →90	89	•
Vanillin sub total	-13 →16	1	40 →71	56	79 →85	82	
TEQ sub total	16 →30	25	71 →100	86	81 →86	83	
CPC total	16 →56	39	6 →27	17	41 →55	49	
TEQ total	36 →59	47	3 →27	17	40 →56	47	

+   Treatment appears to promote CPC removal.
—   Treatment appears to increase CPC loadings.
*   Treatment appears to have no effect on CPC loadings.

TEQ   = toxicity equivalent based on pentachloro phenol.
CPC   = chlorinated phenolic compound.

Based on such an equation, formation of AOX should decrease by approximately 45% for Pulp Grade 1 and 35% for Pulp Grade 2, when chlorine dioxide is increased from 60 to 100%. The levels of AOX and low molecular weight AOX (AOX < 1000) in the effluent before treatment, for both operating conditions and pulp grades, are shown in Fig. 5. Measurements were performed on unfiltered samples using a Dohrmann analyzer according to U.S. EPA Method 9020 [25]. The low molecular weight AOX fraction was prepared by ultrafiltration using an Amicon YM2 membrane.

The data in Fig. 5 indicate that an increase in chlorine dioxide substitution from 60 to 100% significantly decreased the AOX in the untreated effluent: 70% for Pulp Grade 1 and 60% for Pulp Grade 2. The low molecular weight AOX was found to form approximately 30 to 40% of the total AOX, and its decrease, with increased chlorine dioxide substitution, paralleled that of the total AOX. Interestingly the proportion of the low molecular weight AOX generated was not affected by the increase in chlorine dioxide substitution. These findings are in agreement with previously reported research [16] at two mills using 10 and 70% chlorine dioxide substitution, respectively.

This greater than predicted decrease in AOX formation supports work by Liebergott et al. [3] which showed that the relationship between the formation of AOX and applied elemental chlorine changes dramatically at 90 to 100% chlorine dioxide substitution. With chlorine dioxide delignification, the fraction of applied elemental chlorine becoming organically-bound is significantly less than at 60% chlorine dioxide substitution. The results demonstrate that use of predictive equations such as those mentioned above must be applied cautiously as the proportionality factor, k, may not only be dependent on the wood species [3], but may also be a function of the chlorine dioxide substitution in the first stage of bleaching.

In this investigation, the effluent EOX was determined by a cyclohexane extraction method. As indicated in Fig. 6, for the untreated effluent the decrease in EOX due to the increase in chlorine dioxide substitution was variable, with a 63% decrease for Pulp Grade 1 and 17% for Pulp Grade 2. The observed differences may be in part attributed to the substantially lower initial effluent EOX for Pulp Grade 2 at 60% chlorine dioxide substitution. In all cases, the EOX accounted for 0.3 to 0.9% of the total AOX.

Chlorinated phenolic compounds: The chlorination of aromatic compounds, including phenolics, is known to proceed stepwise from the mono- to di-, to tri-, to tetra, and in the case of phenols, to penta-substitution [26]. It has been shown that decreasing the applied molecular chlorine by increasing chlorine dioxide substitution decreases the formation of the more lipophilic, higher chlorinated (tri-, tetra-, and penta-) phenolic compounds [3, 5, 13, 22, 23, 27, 28]. It is also expected that other higher chlorinated compounds which are found in the very lipophilic portion of the EOX will be concomitantly decreased. Evidence supporting this position has been reported for chlorinated thiophenes [27] and chlorinated methyl-substituted furans [29].

CPCs are not all equally deleterious to the receiving environment. For this reason, conclusions based on total CPC loadings in the effluent tend to be misleading. To address this composite parameter problem, a scale has been developed based on chronic toxicity data for trout, fathead minnow, and other aquatic species reported in the literature [30]. Pentachlorophenol, the most toxic of the CPCs, was given a toxicity equivalency factor (TEF) of 1, and the other phenols, were given lower factors, reflecting their lower relative toxicities.

Among the other families of phenolics (i.e., guaiacols, vanillins, etc.) differences in toxicity were found to be related primarily to the degree of chlorination, rather than family type. Hence all classes of compounds having the same extent of chlorine substitution on the aromatic ring were assigned identical toxicity factors. This scale, for CPCs, provides a way to sum the toxicity of a mixture of compounds. The total value is expressed as pentachlorophenol toxicity equivalents (TEQs), and CPC loadings are then calculated as g PCP/adt. This allows a relative assessment of the effect of process modifications on effluent quality.

Table IV indicates the average effluent concentrations, before biological treatment (three daily composites), of total CPCs as well as their pentachlorophenol-based TEQs for the two pulp grades, at the two levels of chlorine dioxide substitution studied. All effluent samples were treated with ascorbic acid to convert any quinones to their respective catechols and were analyzed for chlorinated phenolics by the gas chromatographic method of Voss et al. [31]. Since the CPC loadings were, in general, very low, often close to the detection limit, and were measured by gas chromatography only, the results must at all times be interpreted with caution. For example, the CPC concentrations at 100% chlorine dioxide sub-

stitution were so low, in particular with Pulp Grade 2, that in many cases, only a qualitative assessment of the effect of increased chlorine dioxide substitution on CPC loadings could be made.

As expected from the sequential mechanism of chlorination of aromatic compounds, the more highly chlorinated phenolics were generally non-detectable at 100% chlorine dioxide substitution. Using only the "before biological treatment" effluent data, where a numerical value could be assigned to the decrease in CPCs due to increased chlorine dioxide substitution, a greater than 95% overall decrease in pentachlorophenol-based TEQs for both pulp grades was observed.

In early 1989, HSPP was operating at 10% chlorine dioxide substitution and was discharging approximately 6 kg AOX/adt [32]. The curved line shown in Fig. 7, which is based on laboratory studies investigating the effect of a range of Kappa factors (0.14 to 0.28) and chlorine dioxide substitution levels (0 to 90%) on effluent loadings of CPCs and AOX, estimates the corresponding pentachlorophenol TEQ discharge at 13 g/adt [13, 28]. Data from the current mill trials are plotted on the laboratory generated curve.

Modernization and incorporation of oxygen delignification, in conjunction with 60% chlorine dioxide substitution, account for a 90% decrease in pentachlorophenol TEQ discharge to 1.3 g/adt (average effluent concentration for Pulp Grades 1 and 2 before biotreatment). Increasing chlorine dioxide substitution to 100% decreased the remaining 1.3 g/adt pentachlorophenol TEQ discharge an additional 95%. Overall, modernization, incorporation of oxygen delignification, and adoption of chlorine dioxide delignification have decreased the pentachlorophenol TEQ discharge to less than 1% of its 1989 value.

Treatability of chlorinated organic compounds: The effectiveness of conventional secondary (biological) treatment systems in decreasing AOX and chlorinated phenolic compounds has been documented in recent years, especially at low to moderate chlorine dioxide substitution [24, 33-40]. However, with the exception of the work by Rempel et al [36], information concerning the effectiveness of oxygen activated sludge treatment in decreasing these compounds is notably lacking. Its ability to decrease the more environmentally-significant parameters such as low molecular weight AOX and EOX is also unknown.

This aspect of the investigation was undertaken to examine the effect of wood furnish and chlorine dioxide substitution on the treatability of these chlorinated compounds by an oxygen

activated sludge system. Details on the design and operation of this system can be found in a paper by Strang [41].

Acute toxicity: The effectiveness of the oxygen activated sludge secondary effluent treatment system in removing acute lethal toxicity to fish was shown previously in Table III. All treated effluents during the investigation period had a 96-hour $LC_{50} \geq 100\%$. In all cases, treatment removed greater than 97% of the resin and fatty acids.

AOX and EOX: The ability of the treatment system to remove AOX, and that fraction of the AOX with molecular weight < 1000 Daltons was evaluated for both operating conditions and pulp grades. The results are shown in Fig. 5. The average discharge of AOX in the final, biotreated mill effluent was 1.6 kg/adt at 60% chlorine dioxide substitution and 0.65 kg/adt at 100% chlorine dioxide substitution.

For Pulp Grade 1, treatment resulted in moderate removal of the total AOX, ranging from 17 to 25% for 60% chlorine dioxide substitution and 0 to 18% for 100% chlorine dioxide substitution. A large proportion of the AOX removed was due to a decrease in the low molecular weight fraction.

The decrease in the AOX < 1000 fraction accounted for 40 to 93% of the total AOX removed for Pulp Grade 1 at 60% chlorine dioxide, and for two of the data sets, accounted for all the AOX removal at 100% chlorine dioxide substitution. There was no apparent removal of AOX for one of the data sets at 100% chlorine dioxide substitution, though AOX < 1000 appeared to be reduced slightly.

For Pulp Grade 2, treatment also resulted in moderate removal of the total AOX, ranging from 17 to 27% for 60% chlorine dioxide substitution for two of the data sets, with no apparent removal for the third. Again, the bulk (70 to 72%) of the AOX removed was due to a decrease in the AOX < 1000 fraction. As was the case for Pulp Grade 1, at 100% chlorine dioxide substitution, treatment of the effluents did not give rise to any significant decrease in AOX. However, in two cases, low molecular weight AOX appeared to be decreased across the treatment system.

The preferred removal of the low molecular weight AOX observed in this study is in agreement with previous findings [16-18] which reported that 40 to 80% of the decrease in the total AOX, across an aerated lagoon, could be directly attributed to the degradation of the AOX < 1000 fraction.

The results in Fig. 6 indicate that the average removal of EOX by oxygen activated sludge treatment varied between 35 to 68%. An apparent increase in the average EOX was noted for Pulp Grade 1 at 100% chlorine dioxide substitution.

Chlorinated phenolic compounds: Chlorinated phenolics are known to be biodegradable [15, 42]. Removal efficiencies are dependent on treatment conditions, and are different for individual members of each class of compounds [33-36, 38]. Furthermore, since the distribution of individual chlorinated phenolics changes with chlorine dioxide substitution [13, 22, 24, 27, 28, 38], the question was asked whether the effluents would be equally amenable to biological treatment. This portion of the investigation was designed to address this question.

The relevant chlorinated phenolic data are summarized in Table V. The average percent removals were calculated using the three daily composite treatment efficiencies at each operating condition. Negative numbers indicate an apparent increase in CPC loadings across the treatment system.

The data indicate that despite considerable variability in observed treatment, total pentachlorophenol-based TEQ loadings were decreased for all four operating conditions. The concentrations at 100% chlorine dioxide substitution were so low before treatment, in particular with Pulp Grade 2, that in many cases only a qualitative assessment of the treatment effectiveness could be made. Furthermore, since only the data where a numerical value could be assigned to the percent removal efficiencies of individual CPCs during treatment were used to calculate total average reductions, the apparently lower treatment efficiencies at 100% chlorine dioxide substitution (i.e., 17% vs 40% for Pulp Grade 1), should not be interpreted to mean that the CPCs produced during chlorine dioxide delignification are more recalcitrant to biological treatment.

SUMMARY

Chlorine dioxide delignification at HSPP's modernized and expanded pulp mill has been adopted to respond to customer demand for "molecular-chlorine-gas-free" fully-bleached market softwood pulp.

Comparing chlorine dioxide delignification (100% chlorine dioxide substitution) to 60% chlorine dioxide substitution with a 20 Kappa no. oxygen delignified pulp:
• Fully-bleached market softwood kraft pulp with identical strength and quality was produced.
• Final pulp brightness was slightly lower (~3 points Elrepho) for the cedar-spruce-fir grade but essentially the same for 100% hemlock.
• Water extractable AOX in pulp was unchanged.
• Ethanol/toluene extractable organically-bound chlorine in pulp was

decreased significantly.
• Bleaching efficiency was decreased.
• Cost of bleaching increased by 20%.

The effect of chlorine dioxide delignification and oxygen activated sludge treatment on effluent environmental quality parameters was dramatic.

When chlorine dioxide substitution was increased from 60 to 100%:
• AOX and AOX < 1000 in the untreated effluent were decreased by 60 to 70%.
• The decrease in EOX was variable, ranging from 17 to 63%.
• The chlorinated phenolics in untreated effluent, expressed as pentachlorophenol-based toxicity equivalents, were decreased by about 95%.
• Effluent color was decreased by 30 to 35%.

With oxygen activated sludge secondary biological effluent treatment:
• Treatment of the total mill effluent removed 17 to 27% of the AOX at 60% chlorine dioxide substitution but was only marginally effective at removing AOX produced at 100% chlorine dioxide substitution.
• A large portion of the AOX removed was due to a decrease in the low molecular weight fraction (AOX < 1000).
• The average discharge of AOX in the final, biotreated mill effluent was 1.6 kg/adt at 60% chlorine dioxide substitution and 0.65 kg/adt at 100% chlorine dioxide substitution.
• Removal of pentachlorophenol-based TEQs at 60% chlorine dioxide substitution was 47%. The decrease of chlorinated phenolic compounds at 100% chlorine dioxide substitution could not be quantified as the concentrations at the inlet of the treatment system were very low, often close to the detection limit.
• Final mill effluents were not acutely toxic to rainbow trout.

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Résumé: L'experience en usine avec une pâte kraft provenant de bois de résineux délignifié à l'oxygène, utilisant une délignification au dioxyde de chlore (100% dioxyde de chlore) dans la première étape de blanchiment, a été rapportée et comparée à une autre pâte avec substitution à 60% de dioxyde de chlore. Une pâte kraft entièrement chlorée a été produite avec la même résistance et la même qualité mais avec une blancheur finale légèrement inférieure. La décharge moyenne des COA dans l'effluent final après un traitement de boue activée à l'oxygène était de 1.6 kg/adt avec substitution à 60% de dioxyde de chlore et de 0.65 kg/adt avec substitution à 100% de dioxyde de chlore.

Abstract: Mill experience with an oxygen delignified softwood kraft pulp using chlorine dioxide delignification (100% chlorine dioxide) in the first stage of bleaching is reported and compared to operation with 60% chlorine dioxide substitution. Fully-bleached market kraft pulp with identical strength and quality, but slightly lower final pulp brightness, was produced. The average discharge of AOX in the final mill effluent after oxygen activated sludge treatment was 1.6 kg/adt at 60% chlorine dioxide substitution and 0.65 kg/adt at 100% chlorine dioxide substitution.