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Effects of Washer Efficiency on Characteristics of Effluents from D(EPO)D Bleaching of a Softwood Kraft Pulp

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ABSTRACT

This paper describes the results of a systematic study of AOX, BOD, and COD released by bleaching southern pine kraft pulp in the D_0(EPO)D_1 sequence at a kappa factor of 0.20 and a D_1 stage ClO_2 charge of 1.2%. Measurements of all three parameters were made at three different levels of carryover of D_0 stage filtrate into the (EPO) stage and three different levels of carryover of (EPO) stage effluent into the D_1 stage, and the entire experiment was duplicated.

The combined AOX contributions of the D_0 and (EPO) stages amounted to 11.6% of the chlorine atoms applied in the D_0 stage, while the contribution of the D_1 stage amounted to 2.7% of the chlorine atoms applied in the D_1 stage. The combined AOX contributions of all three stages decreased when the D_0 stage carryover was increased from 0 to 10% and was unaffected by (EPO) stage carryover. With perfect washing between stages, COD contributions to the combined bleach plant filtrates by the D_0, (EPO) and D_1 stages were, respectively, 14.1, 39.8, and 2.9 kg/odumt. The combined COD contributions of all three stages was relatively unaffected by a low level (5%) of D_0 stage carryover, but a higher level (10%) resulted in an overall COD increase of 2 kg/odumt. Increasing (EPO) stage carryover from 0 to 30% decreased total COD by 3 kg/t. With perfect washing between stages, BOD contributions to the combined bleach plant filtrates by the D_0, (EPO), and D_1 stages were, respectively, 3.8, 7.0, and 2.2 kg/odumt. No significant effect of carryover levels on the total BOD release could be detected.

INTRODUCTION

Kraft pulp bleaching sequences that do not make use of molecular chlorine are rapidly becoming the norm throughout the world, and are virtually mandated in the United States by the Environmental Protection Agency's "Cluster Rules."[1] One important sequence type relies on chlorine dioxide, ClO_2, to accomplish both bulk delignification in the first stage and brightening in the latter stages. Detailed knowledge of the environmentally relevant characteristics of the effluents these sequences generate is needed to allow them to be evaluated for specific applications.

The characteristics of the filtrates from individual stages are of less interest than those of the entire bleach plant effluent that results when the filtrates from all stages are combined before being sent to the effluent treatment system. Because the byproducts of any bleaching stage are subject to possible destruction in a subsequent stage, it is reasonable to expect that the characteristics of the combined effluent may be determined not only by the products of the reactions between the bleaching chemical and pulp components in each stage, but also by the proportion of these products that are carried with the pulp into the following stage, as opposed to being discharged directly to the sewer. Consequently, it is of interest to determine the effect of bleach plant washer efficiency on effluent characteristics, and important to recognize it in laboratory evaluations of bleaching sequences from an effluent quality standpoint.

In the present study, we determined properties of individual stage and combined filtrates from laboratory bleaching of a southern pine kraft pulp in the D(EPO)D sequence.

EXPERIMENTAL

Pulping

Southern pine chips from a southeastern U.S. coastal mill were screened and pulped in a 2.0 ft^3 batch digester heated indirectly with steam. The following conditions were used: effective alkali (% o.d. wood): 16; sulfidity (%): 25; maximum temperature (°C): 170; liquor-to-wood ratio (L/kg): 4:1; H-factor: 2058; chip charge (g.o.d.):

6000. The pulp was disintegrated and screened on a 0.010″ slotted flat screen. The Kappa number of the screened pulp was 26.

Bleaching

D_0 stages were performed on 100-g (o.d. basis) samples in a Quantum Technologies high-shear mixer at a kappa factor of 0.20 for 30 minutes at 45°C and 4% consistency. The pulp was preheated in a microwave oven, and its pH was adjusted with H_2SO_4 before adding the ClO_2, to achieve a final pH of 2.0. After ClO_2 addition, the pulp was mixed for 7 seconds and for 7 seconds every 3 minutes thereafter. At the end of the retention period, the filtrate was sampled for pH and residual measurement.

The pulp was transferred to a funnel and filtered to remove as much full-strength filtrate as possible. The filtrate was set aside for use as carryover or for analysis. (The filtrates were stored overnight at 4°C at the pH of the stage.) The pulp was then washed twice by dilution to 3% consistency followed by vigorous mixing and filtering.

The extraction stage was carried out in an agitated pressurized reactor at 70°C and 10% consistency for 60 minutes. The NaOH charge was 3.2% when no D_0 filtrate was present and was otherwise adjusted to give an exit pH between 11.0 and 11.4. The charge of H_2O_2 was 0.5%, and the reactor was pressurized with oxygen at 60 psig. initially. At intervals of 10 min., the oxygen pressure was decreased to 50, 40, and 0 psig. The pulp, NaOH, and carryover (when applied) were first mixed and heated in a microwave oven before being placed in the reactor. The peroxide was added while the pulp was in the reactor. At the end of the stage, the pulp was sampled, filtered, and washed as described above.

The D_1 stage was carried out in polyester bags in a controlled water bath at 70°C. The ClO_2 charge was 1.2%. The pulp, dilution water, and NaOH or H_2SO_4 were first mixed together and put in the bag. Then the chlorine dioxide was added and the bag sealed. After mixing by hand, the bag was carefully opened to measure the pH. Then it was sealed again, heated in the microwave oven, and placed in the water bath until the color of the filtrate indicated that only a trace of residual remained. The pulp was filtered and washed and the filtrate was collected as described above. Exit pH, ClO_2 residual, and ISO brightness were measured.

Filtrate Preparation and Analysis

The individual stage filtrates were collected and refrigerated until the sequence was complete. Typically, there was a delay of one day between collection of the D_0(EOP) and D_1 effluents. A sample of combined filtrate was prepared using individual filtrates in the proportions: D_0:(EOP):D_1= 24(1-c1) : 9(1-c2) : 9, where c1 = (% carryover from stage 1)/100 and c2 = (% carryover from stage 2)/100.

Filtrate samples for AOX analysis were treated with $Na_2S_2O_3$, pH-adjusted to < 2 with concentrated HNO_3 and stored at 4°C. Filtrate samples for COD were pH-adjusted to < 2 with 4N H_2SO_4 and stored at 4 °C. Samples for BOD analysis were adjusted to pH 7.0 with NaOH or H_2SO_4. Immediately after collection and pH adjustment, the samples were refrigerated and shipped in insulated containers.. Testing was completed within 48 hours of collection..

All filtrate tests were done by Savannah Laboratories, Mobile, AL, according to the following methods: AOX-EPA Method 1650 rev. B[2], COD-Standard method 5220C[3], and BOD-Standard method 5210[3].

Experimental Design and Analysis

The experimental design was a replicated 3^2 factorial with a doubly replicated center point. It encompassed 20 independent runs, each starting with a different sample of unbleached pulp. The two variables investigated were the fraction of the total D_0 stage filtrate carried with the pulp into the (EPO) stage (0, 5, and 10%) and the fraction of the total (EPO) filtrate carried into the D_1 stage (0, 15, and 30%). The resulting data were analyzed by multiple regression, for which purpose the variables were coded, to simplify the equations. The variable XD was defined such that its values were, respectively, -1, 0, and +1 when the D_0 stage carryover levels were 0, 5, and 10%. The variable XE was defined such that its values were, respectively, -1, 0, and +1 when the (EPO) stage carryover levels were 0, 15, and 30%. Objective statistical techniques were used to identify outlying observations, which were discarded before doing the regression analysis. Outliers are shown within parentheses in the data tables. The regression model used included the terms XD, XE, XD^2, XE^2, and $XD \cdot XE$. Only those terms significant at a confidence level of 95% or greater were retained.

RESULTS AND DISCUSSION

Pulp properties and residual chemical levels are shown in Table 1. In all cases, only a trace of residual ClO_2 remained at the end of the 30-min D_0 stage retention time. Similarly, no more than a trace of residual H_2O_2 was found at the end of the (EPO) stage.

The concentrations of AOX, COD, and BOD in individual stage filtrates and total and combined discharge rates are shown in Tables 2-4.

Bleaching Efficiency

As Table I shows, the levels of D_0 stage carryover employed had no significant effect on the (EPO) kappa number, although a barely discernible (93% confidence) adverse effect on brightness was noted. The 95% confidence interval for the mean kappa number after the (EPO) stage was 3.60 ± 0.07. The (EPO) brightness decreased from 63.7 with perfect washing after the D_0 stage to 63.0 at the 10% carryover level. As described below, however, D_0 stage carryover had no effect on final brightness.

Table I Experimental Bleaching Data

% D_0 Filtrate Carryover	% (EPO) Filtrate Carryover	(EPO) Stage Kappa No.	(EPO) Stage Brightness	D_1 Stage Exit pH	D_1 Stage ClO_2 Residual, % o.d.p.	D_1 Stage ClO_2 Consumed, % o.d.p.	D_1 Stage Brightness
0	0	3.8	63.1	4.00	0.039	1.16	87.3
		3.6	64.1	4.20	0.039	1.16	87.2
	15	3.5	64.1	4.35	0.058	1.14	87.4
		3.5	64.2	4.60	0.078	1.12	87.1
	30	3.7	63.3	4.50	0.037	1.16	85.5
		3.7	62.9	4.80	0.073	1.13	85.2
5	0	3.5	63.8	4.95	0.136	1.06	87.9
		3.8	63.4	4.70	0.107	1.09	87.2
	15	3.5	64.3	4.30	0.058	1.14	86.8
		3.7	62.4	4.10	0.029	1.17	86.7
		3.5	64.2	4.00	0.044	1.16	87.0
		3.8	63.8	4.50	0.092	1.11	87.2
	30	3.6	62.4	4.55	0.068	1.13	86.4
		3.6	63.4	4.85	0.102	1.10	85.3
10	0	3.7	63.5	4.30	0.058	1.14	87.8
		3.3	63.1	4.30	0.054	1.15	87.4
	15	3.4	63.0	4.50	0.068	1.13	86.4
		3.6	62.9	4.35	0.073	1.13	87.1
	30	3.7	62.9	4.75	0.083	1.12	85.9
		3.6	62.3	4.85	0.088	1.11	85.1

Although we attempted to control the D_1 stage exit pH at 4.5, it varied between 4 and 5, with some effect on the amount of residual ClO_2 that remained at the end of the D_1 stage. Regression analysis of the residual ClO_2 data gave the following equation:

$$\text{Res. } ClO_2 = 0.1(\text{pH}) - 0.014(\text{XE}) - 0.013(\text{XE})^2 - 0.38,$$

which gives the residual as a percentage of o.d. pulp weight, and for which the multiple correlation coefficient, R^2, and the standard error of estimate, s, were, respectively, 0.85 and 0.011.

This equation shows that a pH increase from 4.0 to 5.0 increases the residual ClO_2 by 0.1% (o.d. pulp basis). The pH did not, however, affect the brightness obtained. The above equation also shows that, at constant D_1 stage exit pH, increasing (EPO) stage carryover from 0 to 15% has no effect on the residual ClO_2 level, but a further increase from 15 to 30% causes the residual to decrease by 0.03% (o.d. pulp basis).

A corresponding regression analysis of final brightness showed a similar dependence on carryover level, but no dependence on pH. The following equation was obtained:

$$\text{Brightness} = 87.0 - 1.0(\text{XE}) - 0.5(\text{XE})^2,$$

for which R^2 and s were, respectively, 0.89 and 0.31. This equation shows that increasing (EPO) stage carryover from 0 to 15% decreases final brightness by 0.5 point, while a further increase from 15 to 30% causes a further brightness decrease of 1.5 points. The overall effect of carrying over 30% of the (EPO) stage filtrate into the D_1 stage is thus a 2-point loss in bleached brightness.

AOX

Table II contains the results of determinations of AOX in each of the individual stage filtrates and combined effluent samples. These are expressed both as observed concentrations in mg/L and releases calculated on a pulp weight basis by taking into account the consistency of the stage and the fraction of the filtrate released to the sewer rather than being carried over to the next stage.

The concentration of AOX found in the D_0 stage filtrate is expected to be the same for all experiments, since the experimental variables did not affect D_0 stage conditions. After rejection of a single outlying observation, the mean AOX concentration was 39.9 mg/L, and the standard deviation was 5.4. The 95% confidence interval for the mean is 39.9 ± 2.6 mg/L, corresponding to a formation rate of 0.96 ± 0.06 kg/odumt (oven-dry unbleached metric ton). This corresponds to conversion of (9.2 ± 0.6)% of the applied chlorine atoms to AOX.

The average concentration of AOX found in the (EPO) stage filtrate, after eliminating two suspiciously low values, was 28.2 mg/L, with a standard deviation of 4.8 mg/L. There was no significant effect of D_0 carryover level on the concentration of AOX in the (EPO) filtrate, suggesting that AOX carried into this stage is destroyed. Studies by Cook[4] on the Ultim-O process have also shown that a significant portion of the AOX is destroyed in the extraction stage. The 95% confidence interval for the mean AOX concentration was 28.2 ± 2.4 mg/L, corresponding to a formation rate of 0.25 ± 0.02 kilograms per oven-dry unbleached metric ton (kg/odumt). The total rate of formation in the first two stages was therefore 1.21 kg/odumt, which corresponds to conversion of 11.6% of the applied chlorine atoms to AOX. This value is somewhat lower than the value of 13.6% calculated from a model based on an analysis of literature data obtained by bleaching with ClO_2-rich mixtures of ClO_2 and Cl_2.[5] The difference may reflect differences between pure ClO_2 and mixtures.

Table II Observed AOX Concentrations and Discharges

		Found in Effluent, mg/L			Discharged, kg/ODUMT	
% D_0 Effluent Carryover	% (EPO) Effluent Carryover	D_0 Stage	(EPO) Stage	D_1 Stage	Total of Stage Contributions	Combined Effluent
0	0	43	30	17	1.46	1.34
		41	35	(38)	1.64	1.68
	15	47	25	23	1.53	1.38
		49	25	23	1.57	1.46
	30	34	35	29	1.30	1.26
		42	29	43	1.58	1.49
5	0	40	21	24	1.32	1.35
		34	26	20	1.19	1.35
	15	(21)	(15)	17	(0.75)	(0.75)
		47	32	33	1.61	1.70
		41	21	23	1.30	1.30
		37	23	20	1.20	1.62
	30	41	29	34	1.42	1.33
		29	(16)	27	1.01	1.10
10	0	37	30	11	1.17	1.27
		43	30	13	1.32	1.62
	15	40	24	33	1.34	1.34
		35	24	23	1.15	1.15
	30	33	31	31	1.19	1.44
		46	37	43	1.61	1.25

The concentration of AOX in the D_1 filtrates increased when the level of carryover from the (EPO) stage was increased. The following regression equation was obtained:

$$D_1 \text{ AOX, mg/L} = 26.2 + 7.0(XE)$$

for which R^2 and s were, respectively, 0.37 and 7.4. Despite the relatively low R^2, the effect of carryover was significant at the 99.5% confidence level. This is consistent with the expectation that AOX carried into a D_1 stage will not be destroyed in that stage. Furthermore, comparison of the coefficient for XE in the above equation with the concentration of AOX in the (EPO) filtrate suggests that additional AOX is formed in the D_1 stage from material in the carryover from the (EPO) stage. An increase in (EPO) stage carryover from 0 to 30% corresponds to an increase in XE of two units (from -1 to +1), for which the above equation predicts an increase of 14 mg/L or 0.13 kg/odumt. The (EPO) filtrate entering this stage contained only 30% of 0.25 or 0.08 kg/odumt.

From a practical viewpoint, the amount of AOX discharged to the treatment system per ton of pulp is of more interest than its concentration in the filtrates from individual stages. The amount of AOX released from a given stage is the amount formed, less the amount carried with the pulp into the next stage, except for the last stage in the sequence, which is assumed to release all of the AOX present in the filtrate emerging with the pulp from the bleaching tower. All of these releases are then combined, and the amount of AOX discharged from the pulp mill to the treatment system is their sum, less any loss that occurs as a result of chemical reaction after mixing. Table II contains the individual stage releases, their sums, and the total discharge calculated from the AOX concentration in the combined effluent. The latter two figures will be the same, in the absence of experimental error, unless some AOX is destroyed or created by chemical reaction after mixing of the individual stage filtrates.

Regression analysis of the sum of the individual stage releases ("Total AOX"), after rejection of one outlying observation, gave the following equation:

$$\text{Total AOX, kg/odumt} = 1.36 - 0.11(\text{XD})$$

for which R^2 and s were, respectively, 0.22 and 0.17. This equation reflects the earlier observations that D_0 AOX is destroyed in the (EPO) stage, but that (EPO) AOX is unaffected by the D_1 stage. The low R^2 value reflects the fact that the effect of D_0 stage carryover is small in comparison to the total discharge, but the carryover effect is nevertheless significant at the 95% confidence level.

The Total AOX discussed above was next compared to the total discharge calculated from the AOX concentration in the combined effluent by means of a paired t-test. The two figures may be expected to differ to the extent that AOX is destroyed or created upon mixing of the filtrates from individual stages. The t-test showed that there was no significant difference between them. The 95% confidence interval for the difference was 0.03±0.08 kg/odumt (0.01±0.06 if the three largest differences were discarded). This result, together with the observed effect on the total AOX, leads to the conclusion that increasing D_0 stage carryover decreased overall AOX release. It also shows that there was negligible loss of AOX due to chemical reaction upon mixing acid and alkaline effluents. This conclusion, however, should be viewed in light of the fact that the effluents were combined under laboratory conditions (low temperature and near-neutral pH) that did not favor chemical reaction. This would not be true in the mill, and mill experience suggests that AOX destruction does occur as a result of mixing the effluents from the individual bleaching stages.[5]

COD

Table III contains the results of determinations of COD in each of the individual stage filtrates and combined effluent samples, expressed both as observed concentrations in mg/L and releases in kg/odumt.

Table III Observed COD Concentrations and Discharges

		Found in Effluent, mg/L			Discharged, kg/ODUMT	
% D_0 Effluent Carryover	% (EPO) Effluent Carryover	D_0 Stage	(EPO) Stage	D_1 Stage	Total of Stage Contributions	Combined Effluent
0	0	590	4500	350	57.8	58.8
		540	(5000)	(1000)	(67.0)	58.8
	15	610	(5100)	(910)	(61.8)	52.8
		630	4400	780	55.8	52.8
	30	580	4300	1300	52.7	55.0
		600	4500	1400	55.4	55.0
5	0	590	4400	250	55.3	53.0
		560	4400	350	55.5	53.0
	15	600	4500	760	54.9	51.3
		610	4500	800	55.5	51.3
		590	4300	740	53.0	51.3
		580	4500	780	54.7	55.2
	30	590	4400	1400	53.8	53.3
		620	4400	1300	53.6	53.3
10	0	580	4900	380	60.0	59.4
		610	4900	280	59.8	55.4
	15	580	5000	800	58.0	53.6
		550	4900	760	56.2	61.2
	30	(660)	4800	1400	57.1	59.0
		570	4900	1500	56.7	55.4

The concentration of COD in the D_0 stage filtrate is unaffected by bleach plant washer inefficiency. Its average value, after discarding one outlying observation, was 588 mg/L and its standard deviation was 23 mg/L. The 95% confidence interval for the mean was 588±11 mg/L, corresponding to a formation rate of 14.1±0.3 kg/odumt.

Regression analysis of the (EPO) stage COD concentration data gave an equation that was significantly nonlinear with respect to D_0 stage carryover. It suggested that there was no effect of carrying over 5% of the D_0 stage effluent, but that when the D_0 carryover level was increased to 10% there was a significant increase in (EPO) filtrate COD concentration. When two outlying observations were discarded and the regression analysis was repeated, the conclusion was the same. This analysis gave the equation:

$$\text{(EPO) COD, mg/L} = 4425 + 238(\text{XD}) + 238(\text{XD})^2$$

for which R^2 and s were, respectively, 0.92 and 74. Substitution in this equation predicts COD concentrations of 4425, 4425, and 4900 at D_0 carryover levels of 0, 5, and 10%, respectively. Converting these to a pulp weight basis gives 39.8, 39.8 and 44.1 kg/odumt, respectively. By contrast, the expected values, based on the rate of COD formation in the D_0 stage, are 39.8, 40.5, and 41.2 kg/odumt. The discrepancy at the high carryover level suggests that amounts of D_0 carryover that exceed a threshold limit may effectively catalyze COD formation in the (EPO) stage, for example, by destroying peroxide or inhibiting oxidation.

The concentration of COD in the D_1 filtrates increased at an increasing rate when the level of carryover from the (EPO) stage was increased. After discarding two outliers, the following regression equation was obtained:

$$D_1\ \text{COD, mg/L} = 774 + 531(XE) + 78(XE)^2$$

for which R^2 and s were, respectively, 0.99 and 54. Substitution in the above equation predicts COD concentrations of 322, 774, and 1383 mg/L at (EPO) carryover levels of 0, 15, and 30%, respectively. Converting these to a pulp weight basis gives 2.9, 7.0, and 12.4 kg/odumt. The expected values, based on the average COD concentration in the (EPO) filtrate, are 2.9, 9.1, and 15.3 kg/odumt. The comparison suggests that COD in the carryover is partially destroyed in the D_1 stage, and that proportionally more is destroyed when the carryover level is lower.

The amounts of COD released per ton of pulp are also shown in Table III. Regression analysis of the total of the individual stage COD releases, after discarding two outliers identified earlier, gave the following equation:

$$\text{Total COD, kg/odumt} = 54.5 + 1.1(XD) - 1.4(XE) + 2.3(XD)^2$$

for which R^2 and s were, respectively, 0.83 and 1.0. This equation predicts that total COD will be relatively unaffected by low levels (~5%) of D_0 stage carryover, but that a higher level (~10%) will result in an overall COD increase of 2 kg/odumt. It also predicts that increasing (EPO) stage carryover from 0 to 30% will decrease total COD by 3 kg/t. The former effect is indicative of a detrimental effect of D_0 carryover on (EPO) COD, and the latter to partial destruction of (EPO) COD in the D_1 stage.

The Total COD discussed above was next compared with the total discharge calculated from the COD concentration in the combined effluent by means of a paired t-test. The two figures may be expected to differ to the extent that COD is destroyed or created upon mixing of the filtrates from individual stages. After discarding the results for the two outliers, the t-test showed that there was no significant difference between them. The 95% confidence interval for the difference (Total - Combined) was 1.0 ± 1.3 kg/odumt. This result, together with the observed effect on the total COD, leads to the conclusion that increasing D_0 stage carryover increases overall COD discharge, while increasing (EPO) carryover decreases it.

BOD

Measurement of BOD concentration in the single-stage filtrates and combined effluents gave the data shown in Table IV.

Analysis of the D_0 filtrate BOD data was complicated by the observation that their distribution was skewed to the right. This departure from normality was corrected by first taking their reciprocals, which were normally distributed. The resulting 95% confidence interval for the mean BOD concentration in the D_0 filtrate was 159 ± 15 mg/L, corresponding to a formation rate of 3.82 ± 0.36 kg/odumt.

The (EPO) stage filtrate BOD's showed no significant dependence on D_0 carryover level. The 95% confidence interval for the mean (EPO) stage filtrate BOD was 778 ± 52 mg/L, corresponding to a formation rate of 7.00 ± 0.47 kg/odumt. Either D_0 BOD carryover was destroyed in the (EPO) stage or the precision of the BOD determinations was not good enough to detect the small difference (0.2-0.4 kg/odumt) expected.

The concentratiom of BOD in the D_1 filtrate increased with increasing (EPO) stage carryover, as described by the regression equation:

$$D_1\ \text{BOD, mg/L} = 336 + 87\ (XE)$$

for which R^2 was 0.48 and s was 74. Substitution in the above equation predicts BOD concentrations of 249, 336 and 423 mg/L at (EPO) carryover levels of 0, 15, and 30%, respectively. Converting these to a pulp weight basis gives 2.2, 3.0, and 3.8 kg/odumt. The expected values, based on the average BOD concentration in the (EPO) filtrate, are 2.2, 3.2, and 4.3 kg/odumt. The comparison indicates that roughly 20% of the BOD in the carryover is destroyed in the D_1 stage.

The amounts of BOD released per ton of pulp are also shown in Table IV. Regression analysis of the total of the individual stage BOD releases showed no significant effect of the carryover levels on the total BOD release. Failure to detect effects corresponding to the observed effects on COD could be due either to their absence or to the fact that the precision of the BOD measurements, relative to their mean, is poorer than in the case of COD. After deletion of one outlier, calculation of a 95% confidence interval for the total BOD release was 12.54 ± 0.65 kg/odumt.

Table IV Observed BOD Concentrations and Discharges

		Found in Effluent, mg/L			Discharged, kg/ODUMT	
% D_0 Effluent Carryover	% (EPO) Effluent Carryover	D_0 Stage	(EPO) Stage	D_1 Stage	Total of Stage Contributions	Combined Effluent
0	0	190	670	290	13.20	13.44
		140	720	280	12.36	11.34
	15	130	1000	270	13.20	11.79
		180	750	470	14.29	(15.04)
	30	150	670	470	12.05	12.58
		130	730	300	10.42	11.79
5	0	140	730	220	11.74	(4.49)
		250	860	300	(16.14)	12.65
	15	140	940	330	13.35	12.23
		150	610	240	10.25	10.26
		160	930	390	14.27	11.05
		130	660	320	10.89	11.84
	30	130	690	450	11.36	9.91
		150	940	340	12.40	12.95
10	0	130	820	220	12.17	13.07
		140	730	200	11.39	(16.63)
	15	230	810	230	13.23	10.33
		250	690	400	14.28	10.71
	30	170	750	460	12.54	11.44
		220	850	530	14.88	11.44

An independent estimate of the total BOD discharge was obtained by analyzing combined filtrate samples and converting the resulting concentrations to mass-based discharges. After elimination of three outlier, these data were also subjected to regression analysis. As in the case of the total of the single-stage releases discussed above, no significant effects of the carryover levels were detected. After elimination of three outliers, the 95% confidence interval for the combined BOD discharge was calculated to be 11.69 ± 0.54 kg/odumt.

The two estimates of total BOD discharge were compared by a paired t-test, after excluding the four cases in which either estimate was an outlying observation. The result indicated that the total BOD in the combined filtrates was slightly less than the sum of the contributions of all of the single-stage filtrates, the 95% confidence interval for the difference being 0.92 ± 0.89 kg/odumt, or about 7% of the sum of the contributions of the individual stages.

CONCLUSIONS

From this study of $D_0(EPO)D_1$ bleaching of southern pine kraft pulp at 0.20 kappa factor and a ClO_2 charge of 1.2% in the D_1 stage, with D_0 stage carryover levels ranging from 0 to 10% and (EPO) stage carryover levels ranging from 0 to 30%, the following conclusions may be drawn.

Bleaching Efficiency

1. D_0 stage carryover, at a level of 10%, has no significant effect on the (EPO) kappa number.
2. Increasing (EPO) stage carryover from 0 to 15% decreases final brightness by 0.5 point, while a further increase from 15 to 30% causes a further brightness decrease of 1.5 points. The overall effect of carrying over 30% of the (EPO) stage filtrate into the D_1 stage is thus a 2-point loss in bleached brightness.

AOX

1. With perfect washing between stages, AOX contributions to the combined bleach plant filtrates by the D_0, (EPO), and D_1 stages are predicted to be, respectively, 0.96, 0.25 and 0.17 kilograms per oven-dry unbleached metric ton (kg/odumt). The combined contributions of the D_0 and (EPO) stages amount to 11.6% of the chlorine atoms applied in the D_0 stage, while the contribution of the D_1 stage amounts to 2.7% of the chlorine atoms applied in the D_1 stage.
2. Our failure to detect any significant effect of D_0 carryover level on the concentration of AOX in the (EPO) filtrate suggests that AOX carried into this stage is destroyed. AOX carried into a D_1 stage will not be destroyed in that stage. Furthermore, a small additional amount of AOX may be formed in the D_1 stage from material in the carryover from the (EPO) stage.

3. The combined AOX contributions of all three stages decreases by 0.22 kg/odumt when D_0 stage carryover is increased from 0 to 10% and is unaffected by (EPO) stage carryover.

COD

1. With perfect washing between stages, COD contributions to the combined bleach plant filtrates by the D_0, (EPO), and D_1 stages are predicted to be, respectively, 14.1, 39.8, and 2.9 kg/odumt.
2. Increasing D_0 stage carryover beyond 5% causes a larger-than-expected increase in (EPO) stage COD, suggesting that amounts of D_0 carryover that exceed a threshold limit may effectively catalyze COD formation in the (EPO) stage, for example, by destroying peroxide or inhibiting oxidation.
3. As (EPO) carryover is increased, there is a slightly smaller-than-expected increase in D_1 stage COD, suggesting that COD in the carryover is partially destroyed in the D_1 stage.
4. The combined COD contributions of all three stages is relatively unaffected by low levels (~5%) of D_0 stage carryover, but a higher level (~10%) results in an overall COD increase of 2 kg/odumt. Increasing (EPO) stage carryover from 0 to 30% will decrease total COD by 3 kg/t.

BOD

1. With perfect washing between stages, BOD contributions to the combined bleach plant filtrates by the D_0, (EPO), and D_1 stages are predicted to be, respectively, 3.8, 7.0, and 2.2 kg/odumt.
2. The (EPO) stage BOD shows no significant dependence on D_0 carryover level.
3. Although D_1 filtrate BOD increases with increasing (EPO) stage carryover, roughly 20% of the BOD in the carryover is destroyed in the D_1 stage.
4. No significant effect of the carryover levels on the total BOD release could be detected either because they were absent or because the precision of the BOD measurements, relative to their mean, is poorer than in the case of COD.
5. The total BOD in the combined filtrates was 11.7 kg/odumt, which was slightly less than the sum of the contributions of all of the single-stage filtrates (12.5 kg/odumt).

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