

Mill-scale implementation of the recycled oxygen process

M. Muguet, P. Joly, D. Lachenal, and G. Bohman

In mill trials with the optimized prebleaching sequence, it was possible to produce high-brightness softwood kraft pulp with AOX emission as low as 1.5 kg/ton before effluent treatment.

Oxygen delignification is an attractive process for reducing the pollution load of a bleached pulp mill effluent, but its effect has always been limited. The reason lies in the poor selectivity of oxygen, which prevents it from removing more than 50% of the lignin. Legislation on AOX is becoming more and more stringent, requiring further reduction in chlorine compounds.

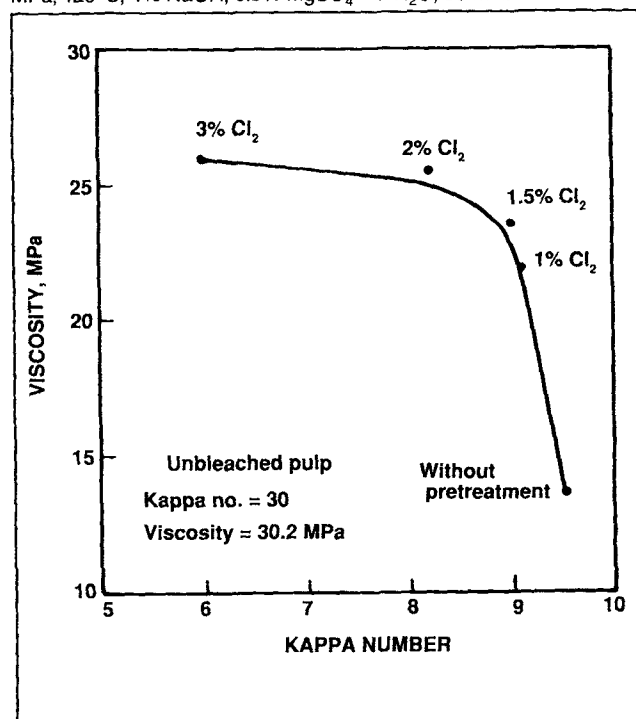
Several attempts have been made to improve the selectivity of lignin removal in oxygen bleaching. These efforts have included the removal of metal ions (1), the use of chelating agents (2), and pretreatment with NO_2 (3-4). However, none of these efforts has supplanted the need to add magnesium salts.

It has been found that using Cl_2 or ClO_2 can improve the selectivity somewhat. For instance, a low charge of chlorine (2%) prior to an O_2 stage produces pulp having a low kappa number (of 8-9) but still with a good viscosity (Fig. 1) (5-6). The mechanism involved has not yet been clearly demonstrated, but the production of new hydroxyl phenolic groups during chlorination and after alkaline treatment seems to induce a more selective oxidation reaction with O_2 (7).

Since the effluent coming from the O_2 stage is usually recycled, the logical way to benefit from this activation is to apply it on an oxygen-bleached pulp to avoid introducing chlorides in the recovery system. This procedure leads to the O x O prebleaching sequence where "x" stands for the activation treatment with halogens (chlorine, chlorine dioxide, or a mixture of both).*

A thorough study of the O x O process has been carried out at Centre Technique du Papier in Grenoble, France. The main conclusion was that with the optimized (O x O) DED sequence, a fully bleached pulp was obtained. This

1. Effect of Cl_2 pretreatment (10% consistency, 70°C, 10 min) on the selectivity of the oxygen bleaching process at 12% consistency, 0.5 MPa, 120°C, 4% NaOH, 0.5% $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$, 60 min.



process leads to a substantial decrease in the AOX (absorbable organic halogens) emission (8).

We decided to apply the process on an industrial scale. Here, we summarize the major laboratory findings related to the recycled oxygen study and present the primary results obtained in two mills.

Muguet is senior scientist at American Air Liquide, 5230 South East Avenue, Countryside, Ill. 60525. Joly is a scientist at L'Air Liquide, Centre de Recherche Claude Delorme, Les Loges en Josas, 78350 Jouy en Josas, France. Lachenal is professor and scientific adviser, Centre Technique du Papier, BP 7110, 38020 Grenoble, Cedex, France. Bohman is program manager, Alfax, Lundavagen 143, 21224 Malmoe, Sweden.

*This nomenclature is specific to this paper and has not been reviewed and approved by the TAPPI Pulp Manufacture Division.

Laboratory optimization of the O x O process

We had demonstrated already that the recycled oxygen process was able to produce high-brightness pulp with good strength properties while maintaining the emission of AOX at around 2 kg/ton (8). This process is mainly characterized by the combination of low charges of chlorine (or a mixture of chlorine and chlorine dioxide) and the use of harsh conditions in the subsequent oxygen stage.

The laboratory study indicated also that this concept could easily be retrofitted in a mill having an O(C+D)(EO)DED sequence by simply adjusting the conditions in the chlorination and alkaline extraction stages.

This success is illustrated in the following example. A softwood kraft pulp already oxygen-delignified to kappa no. 20 is submitted to a regular (C+D)(EO)DED bleaching sequence. Conditions are given in Table I. The kappa number after O(C+D)(EO) is 1.6, and final brightness is 88.8.

The O x O concept has been applied in preparing this pulp. Table II gives the development of delignification after the first three stages. It also presents the modification of chlorine multiple and temperature in the second oxygen stage. These results indicate:

- The chlorine multiple can be lowered to 0.15 (30% reduction) while increasing the (EO) temperature from 65°C to 90°C.
- The process is sensitive to (EO) temperature.
- Chlorine is a better activation agent than chlorine dioxide. A 50:50 mixture is not as efficient as 22:78.

After final bleaching in most of the cases, the same full brightness was obtained, as listed in Table II, provided that some more ClO₂ was added in the first and second D stages.

These results show that using the best conditions, less than 2 kg/ton of TOCl could be reached. There was no clear evidence of a decrease in pulp strength, nor did we notice brightness loss. These good results encouraged us to check this process modification in a full-scale trial.

Mill implementation

In cooperation with two Swedish pulp mills, we undertook an implementation of this process. This simple optimization in its concept was relatively easy to perform, because additional equipment and investments were not necessary.

The first objective was to check how far the chlorine multiple could be lowered and how the reinforcement of the (EO) stage could compensate for this less effective chlorination. Getting low AOX figures without disturbing pulp production was indeed our final target.

In each case, we used the same strategy. To avoid getting excessively high kappa numbers which could lead to lower final brightness, we decided first to increase temperature (and pressure when possible) in the (EO) stage. Then, gradually, the chlorine multiple would be reduced to about 70% of its original value. In the third step, the ClO₂ substitution ratio was increased. Finally, H₂O₂ was added in conjunction with O₂ to try to reduce further the chlorine multiple.

I. (C+D)(EO)DED bleaching sequence of the oxygen-treated pulp

	(C+D)	(EO)	D	E	D
Consistency, %	8-3.5 ^a	10	10	10	10
Temperature, °C	35	65	60	65	75
Time, min	25	100	160	30	220
Chemicals, %					
Cl ₂	3.5	...	...	...	...
ClO ₂ ^b	1.0	...	1.3	...	0.3
NaOH	...	2.0	...	0.3	...
O ₂	...	at 2 bars	...	...	...

^aClO₂ added first at 8% consistency, then Cl₂ at 3.5%.

^bAs active chlorine.

II. Kappa number after (EO) stage and brightness, viscosity, and TOCl after final bleaching

	ClO ₂ substitution, %			
	22	22	50	50
Ref. pulp, chlorine multiple = 0.22				
(EO) stage				
Temp., °C	65	...	...	...
Kappa no.	1.6	...	...	...
ClO ₂ , %	1.6	...	...	...
Brightness, % ISO	88.8	...	...	...
Viscosity, mPa·s	22.2	...	...	...
TOCl, * kg/ton	3.6	...	...	...
Chlorine multiple = 0.15				
(EO) stage				
Temp., °C	80	90	80	90
Kappa no.	2.5	1.8	2.7	2.1
ClO ₂ , %	3.0	2.0	3.0	2.2
Brightness, % ISO	88.6	88.8	88.4	88.7
Viscosity, mPa·s	21.5	22.0	21.5	21.7
TOCl, * kg/ton	2.7	2.6	2.2	1.8
Chlorine multiple = 0.12				
(EO) stage				
Temp., °C	80	90	80	90
Kappa no.	3.2	2.3	3.7	2.9
ClO ₂ , %	3.0	2.4	3.0	3.0
Brightness, % ISO	87.5	88.5	87.0	88.3
Viscosity, mPa·s	22.0	22.1	21.5	21.5
TOCl, * kg/ton	2.3	2.2	1.8	1.8

* Calculated by TOCl = 0.09 (Cl₂ + ClO₂)/5 (9).

Gas analysis

The "helium tracer technique" was used during these trials to control carefully the O₂ consumption (10). This method enabled us to meet the O₂ requirement in the more powerful (EO) stages.

III. Conditions in the (C+D) and (EO) stages

	Mill A		Mill B	
	Chlori- nation	Extrac- tion	Chlori- nation	Extrac- tion
Consistency, %	3.5	12	10	12
Temperature, °C	50	65	40	65
Time, min	16	60 ^a	25	120
Chemicals, kg/ton				
Cl ₂	30	...	20	...
ClO ₂	6	...	8.8	...
NaOH	...	25	...	16
O ₂	...	4	...	4
Chlorine multiple	0.20	...	0.16	...
ClO ₂ substitution, %	15	...	30	...
Pressure, ^b bars	...	1.2	...	2 ^c

^a12 min in the retention tube.

^bTop of tube.

^cBottom of tube.

Mill A

This mill produces 500 metric tons/day of softwood kraft pulp for internal use. The kappa number after cooking is 30–32, decreasing to 18 after the oxygen delignification stage. Initial conditions of the chlorination and alkaline extraction stages are given in Table III.

Test program

Table IV illustrates the progress of the parameters controlled during the trial. Each of the seven steps is listed, showing the changes made in the process parameters.

Trial results

Carefully controlled, the implementation was conducted without any trouble, and results corresponded well with expectations (Table V). In the initial part of the trial, we recorded a 0.5–0.8 drop in kappa number as temperature and pressure were increased in the (EO) stage. At the same time, oxygen consumption rose from 1.5 kg/ton to 3 kg/ton. Temperature had the most important effect, but pressure plays a greater role at high temperature (Fig. 2).

Figure 3 presents the evaluation of kappa number with the reduction in chlorine multiple. Starting from 0.20, a reduction to 0.15 is easily obtained while maintaining the kappa number at its original value (Step 4). As Table V shows, oxygen consumption rose at this point to 3.3 kg/ton. In Step 5, the reduction in molecular chlorine attributable to the increase in the substitution ratio from 15% to 50% revealed lower efficiency since the kappa number rose to 2.5 and O₂ consumption went back to 3 kg/ton. This result confirms our conclusions from the laboratory study.

In the last two steps, the addition of 3 kg/ton of hydrogen peroxide ahead of the steam mixer did not help us to reach a chlorine multiple of 0.12. The kappa number increased to 3–3.5, and oxygen consumption diminished to 2.55 kg/ton.

The explanation for this poor effect may lie in a slight steam shortage, but part of the problem may also have

been in the location of the addition point for H₂O₂. This one should be changed to avoid the substantial consumption of H₂O₂ before oxygen is introduced.

Pulp quality

Final brightness was maintained to a high level throughout the trial except at a chlorine multiple of 0.12. Some ClO₂ adjustment problems in first and second D stages explain the slight loss from Step 6 to Step 7.

No detectable change in viscosity was recorded even at low chlorine multiple. Pulp strength also remained constant, and beatability was not affected by reduced chlorine multiple and the increased substitution of chlorine dioxide for chlorine.

Effluent

The AOX discharge in total bleaching effluent before external treatment is given in Fig. 4. From 3.3 kg/ton for the reference, it went down to 1.8 kg/ton for the optimized sequence (chlorine multiple = 0.15), which is a reduction of almost 50%.

COD and color remained constant during the trial (Figs. 5 and 6).

Mill B

This mill produces 360 tons/day of softwood kraft pulp (market pulp). After cooking, the kappa number is 33; after oxygen delignification, it is 18.

The main features of (C+D) and (EO) stages are presented in Table III. The chlorine multiple is already low (0.16) from efficient washing and by virtue of an accurate process control system. The (EO) tower is upflow in design, so no pressure can be applied at the top.

Trial results

Results exceeded our expectations. We were able to reach chlorine multiples as low as 0.10. Few production disturbances, constant incoming kappa number, and low washing losses helped us to achieve this goal.

Table VI summarizes the progress of the changes in the parameters in the (C+D) and (EO) stages. A drop of 0.2–0.3 kappa unit was obtained by increasing the temperature in the (EO) stage, which allowed the chlorine multiple to be reduced to 0.12. Then, by reaching lower chlorine multiple, at a 50% substitution ratio, the kappa number increased to 3–4. Again, this was in accordance with our laboratory study (Fig. 7).

On the other hand, final brightness decreased slightly despite higher charges of chlorine dioxide in first and second D stages (from 16 kg/ton for the reference to 20–25 kg/ton). A longer trial should enable us to predict the exact ClO₂ requirement in the last step of optimization.

The addition of 2 kg/ton H₂O₂ is beneficial in this case because it reduces kappa by 0.3 unit (Steps 6 and 7). An increase from 81° to 85°C in the (EO) stage seems to have the same effect (Step 8). This increase allows a reduction of 3 kg/ton of chlorine dioxide in the final stages at constant brightness.

Oxygen consumption followed the same trend we recorded in the other mill but to a lesser extent. The range of variation was smaller—2.4 kg/ton for the reference up to 3 kg/ton for Step 5. Higher temperatures which could

IV. Trial program for Mill A

Step	Description	(C+D) stage		(EO) stage		
		Chlorine multiple	ClO ₂ sub., %	Temp., °C	Pressure, bar	H ₂ O ₂ , kg/ton
Ref.	Reference pulp	0.20	15	65	1.2	0
Step 1	Increase pressure	0.20	15	65	3	0
Step 2	Increase temperature	0.20	15	90	1.2	0
Step 3	Increase temperature and pressure	0.20	15	90	3	0
Step 4	Reduce chlorine multiple	0.15	15	90	3	0
Step 5	Increase substitution	0.15	50	90	3	0
Step 6	Add hydrogen peroxide	0.15	50	90	3	3
Step 7	Reduce chlorine multiple	0.12	50	86	3	3

V. Trial results for Mill A

	Ref.	Step			
		4	5	6	7
Chlorine multiple	0.20	0.15	0.15	0.15	0.12
ClO ₂ substitution, %	15	15	50	50	50
Cl ₂ , kg/ton	30	23	13.5	13.5	11
ClO ₂ , kg/ton	6	4	13.5	13.5	11
(EO) stage					
Temperature, °C	65	90	90	90	90
Pressure, bar	1.2	3	3	3	3
Oxygen					
Charged, kg/ton	4	5	5	5	5
Consumed, kg/ton	1.6	3.3	3.0	2.6	2.55
H ₂ O ₂ , kg/ton	...	...	...	3	3
(EO) kappa no.	2.2	2.2	2.5	2.5	3-3.5
ClO ₂ *, kg/ton	18	18	15.5	15.5	19
Final brightness, % ISO	90.5	90.5	89.5	89.5	88.5
AOX, kg/ton	3.3	...	1.8	1.8	1.3

*For both first and second D stages.

increase oxygen consumption and efficiency should be indeed studied.

Pulp quality

Throughout this trial, a good market pulp was produced while viscosity and pulp strength remained unchanged (Table VI and Fig. 8). Pulp cleanliness was not affected by a lower chlorine multiple during the whole trial, as shown in Fig. 9.

Effluent situation

Again, a dramatic reduction in the AOX emission was recorded in the bleach plant effluent before any external treatment. From 2.5 kg/ton for the reference, it went down to less than 1.5 kg/ton at a chlorine multiple of 0.10, which corresponds to a 50% reduction in the molecular chlorine charged in chlorination (Fig. 10). Although it was not studied, the dioxin level should be rather low because the mill operates in the "safe zone" as defined by Berry (11).

In this mill, we detected a substantial decrease in the

effluent color (Fig. 11). Chlorine dioxide substitution is probably responsible for this variation, but a more serious study should be undertaken to check the effect of high temperature in the (EO) stage. As expected, COD did not vary, as Fig. 12 shows.

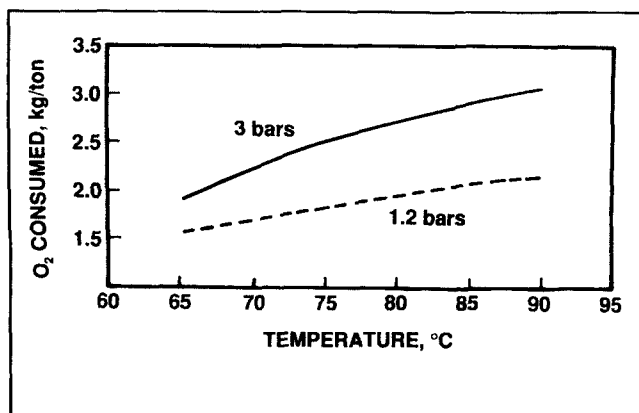
As long as ClO₂ use is increased, it is not surprising to record a higher production of chlorate in the effluent. Figure 13 outlines the linear relationship relating chlorate and total ClO₂ charge in the bleaching plant.

Costs

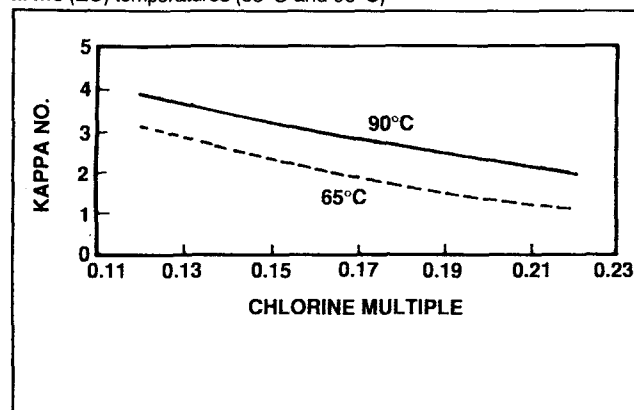
The costs were evaluated throughout the trial. Taking into account steam and chemicals, costs increased by 25% from 130 SEK/ton for the reference to 160-165 SEK/ton (Steps 4-6). Steam costs accounted for 40% of this increase.

The addition of H₂O₂, although helpful in reducing kappa number, brought another 10% increase but was difficult to justify economically.

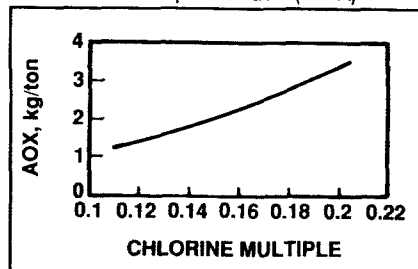
2. The variation of oxygen consumption in the (EO) stage (Mill A)



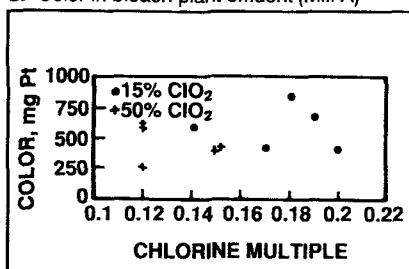
3. Development of kappa number with the reduction in chlorine multiple at two (EO) temperatures (65°C and 90°C)



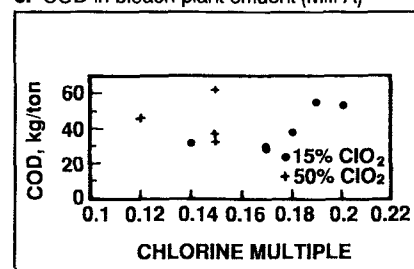
4. AOX in bleach plant effluent (Mill A)



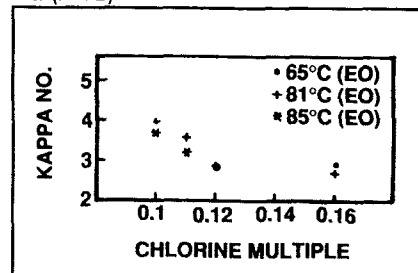
5. Color in bleach plant effluent (Mill A)



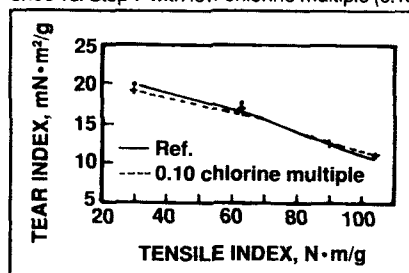
6. COD in bleach plant effluent (Mill A)



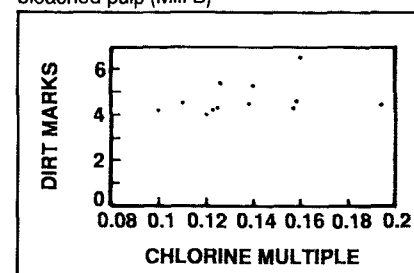
7. Development of kappa number during the trial (Mill B)



8. Comparison of pulp strength for the reference vs. Step 7 with low chlorine multiple (0.10)



9. Development of dirt content in the final bleached pulp (Mill B)



Conclusions

Plant trials were successful in confirming laboratory results. By running the (EO) stage in harder conditions, it has been possible to reduce the chlorine multiple down to 0.10 without impairing pulp characteristics.

This process is a possible alternative in environmental control in that 1.5 kg/ton of AOX (before external treatment) was reached. Compared with other process modifications, this optimization features the following advantages:

- No investment
- Slight increase in ClO₂ requirement
- Better oxygen efficiency
- Small increase in bleaching cost.

To get even lower AOX, further studies should be oriented towards:

- Determining the optimum kappa number after oxida-

tive extraction (EO) from a practical and economical standpoint

- Achieving a lower chlorine multiple
- Evaluating higher ClO₂ substitution
- Evaluating the use of higher temperature and higher pressure in the (EO) stage as in a regular oxygen delignification stage
- Evaluating the best combination between oxygen and hydrogen peroxide.
- Combining extended cooking with the O x O process. □

Literature cited

1. Smith, L., Calvert, D.W., Rousseau-Pauw, D., et al., U. S. pat. 3,725,194 (1970).
2. Sjöström, E. and Valttilä, O., Paperi Puu 1: 37(1978).
3. Lachenal, D., DeChoudens, C., and Monzie, P., Svensk Papperstid. 83: 494(1980).
4. Abrahamsson, K., Lowendahl, L., and Samuelson, O., Svensk Papperstid. 84 R 152 (1981).
5. Lachenal, D., de Choudens, C., Bourson, L., and Lachapelle,

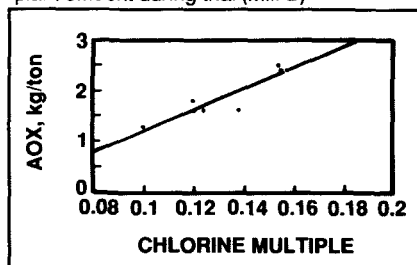
VI. Trial results for Mill B

	Ref.	Step							
		1	2	3	4	5	6	7	8
Incoming kappa no.	17.9	18.1	18.2	17.7	18.4	18.7	17.4	18.5	18.5
Viscosity,* cm ³ /g	982	968	947	946	954	949	...	959	...
(C+D) stage									
Cl ₂ multiple	0.16	0.15	0.12	0.14	0.11	0.11	0.10	0.10	0.10
ClO ₂ sub., %	32	31	31	50	50	50	50	50	50
Cl ₂ , kg/ton	20	20	15	12	11	11	9	9	9.5
ClO ₂ , kg/ton	8.8	8.8	7	12	11	11	9	9	9.5
(EO) stage									
Temperature, °C	65	81	81	81	81	85	85	85	81
NaOH, kg/ton	16	19	18	19	19	21	20	23	18
O ₂ , kg/ton	5.2	5.5	5.2	5.2	5.3	6.1	5.2	5.2	5.4
O ₂ consumed, kg/ton	2.4	2.9	...	2.55	2.6	3.0	2.75	2.5	...
H ₂ O ₂ , kg/ton	...	...	...	...	...	...	...	2.1	2.1
Kappa no.	2.9	2.7	2.9	2.9	3.6	3.2	4.0	3.7	4.0
Viscosity,* cm ³ /g	897	881	894	884	904	899	...	890	...
Final stages									
ClO ₂ , ^a kg/ton	16	17.5	17.3	22.3	23.1	20.1	25.1	22.6	24.3
Brightness, % ISO	90.0	89.7	88.6	89.2	88.4	88.9	88.5	88.6	88.4
Final viscosity,* cm ³ /g	840	846	855	842	840	822	834	831	852
Chemicals and steam, SEK/ton	130	153	...	165	165	162	164	177	175

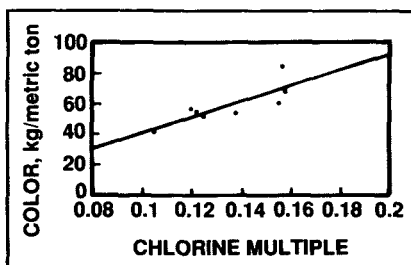
*SCAN method C15:62.

^a For both first and second D stages.

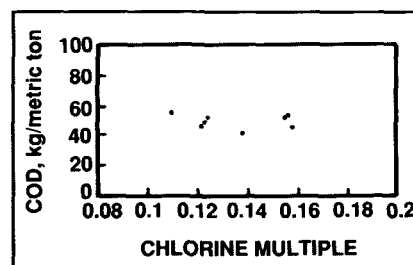
10. Reduction of AOX emission in bleach plant effluent during trial (Mill B)



11. Color in bleach plant effluent (Mill B)



12. COD in bleach plant effluent (Mill B)



- R., 1987 International Oxygen Delignification Conference, TAPPI PRESS, Atlanta, p. 69.
- Fossum, G. and Marklund, A., 1988 International Pulp Bleaching Conference Proceedings, TAPPI PRESS, Atlanta, p. 253.
 - Sarkanen, K. V. and Goyal, G., 1988 International Pulp Bleaching Conference Proceedings, TAPPI PRESS, Atlanta, p. 77.
 - Lachenal, D. and Muguet, M., 1989 CPPA Annual Meeting, CPPA, Montreal, p. B 187.
 - Germgard, U. and Larson, S., Paperi Puu 65(4): 287(1983).
 - Hornsey, D., Perkins, A., and Davidson, J., 1989 TAPPI Annual Meeting Proceedings, Atlanta, Ga., p. 55.
 - Berry, R. M., Fleming, R. H., Voss, R. H., Luthe, C. E., et al., 1989 CPPA Annual Meeting, CPPA, Montreal, p. 349.

Received for review July 22, 1990.

Accepted Aug. 21, 1990.

Presented at the TAPPI 1990 Oxygen Delignification Seminar.

13. Chlorate emission in bleach plant effluent (Mill B)

