Partial closure in modern bleaching sequences

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ABSTRACT

Despite the progress being made in research aimed at achieving a zero-liquid-effluent mill, there is justification for investigating the more gradual approach of partial recirculation of bleaching effluents (partial closure). Eka Chemicals, in cooperation with the University of Idaho, is carrying out research using mill trials, laboratory testing, and computer simulations to evaluate combinations of bleaching stages, operating conditions, washing, and filtrate recycling and treatment.

One idea being investigated for ECF bleaching is that of keeping the alkaline and acidic effluent streams separate and evaluating acid effluent treatment and alkaline filtrate recycling. The laboratory potential of this approach on conventional southern pine softwood kraft pulp, O_2-predelignified Scandinavian pulp, and conventional and O_2-predelignified eucalyptus pulp is reported in this paper.

For fully bleached ECF southern pine kraft pulp, comparisons of the results of external effluent treatment (anaerobic + activated sludge) on the total effluents, and on the acidic effluent, show that the acidic effluent is more easily treatable in terms of AOX and COD.

Under well-controlled laboratory conditions with efficient washing, partial closure is promising. The extent to which these results will be influenced by more realistic mill conditions (i.e., carryover) and the degree of compatibility of the alkaline effluents with the recovery system are being evaluated through extensive simulation studies and mill trials.

Application:

Partial closure of alkaline effluents seems to offer a synergistic effect since it not only reduces the level of environmental parameters but also improves the biodegradability of residual effluent in an external treatment.

BACKGROUND

REDUCTION OR ELIMINATION OF liquid effluent from bleached pulp mills (i.e., mill closure) has been under investigation for several decades. Rapson, Reeve, and others *(1–4)* attempted to close the kraft mill at Thunder Bay, ON, Canada. MoDo AB *(5, 6)* evaluated membrane filtration to upgrade bleach plant alkaline filtrate for reuse in its mills. Different options have been proposed for separate handling of the alkaline and acidic bleach plant effluents *(7–10)*. Significant efforts have been made to eliminate bleach plant effluents from elemental chlorine-free (ECF) bleaching *(11)*. Champion International Corp.'s BFR process *(12–14)* is a recent attempt to close an ECF mill.

Overview

This paper is concerned with Eka Chemicals' international mill closure effort to find cost effective alternatives to minimize the bleach plant effluents from kraft mills. The mill closure program has three synergistic components:

- Laboratory investigations
- Detailed full-mill simulations to help evaluate the millwide impact of alternative closure options
- Comprehensive mill testing to evaluate the closure options and validate the simulation results.

Scope

Specifically, this paper deals with partial closure of ECF bleaching sequences. Partial closure consists of segregating the acid and alkaline effluents, recycling the alkaline effluent, and discharging the acid filtrate after treatment. The lower half of **Fig. 1** depicts the partial-closure concept.

This paper reports the results of laboratory studies that demonstrate the viability of partial closure. Full-mill evaluations of partial closure will be reported in subsequent papers.

PARTIAL CLOSURE: SCREENING FOUR PULPS

Four different kraft pulps were laboratory bleached at optimum conditions to 89.5% ISO brightness using the bleach sequence D (EPO) D (EP) D. There was good washing (i.e., displacement ratio (DR) = 0.96) between bleach stages. The acid and alkaline filtrates were collected separately, as well as combined, as shown in Fig. 1.

Table I shows that, for all four pulps, 50–70% of the total chemical oxygen demand (COD) and color are in the alkaline effluents and, using partial closure, will be burned in the recovery boiler. Table I also shows the low levels of adsorbable organic halogen (AOX) generation and shows that partial closure returns only 10–15% of the AOX to the recovery boiler. Lower chlorine levels in the recovery boiler mean lower risk for plugging and corrosion.

In summary, for all four pulps, Table I demonstrates the significant potential benefits from partial closure and justifies the more detailed laboratory evaluation presented in the following paragraphs.

PARTIAL CLOSURE: IN-DEPTH STUDY OF SOUTHERN PINE

Southern pine kraft pulp with a Kappa no. of 28 (Pulp 1 in Table I) was selected for in-depth laboratory evaluation of partial closure. **Table II** summarizes the bleaching details.

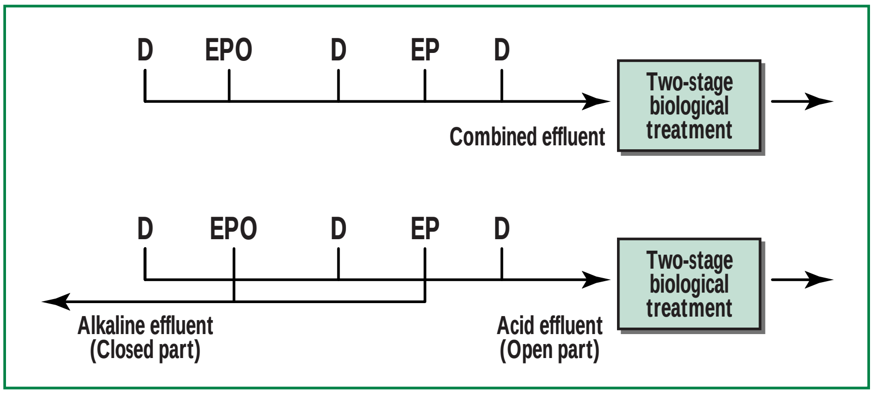
The bleaching sequence was D (EPO) D (EP) D with 57, 19, and 10 kg ClO_2 as active chlorine in the D_1, D_2, and D_3 stages, respectively. The hydrogen peroxide charge was 5 kg/ton pulp in the E_1 stage and 2 kg/ton pulp in the E_2 stage. The kappa factor was 0.2.

The individual effluents, as well as the combined effluents, were treated in the system shown in **Fig. 2.** The two-stage laboratory system was chosen to give the best possible degradation, thus showing the potential of biological treatment. It consisted of an initial 2-hour anaerobic stage, aimed at eliminating the chlorate, and a 12-hour aerobic-activated sludge stage, aimed at reducing the organic compounds measured as COD, AOX, etc. *(15)*.

Table III and **Fig. 3** summarize the effluent treatment results. The two-stage effluent treatment system removes about 95% of the biochemical oxygen demand (BOD) and virtually all of the chlorate. AOX and COD in the acidic effluent are more effectively removed than in the combined effluent. That is, the acid effluent resulting from partial closure was more easily treated than the total bleaching effluent.

Table IV contains a detailed analysis of the acid effluent before and after the two-stage treatment scheme shown in Fig. 2. The two-stage treatment removes all the low-molecular-weight compounds and thus may have an impact on the volatile organic compound (VOC) (methanol) emissions from the mill. The two-stage treatment of the acid bleaching effluent also eliminated toxicity (Microtox and Selenastrum).

How will the recycled alkaline filtrate impact the kraft recovery system? **Table V** shows that partial closure will add about 5% solids and 2.5% heat release to the boiler. These increases seem to be in the range of incremental recovery capacity *(16)*. Note that the heating value of the alkaline effluent is approximately one-half the heating value of normal black liquor, based on dry solids. As seen in **Table VI,** the effect of partial closure on nonprocess



1. Partial closure principle

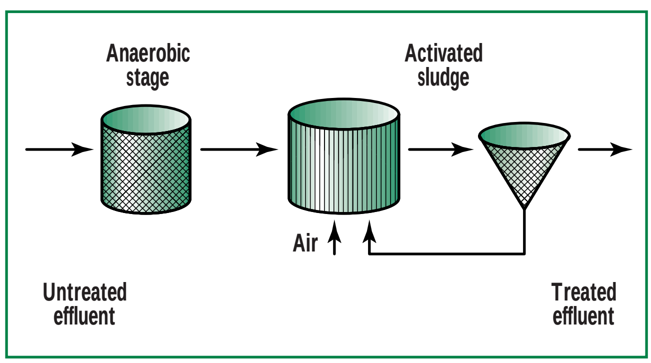
Effluent	Pulp*	Kappa number	AOX, kg/ton pulp	COD, kg/ton pulp	Color, kg/ton pulp
Combined	1	28	1.04	62	51
Acidic	1	28	0.90	24	17
Combined	2	12	0.61	31	20
Acidic	2	12	0.55	13	6
Combined	3	13	0.98	29	15
Acidic	3	13	0.84	15	7
Combined	4	8	0.72	20	4
Acidic	4	8	0.66	10	2

*1 = Conventional southern pine
2 = O_2-delig. Scandinavian softwood
3 = Conventional eucalyptus pulp
4 = O_2-deigl. eucalyptus pulp

I. Comparison of combined bleach plant effluent and acidic effluent before treatment (see Fig. 1)

State	Kappa no.	Brightness, % ISO	Viscosity, dm³/kg	OCl, ppm
Unbleached	28.3	22.3	996	-
Bleached	0.8	89.5	865	145

II. Southern pine kraft pulp characteristics



2. Laboratory effluent treatment

Prior to effluent treatment

Analysis	Combined effluent	Acidic effluent	Alkaline effluent
COD, kg/ton pulp	62	24	38
AOX, kg/ton pulp	1.04	0.8	0.15
BOD_5, kg/ton pulp	11	5	6*
Color, kg/ton pulp	51	17	36
Microtox EC_{50}, %	64	29	-

After effluent treatment

Analysis	Combined effluent	Acidic effluent
COD, kg/ton pulp	40	12
AOX, kg/ton pulp	0.5	0.2
BOD_5, kg/ton pulp	0.4	0.2
Color, kg/ton pulp	59	22
Microtox EC_{50}, %	100	100

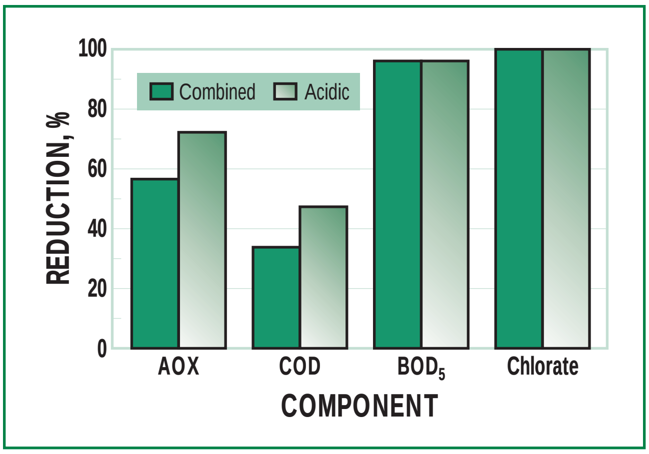
*Calculated

III. ECF southern pine kraft pulp effluent characteristics

Analysis	Prior to effluent treatment	After effluent treatment
COD, kg/ton pulp	24	12
Lignin, kg/ton pulp	9.7[a]	9.7[a]
Carbohydrates, kg/ton pulp	2.6[a]	0.1[a]
Extractives, kg/ton pulp	4.7[a]	2.1[a]
Methanol, kg/ton pulp	5.3[a]	0
Acetic acid, kg/ton pulp	0	0
Formic acid, kg/ton pulp	1.6[a]	0
AOX, kg/ton pulp	0.8	0.2
EOX, g/ton pulp	1.9	0.3
Microtox EC_{50}, %	29	100
Sterols, g/ton pulp	0.2	0.05
Resin acids, g/ton pulp	1.3	0.2
Selenastrum EC_{50}, %	NA[b]	100

[a]Recalculated to COD
[b]Not applicable

IV. ECF southern pine kraft pulp acidic effluent characteristics



3. AOX, COD, BOD_5, and chlorate reductions–ECF southern pine kraft pulp

element buildup in the recovery boiler is much lower than total closure (i.e., recycling the combined filtrate).

KEYWORDS

Bleach plants, bleaching, bleaching effluents, chemical recovery, chemical treatment, chlorine dioxide, closed systems, eucalyptus, evaluation, hardwoods, kraft mills, oxides, pinus, *softwoods, water reuse.*

For the laboratory conditions used in this study, Table VI shows that partial closure theoretically returns only 14% of the calcium, 4% of the magnesium, and 47% of the oxalate to the recovery boiler, where these substances can create scaling problems. Also from Table VI, about 6% of the total bleach plant chlorine would be returned to the recovery boiler by using partial closure. Model predictions on what the concentrations of each of these will be in the real mill situation with close up are underway and will be presented in subsequent papers.

Table VII illustrates that the alkaline filtrate generally returns 50–60% of the organics to the recovery boiler, even though the volume of the alkaline filtrate is only 40% of the total. In the case of methanol, about 20% was found in the alkaline effluent.

EXPERIMENTAL

Pulp treatments and bleaching conditions have been presented previously *(15, 17, 18)*. Procedure and laboratory equipment used for the effluent treatment are the same as those used in a previous study *(15)*. Analyses were carried out according to the standard procedures refer-rencedto in the appendix.

CONCLUSIONS

Laboratory testing of a process that recycles ECF bleach plant alkaline filtrate to the recovery boiler and sends the acidic filtrate to secondary treatment (*partial closure*) shows the following:

For hardwood and softwood kraft pulp, both oxygen delignified and nonoxygen delignified, partial closure sends 50–70% of the bleach plant COD and color to the recovery boiler but only 10–15% of the AOX (Table I).

For fully bleached nonoxygen-delignified kraft pulp from southern pine, partial closure produces an effluent (acid effluent) that is more responsive to the two-stage treatment than the total bleach plant effluent (Figs. 2 and 3).

Dry solids	
Percent	**0.42**
Kg/ton pulp	**76**
Loss of ignition, % of DS	**44**
Elementary analysis, % of DS	
Na+K	**22.3**
S	**0.2**
C	**24.9**
H	**3.5**
N	**0.1**
O	**46.6**
Net heating value, MJ/kg DS	**6.3**

V. Data relevant for recovery of the alkaline effluent—ECF southern pine kraft pulp

Metal	Combined, 45 m³	Alkaline, 18 m³
Cations, g/ton pulp		
Al	23	1.4
Ba	5.7	0.7
Ca	2318	324
Fe	21.8	2.9
Mg	927	36
Mn	43	2.7
Si	332	113
Anions, g/ton pulp		
C_2O_4	2,840	1,330
SO_4	1,020	320
CO_3	8,600	7,920
Cl	15,620	950

VI. Nonprocess elements in effluents—ECF southern pine kraft pulp

For fully bleached nonoxygen-delignified kraft pulp from southern pine, partial closure will increase recovery boiler solids by about 5% and heat load by about 2.5% (Table V). About 6% of the chlorine atoms added in the bleach plant go to the recovery boiler (Table VI).

Partial closure shows promise and should be investigated further using full-mill simulation and mill trials. TJ

Analysis	Alkaline effluent	Combined effluent
COD, kg/ton pulp	38.0	62.0
Lignin, kg/ton pulp	25.7*	33.3*
Carbohydrates, kg/ton pulp	3.5*	6.6*
Extractives, kg/ton pulp	6.8*	10.8*
Methanol, kg/ton pulp	1.6*	7.4*
Acetic acid, kg/ton pulp	0.5*	0.7*
Formic acid, kg/ton pulp	0.7*	1.9*

*Recalculated to COD

VII. Organics in effluents—ECF southern pine kraft pulp

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APPENDIX

Analyses

Pulp

Brightness	SCAN-C 11:75
Kappa no.	SCAN-C 1:77
Viscosity	SCAN-CM 15:88
Chlorinated organics	German Standard PTS-RH:012/90

Effluent

AOX	ISO (1989A), ISO9562:1989 (E)
EOX	Lopez, M., Larsson, K.O., and Sundstrand, S., *Nordic Pulp and Paper Res. J.* no. 3-1994 9 (1994) p. 187–190
COD	APHA, AWWA and WPCF (1985a): 16th edn., American Public Health Association, Washington DC 20005, USA, pp. 537–538.
BOD_5	ISO(1989B), ISO9562:1989 (E)
Color	Spectrophotometrically at 400 nm using different concentrations of platinum-cobalt as standard
Lignin*	As soluble, UV 280 nm
Carbohydrates*	Meier, D., and Weissmann, G., *Holzforschung 40* (1986) 55–57
Extractives*	Extraction with MTBE / ph. 9. Gravimetric determination
Methanol*	GC (Column DB1 at room temperature)
Acetic and Formic Acid*	GC, R. Alén, P. Jännäri and Eero Sjöström, *Finn. Chem. Lett.* 1985
Sterols Resin Acids	Voss, R., and Rapsomatiotis, A., *J. Chromatogr.* 346 (1985) 2205–214.
Cations	ICP-AES
SO_4	Ion Chromatography
CO_3	Dohrman DC-190
C_2O_4	Ion Chromatography
Loss Of Ignition	550C, 2h
C, H, N	ASTM D 5373-93
Heating Value	ISO 1928
Microtox	ISO/TC 147/SC5WG 1N 110
Selenastrum	ISO 8692

*Measured values were recalculated to COD by factors shown in "COD factors."

COD factors

Constituent	Factor
Lignin	1.90
Carbohydrate	1.20
Extractives	2.70
Acetic Acid	1.07
Formic Acid	0.35
Methanol	1.50