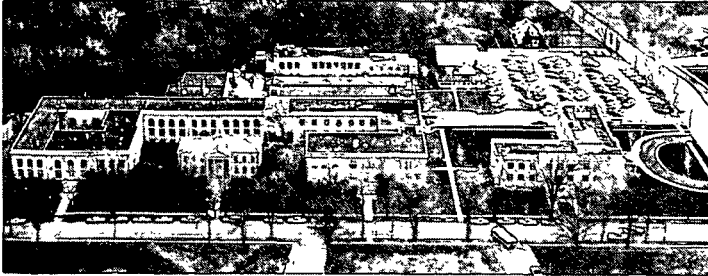


*W. Fisher  
Mauno*



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**EFFECTS OF PEROXIDE BLEACHING  
OF SOFTWOOD KRAFT PULP**

**H. S. DUGAL AND MAUNO RUHANEN**

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## EFFECTS OF PEROXIDE BLEACHING OF SOFTWOOD KRAFT PULP

H. S. Dugal  
Director, Environmental Sciences Division  
The Institute of Paper Chemistry  
Appleton, Wisconsin 54912

Mauno Ruhanen  
Research and Development Manager  
Joutseno Pulp Company  
54120 Pulp, Finland

### ABSTRACT

A method for bleaching softwood kraft pulp with hydrogen peroxide, instead of chlorine, in the first bleaching stage has been tried. Kraft pulp was obtained from a mill using 92% softwoods and 8% hardwoods. It was bleached in the laboratory by APP, CEH, APPDED, and CEDED sequences and compared for effluent quality, toxicity, corrosion, pulp strength properties and color reversion. Results indicate that if all effluents from acid pretreatment and peroxide stages (APP) are recycled to the recovery system of a kraft mill, the pollutant load can be significantly reduced. Calculations show that color reductions of over 90%, BOD 40%, TOC 64%, and DS 71% could be achieved over the conventional CEDED bleaching sequence. Toxicity and corrosivity of the combined effluents from peroxide sequences were also lower than or similar to those from the conventional methods. Although yields of peroxide bleached pulps were somewhat higher, no appreciable differences in pulp properties were noticed. The results also show that in order for peroxide bleaching to become justifiable, the cost of peroxide must drop relative to present peroxide/chlorine prices. A requirement to eliminate chlorinated compounds from bleach effluents will also tilt the economic picture in favor of nonchlorine approaches such as peroxide.

### INTRODUCTION

In a modern bleached kraft pulp mill a major part of wastewater load originates from the bleach plant. Bleach plant effluents have high volume, BOD and color. In addition, the conventional use of chlorine produces chlorinated organic compounds, which are reported to have toxic properties.

In order to minimize the above environmental impacts, ways to reduce wastewater loads are being critically examined. In principle, two main approaches can be taken, namely preventive and cure. "Preventive" approaches include process modifications, process control and development of new production technology (internal approaches). "Cure" approaches include physical-chemical or biological treatment systems (external approaches).

Disadvantages of external approaches are mainly the high capital cost and handling and disposal of sludges. Mills which are faced with such heavy expenditures and/or are treatment capacity limited, should look at internal controls as possible alternatives. These alternatives include best management practices, treatment of individual process-streams, and changes and modifications of the manufacturing process.

Many new processes and process modifications have been suggested, but none has been very successful. The closed-cycle system by Rapson is seriously hampered by high chloride content of bleaching effluents. We understand corrosion is one of the problems. Nonchlorine bleaching (at least in the first stage) may be one answer to the chloride problems.

Oxygen is being used commercially, but the equipment needed is expensive, production costs are not low and pulp quality is slightly different. Other possible bleaching chemicals are peroxides and ozone. These are relatively expensive, but their real potential has not been extensively studied.

Hydrogen peroxide is used quite commonly in the bleaching of mechanical pulps and sometimes in the final bleaching stages of chemical pulps. In these

cases hydrogen peroxide is used primarily as a "surface" bleaching agent or as a final stage of a bleaching sequence. However, there are some indications that peroxide could work as a delignification agent as well.

### BACKGROUND

Hydrogen peroxide is known to delignify sulfite pulps quite satisfactorily<sup>1-6</sup> but not the kraft pulps<sup>7-8,23</sup>. Although use of large amounts of tertiary butyl hydroperoxide has effectively delignified kraft pulps<sup>9,10</sup>, we chose to use hydrogen peroxide in the first stage, instead of chlorine, because of its advantages.

The main advantages over chlorine are:

- (i) it easily dissipates leaving no residuals, especially chlorinated compounds,
- (ii) it produces less colored wastewaters, and
- (iii) it offers possibilities of a complete recycle of bleach plant effluents.

### SULFONATION OF KRAFT PULP

Because sulfite pulps are easily bleached with peroxide, sulfonation of kraft pulp prior to peroxide bleaching was considered as one of the possible approaches. Little information on this was found in the literature<sup>11,12</sup>.

High yield (60%) kraft pulps are reported to sulfonate very rapidly (10-15 minutes) even at relatively low temperatures. The resulting degree of sulfonation of the residual lignin corresponds to approximately one sulfonic acid group per ten phenylpropane units. Sulfonation, according to these results, improved the strength properties of high yield pulps, but at the normal yield level (48%) the effect was less pronounced<sup>11</sup>.

During normal sulfonation, sulfonic acid groups are introduced only on the aliphatic side-chains of the phenylpropane units. For more effective sulfonation of kraft lignin, sulfomethylation can be used<sup>13</sup>.

## PEROXIDE-LIGNIN REACTIONS

Several studies on lignin model compounds and isolated lignins under conditions resembling those used in bleaching pulp with peroxide have provided much information concerning the probable reaction mechanisms between peroxide and lignin in pulp. The specific reactions depend to a large extent on the chemical structure of lignin<sup>14-20</sup>.

Experiments conducted on spruce milled wood lignin and spruce groundwood substantiate the view that the attack of alkaline peroxide on lignin is confined mainly to unetherified phenolic units and to monomer units having side chains possessing carbonyl and certain other functional groups. By alternate routes, involving demethylation, quinone formation, cleavage of side chains (Dakin reaction) and ring rupture, alkaline peroxide is capable of breaking down lignin-like structures to yield colorless aliphatic substances<sup>14</sup>.

A reaction scheme to account for the attack of peroxide on deciduous lignin phenolic units is presented by Kemf and Dence<sup>15</sup>. According to this, unetherified syringyl units are extensively degraded by peroxide to carbon dioxide and a variety of dicarboxylic acid derivatives. Such excessive degradation results in the superfluous consumption of peroxide and affects the amount of buffering agent needed during bleaching.

Results of subsequent studies have given more indications that alkaline peroxide is capable of causing significant solubilization of lignin under certain conditions<sup>16</sup>.

The above results are in contradiction to the small yield loss observed during the conventional peroxide bleaching of groundwood. Recent studies have shown that under alkaline conditions hydrogen peroxide may participate in two different types of reactions with lignin structures<sup>17,18</sup>. In the presence of sodium silicate and in the absence of heavy metal ions, hydrogen peroxide is almost completely stabilized and its reactions with lignin are restricted to the elimination of conjugated carbonyl structures resulting from attack by hydroperoxy anions.

On the other hand, if heavy metal ions are present and/or silicate is absent in the reaction medium, hydrogen peroxide rapidly decomposes via hydroxyl radicals and superoxide ions to oxygen (partly in the excited singlet state) and water<sup>18</sup>. These decomposition products are able to react with phenolic structures thereby causing degradation of lignin. When the reaction between alpha-methylsyringyl alcohol, a model for the phenolic units in lignin, and hydrogen peroxide in the alkaline pH-range was studied, it was found that the reaction rate exhibits a strong maximum around pH 11.5.

In addition to heavy metal ions, inert salts such as sodium sulfate and an increase in temperature were able to accelerate the reaction rate of lignin degradation. These results suggest that alkaline hydrogen peroxide, without stabilizing agents, could be used as a lignin-removing bleaching chemical. Unfortunately, the attack on carbohydrates also increases, when the stability of hydrogen peroxide is decreased<sup>19,20</sup>.

## PEROXIDE BLEACHING OF KRAFT PULP

Peroxide has been used commercially and experimentally in a variety of ways in the bleaching of kraft pulps. Most commonly it is applied in the later stages of a multistage bleaching sequence. A peroxide stage can be easily used instead of an alkaline extraction or hypochlorite stage. In both cases reduction in the consumption of chlorine chemicals can be achieved.

When peroxide is used in the second bleaching stage after oxygen treatment<sup>21</sup> or chlorination<sup>22</sup>, semibleached pulps have been obtained.

The only reported attempt to use alkaline peroxide treatment instead of chlorination at the beginning of a bleaching sequence for kraft pulp was made in France by Monzie *et al.*<sup>7,8,23</sup>. Commercial hardwood kraft pulps (unbleached kappa number 20-23) were fully bleached by four-stage EDPD and PDPD sequences. Their key results are summarized below:

- Higher temperatures and consistencies are beneficial for achieving low lignin content. Consistency of 20% is reported to be the practical limit for good bleaching.
- During the first hour of bleaching there is a rapid decrease of kappa number after which it levels off.
- Addition of silicate accelerates the delignification process. (This is inconsistent with the results that unstabilized peroxide should be a more effective delignifying agent.)
- Sodium carbonate can be substituted for sodium silicate. (This is very important with respect to recycling waste liquor from the peroxide stage to the kraft recovery system.)

In case of softwood kraft pulps, four multistage processes CEDED, PCEDED, ECEDED, and PDPDP were tried by the same French authors. The effects of silicate and carbonate were found to be marginal compared with the ones observed for hardwood kraft pulps. Also, the results on the first stage bleaching sequence for softwood kraft pulp are not reported in detail. The heavy metal content in different pulps may have been one reason for the different behavior during peroxide bleaching. No particular data are given for the wastewater quality and loads.

## EXPERIMENTAL

### PULP

Unbleached kraft pulp was obtained from Thilmany Pulp and Paper Company, Kaukauna, Wisconsin. The mill was using about 8% hardwoods and 92% softwoods. The pulp was in the form of wet sheets with a consistency of 32%. The sheets were torn into about 1 x 1 inch pieces by hand and stored in polyethylene (PE) bags at 5°C.

### SULFONATION AND SULFOMETHYLATION

The pulp was disintegrated in cold tap water and the slurry adjusted to desired pH (2-11) with

NaOH or H<sub>2</sub>SO<sub>4</sub>. After mixing in Na<sub>2</sub>SO<sub>3</sub> and/or HCHO, the pH was checked and readjusted if needed. Reactions were carried out in PE bags for temperatures below 90°C and in stainless steel bombs for temperatures above 90°C. After the desired reaction time of 45-420 minutes the samples were cooled, final pH measured and diluted with tap water to a 2.5% consistency before filtration. The pulp cake was washed with tap water (40 mL/g o.d. pulp), diluted again to 2.5% consistency and left standing for 15 minutes. It was then filtered and washed as above.

#### SULFONIC GROUP ANALYSIS

The SO<sub>2</sub>OH groups introduced into the pulp by sulfonation or sulfomethylation were determined using the method described by Kringstadt and Olason<sup>11</sup>. The amount of SO<sub>2</sub>OH groups was calculated as the number of SO<sub>2</sub>OH groups per phenyl-propane units of the residual lignin in pulp. These amounts were: 0.11 for sulfonation and 0.2 for sulfomethylation.

#### ACID PRETREATMENT

A known amount of unbleached pulp was disintegrated with water at room temperature. Acid was added to get the desired pH. After the desired retention time, final pH was checked. Washing after acid treatment was performed in the same way as after sulfonation.

#### PULP BLEACHING

All peroxide bleaching experiments were performed in PE bags using 2% H<sub>2</sub>O<sub>2</sub>, at 12% consistency, 80°C, pH of about 11 for four hours (for conditions of other bleaching stages see Table I). After the desired reaction time the peroxide treated sample was cooled, final pH measured and the pulp diluted to 2.5% consistency. After standing for 15 minutes, the sample was filtered and washed with cold tap water (40 mL/g o.d. pulp). The filtered cake was treated with SO<sub>2</sub>-water at pH 3.5 for at least 15 minutes and then washed.

TABLE I  
PEROXIDE BLEACHING CONDITIONS FOR SOFTWOOD KRAFT PULP

Stages	Consist., %	Temp., °C	Time, hr	Chemical Charge
A	~3.5	25	1	SO <sub>2</sub> to pH ≤ 3.0
P <sub>1</sub> ; P <sub>2</sub>	12.0	80	4	2% at pH > 10.0
C	3.5	25	0.75	5.6% active Cl <sub>2</sub>
E <sub>1</sub>	10	70	1.5	3.3% NaOH
E <sub>2</sub>	10	60	1	1.0% NaOH
D <sub>1</sub>	10	60	3	3.16% active Cl <sub>2</sub>
D <sub>2</sub>	10	60	3	0.86% active Cl <sub>2</sub>
H	10	60	2	1.5% active Cl <sub>2</sub> , at pH 9.5

A-stage = acid pretreatment.  
C-stage = chlorination stage.  
D<sub>1</sub>, D<sub>2</sub> = chlorine dioxide stages.  
E<sub>1</sub>, E<sub>2</sub> = extraction stages.  
H-stage = hypochlorite stages.  
P<sub>1</sub>, P<sub>2</sub> = peroxide stages.

#### STANDARD METHODS

Standard Methods used are listed below:

*Kappa Number* of Pulp, T 236 os-76

*Forming Handsheets* for Reflectance Tests of Pulp, T 218 os-75

*Brightness* of Pulp, T 462 os-77

*Freeneess* of Pulp, T 227 os-58

*Laboratory Beating* of Pulp (FFI), T 248 pm-74

*Forming Handsheets* for Physical Tests of Pulp, T 205 os-71

*Physical Testing* of Pulp Handsheets, T 220 os-71

*Tests for Waste Waters:*

BOD<sub>5</sub> - APHA, 14th Edition, No. 507

Solids - APHA, 14th Edition, No. 208C

TOC - APHA, 14th Edition, No. 505

Color - NCASI, Tech. Bull. 253

#### GEL PERMEATION CHROMATOGRAPHY

The molecular weight distribution of effluents from bleaching sequences was determined using gel permeation chromatography (aqueous). A 1.0 x 60 cm column filled with Sephadex G-25 (50-150 μ) provided fractionation in the 5000 to 250 relative molecular weight range. Freeze dried bleach effluents were recombined to provide the various bleaching sequence samples. A 20 mg effluent sample was fractionated at 0.23 mL/min and continuously monitored at 277 nm absorption with a LKB Uvicord II photometer.

This fractionation resolved three (3) distinct molecular weight regions 5000-2000, 2000-250, less than 250. The 277 nm absorption was calculated for each fraction from the elution curve and normalized to 100%. An extinction coefficient cm<sup>-1</sup>/g was determined from the total 277 nm absorption units per gram of ash-free organic component.

#### CARBOXYL CONTENT

The samples (approximately 4 mg) were weighed and mixed with equal amounts (300 mg) of potassium bromide. The mixtures were vacuum dried over P<sub>2</sub>O<sub>5</sub> at 50°C overnight. Pellets of the mixtures were made and infrared spectra recorded.

All of the spectra showed apparent ionized carboxyl bands at about 1600 cm<sup>-1</sup>. Some of the spectra showed broad shoulders at about 1700 cm<sup>-1</sup> (possible acid and/or ester carbonyl).

The ratio of the absorbance of the broad 1600 cm<sup>-1</sup> band to the weight of sample was calculated for each sample. Results are given in Table V. Although the title is carboxyl content, the values represent only the ratio of sample weight to absorbances as stated.

#### TOXICITY TEST

Each effluent was tested for % EC<sub>50</sub> (Effluent

Concentration at which 50% of test organisms survive) by running tests at different concentrations (about 9 plus a control). Data for % EC<sub>50</sub> was obtained by graphical interpolation.

Dilution water was dechlorinated tap water with 1 ppm sodium thiosulfate. The pH of the test sample was adjusted to 7.0 with an acid or base.

A total of 20 *Daphnia magna*-early instars were used for each concentration (four 200 mL beakers each containing 100 mL of test sample and five *Daphnia*).

#### CORROSION TESTS

Test samples of effluents were adjusted (diluted) to correspond to the same amount of effluent per ton of pulp (27.6 m<sup>3</sup>/ton o.d. pulp). However, the effluent from acid pretreatment stage was left on the existing level of dilution (30.6 m<sup>3</sup>/ton o.d. pulp). The environments were tested using mild steel electrodes. Potential decay and corrosion rate (M.P.Y.) data were taken using the MI010 instrument. Testing conditions were as follows:

Effluent from	Temp., °C	pH		Conductivity	
		Start	After 250 hr	Start	After 250 hr
A-stage	25	2.19	4.25	3,340	2,000
P <sub>1</sub> -stage	70	9.90	8.59	3,420	3,640
P <sub>2</sub> -stage	70	9.80	8.98	4,000	4,530
C-stage	25	1.71	1.88	13,600	8,620
E-stage	50	10.52	8.49	4,170	3,140

#### CHEMICAL COST

Chemical cost calculations were based on chemical consumption data and the following prices from Chemical Marketing Reporter, July 7, 1980:

Cl<sub>2</sub> \$145 per ton, NaOH \$150 per ton, H<sub>2</sub>O<sub>2</sub> (50%)  
 25¢ per lb, NaClO<sub>3</sub> \$340 per ton, S \$9 per 100 lb,  
 H<sub>2</sub>SO<sub>4</sub> \$60 per ton.

#### RESULTS AND DISCUSSION

Degree of sulfonation of kraft pulp was always low. Sulfonation had no effect on subsequent peroxide bleaching. Decrease in kappa number during bleaching was somewhat larger in the absence of silicate and MgSO<sub>4</sub> than when they were present. All other experiments were, therefore, carried out without silicate or MgSO<sub>4</sub> additions.

Sulfite pulps could be bleached more easily with peroxide than kraft pulp without acid-pretreatment (Table II). After acid-pretreatment, however, the peroxide bleachability of kraft pulps improved considerably (Fig. 1). Further controlled experiments indicated that acid-pretreatment was advantageous because it removed metals which presumably catalyzed the degradation of peroxide. Out of eight metals found in the pulp (Al, Ca, Cu, Fe, Mg, Mn, Na, Ti) Cu, Mn, and to a lesser degree Fe, showed definite trends with brightness. Data in Fig. 2 show that maximum brightness is obtained when acid-pretreatment is carried out at pH below 3.0. Below this pH, Cu/Mn

are reduced from 1.3/99.0 ppm to 0.9/7.2 ppm, respectively.

TABLE II

#### PEROXIDE BLEACHING OF PULPS

(pH ~11.5; 80°C; 10-15% consistency; 2 hr)

Pulp	Acid-Pretreatment	H <sub>2</sub> O <sub>2</sub> , %	Kappa No.	GE-Brightness, %
Sulfite, unbl.	--	--	18.5	53.8
	--	0	16	53.0
	--	2	6.8	81.8
Kraft, unbl.	--	--	25	30
	--	0	21	30
	--	2	16	37
	H <sub>3</sub> PO <sub>4</sub>	2	16	50
	HCl	2	11.5	53

Acid-pretreatment pH ≤ 3.0; 30°C; 30 min.

#### BRIGHTNESS VS: RETENTION TIME

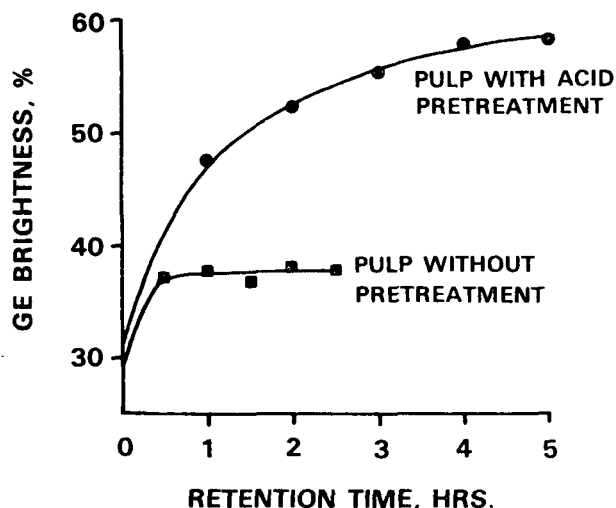


Figure 1. Effect of Bleaching Time on Brightness

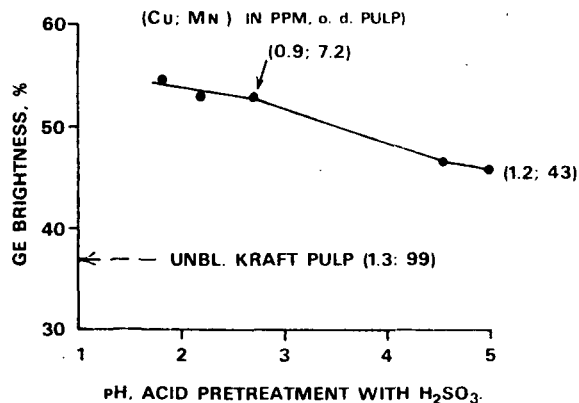


Figure 2. Effect of pH on Acid Pretreatment

Sulfurous acid (SO<sub>2</sub>OH) was used for acid-pre-treatment instead of HCl, H<sub>2</sub>SO<sub>4</sub>, or H<sub>3</sub>PO<sub>4</sub> because no major differences in efficiency were noticed between these acids. In addition SO<sub>2</sub>OH has the benefits that it can be generated from vent gases containing SO<sub>2</sub> and that after use it can be recycled back to the chemical recovery plant.

Effect of metal ions on peroxide bleaching was checked by washing the acid-treated pulps with waters containing 100 ppm of Mg, Fe, or Mn. Only in the case of Mg, deionized water was used. Pulps washed with waters containing Fe or Mn did not show any improvement in brightness after peroxide bleaching, whereas those with Mg did. Apparently, some metal ions are responsible for lower bleaching response of unbleached kraft pulp with peroxide.

As expected, the effect of pH on peroxide bleaching was dramatic. Up to a pH of about 11.0, the brightness of the pulp increased steadily and then levelled off.

Multistage bleaching sequences (PPPPP; APP; APPPP; APAPAPAP) involving peroxide (P) with and without acid-pretreatment (A) were also carried out. According to these results, it does not really matter greatly how the H<sub>2</sub>O<sub>2</sub> charge is divided up between different bleaching stages as long as the total H<sub>2</sub>O<sub>2</sub> amount remains the same. However, some slight differences in the first two stages were noticed. For example, when a H<sub>2</sub>O<sub>2</sub> charge of total 2% was applied equally in two stages (1% in each stage), a slightly higher pulp brightness was obtained than when 2% H<sub>2</sub>O<sub>2</sub> charge was applied in one stage. In addition, the two stage approach with lower H<sub>2</sub>O<sub>2</sub> concentration has the potential advantage of being less "drastic." We, therefore, chose to carry out peroxide bleaching by the APP sequence, with a retention time of four hours in each peroxide stage.

Four different bleaching sequences were selected for comparison. Two were conventional (CEH, CEDED) and commercially used, and the other two were the non-conventional developed by us (APP, APPDED). For reasons of compatibility in product market, APP was compared with CEH, and APPDED with CEDED. These sequences were compared for their effluent characteristics, toxicity, corrosion, and pulp quality (yield, brightness, brightness reversion, and strength properties).

#### EFFLUENT CHARACTERISTICS

After each bleaching stage the pulp was washed with tap water, the filtrate was collected and its amount measured. Each effluent was then analyzed for dissolved solids (DS); TOC; BOD; and color. Loads were calculated as m<sup>3</sup>/metric ton or kg/ton of pulp.

Total volumes from individual sequences, APP and CEH were 72 m<sup>3</sup> and 66.6 m<sup>3</sup>/t, respectively. These values for APPDED and CEDED were 119.2 m<sup>3</sup> and 104 m<sup>3</sup>.

For comparative purposes, relative waste loads of DS, TOC, BOD and color are presented in Fig. 3. Loads from conventional CEDED sequences were taken as a base line of 100. Compared to conventional CEH and CEDED sequences, the peroxide sequences contain little or no chlorides. These have much higher DS and BOD; about the same TOC, and almost negligible color loads. In fact, higher DS and BOD should not be of much consequence as these streams could be easily recycled. The data also indicate that the type of TOC present in peroxide sequences is also easily biodegradable.

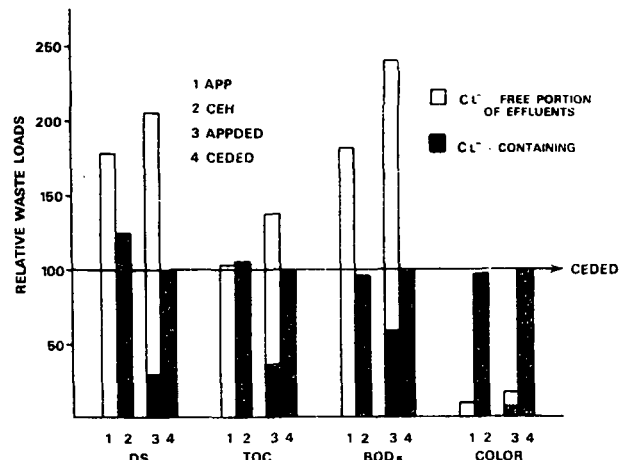


Figure 3. Relative Waste Load of Different Bleaching Sequences (CEDED = 100)

The data further indicate that if CEDED sequence is replaced by APPDED and the effluents from APP stages are recycled back into the process, large reductions in total effluent loads can be achieved (when compared with CEDED). Calculations show that in this way reductions of over 90% in color, 40% BOD, 64% TOC and 71% DS can be obtained.

Table III shows the percent distribution of DS, TOC, BOD, and color loads within a bleaching sequence. As expected, the maximum load bearing streams are from the extraction stages in conventional sequences and peroxide stages in peroxide sequences.

TABLE III  
PERCENT DISTRIBUTION WITHIN BLEACH SEQUENCE

	APPDED			CEDED			CEH			APP	
	A	PP	DED	C	E	DED	C	E	H	A	PP
DS	31	55	14	21	56	23	17	45	38	36	64
TOC	3	72	26	20	71	13	19	67	14	4	96
BOD <sub>5</sub>	12	63	25	36	41	23	37	43	20	16	84
Color	2	57	36	20	76	4	21	77	2	3	97

Note: Values have been rounded to the nearest whole numbers.

Gel Permeation Chromatography (GPC) was used to fractionate effluent constituents by molecular weights into major components. Sephadex G-25 gell was used with a M<sub>w</sub> exclusion limit of 5000. In other words, substances below 5000 were fractionated. Water was used as the solvent. Data in Table IV show that all sequences generate dissolved materials in two major M<sub>w</sub> ranges - higher (5000-2000) and lower (<250). Very little material was found in the medium range of M<sub>w</sub> 1000-250, especially in the case of peroxide sequences.

TABLE IV  
PERCENT DISTRIBUTION BY MOLECULAR WEIGHT

Bleaching Sequence	Approx. M <sub>w</sub> Range		
	5000-2000	1000-250	< 250
APP	55%	5%	40%
CEH	40	19	41
APPDED	53	7	40
CEDED	26	18	56

IR and UV absorptivity data are given in Table V. Bleaching sequences containing chlorine dioxide stages show the presence of carbonyl groups. Data in Table V further show that higher amounts of ionized carboxyl groups and higher UV absorptivities are reflected by effluents from peroxide sequences than those from conventional CEH and CEDED sequences. Also note that the peroxide sequence effluents were extremely low in visible color (see Fig. 3).

TABLE V  
EFFLUENT CHARACTERIZATION

Bleaching Sequence	UV-Absorptivity at 277 nm, (lignin, etc.)	IR-Absorptivity	
		at 5882 nm (-C=O)	at 6250 nm (-COO-)
APP	225	No	410
CEH	221	±	285
APPDED	239	Yes	643
CEDED	161	Yes	260

Note: -C=O ~ ester or -COOH  
COO- ~ ionized carboxyl  
absorptivity = absorbance/organic concentration  
5882 nm = ~ 1700 cm<sup>-1</sup>  
6250 nm = ~ 1600 cm<sup>-1</sup>

#### EFFLUENT TOXICITY AND CORROSION

Toxicity of different bleaching sequences was checked using Daphnia - early instars. EC<sub>50</sub> values in Table VI are a bit higher for peroxide sequences indicating somewhat lower potential for toxicity. Whether or not these values are very significant is hard to answer with the data at hand. We can, however, safely comment that peroxide sequence effluents show similar EC<sub>50</sub> values to (if not higher than) the conventional sequences indicating similar or lower "toxicity" potential.

TABLE VI  
EFFECT OF BLEACHING SEQUENCE ON TOXICITY  
(Daphnia - Early Instars)

Sequence	EC <sub>50</sub> , % by volume
APP	51.5
CEH	41.0
APPDED	66.0
CEDED	39.0

Corrosion tests were run on effluents from A, P<sub>1</sub>, P<sub>2</sub>, C, and E (after C) stages using mild steel. The mils penetration per year (mpy) data indicate that effluents from A and C stages are highly corrosive (see Table VII) whereas P and E stages showed only slight or no corrosion. As a rule of thumb, values of 50 mpy and above indicate that the material has less resistance to corrosion and may not be satisfactory. Based on data in Table VII, we do not see any concern over higher corrosion rates in APP sequence compared with the worst stages of a conventional bleach plant.

#### PULP QUALITY

Yields of peroxide bleached pulps were 2-3% higher than those of conventional sequences (Table VIII).

TABLE VII  
EFFECT OF BLEACHING STAGES ON CORROSION RATE  
(250 hr runs on mild steel)

Stages	Temp., °C	Final pH	Corrosion Rate, (mpy)
A	25	4.3	159.4
P <sub>1</sub>	70	8.6	0.0
P <sub>2</sub>	70	9.0	33.4
C	25	1.9	129.4
E	50	8.5	3.7

TABLE VIII  
EFFECT OF BLEACHING SEQUENCE AND STORAGE

Sequence	Yield, %	GE-Brightness, %	Reversion <sup>a</sup> in % Brightness, GE-units
APP	96	68	2.7
CEH	93	77	7.4
APPDED	95	88	4.6
DEDED	93	85	5.4

<sup>a</sup>90 Min. at 105°C.

Table VIII further shows that the brightness levels of APPDED and CEDED are somewhat comparable. CEH sequence on the other hand gave brighter pulps than APP. This difference must be considered in evaluating these two sequences.

The brightness reversion during accelerated aging was measured for some pulps (Table VIII). APP sequence pulps showed significantly better brightness stability than the CEH sequence. In the case of fully bleached pulps, although the same trend was noticeable, the difference was not so great. In general, however, the peroxide bleached pulps were more stable.

Strength properties of pulps were determined according to the standard procedures. Pulps bleached with sequences APP, CEH, APPDED, and CEDED were beaten in a PFI-mill before testing for strength properties. Opacity of the sheets was also measured. Only some critical properties (tear factor and breaking length) are plotted in Fig. 4 and 5.

In the case of semibleached pulps (APP and CEH) the differences are not significant (Fig. 4). However, the CEDED bleached pulp seems to be 10-15% stronger than APPDED pulp (Fig. 5). In general, the differences in properties of pulps bleached with chlorine or peroxide are small or negligible.

Electron microphotographs were taken to check possible differences in fiber wall and sheet structures (see Fig. 6, 7, 8). Except in the case of CEDED, all others showed some damage on the outer surface of the fiber. Photographs of the sheets from fully bleached pulps indicate that the peroxide bleached (APPDED) fibers may be somewhat stiffer

than those bleached by the conventional process (CEDED).

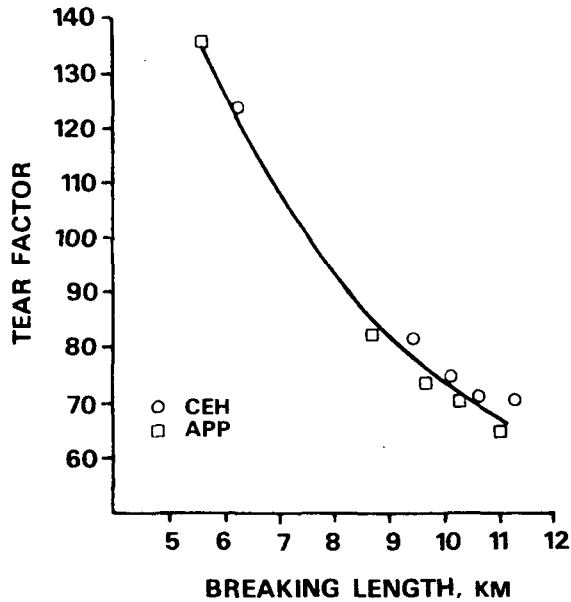


Figure 4. Tear Factor vs. Breaking Length of Semi-bleached Pulps

the pulp is required. Bleached pulps have acceptable quality but the chemical cost is 2-3 times higher than sequences with chlorine.

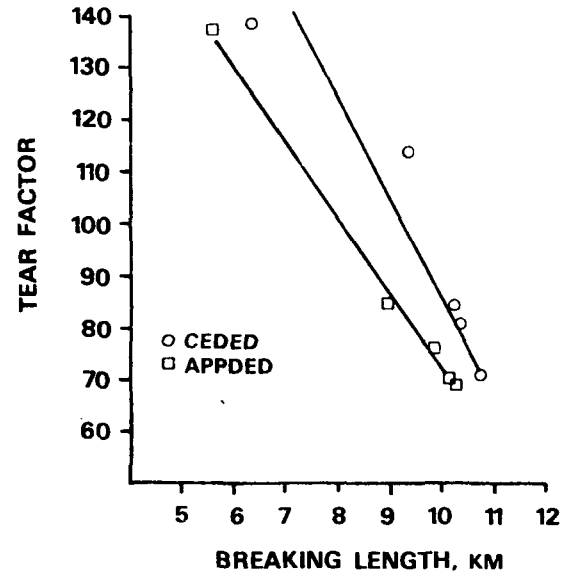


Figure 5. Tear Factor vs. Breaking Length of Fully Bleached Pulps

#### CHEMICAL COSTS

The costs of bleaching chemicals for different bleaching sequences were estimated at the current price level and chemical charges applied in this study. The total chemical costs (Table IX) show that the conventional method remains a lot cheaper than peroxide sequences at this moment. However, peroxide can become economical in the future provided the laws require elimination of chlorinated compounds from effluents or the cost of peroxide drops.

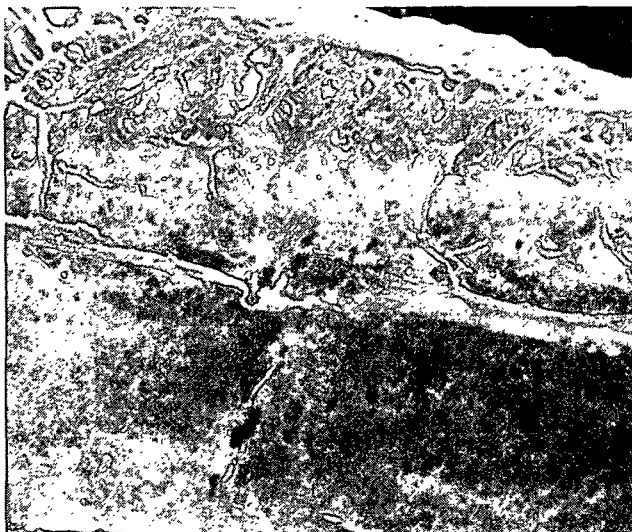
#### CONCLUSIONS

Softwood kraft pulps can be bleached with peroxide in the first stage of a bleaching sequence, instead of chlorine. However, an acid-pretreatment of

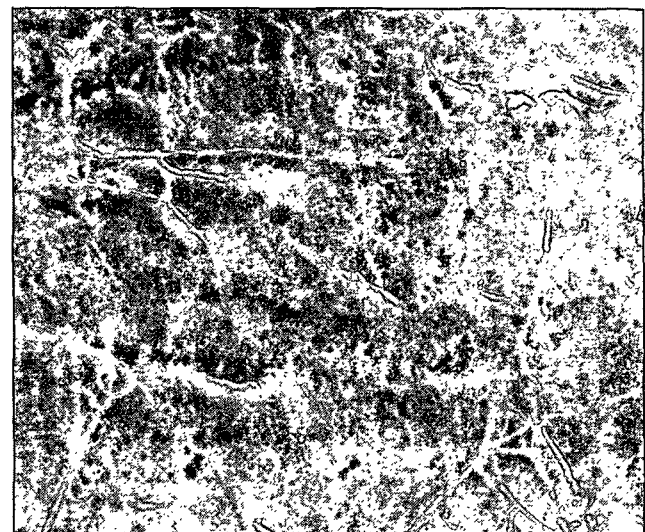
TABLE IX

#### CHEMICAL COST (ESTIMATED)

Sequence	U.S. \$/Metric Dry Ton
APP	53
CEH	18
APPDED	66
CEDED	28



APP Sheet



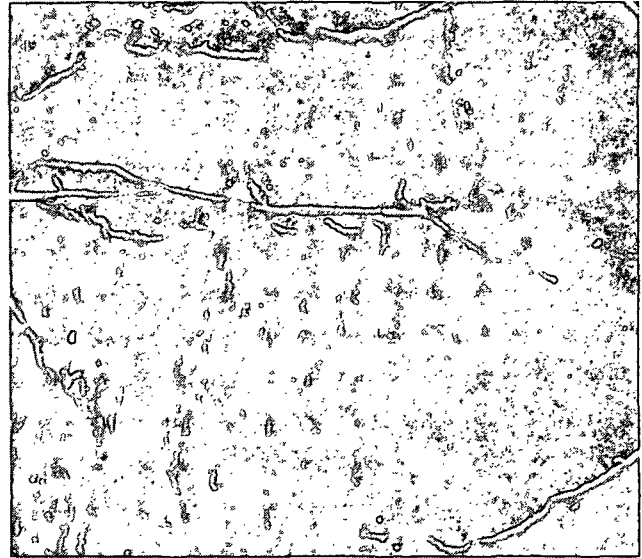
CEH Sheet

Figure 6. Semibleached Pulps by Bleaching Sequences APP and CEH. Magnification 10,000X



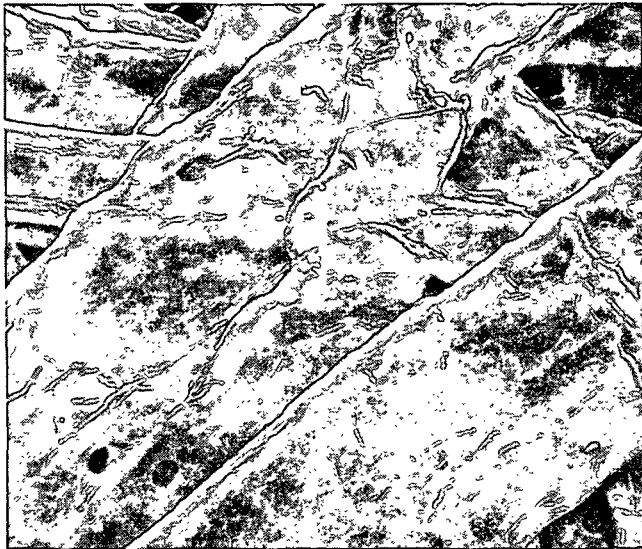


APPDED Sheet



CEDED Sheet

Figure 7. Fully Bleached Pulps by Bleaching Sequences APPDED and CEDED. Magnification 10,000X



APPDED Sheet



CEDED Sheet

Figure 8. Fully Bleached Pulps by Bleaching Sequences APPDED and CEDED. Magnification 1,000X

Compared to chlorine sequences, H<sub>2</sub>O<sub>2</sub> sequence effluents have higher BOD, higher dissolved organics, higher percent EC<sub>50</sub> (lower toxicity potential), similar corrosion potential, but extremely low color.

Recycling of peroxide and acid pretreatment stages back to the recovery system can drastically reduce the present CEDED sequence loads. Reductions of 90% in color loads, 40% BOD, 64% TOC, and 71% DS can be achieved. In addition, there is no possibility of the presence of chlorinated compounds in the effluents.

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