

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597282>

### Preliminary Results on Hydrogen Peroxide Addition to Chlorine Dioxide Bleaching Stages

R. C. Francis<sup>a</sup>; S. Chairrekij<sup>a</sup>; B. V. Ramarao<sup>a</sup>

<sup>a</sup> Faculty of Paper Science and Engineering, College of Environmental Science and Forestry, State University of New York, New York, USA

Online publication date: 06 March 2003

**To cite this Article** Francis, R. C. , Chairrekij, S. and Ramarao, B. V.(2003) 'Preliminary Results on Hydrogen Peroxide Addition to Chlorine Dioxide Bleaching Stages', *Journal of Wood Chemistry and Technology*, 23: 2, 113 – 129

**To link to this Article:** DOI: 10.1081/WCT-120021920

**URL:** <http://dx.doi.org/10.1081/WCT-120021920>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY

Vol. 23, No. 2, pp. 113–129, 2003

## Preliminary Results on Hydrogen Peroxide Addition to Chlorine Dioxide Bleaching Stages

R. C. Francis,\* S. Chairrekij, and B. V. Ramarao

Faculty of Paper Science and Engineering, State  
University of New York, College of Environmental  
Science and Forestry, Syracuse, New York, USA

### ABSTRACT

There are convincing results in the literature indicating that the fiber yield for fully bleached hardwood kraft pulps can be increased by approximately 2% (measured on chip weight as basis) by pulping at milder conditions and bleaching under more aggressive conditions. The kappa number of the unbleached pulp in this scheme would be higher by about 3–5 units. The viability of this process is predicated upon increased throughput in an existing bleach plant without a major retrofit. The feasibility of the principle of this process was investigated by adding hydrogen peroxide to the first two chlorine dioxide stages ( $D_0$  and  $D_1$ ) along with sodium molybdate as a catalyst. The incremental peroxide required for bleaching the

---

\*Correspondence: R. C. Francis, Faculty of Paper Science and Engineering, State University of New York, College of Environmental Science and Forestry, One Forestry Drive, Syracuse, New York 13210, USA; E-mail: francis@syr.edu.



higher kappa number pulps could in principle be added to either of the two stages without any change in their operating conditions. Our preliminary data suggest that peroxide action in the  $D_1$  stage results in a lower rate of cellulose depolymerization and hence is preferable. The recovery of the molybdate catalyst is critical to the feasibility of this process. One possible process of molybdate recovery utilizing selective ion flotation with a cationic surfactant (dodecylamine) was investigated. A recovery of 58% was achieved after two preliminary trials using the column flotation technique. Other literature results suggest that a higher recovery, of the order of >90% is achievable using ion flotation indicating that a highly efficient recovery process for both the molybdate catalyst and the flotation agent can be developed. Thus, this technique of obtaining enhanced yields could provide an economically feasible alternative for production enhancement in pulp mills.

*Key Words:* Chlorine dioxide; Hydrogen peroxide; Sodium molybdate hardwoods; Kraft pulps.

## INTRODUCTION

According to some projections, it appears that the global supply of hardwoods may be less than the demand by as early as 2010.<sup>[1]</sup> Furthermore, regional shortages resulting in increased costs of hardwood chips in papermaking seem even more likely. Research on improving fiber yields from the kraft pulping and bleaching of hardwoods and enhancing their utilization acquires significance in relieving such shortages in the future. Some recent work on elemental chlorine-free bleaching<sup>[2]</sup> (ECF) and totally chlorine-free (TCF) bleaching processes represent efforts in this direction.

Oxygen delignification is a critical stage in TCF bleaching because it affords a low kappa number ( $\sim 10$ ) before the application of the more expensive oxidants such as peracetic acid, ozone, and hydrogen peroxide. The unbleached pulps from black locust (*Robinia pseudoacacia*) and silver maple (*Acer saccharinum*) that were used in our ECF study both had kappa number of  $\sim 20$  and viscosity  $> 50$  cP.<sup>[2]</sup> The sequence that was used is  $OD_0EoD_1$  (O = alkaline oxygen,  $D_0 = ClO_2$  delignification,  $Eo =$  alkaline extraction with  $O_2$ , and  $D_1 = ClO_2$  brightening stage) and both pulps had kappa number  $\sim 10.5$  and viscosity  $> 34$  cP after the  $O_2$  stage.<sup>[2]</sup> We initiated the TCF sequence with more aggressive  $O_2$  treatments but were unable to achieve a kappa number  $< 9.0$ . What we discovered is that we could terminate pulping at kappa number 22–23



## Chlorine Dioxide Bleaching

115

instead of 20, use an extra 0.5% NaOH on pulp in the O<sub>2</sub> stage and end up at kappa number 10. The benefit of this approach was a yield increase of ~1.5% on chips as compared to pulping to kappa number 20.

This concept of milder pulping and more aggressive bleaching of hardwoods to obtain a higher yield is documented in the literature for both TCF and ECF chemicals.<sup>[3,4]</sup> Colodette et al. used an OQP (Q=treatment with chelating agent, P=alkaline peroxide stage) partial sequence to delignify four eucalyptus kraft pulps with kappa numbers varying from 16.8 to 27.2.<sup>[3]</sup> By increasing the severity of OQP treatments for brownstocks with higher kappa numbers they were able to lower the kappa number of all four pulps to 6.8–7.5. The fiber yield after OQP was 46.3% on chips for the 16.8 kappa number pulp and 51.6% for the 27.2 kappa number pulp. The chip requirement decreased by 10.2%, from 2.16 tons/ton pulp for brownstock kappa number 16.8–19.4 tons/ton pulp for the 27.2 kappa number brownstock. In a second investigation, Marcoccia et al.<sup>[4]</sup> varied a wide range of kraft pulping parameters to obtain pulps with varying kappa numbers and yields. When these pulps were bleached to 88%, ISO brightness by D<sub>0</sub>EoD<sub>1</sub> the fiber yield varied from 46.0 to 49.5% on chips.<sup>[4]</sup> The yield increase in this case was obtained by using more ClO<sub>2</sub> for higher kappa number pulps and this would increase the concentration of adsorbable organic halogens (AOX) in the effluent.

The objective of this investigation was to perform preliminary trials on an extended delignification technique that did not call for a major re-design of an ECF bleach plant or uses more ClO<sub>2</sub>. The approach was to add H<sub>2</sub>O<sub>2</sub> and sodium molybdate simultaneously with ClO<sub>2</sub> to the D<sub>0</sub> or D<sub>1</sub> stage.

## EXPERIMENTAL

### Wood Supply and Pulping

The black locust and silver maple logs were obtained from the W. Kellogg Experimental Forest of the Department of Forestry, Michigan State University<sup>[2]</sup> while the aspen (*Populus tremuloides*) was harvested in Central New York. Kraft pulping was conducted in pressurized digesters with liquor circulation. A 5:1 liquor to wood ratio was used with 16% active alkali on chips (NaOH and Na<sub>2</sub>S added on a Na<sub>2</sub>O basis) and 28% sulfidity. The time to reach the maximum temperature of 165°C was always 90 min and the duration at 165°C was 120 min.



### Oxygen Delignification

Conducted in a Quantum Mark IV reactor at 12% consistency, 0.72 MPa of O<sub>2</sub>, 2.5% NaOH, and 0.5% MgSO<sub>4</sub>·7H<sub>2</sub>O on pulp at 90°C for 1 h.

### Chelation Treatment

Q Stage: 0.2% sodium diethylenetriaminepentaacetate (Na<sub>5</sub>DTPA) on pulp, pH adjusted to 5.5 with NaHSO<sub>3</sub>, 3% consistency, and 1.0 h at 20–25°C. These were the only conditions used for both unbleached and O<sub>2</sub>-delignified pulps.

### Treatments of Unbleached Pulp

D<sub>0</sub> or D/P<sub>M</sub> Stage: In plastic bottles at 3.5% consistency, 70°C, 2 h with initial pH ~4 before the addition of oxidants and 250 ppm Na<sub>2</sub>MoO<sub>4</sub> on pulp for D/P<sub>M</sub> stages.

E Stage: In plastic bags at 12% consistency, 80°C, 2 h, and NaOH application of 1.5% or 2.0% on pulp.

P Stage: In plastic bags at 12% consistency, 80°C, 2 h, 0.5% H<sub>2</sub>O<sub>2</sub>, 1.5% NaOH, and 0.1% MgSO<sub>4</sub>·7H<sub>2</sub>O on pulp.

D<sub>1</sub> Stage: In plastic bags at 10% consistency, 70°C, 2 h, 0.8% ClO<sub>2</sub>, and 0.1% NaOH on pulp.

### Treatments of O<sub>2</sub>-Delignified Pulp

D or D/P<sub>M</sub> Stage: In plastic bags at 10% consistency, 70°C, 2 h, and 250 ppm Na<sub>2</sub>MoO<sub>4</sub> on pulp for D/P<sub>M</sub> stages.

E Stage: Similar to unbleached pulp with 1.5% NaOH on pulp.

### Ion Flotation of Molybdate

Figure 1 shows a schematic of a bench scale flotation column set up in our laboratory. The flotation column can be used in both continuous and batch modes. The column is 1.946 m tall and 92.075 mm in diameter. It is provided at the top with a collection trough that leads to an overflow tank. An air sparger is provided at the bottom of the column to supply air



Chlorine Dioxide Bleaching

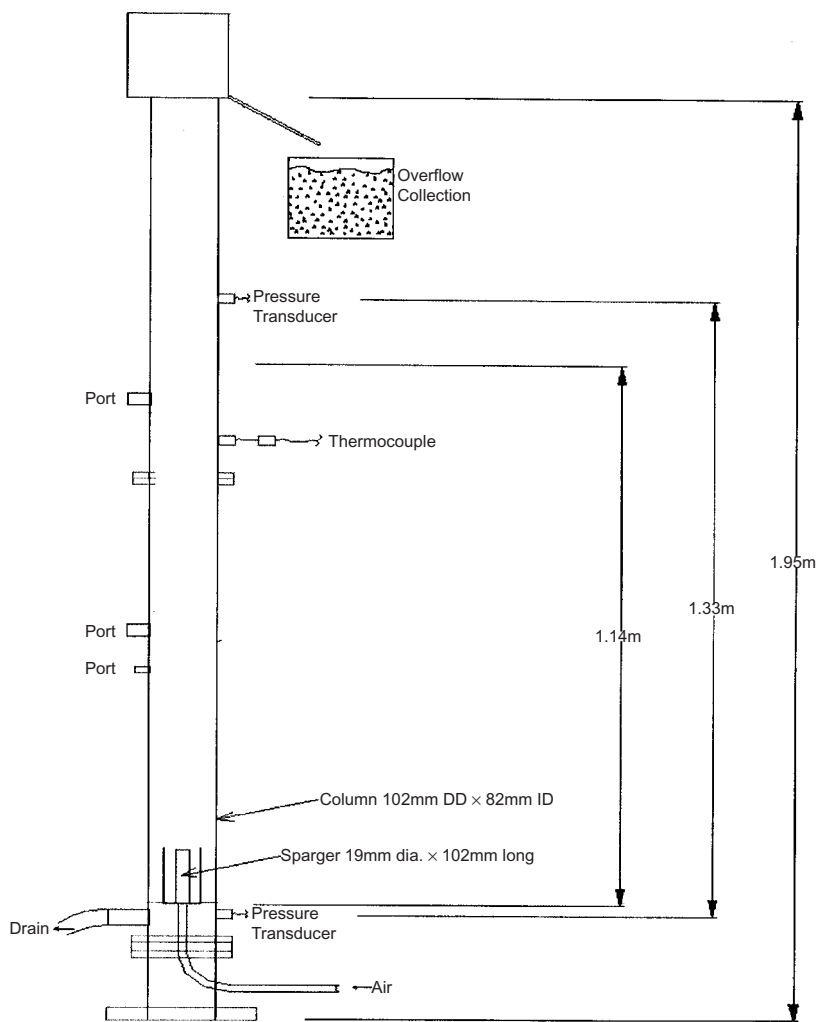


Figure 1. Schematic of flotation column with instrumentation for pressure and temperature measurements.

bubbles. Two pressure transducers are provided in the column to measure the pressure differential between two locations. The pressure differential can be used to obtain the air holdup within the column at any chosen time. A thermocouple is also provided to record the temperature of the slurry in the column.

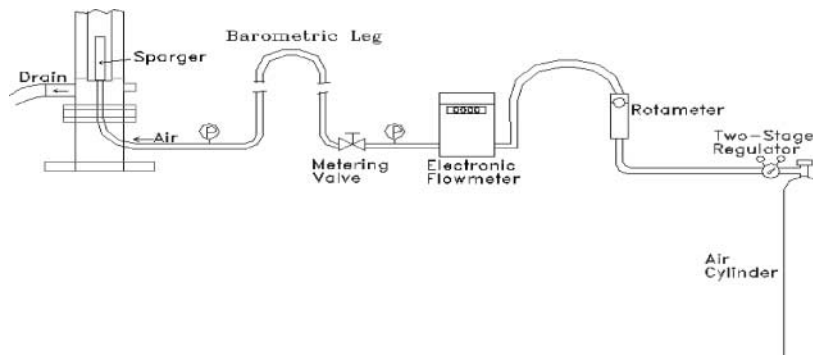


Figure 2. Schematic of the gas flow supply to the flotation column.

Figure 2 shows a schematic of the gas supply system to the column. A compressed air cylinder is connected via a two-stage regulator to a rotameter. An electronic flow meter was also connected in series to provide a calibration of the flow rate indicated by the rotameter. The compressed air is passed through a metering valve and a barometric leg, after which it is lead to the sparger. Pressure gauges are provided on either side of the metering valve to aid setting of the air flow conditions in a reproducible manner.

### Analyses

Tappi Standard Methods were used for kappa number and viscosity while brightness was determined on an Elrepho brightness meter. Transition metals and Mo concentrations in effluents were determined by ICP atomic emission spectroscopy. Trace metals in pulps were determined by Econotech Services Ltd., British Columbia, Canada.

## RESULTS AND DISCUSSION

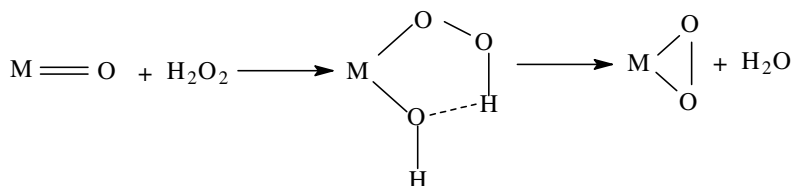
### A Rationale for $\text{H}_2\text{O}_2/\text{Na}_2\text{MoO}_4$ Addition to a D Stage

Molybdate-catalyzed, peroxide delignification ( $P_M$ ) was first patented in 1982<sup>[5]</sup> and has been previously investigated.<sup>[6,7]</sup> The decrease in kappa number was approximately equivalent at initial pH 2 and pH 5. However, the rate of cellulose depolymerization was lower and pulp



## Chlorine Dioxide Bleaching

119



**Figure 3.** The reactive, cyclic peroxide believed to be generated when molybdate or tungstate is used as a catalyst for oxidation.

washing could be avoided prior to extraction ( $P_M \rightarrow E_O$ ) when initial pH 5 was used.<sup>[7]</sup> The catalytic effect of molybdate or tungstate is believed to be due to their ability to form cyclic peroxides as shown in Fig. 3 where  $M = Mo$  or  $W$ .<sup>[6,7]</sup> Three-membered cyclic peroxides are reactive oxidants in most cases. Interestingly, both ozone and oxygen delignification at pH 5 were reported to be catalyzed by  $Na_2MoO_4$ .<sup>[8]</sup> Chlorine dioxide may be able to facilitate the oxidation in Fig. 3 by donating an O atom. When the cyclic molybdo-peroxide oxidizes lignin no AOX would be generated. The  $MoO_4^{2-}$  would be present during  $ClO_2$  oxidation of pulp if a  $P_M$  stage is combined with a D stage and this may afford some environmental improvement. Not all of the Mo in the wash water would be recovered (to be discussed later) but  $MoO_4^{2-}$  or Mo in general demonstrates low toxicity to humans<sup>[9,10]</sup> and aquatic species.<sup>[11]</sup> Note that conventional bleaching results in AOX levels in the effluent at relatively higher concentrations of the order of kg/ton (of pulp) whereas the effluent from the Mo catalyzed bleach effluent is expected to be of substantially lower order (g/ton). Of course, a detailed comparison of the environmental benefit would account for the relative toxicity of the compounds involved. Such comparisons would provide a more complete understanding of the environmental benefits but the preliminary commercial viability of the D/ $P_M$  concept would be the first step. Another interesting question is whether a Z/ $P_M$  stage where Z=ozone would prove economically viable and environmentally beneficial. A Z stage is typically performed in the pH 2–5 range and is also catalyzed by molybdate.<sup>[8]</sup> The Z/ $P_M$  effluent would be low in  $Cl^-$  and could be recycled to the kraft recovery system. There is a report of a kraft mill that used a  $P_M$  stage for two years without any adverse effects associated with the Mo being recycled to the recovery system.<sup>[11]</sup>

A  $P_M$  stage is normally conducted between pH 2 and pH 5. Most of the delignification and brightening in a  $D_0$  or  $D_1$  stage occur in the same pH range. The  $D_0$  stage is normally initiated at pH 3–4 and ends at





around pH 2.5. The  $D_1$  stage typically has an initial pH  $\sim 10$  but this value decreases to  $\sim 5$  after 10 min and end at  $\sim 4$ .<sup>[12]</sup>

A major risk associated with combining a  $P_M$  and a D stage is wasteful reactions between the two oxidants. However, a few preliminary bleaching trials would indicate whether or not this should be a major concern.

### A Rationale for Molybdate Recovery from Effluent

In our earlier research, 250 g  $\text{Na}_2\text{MoO}_4$ /ton pulp (ppm) was required for efficient  $\text{H}_2\text{O}_2$  utilization at  $85^\circ\text{C}$ .<sup>[7]</sup> If  $10\text{ m}^3$ /ton of both acidic and alkaline effluents are assumed for the bleach plant then the combined effluent would contain 117 g Mo (250 g  $\text{Na}_2\text{MoO}_4$ ) in  $20\text{ m}^3$  or 5.8 ppm Mo. This assumes no adsorption of molybdate on the pulp. This value would be too high for discharge. Furthermore, at approximately \$10/kg for  $\text{Na}_2\text{MoO}_4$ <sup>[13]</sup> it makes sense to investigate its recovery.

Some practical absorption/desorption processes have been reported in the literature for aqueous Mo process streams that could facilitate application of this technology to ECF pulp mills.<sup>[14–20]</sup> We will investigate an ion flotation method that is reported to be quite effective in the concentration range that is of interest to us.<sup>[14–16]</sup> The method involves molybdate adsorption to the cationic surfactant, dodecylamine, followed by air flotation (pH 2.5–4.5). The amount of froth produced is reported to be quite low and the  $\text{MoO}_4^{2-}$  releases from the surfactant at pH 11 when the amine changes state from  $\text{RH}_3\text{N}^+$  to  $\text{RNH}_2$ . This is followed by a phase separation and the molybdate can be recycled back to the bleaching stage. The dodecylamine can be re-dissolved in larger quantities of hot water and recycled to the feed stream of the flotation unit. While the amine is minimally soluble in water at room temperature, 1 g easily dissolved in 100 mL at  $80^\circ\text{C}$ . In the concentration range that would be of interest to pulp bleaching operations, only a 1:1 mole ratio of dodecylamine is required for quantitative recovery of molybdate.<sup>[14–16]</sup> The process is insensitive to  $\text{Cl}^-$  and up to 3 g/L of  $\text{Na}_2\text{SO}_4$ ,<sup>[14–16]</sup> requires minimal capital expenditure and could be readily implemented at the end of  $D_0$  or  $D_1$  stage.

### Preliminary Delignification/Brightening Results

Three oxygen-delignified hardwood kraft pulps were mixed in approximately equal proportions. The pulps were from aspen, black



## Chlorine Dioxide Bleaching

121

**Table 1.** D/P<sub>M</sub> delignification of O<sub>2</sub> delignified mixed hardwood pulp.<sup>a</sup> Kappa number 9.1, viscosity 34.9 cP, brightness 51.3% Elrepho.

ClO <sub>2</sub> (% on pulp)	H <sub>2</sub> O <sub>2</sub> (% on pulp)	Kappa <sup>b</sup> number	Viscosity <sup>b</sup> (cP)	Brightness <sup>b</sup> (% Elrepho)
10 min pH = 2.6; end pH = 2.5				
0.75	0	2.6	29.9	72.1
0.75	0.25	2.1	28.4	75.3
10 min pH = 4.9; end pH = 4.4 <sup>c</sup>				
0.75	0	3.6	30.5	77.2
0.75	0.25	3.0	30.7	77.5

<sup>a</sup>D/P<sub>M</sub> performed after a Q stage.<sup>b</sup>After extraction with 1.5% NaOH on pulp (straight E stage).<sup>c</sup>Only 0.1% NaOH on pulp required.

locust, and silver maple and were cooked and O<sub>2</sub>-delignified under similar conditions (Experimental). The pulp mixture was given a chelation treatment (Q stage) to remove transition metals, particularly iron. The Fenton mechanism has been observed in pulp slurries at pH < 4.<sup>[21]</sup> The demineralized pulp was then treated with ClO<sub>2</sub> and ClO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/NaMoO<sub>4</sub> in the range of pH 2.5 and 4.4–4.9. The results are presented in Table 1 and the P<sub>M</sub> effect was quite impressive. Below a value of ~3, kappa number decreases very slowly with increasing oxidant application. Therefore, the decrease in kappa number from 2.6 to 2.1 caused by 0.25% H<sub>2</sub>O<sub>2</sub> in the pH 2.5 range (P<sub>M</sub> added to a D<sub>0</sub> stage) was significant. This was accompanied by only a minor decrease in viscosity and increased brightness. In the pH 4.4–4.9 range, 0.25% H<sub>2</sub>O<sub>2</sub> decreased kappa and increased brightness without decreasing viscosity.

In these trials we started with pulps of the same kappa number and the P<sub>M</sub> effect was increased delignification and brightening as compared to a straight D stage. In the context of pulping to a higher kappa number the expected P<sub>M</sub> effect would be to lower the kappa number from a higher initial value to the same end value as a straight D stage on a pulp with a lower initial kappa number.

The simulation of D/P<sub>M</sub> under D<sub>0</sub> conditions in Table 1 is not a practical approach because a Q stage before the D<sub>0</sub> stage would call for a major capital investment. An unbleached black locust kraft pulp without chelation treatment was used to simulate D/P<sub>M</sub> under D<sub>0</sub> conditions. Based on the low kappa numbers obtained at pH 4.4–4.9 in Table 1, we targeted an end pH of 3.0–3.5 for the D/P<sub>M</sub> treatments in this



trial. It was hoped that Fe desorption from the pulp would be minor at these pHs.

In order to see if there was any synergism between the two oxidants in lowering kappa number, a kappa factor of 0.15 was chosen and converted to oxidizing equivalents (OXE). The total OXE charge was fixed and  $\text{ClO}_2$  was replaced by  $\text{H}_2\text{O}_2$  at 10, 20, 30, and 50%. The pulp had a kappa number of 18.9. Therefore, a kappa factor of 0.15 corresponds to 2.84% equivalent  $\text{Cl}_2$  on pulp ( $0.15 \times 18.9$ ) or 28.4 g equiv.  $\text{Cl}_2/\text{kg}$  pulp. Since the equivalent weight of  $\text{Cl}_2$  is 35.5 g, the oxidant charge corresponded to 0.80 OXE/kg pulp. This trial was performed at 3.5% consistency (10% in Table 1) because this lower value is quite common in commercial practice. All treatment conditions are listed under Experimental.

The results are documented in Table 2 and based on kappa number and brightness after alkaline extraction it appears that up to 30% of the  $\text{ClO}_2$  (sample S0 vs. S4) can be replaced by  $\text{H}_2\text{O}_2$  (on an OXE basis). In the context of delignifying a pulp with a higher unbleached kappa number, one could increase the OXE application in a  $\text{D}_0$  stage by up to 42% by adding  $\text{H}_2\text{O}_2$  ( $42/142 = 0.30$ ). The S0 and S4 samples were brightened by the QPD partial sequence. Hydrogen peroxide was applied at 0.5% on pulp and 0.19% and 0.20% on pulp were consumed by S0 and S4. The brightness after the P stage was 76.2% Elrepho for S0 and 76.1% for S4. After a final D stage (0.8%  $\text{ClO}_2$  on pulp), the S0 sample had a brightness of 88.8% while the value was 88.6% for S4.

**Table 2.** Replacement of  $\text{ClO}_2$  by  $\text{H}_2\text{O}_2$  in a  $\text{D}_0$  stage at a fixed OXE application.<sup>a</sup> Kappa number 18.9, viscosity 47.5 cP, brightness 31.9% Elrepho.

Sample	$\text{ClO}_2$ replaced by $\text{H}_2\text{O}_2$ (%)	Kappa <sup>b</sup> number	Viscosity <sup>b</sup> (cP)	Brightness <sup>b</sup> (% Elrepho)	End pH
S0	0 <sup>c</sup>	5.1	39.0	60.4	2.6
S1	0	4.7	38.5	59.9	2.6
S2	10	4.9	35.8	59.1	2.7
S3	20	5.3	34.3	58.9	2.8
S4	30	5.3	32.1	59.4	3.0
S5	50	7.2	29.9	53.8	3.5

<sup>a</sup>0.80 OXE/kg pulp; Equiv. wt. of  $\text{ClO}_2 = 13.5$ , and  $\text{H}_2\text{O}_2 = 17.0$ .<sup>[22]</sup>

<sup>b</sup>After an E stage with 1.5% NaOH on pulp.

<sup>c</sup>No  $\text{Na}_2\text{MoO}_4$  in S0, 250 ppm on pulp for S1–S5.



### Chlorine Dioxide Bleaching

123

Although there was no synergism between  $\text{ClO}_2$  and  $\text{H}_2\text{O}_2$  in lowering the kappa number in the D/ $P_M$  stage, the rate of  $\text{H}_2\text{O}_2$  consumption appeared to be higher than in a  $P_M$  stage without  $\text{ClO}_2$ . There were only traces of residual oxidants in samples S0–S4 and 96% of the peroxide applied on S5 (0.68%  $\text{H}_2\text{O}_2$  on pulp) was consumed. In our earlier research,<sup>[7]</sup> such high consumption rates were never attained with 250 ppm  $\text{Na}_2\text{MoO}_4$  on pulp even though a temperature of 85°C (70°C in this case) was used. Furthermore, 10% consistency was used earlier as compared to 3.5% in the present case. Assuming no  $\text{MoO}_4^{2-}$  adsorption to the pulp, the solution phase molybdate concentration was 0.135 mM in the earlier study compared to 0.044 mM in the present case.

Another interesting observation is that  $\text{ClO}_2$  delignification was catalyzed by molybdate (S0 vs. S1). This result in conjunction with those for acidic  $\text{O}_2$  and  $\text{O}_3$ , that were previously mentioned,<sup>[8]</sup> would suggest that molybdate is catalytic in a wide range of acidic oxidizing systems. Further research is needed to see the effect of molybdate on the quantity and nature of AOX generated by  $\text{ClO}_2$ .

The only negative outcome in Table 2 is decreased viscosity with increasing  $\text{H}_2\text{O}_2$  application. Fenton chemistry was anticipated and the effluent for sample S1 (pH 2.6) was analyzed for Fe. The solution phase Fe concentration was 0.68 ppm which corresponds to a desorption of 18.8 ppm from pulp. Iron is normally strongly bound to kraft pulps even at a pH as low as 2.0.<sup>[23]</sup> Such a high desorption at pH 2.6 was somewhat surprising. The unbleached pulp was sent to an external laboratory for transition metal analysis. A demineralized sample (Q stage) was also sent to see how much Fe was desorbed from the pulp by  $\text{Na}_5\text{DTPA}$  at pH 5.5. The pulp was very rich in Fe (100 ppm) and a desorption of 18.8 ppm was now considered reasonable. The Fe was strongly bound at pH 5.5 (Table 3). While the  $\text{Na}_5\text{DTPA}$  lower the Cu concentration from 38 ppm on pulp to 4.7 ppm, it removed none of the iron.

The high iron content and its negative effect were actually helpful in shaping future research. Emphasis should be placed on  $P_M$  incorporation

**Table 3.** Transition and alkaline earth metals in black locust kraft pulp (mg/kg).

Sample	Ca	Mg	Mn	Fe	Cu
Untreated	1940	270	< 2	100	38
Q-treated <sup>a</sup>	820	91	< 2	100	4.7

<sup>a</sup>Q stage as described in Experimental.



with the  $D_1$  stage. The pulp would lose weakly bound Fe in the  $D_0$  stage and strongly bound Fe would leave with lignin in the  $E_0$  stage. Further desorption in the  $D_1$  stage at  $\text{pH} > 3.5$  should be minimal. Also, the Fenton mechanism in pulp slurries is much less significant at  $\text{pH} > 3.5$  as compared to  $\text{pH} 2-3$ .<sup>[21]</sup> The  $P_M$  treatment generated a high concentration of quinones from lignin model compounds.<sup>[6]</sup> Therefore, if  $P_M$  is incorporated with the  $D_1$  stage then this stage should be followed by another brightening stage (D or P). However, most mills making fully bleached, hardwood kraft pulp do have another brightening stage after the  $D_1$ .

### Preliminary Results on Molybdate Recovery

Two air flotation experiments with dodecylamine were performed. The experiments by Zhao et al.<sup>[14-16]</sup> were conducted on a small scale (100 mL of solutions) at high air flow rates (3 L of air at STP sparged over a 10 min period). One of our objectives was to check if larger volumes as expected from the bleaching effluent could be handled under suitable air flow rate conditions. Most of our present research was performed with 10 L of solution or slurry and 25-50 L of air sparged over 10 min.<sup>[24,25]</sup> A solution of 11.0 ppm Mo (from  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in deionized water was prepared and  $\text{H}_2\text{SO}_4$  was added to achieve pH 3.2. An ethanolic solution of dodecylamine was added at 21.3 ppm (1:1 mole ratio with Mo). The resulting ethanol concentration in the solution was 0.213% (v/v). When 3.0 L/min of air was sparged through 10 L of solution for 10 min, a Mo separation factor (conc. in foamate/conc. in clean solution) of 5.7 was obtained. However, only 37% of the Mo end up in the foamate that constituted 9.5% of the original volume (Table 4). When the air flow rate was increased to 5.0 L/min the separation factor decreased to 3.7 but 58% of the Mo was in the foamate (Table 4). This higher air flow rate increased the foamate volume to 26.7% of the original. The results of Zhao et al.<sup>[14-16]</sup> can thus be scaled and it appears that column flotation presents a viable unit operation in the recovery of the molybdate anion. Foamate can be handled by using columns with smaller aspect ratios i.e., of a larger diameter for a given length. Note that column flotation provides substantial advantages over conventional flotation cells. Column flotation provides a gentler bubble flow regime as opposed to the more chaotic flow found in horizontal agitated tanks. Thus higher selectivity can be obtained. Flotation columns accommodate the effluent solution volumes in a vertical configuration resulting in lower floor



## Chlorine Dioxide Bleaching

125

**Table 4.** Removal of molybdate from aqueous solution by ion flotation ( $\text{RH}_3\text{N}^+$  and  $\text{MoO}_4^{2-}$ ). Sparging of air for 10 min with feed concentration of Mo = 11.0 ppm.

Air flow rate (L/min)	Clean solution		Foamate		Mo in foamate <sup>b</sup> (%)	Separation factor <sup>c</sup>
	Volume (L)	Concentration (ppm)	Volume (L)	Concentration <sup>a</sup> (ppm)		
3.0	9.05	7.6	0.95	43.2	37	5.7
5.0	6.60	6.4	2.40	23.8	58	3.7

<sup>a</sup>By difference between concentrations in feed and clean solution.

<sup>b</sup>% of Mo in feed.

<sup>c</sup>Mo concentration in foamate/concentration in clean solution.



space requirement which is often at a premium in mills. The absence of moving parts can result in lower capital costs as well as operational cost savings due to the elimination of the agitator. Reduction of operating costs of up to 80% over conventional cells have been reported.<sup>[26,27]</sup>

### Preliminary Economic Analysis

The appropriate methodology, and the one chosen, is based on increased pulp production from the same amount of chips. The bleach plant is rarely a bottle-neck in a kraft operation it is unlikely that a mill would chose to take advantage of higher fiber yields by using less chips to produce the same amount of pulp. Data in the literature clearly support the hypothesis that if the unbleached kappa number of a hardwood kraft is increased from 15 to 20 a 2% increase in fiber yield would be obtained.<sup>[2-4,28]</sup> Let us assume a mill producing a 1,000 bleached tons/day at 47% yield on chips. If pulp yield is increased to 49% then an extra 42 tons of pulp would be produced at a market value of ~\$21,000 (\$500/ton). Some of the increased expenditures would be for H<sub>2</sub>O<sub>2</sub>, approximately 5 kg/ton on ~1,100 tons of unbleached or semi-bleached pulp. The cost would be approximate \$4,100 if \$0.75/kg is assumed for H<sub>2</sub>O<sub>2</sub>. At a kappa factor of 0.2, a 5 unit increase in kappa number would require an extra 1.0% equiv. Cl<sub>2</sub> or ~0.5% H<sub>2</sub>O<sub>2</sub> on pulp (equiv. wt. of Cl<sub>2</sub> = 35.5; H<sub>2</sub>O<sub>2</sub> = 17).

If a molybdate application rate of 250 g/ton were to be used then 275 kg of Na<sub>2</sub>MoO<sub>4</sub>/day would be required for 1100 tons. This would cost \$2750 since Na<sub>2</sub>MoO<sub>4</sub> sells for approximately \$10/kg.<sup>[13]</sup> However, your molybdate cost would be only \$550/day if an 80% recovery and recycle rate is attained. The dodecylamine requirement for 275 kg/day of Na<sub>2</sub>MoO<sub>4</sub> would be 532 kg (1:1 mole ratio). However, if an 80% recycle rate is also assumed then only 106 kg of the amine would be required at a cost of ~6/kg.<sup>[29]</sup> Therefore, the chemical cost would be around \$5,300/day and ~\$16,000/day would be available to operate the air flotation system on the D<sub>1</sub> stage wash water.

### SUMMARY

The fiber yield for fully bleached, hardwood kraft pulps can be increased by ~2% on chips if milder pulping and more aggressive



### Chlorine Dioxide Bleaching

127

bleaching conditions are utilized. The unbleached kappa number has to be increased by only 3–5 units. Experimental data in support of this concept have been provided in the past but either additional bleaching stages<sup>[3]</sup> or more  $\text{ClO}_2$ <sup>[4]</sup> were used. This study investigated the addition of  $\text{H}_2\text{O}_2$  to an existing  $\text{ClO}_2$  stage ( $\text{D}_0$  or  $\text{D}_1$ ) along with sodium molybdate as a catalyst.

The incremental  $\text{H}_2\text{O}_2$  required for higher kappa number pulps can be added and consumed in either the  $\text{D}_0$  or  $\text{D}_1$  stages without any change in conditions. Based on preliminary data,  $\text{H}_2\text{O}_2$  addition to the  $\text{D}_1$  stage is preferred because of a lower rate of cellulose depolymerization. Preliminary research was performed on molybdate recovery by ion flotation with the cationic surfactant, dodecylamine. A recovery rate of 58% was attained after only two trials. Prior research with this technique suggests that almost all of the molybdate and dodecylamine can be easily recycled.

### ACKNOWLEDGMENTS

The financial support from the member companies of the Empire State Paper Research Associates (ESPRA) and the Michigan State University USDA Eastern Hardwood Utilization Grant #00-34158-9236 is deeply appreciated.

### REFERENCES

1. McNutt, J. *PIMA* **1996**, 78 (1), 28.
2. Francis, R.C.; Hausch, D.L.; Granzow, S.G.; Makkonen, H.P.; Kamdem, D.P. *Holz als Roh-und Werkstoff* **2001**, 59, 49.
3. Colodette, J.L.; Gomide, J.L.; Salles, D.V.; de Brito, A.C.H. *Proceed. 1995, Tappi Pulping Conf.; Tappi Press: Atlanta, 1995; 405.*
4. Marcoccia, B.; Stromberg, B.; Prough, J.R. *Proceed. 1998 Tappi Pulping Conf.; Tappi Press: Atlanta, 1998; 1485.*
5. Eckert, R.C. *Delignification and Bleaching Process and Solution for Lignocellulosic Pulp with Peroxide in the Presence of Metal Additives. Can. Patent 1,129,161, 1982.*
6. Sundman, G.I. *Molybdenum- and Tungsten-Catalyzed Reactions of Acidic Hydrogen Peroxide with Kraft Lignin Model Compound and Enzymatically Liberated Kraft Lignin. Ph.D. dissertation, SUNY College Environ. Sci. and Forestry, Syracuse, New York, 1988.*





7. Kubelka, V.; Francis, R.C.; Dence, C.W. *J. Pulp Pap. Sci.* **1992**, *18*, 108.
8. Agnemo, R. *J. Pulp Pap. Sci.* **2002**, *28*, 23.
9. Friberg, L.; Lener, J. *Handbook on the Toxicology of Metals*, 2nd Ed.; Friberg, L., Nordberg, G.F., Vouk, V., Eds.; Elsevier: Amsterdam, 1986; 446–458 and references contained therein.
10. Vyskocil, A.; Viau, C. *J. Appl. Toxicol.* **1999**, *19*, 185.
11. Paren, A.; Jakara, J.; Anderson, R. Molybdate-Activated Peroxide Delignification in ECF Bleaching of Hardwood Kraft Pulp. Manuscript Provided by Kemira Chemicals Canada, Maitland, Ontario, 1999.
12. Reeve, D.W. Chlorine dioxide in bleaching stages. In *Pulp Bleaching—Principles and Practice*; Dence, C.W., Reeve, D.W., Eds.; Tappi Press: Atlanta, 1996; 388.
13. Chemical Marketing Reporter. Price of Sodium Molybdate Dihydrate, September 4, 2000.
14. Zhao, Y.; Zouboulis, A.I.; Matis, K.A. *Sep. Sci. Technol.* **1996**, *31*, 769.
15. Zhao, Y.; Zouboulis, A.I.; Matis, K.A. *Hydrometallurgy* **1996**, *43*, 143.
16. Zhao, Y.; Zouboulis, A.I.; Matis, K.A. *Hydrometallurgy* **1996**, *43*, 155.
17. Zhao, Y.; Chen, J. *Hydrometallurgy* **1996**, *42*, 325.
18. Heining, M.W.; Mellan, C.E. *Sep. Sci. Technol.* **1992**, *27*, 663.
19. Wu, C.-H.; Lo, S.L.; Lin, C.-F. *Coll. & Surfaces A* **2000**, *166*, 251.
20. Mulcany, F.M.; Fay, M.J.; Proctor, A.; Houalla, M.; Hercules, D.M. *J. Catal.* **1990**, *124*, 231.
21. Zhang, X.-Z.; Francis, R.C.; Dutton, D.B.; Hill, R.T. *Proceed. 1998 Tappi Pulping Conf.*; Tappi Press: Atlanta, 1998; 1561.
22. Reeve, D.W. Introduction. In *Pulp Bleaching—Principles and Practice*; Dence, C.W., Reeve, D.W., Eds.; Tappi Press: Atlanta, 1996; 16.
23. Bryant, P.S.; Edwards, L.L. *J. Pulp Pap. Sci.* **1996**, *22*, 37.
24. Chairrekij, S.; Dhingra, H.; Ramarao, B.V. *Resources, Conservation and Recycling* **2000**, *28*, 219.
25. Chairrekij, S.; Gupta, H.; Amato, W.S.; Ramarao, B.V. *Proceed. Wood and Cellulose-Building Blocks for Chemicals, Fuels and Advanced Materials*, SUNY College Environ. Sci. and Forestry, Syracuse, New York, 2000.
26. Dussureault, S.; Barbe, M.C.; Levesque, M. Column flotation: a new technology for deinking recycled pulp. *Tappi Proc. Recycling Symp.* **1995**, 251–255.



**Chlorine Dioxide Bleaching**

**129**

27. Finch, J.A.; Dobby, G.S. *Column Flotation*; Pergamon Press, 1990; Vol. 1, 1–18.
28. Gellerstedt, G.; Gustafsson, K.; Northey, R.A. *Nordic Pulp Pap. J.* **1988**, 3, 87.
29. Booth, S. *Akzo Nobel Surface Chemistry*; Chicago, IL, Private Communication, 2002.



MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

---

©2003 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.