# IMPROVED OXYGEN DELIGNIFICATION WITH INTERSTAGE PEROXYMONOSULFURIC ACID TREATMENT. PART 2. EFFECT OF HYDROGEN PEROXIDE

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## ABSTRACT

An improved oxygen delignification system with increased selectivity has been developed where pulp is treated with small amounts of peroxymonosulfuric acid (Ps) between two oxygen stages. However, commercially prepared peroxymonosulfuric acid solutions normally contain significant amounts of hydrogen peroxide and thus work here studied the effects of hydrogen peroxide in the system.

Results showed that no benefits to overall process selectivity were observed when hydrogen peroxide was present in the Ps stage itself. However, the presence of hydrogen peroxide in the final oxygen stage of the OPsO sequence extended the selective delignification set up by the intermediate peroxymonosulfuric acid treatment. This suggests that ideal operation of the OPsO sequence would include treatment with peroxide-free peroxymonosulfuric acid, interstage washing after the Ps stage to recover and reuse residual peroxymonosulfuric acid, and final oxygen delignification with low levels of hydrogen peroxide addition.

Initial pilot scale experiments confirmed that two stage oxygen delignification with interstage Ps treatment reduced pulp kappa number to low levels. Final kappa numbers for softwood and hardwood kraft pulps were 5.3 and 2.9, respectively, after OQPs(OP) treatment with 1.5% $HSO_5^-$ and 0.5% $H_2O_2$ (0.95% total equivalent $H_2O_2$). Pilot scale work has shown that careful control of peroxymonosulfuric acid reactions is required to maximise overall process selectivity.

## INTRODUCTION

Oxygen delignification is being used increasingly worldwide in modern bleached kraft pulp mills. This intermediate step between kraft pulping and final bleaching removes up to 50% of the residual lignin in kraft pulp, thus reducing the requirements for chlorine-based bleaching. Extending conventional oxygen treatments to more than 50% delignification would further decrease bleach chemical demands and increase environmental benefits. However, this is seldom practiced commercially since unacceptable losses in pulp quality, mainly strength potential, may occur.

Recent work at PAPRO has investigated the effectiveness of improving oxygen delignification with peroxyacid treatments [1,2]. The aim has been to increase the overall selectivity of a two stage oxygen delignification system through use of a mild interstage treatment with peroxymonosulfuric acid (Ps), a so-called OPsO sequence. Improved process selectivity will allow oxygen delignification to achieve lower pulp kappa number without excessive strength loss. The OPsO sequence is a chlorine-free analogue of the OxO sequence proposed by Lachenal [3,4] where the x stage is a limited treatment with molecular chlorine designed to "activate" the final oxygen stage.

Initial work on the OPsO sequence used a laboratory prepared solution of peroxymonosulfuric acid which contained an equilibrium mixture of the peroxyacid acid and hydrogen peroxide in excess sulfuric acid according to:

$$H_2O_2 + H_2SO_4 \Leftrightarrow H_2SO_5 + H_2O \qquad \{1\}.$$

At commercial concentrations of hydrogen peroxide and sulfuric acid, over 50% of the peroxide was converted to the peracid. No pulp washing was performed after peroxymonosulfuric acid treatment so that any residual active chemical was carried over into the final oxygen delignification stage (*i.e.*, an O(PsO) sequence). The addition of hydrogen peroxide to oxygen treatments has been reported previously to improve delignification selectivity and effectiveness [5,6]. This process design effectively utilises all of the active chemical and thus overcomes the need to maximise peroxymonosulfuric acid yield according to equilibrium {1}.

Initial results with the O(PsO) sequence showed that overall selectivity was superior to simple two stage oxygen delignification in terms of pulp viscosity and handsheet strength at a given final kappa number [1,2]. A pulp treatment with sequestering agent to remove catalytic metal ions (a so-called Q stage) was required prior to peroxymonosulfuric acid treatment in order to achieve maximum selectivity. In addition, it was confirmed that eliminating pulp washing after the peroxymonosulfuric acid treatment to allow residual chemical carry over to the final oxygen stage was beneficial to overall performance. Analysis of the residual chemical carryover showed that most of the original hydrogen peroxide in the treatment

mixture survived the short Ps stage and was thus present during the final oxygen delignification stage [1].

### Pilot Scale Research

In 1993, collaborative studies were initiated between PAPRO and Centre Technique du Papier (CTP) in France to study the OPsO sequence on a pilot scale. CTP has been conducting research on improved oxygen delignification systems for several years and has recently installed a modern bleaching pilot plant for more detailed studies of promising bleaching technologies [3,4,7].

Before pilot scale experiments began, it was vital to determine the precise role of hydrogen peroxide in the OPsO system. Was the hydrogen peroxide normally present in peroxymonosulfuric acid solutions imparting benefits to overall selectivity by being active in both the Ps and final oxygen stages, or by being active in only one of these treatments? An initial laboratory study was designed to answer that question. Peroxymonosulfuric acid treatments were performed with Du Pont's Oxone™ product which is a peroxide-free triple salt containing potassium peroxymonosulfate, *i.e.*, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. The use of Oxone™ allowed peroxymonosulfuric acid treatments to be performed with and without hydrogen peroxide present. By using interstage washing after the Ps treatment, final oxygen delignification could be performed under controlled conditions of peroxymonosulfuric acid and hydrogen peroxide levels.

Based on these laboratory results, pilot scale studies of OPsO processing were conducted in the semi-continuous bleaching pilot plant at CTP. Results from both the laboratory and pilot scale work are described here.

## EXPERIMENTAL

### Pulp

Kraft pulp for laboratory studies was prepared at conventional conditions using softwood chips from a local French mill. Pulp kappa number was 30.9 and cellulose degree of polymerisation (DP) was 1490, which was equivalent to 24.0 mPa.s pulp viscosity. Commercial softwood and hardwood MCC™ pulp after oxygen delignification was also obtained locally for pilot scale studies.

### First-stage Oxygen Delignification

Oxygen delignification in the laboratory was performed in pressurised reactors at the following conditions:

| | |
|---|---|
| 2.5% NaOH | 100°C |
| 0.5 MPa $O_2$ | 60 minutes |
| 0.1% $MgSO_4$ | 10% consistency |

### Metal Ion Removal (Q stage)

Metal ion removal in the laboratory was performed in plastic bags heated in a water bath. Pulp pH was adjusted to pH 5-6 by sulfuric acid addition and soaking overnight. Pulp was treated with 1.0% $Na_4$-EDTA, the tetrasodium salt of ethylenediaminetetraacetic acid, at 10% consistency and 90°C for 60 minutes.

### Peroxymonosulfuric Acid Treatment (Ps stage)

Peroxymonosulfuric acid treatments in the laboratory were performed in plastic bags heated in a water bath under variable conditions of $HSO_5^-$ (as Oxone™) and $H_2O_2$ charge. Treatment pH was unadjusted. Other standard conditions were 10% consistency, 75°C and 30 minutes.

### Final Oxygen Delignification

Oxygen delignification was performed as above except alkali charge was varied from 1.0 to 5.5% NaOH. Peroxymonosulfate as Oxone™ and hydrogen peroxide were added where indicated.

### Analyses

Kappa number, brightness and viscosity were measured according to appropriate AFNOR standards. Relative pulp viscosity (RV) in mPa.s was converted to cellulose degree of polymerisation (DP) according to the following formula:

$$DP = [0.75\ (954 \log RV - 325)]^{1.105}$$

## RESULTS AND DISCUSSION

A large batch of conventional kraft pulp was prepared in the laboratory then oxygen delignified to 15.3 kappa number with 2.5% NaOH. Pulp was then treated with EDTA at conditions designed to chelate and remove catalytic transition metals (Fe, Mn, Cu) while preserving beneficial alkaline earth metals (Ca, Mg) [8]. After chelation, pulp kappa number remained unchanged and pulp DP was 1530 (25.4 mPa.s viscosity).

Control pulps were prepared where final oxygen delignification was performed without peroxymonosulfuric acid pretreatment, *i.e.*, kraft-OQO processing (Table 1). Alkali charge in the final oxygen stage was varied from 1.0 to 5.0% NaOH.

Table 1. Final oxygen delignification for control kraft-OQ pulps without Ps pretreatment[1].

| NaOH % | Kappa Number | DP | Brightness % |
|---|---|---|---|
| - | 30.9 | 1530 | 32.9 |
| 1.0 | 13.1 | 1420 | 36.8 |
| 2.0 | 12.6 | 1275 | 38.0 |
| 2.5 | 12.5 | 1200 | 38.0 |
| 3.0 | 12.2 | 1240 | 39.0 |
| 4.0 | 11.2 | 1160 | 40.2 |
| 5.0 | 10.9 | 1150 | 42.2 |

**Hydrogen Peroxide in the Ps Stage**

A factorial experimental design with star points [9] was implemented to study the effect of hydrogen peroxide in the Ps stage. The overall delignification effectiveness and selectivity were measured after the Ps stage as well as after the final oxygen delignification stage. Hydrogen peroxide and peroxymonosulfuric acid charges were varied from nil to 1.0% $H_2O_2$ and nil to 3.0% $HSO_5^-$, respectively, as shown in Table 2. After peroxymonosulfuric acid treatment, pulps were washed then final oxygen delignification was performed with 2.5% NaOH alkali charge. Experimental results after the Ps stage and after the final oxygen delignification treatment are presented in Table 3.

Response models for pulp kappa number and DP were developed by least squares analysis of experimental data (Table 4). For kappa number, only the influence of peroxymonosulfuric acid charge was significant at the 95% level. As peroxymonosulfuric acid charge increased, kappa number decreased non-linearly for pulps after both the Ps stage and the final oxygen delignification stage (Figure 1). Hydrogen peroxide in the Ps stage, however, did not affect the extent of overall delignification. As shown in Figure 1, variation in the hydrogen peroxide charge at each peroxymonosulfuric acid level had little influence on final kappa number for OQPsO pulp. The models for kappa number fit the data very well with coefficients of determination ($R^2$) greater than 0.95.

DP of the final OQPsO pulp responded non-linearly to the charges of both peroxymonosulfuric acid and hydrogen peroxide in the Ps stage (Table 4). The response surface showed a shallow optimum at about 1.5% $HSO_5^-$ and 0.4% $H_2O_2$ (Figure 2). Overall, final pulp DP was much less responsive than kappa number to the charges of peroxymonosulfuric acid and hydrogen peroxide in the Ps stage. Additionally, the model for final pulp DP had a coefficient of determination of only 0.71, and thus, did not fit the data as well as the models for kappa number (Table 4).

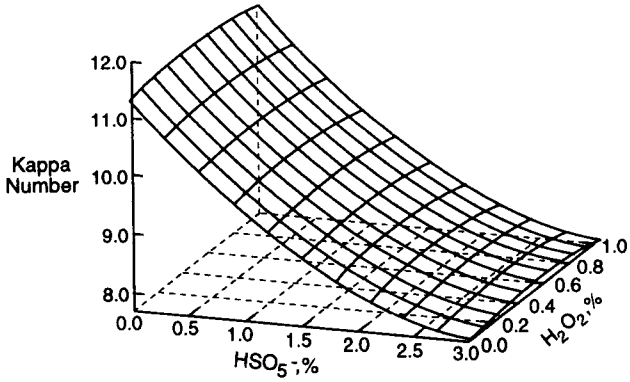



Figure 1. Effect of peroxymonosulfuric acid and hydrogen peroxide in the Ps stage on final kappa number after OQPsO processing.

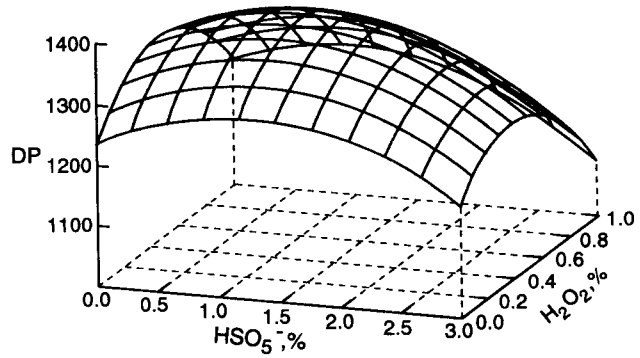



Figure 2. Effect of peroxymonosulfuric acid and hydrogen peroxide in the Ps stage on final pulp DP after OQPsO processing.

The selectivity of delignification was the attribute of greatest importance and was estimated by the ratio of lignin removal to DP loss, *i.e.*, $\Delta K\#/\Delta DP$. Since Ps charge had a very positive effect on lignin removal and a somewhat neutral effect on DP loss, overall selectivity tended to improve as more peroxymonosulfuric acid was applied in the Ps stage. This is illustrated in Figure 3 where kappa number-DP plots for the experimental pulps are compared with those of control pulps which have not been pretreated with combinations of peroxymonosulfuric acid and hydrogen peroxide. As peroxymonosulfuric acid charge increased, final kappa number for OQPsO pulp was substantially reduced with little concomitant decrease in pulp DP.

Table 2. Factors for peroxymonosulfuric acid and hydrogen peroxide charges.

| Factor | $-2^{1/2}$ | -1 | 0 | +1 | $+2^{1/2}$ |
|---|---|---|---|---|---|
| X1: % $HSO_5^-$ | 0.00 | 0.44 | 1.50 | 2.56 | 3.00 |
| X2: % $H_2O_2$ | 0.00 | 0.15 | 0.50 | 0.85 | 1.00 |

Table 3. Results from factorial experiments investigating the effects of hydrogen peroxide in the Ps stage.

| Chemicals | | Ps Stage[1] | | | | | Final Oxygen Stage[2] | | |
|---|---|---|---|---|---|---|---|---|---|
| $HSO_5^-$ % | $H_2O_2$ % | Kappa No. | DP | Final pH | Residuals, % $HSO_5^-$ | Residuals, % $H_2O_2$ | Kappa No. | DP | Bright % ISO |
| 0.44 | 0.15 | 14.3 | 1460 | 6.3 | 0.08 | 0.10 | 10.3 | 1280 | 44.0 |
| 2.56 | 0.15 | 12.7 | 1350 | 3.3 | 1.43 | 0.13 | 8.0 | 1290 | 47.8 |
| 0.44 | 0.85 | 14.4 | 1420 | 6.1 | 0.12 | 0.64 | 10.2 | 1260 | 43.9 |
| 2.56 | 0.85 | 12.7 | 1300 | 3.4 | 1.43 | 0.85 | 7.9 | 1235 | 47.1 |
| 0.00 | 0.50 | 15.2 | 1430 | 7.6 | 0.00 | 0.36 | 11.7 | 1380 | 40.3 |
| 3.00 | 0.50 | 12.5 | 1295 | 3.2 | 1.59 | 0.39 | 7.9 | 1235 | 47.7 |
| 1.50 | 0.00 | 13.1 | 1420 | 3.8 | 0.69 | 0.00 | 8.9 | 1320 | 46.5 |
| 1.50 | 1.00 | 12.8 | 1350 | 4.1 | 0.78 | 0.83 | 9.0 | 1250 | 46.3 |
| 1.50 | 0.50 | 13.0 | 1380 | 4.1 | 0.65 | 0.39 | 8.8 | 1390 | 47.2 |
| 1.50 | 0.50 | 13.1 | 1370 | 3.8 | 0.63 | 0.38 | 8.9 | 1390 | 46.5 |
| 1.50 | 0.50 | 13.0 | 1350 | 4.1 | 0.68 | 0.39 | 9.1 | 1370 | 44.4 |
| 1.50 | 0.50 | 13.0 | 1380 | 4.1 | 0.76 | 0.41 | 9.0 | 1370 | 45.2 |

[1] Kraft-OQ pulp, 15.3 kappa number, 1530 DP.

[2] 2.5% NaOH

For example at DP 1250 (17.0 mPa.s), final pulp kappa number was reduced from about 12.5 for the control pulp to 8.0 for pulp pretreated with 2.6% $HSO_5^-$. Variations in hydrogen peroxide charge in the Ps stage had little consistent effect on overall selectivity.

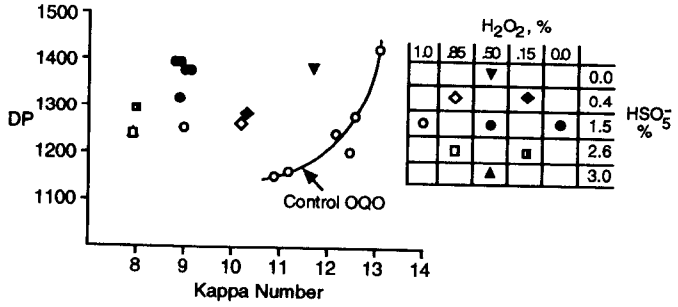



Figure 3. Effect of peroxymonosulfuric acid and hydrogen peroxide in the Ps stage on overall selectivity after OQPsO processing.

## Hydrogen peroxide in the Final Oxygen Stage

To study the effect of hydrogen peroxide in the final oxygen stage, kraft-OQ pulp was treated at standard conditions with 1.5% $HSO_5^-$ without hydrogen peroxide addition, then fully washed. This resulted in a Ps-treated pulp of 13.5 kappa number and 1330 DP (19.0 mPa.s).

This kraft-OQPs pulp (no $H_2O_2$ in Ps stage) was then oxygen delignified with the addition of the following:

- 0.5% $H_2O_2$,
- 0.9% $HSO_5^-$ (equivalent to the residual in the Ps stage),
- 0.5% $H_2O_2$ plus 0.9% $HSO_5^-$,
- Nil.

These four variants of final oxygen delignification were performed at three alkali levels to give a range of 12 final kraft-OQPsO pulps (Table 5). Kappa number-DP relationships, *i.e.*, selectivity, are plotted in Figure 4 along with that for the control pulp. All kraft-OQPsO pulps form a common selectivity relationship which is superior to that of the control pulp. Neither residual peroxymonosulfuric acid nor hydrogen peroxide in the final oxygen stage further improved the selectivity of overall delignification set up by the Ps treatment itself.

Table 4. Regression coefficients (95% significance) for the main effects and interactions of peroxymonosulfuric acid and hydrogen peroxide in the Ps stage.

$$\text{Response} = \text{Const.} + C1(X1) + C2(X2) + C3(X1)^2 + C4(X2)^2 + C5(X1X2)$$

| | Regression Coefficients | | | |
|---|---|---|---|---|
| | Ps Stage | | Final $O_2$ Stage | |
| | Kappa Number | DP | Kappa Number | DP |
| Main factors | | | | |
| X1: $HSO_5^-$ | -2.02 | -49.6 | -2.13 | 91.4 |
| X2: $H_2O_2$ | - | -67.2 | - | 379 |
| 2 Factor Interactions | | | | |
| $(X1)^2$ | 0.39 | - | 0.32 | -39.1 |
| $(X2)^2$ | - | - | - | -441 |
| (X1*X2) | - | - | - | - |
| Constant | 15.17 | 1478 | 11.43 | 1252 |
| $R^2$ | 0.97 | 0.94 | 0.96 | 0.71 |
| Std. Error | 0.13 | 12.7 | 0.22 | 34.0 |

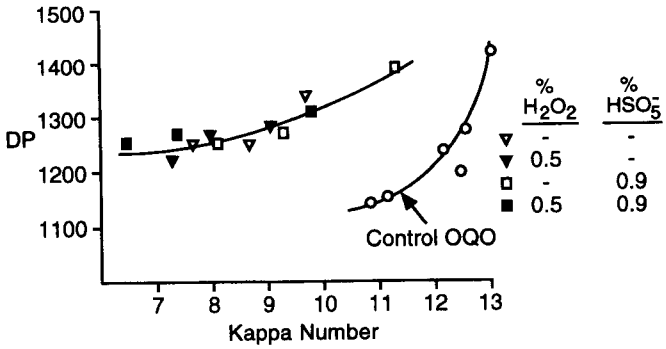



Figure 4. Effect of peroxymonosulfuric acid and hydrogen peroxide in the final oxygen stage on overall selectivity after OQPsO processing.

The data do, however, show that the addition of hydrogen peroxide to the final oxygen stage extends the selective delignification induced by the peroxymonosulfuric acid pretreatment. Lower final kappa number is obtained with 0.5% $H_2O_2$ addition without further loss of DP (Figure 4). For example, the addition of 0.5% $H_2O_2$ to the final oxygen stage at 2.5% NaOH reduced kappa number by one further unit while maintaining DP at about 1250 (Table 5). The addition of 0.9% $HSO_5^-$ had a negative effect on oxygen delignification, presumably due to alkali consumption by the acidity of the added Oxone™ solution, *i.e.*, peroxymonosulfate and bisulfate anions (Table 5).

The addition of hydrogen peroxide also resulted in improved final pulp brightness. Again, using the example where 0.5% $H_2O_2$ was added to the final oxygen stage at 2.5% NaOH, brightness increased from 47.2% to 53.9% ISO with hydrogen peroxide addition (Table 5). Hydrogen peroxide was thus acting to destroy chromophores (*i.e.*, brightening) while also enhancing lignin degradation (*i.e.*, delignification). Further work is required to determine if this increased brightness is maintained through final bleaching.

**Optimum Processing**

Results indicate that peroxymonosulfuric acid and hydrogen peroxide are more efficiently applied in separate stages of the OPsO system. Hydrogen peroxide does not enhance the action of peroxymonosulfuric acid in the Ps stage but does extend selective delignification when present in the final oxygen stage. The presence of peroxymonosulfuric acid in the final oxygen stage, on the other hand, retards delignification somewhat due to its acidity.

This suggests that the ideal configuration for an OPsO system would be to apply just peroxymonosulfuric acid in the Ps stage and add hydrogen peroxide directly to the final oxygen stage. Post washing after the Ps stage should allow some of the unreacted peroxymonosulfuric acid to be recovered for re-use, thus lowering overall peroxymonosulfuric acid demand. It is estimated that careful washing can recover and reuse at least half of the residual active chemical. For example, if 0.8% $HSO_5^-$ is residual after a Ps stage where 1.5% $HSO_5^-$ is applied, then reuse of 0.4% $HSO_5^-$ would reduce overall peroxymonosulfuric acid requirements to 1.1% $HSO_5^-$.

Table 5. Final oxygen delignification with peroxymonosulfuric acid and hydrogen peroxide addition[1].

| $HSO_5^-$ % | $H_2O_2$ % | NaOH % | Kappa Number | DP | Brightness % |
|---|---|---|---|---|---|
| - | - | 1.0 | 9.7 | 1340 | 43.6 |
| - | - | 2.5 | 8.7 | 1250 | 47.2 |
| - | - | 4.0 | 7.7 | 1250 | 50.3 |
| - | 0.5 | 1.0 | 9.1 | 1280 | 51.8 |
| - | 0.5 | 2.5 | 8.0 | 1260 | 53.9 |
| - | 0.5 | 4.0 | 7.3 | 1220 | 55.7 |
| 0.9 | - | 1.0 | 11.3 | 1390 | 41.5 |
| 0.9 | - | 2.5 | 9.3 | 1270 | 45.6 |
| 0.9 | - | 4.0 | 8.1 | 1250 | 49.1 |
| 0.9 | 0.5 | 1.0 | 9.8 | 1310 | 48.1 |
| 0.9 | 0.5 | 2.5 | 7.4 | 1265 | 52.8 |
| 0.9 | 0.5 | 4.0 | 6.5 | 1250 | 55.2 |

[1] Kraft-OQPs pulp (1.5% $HSO_5^-$).

Table 6. Pilot scale QPs(OP) treatment conditions.

| Stage | Chemicals, % Initial | Chemicals, % Consumed | Consist'y % | Temp. °C | Time min. | Final pH |
|---|---|---|---|---|---|---|
| Q | | | | | | |
| Swd & Hwd | 0.5 EDTA | - | 10 | 90 | 60 | 6.3 |
| Ps | | | | | | |
| Swd | 1.5 $HSO_5^-$ | 100 | 10 | 75 | 60 | 2.9 |
| Hwd | 1.5 $HSO_5^-$ | 100 | 10 | 75 | 30 | 2.7 |
| (OP) | | | | | | |
| Swd & Hwd | 2.5 NaOH | - | 10 | 100 | 60 | >10.5 |
| | 0.5 $H_2O_2$ | 100 | | | | |
| | 0.1 $MgSO_4$ | - | | | | |
| | 0.5 MPa $O_2$ | - | | | | |

Operating the OPsO process in this manner would require the development of a cost-effective means to generate peroxide-free peroxymonosulfuric acid. Song, *et al,* [10] have shown that adding acetic acid to Ps solutions increases peroxide conversion to peracid. The excess sulfuric acid catalyses acetic acid conversion to peracetic acid. Further work, however, is required to determine if the resulting mixed peracid solution would function effectively in the proposed OPsO process.

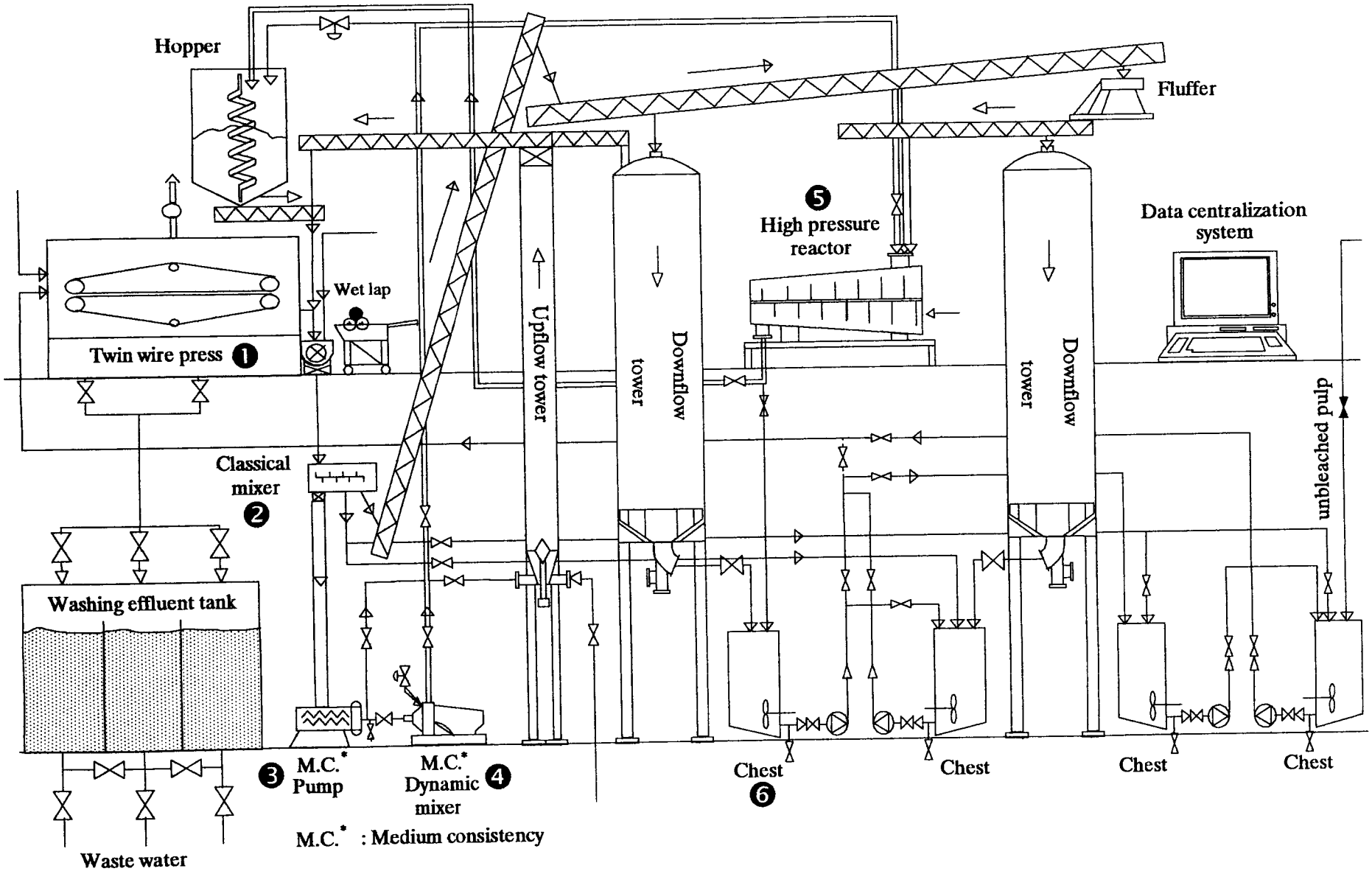
**Pilot Scale Trials**

Based on the above results, pilot scale studies of improved oxygen delignification were performed using commercial hardwood and softwood MCC™ kraft pulp. These pulps were oxygen delignified in the mill prior to shipment to CTP for final treatment in the bleaching pilot plant. Improved oxygen delignification to low kappa number was targeted with a final QPs(OP) sequence where EDTA pretreatment was followed by peroxymonosulfuric acid treatment then final oxygen delignification with hydrogen peroxide addition. Chosen conditions for the pilot trials are presented in Table 6.

The CTP pilot plant is a very flexible system which can simulate most bleach treatments in a semi-continuous mode. The plant is located on two floors and normally operates at 150 kg/hr for medium consistency processing. As shown in Figure 5, the pulp press, process controls and high pressure reactor are located on the top floor while filtrate tanks, pulp chests, pumps and mixers are in the basement. Two tall reactor systems extend over both floor levels.

For a typical MC treatment, pulp is dewatered to 30% consistency over the twin wire press (#1 in Figure 5), then rewetted to about 10% consistency as well as mixed with chemicals or steam in a peg mixer (#2).

# Figure 5 : The CTP Bleaching Pilot Plant



An MC pump (#3) then transports the pulp either through a dynamic mixer (#4) or directly to the high pressure reactor (#5). This reactor is operated in a batch mode, so that a normal run of 100 kg of pulp requires about 40 minutes to fill the reactor. After the required retention, pulp is diluted to about 2% consistency and dumped to the stock chest (#6). Interstage washing is accomplished in the twin wire press as pulp is thickened to 30% consistency prior to the next stage of treatment.

QPs(OP) processing required three passes through the MC loop. The Q-stage had 0.5% EDTA applied on pulp in the peg mixer. The pH was also adjusted at this point with sulfuric acid addition. EDTA-impregnated pulp bypassed the dynamic mixer and was held in the high pressure reactor for 60 minutes at atmospheric pressure. After dilution washing, the Ps stage was performed in a similar manner with $HSO_5^-$ applied instead of EDTA. Peroxymonosulfate was added as a solution of Oxone™ and no pH adjustment was made. After dilution washing, the final (OP) stage was operated with alkali, magnesium sulfate and peroxide addition in the peg mixer followed by oxygen addition in the dynamic mixer. Reaction occurred under 0.5 MPa pressure in the high pressure reactor. Final pulp properties were analysed after dilution washing over the twin wire press.

Results from softwood and hardwood pulp trials are presented in Table 7. The softwood MCC™-O pulp was of relatively high kappa number for a pulp of this type, *i.e.*, 16.9. Treatment with 1.5% $HSO_5^-$ after a metal ion removal step resulted in substantial delignification to 10.8 kappa number. This extent of delignification in the Ps stage (36%) was much larger than that observed in the laboratory under similar conditions. Results in Table 3 show that an equivalent Ps treatment reduced kappa number from 15.3 to 13.1, or by only 14%. Reductions in pulp DP after Ps treatment were also greater in the pilot plant, *i.e.*, 23% *versus* 7% in the laboratory. It is noteworthy that in the pilot scale experiments peroxymonosulfate consumption was 100% and final reaction pH was less than three, whereas these values in the laboratory work were about 50% and pH~4, respectively (Tables 3,7). Similar results were observed for hardwood pulp. All of the peroxymonosulfate was consumed at final pH 2.7 while kappa number was reduced by over 45% and pulp DP by 17% (Table 7).

There are several possible reasons for the increased extent of Ps reaction in the pilot plant. First, reaction time in the pilot plant was longer than that in the laboratory. The semi-continuous nature of the pilot plant meant that 40 minutes were required to fill the high pressure reactor before actual retention timing began. Average retention was thus about 20 minutes greater than the target. In addition, the softwood trial was inadvertently extended to 60 minutes target retention instead of the planned 30 minutes, as was used in the laboratory. Second, chemical mixing is much more efficient in the pilot plant and this may have increased overall chemical reaction. Third, metal ion contamination may not have been as well controlled in the pilot plant, resulting in greater peracid decomposition and attack on the pulp. Lower reaction pH in the pilot plant may have also contributed to increased viscosity loss.

Final oxygen delignification with 0.5% $H_2O_2$ addition removed a further 50% of the residual lignin from the QPs-treated softwood pulp. Final kappa number was 5.3 at 890 DP (9.9 mPa.s). QPs-treated hardwood pulp was at such a low kappa number (3.8) that subsequent (OP) treatment only achieved a further 24% delignification to 2.9 kappa number. Final hardwood pulp DP was also very low at 990 (11.4 mPa.s).

Table 7. Results from pilot scale QPs(OP) treatment of softwood and hardwood MCC™-O pulps.

| | Kappa Number | | Degree of Polymerisation | | Brightness |
|---|---|---|---|---|---|
| | Value | Change, %[1] | Value | Change, %[1] | % ISO |
| Initial pulp | | | | | |
| Swd | 16.9 | - | 1510 | - | 31.0 |
| Hwd | 7.1 | - | 1610 | - | 47.0 |
| QPs | | | | | |
| Swd | 10.8 | 36 | 1160 | 23 | 33.1 |
| Hwd | 3.8 | 47 | 1330 | 17 | 56.6 |
| (OP) | | | | | |
| Swd | 5.3 | 69 | 890 | 41 | 50.7 |
| Hwd | 2.9 | 59 | 990 | 39 | 66.8 |

[1] Change = (Initial pulp - Treated pulp)/ Initial pulp x 100%

These pilot plant trials demonstrated that oxygen delignified pulps of very low kappa number could be produced from both hardwoods and softwoods. These pulps should be easily bleached in any subsequent brightening treatments. Unfortunately, overall selectivity was not optimal due to excessive reaction during the peroxymonosulfuric acid treatment. Further work is required to optimise pilot plant conditions, especially during the critical Ps stage. Peroxymonosulfuric acid reactions must be limited to ensure a relatively mild treatment and thus optimum overall delignification selectivity.

## CONCLUSIONS

The addition of hydrogen peroxide to the final oxygen stage of an OPsO sequence was shown to extend the selective delignification set up by the intermediate peroxymonosulfuric acid treatment. No benefits to overall process selectivity were observed when hydrogen peroxide was present in the Ps stage itself. In addition, no benefits to overall process selectivity were observed when peroxymonosulfuric acid was present in the final oxygen stage.

Ideal operation of the OPsO sequence would, therefore, include:

- Metal ion removal prior to treatment with peroxide-free peroxymonosulfuric acid,
- Interstage washing after the Ps stage to recover and reuse residual peroxymonosulfuric acid,
- Final oxygen delignification with low levels of hydrogen peroxide addition.

This ideal option would require the development of cost-effective technologies for generating peroxide-free peroxymonosulfuric acid.

Initial pilot scale trials of QPs(OP) processing of commercial hardwood and softwood MCC™-O pulps showed that very low kappa numbers could be achieved after final oxygen delignification. However, excessive reaction in the Ps stage reduced overall process selectivity. Further pilot scale trials are planned whereby better control of peroxymonosulfuric acid treatments should ensure more selective final oxygen delignification.

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## REFERENCES

1. McGrouther, K. and Allison, R., Improved oxygen delignification with peroxyacid treatment. *Appita J. 46* (6): 424-428 (1993).
2. Allison, R. and McGrouther, K., Improved oxygen delignification with interstage peroxymonosulfuric acid treatment. Poster proc. 1994 Int. Pulp Bleaching Conf., Vancouver, 121-128.
3. Lachenal, D. and Muguet, M., Reducing TOCl with the OxO process. *Pulp Paper Can. 92* (12): T297-301 (1991).
4. Lachenal, D., Muguet, M. and Joly, P., EOxEO prebleaching: a way to reduce the formation of AOX. *Paperi Puu 73* (5): 437-440 (1991).
5. Parthasarathy, V., Sundaram, V., Jameel, H., Gratzl, J. and Klein, R., Hydrogen peroxide reinforced oxygen delignification of southern pine kraft pulp and short sequence bleaching. *Tappi J. 73* (7): 177-187 (1990).
6. Odermatt, J., Patt, R., Kordsachia, O. and Troughton, N., TCF bleaching of conventional and EMCC softwood kraft pulp. Proc. 1994 Int. Pulp Bleaching Conf., Vancouver, 77-85.
7. Lachenal, D., The CTP bleaching pilot plant. Proc. Non-chlorine Bleaching Conf., Hilton Head, (1992).
8. Basta, J., Holtinger, L. and Hook, J., Controlling the profile of metals in the pulp before hydrogen peroxide treatment. Proc. 6th Int. Symp. Wood and Pulping Chem., Melbourne, Vol. 1, 237-244 (1991).
9. Cochran, W. and Cox, G., *Experimental Designs*, John Wiley & Sons, New York, Ch. 5, (1950).
10. Song, J., Pan, D., Chang, H-m. and Jameel, H., Peroxymonosulfuric acid and a mixed peracid solution as bleaching agent. Proc. 7th Int. Symp. Wood Pulping and Chem., Beijing, 34-43 (1993).