TCF bleaching of conventionally cooked softwood kraft pulps

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RESUMO:

TCF BLEACHING OF CONVENTIONALLY COOKED SOFTWOOD KRAFT PULPS

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ABSTRACT

Increasingly stringent environmental regulations, as well as demand for TCF ("totally chlorine free") pulp and paper in some areas of the world has led to an emergence of many new bleaching sequences. The most effective and economical non-chlorine bleaching chemicals today, are ozone and peroxide, both of which are commercially used. The use of high temperature peroxide reduces the operating expense compared to conventional peroxide bleaching technology, but the use of peroxide alone, especially at high brightness results in a very high bleach chemical cost. For high brightness, the use of small amounts of ozone is an economical choice to dramatically reduce the operating cost.

The capital cost for conversion of existing cooking facilities to produce extended delignified softwood pulps is site specific, but is frequently a barrier to the conversion of the fiberline to high quality TCF pulp production. The application of TCF sequences using ozone and peroxide for pulp production of conventionally cooked pulps (>25 kappa) is thus of great interest for many mills. The development of bleaching sequences that permit the use of existing bleach plant equipment for application of ozone and peroxide with minor additions of equipment enables the commercial implementation of this technology.

This study evaluates the commercial implementation of medium consistency ozone and high temperature peroxide (the P_{HT} process) for retrofit of a conventional softwood kraft fiberline producing brown stock pulp at 25-30 kappa to TCF bleaching sequences. For high brightness pulp production, the use of oxygen delignification proceeding the bleach plant is necessary. Specifically examined are brightening, kappa reduction, strength and chemical use impact. With a reasonable capital investment, it is possible to produce mid-80's brightness captive use pulp for papermaking, or fully bleached 88+% ISO pulp for market pulp. Fully bleached, 90+% ISO pulp production generally requires further lowering of the kappa number to the bleach plant with extended cooking.

INTRODUCTION

Hydrogen peroxide is growing in acceptance as a major bleaching option for the coming century. The limitation of peroxide to use in small doses for alkaline extraction of

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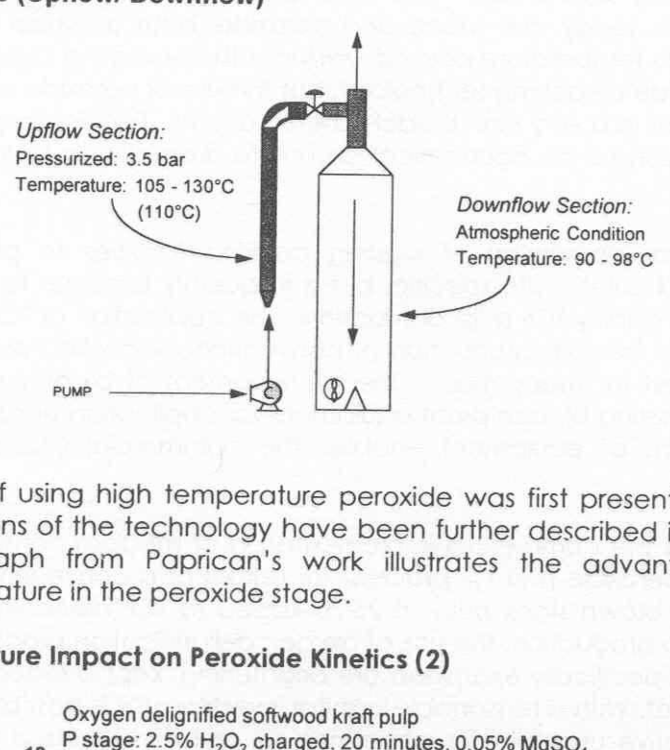
conventional sequences (4,5) has become a restriction of the past as new processes are introduced to increase the efficiency of peroxide bleaching. Currently, all TCF capacity is produced with hydrogen peroxide as the major brightening chemical alone, in combination with oxygen and/ or extended cooking, or with oxygen/ extended cooking and ozone(6).

The introduction of high temperature peroxide bleaching has yielded substantial benefits in the efficiency of peroxide bleaching (2,3,7). These benefits have translated to significantly less chemical demand for mills bleaching exclusively with peroxide, as is further illustrated in this technical presentation. The ability to reuse existing mill tanks in a peroxide retrofit offers additional gains for overall mill economics (3).

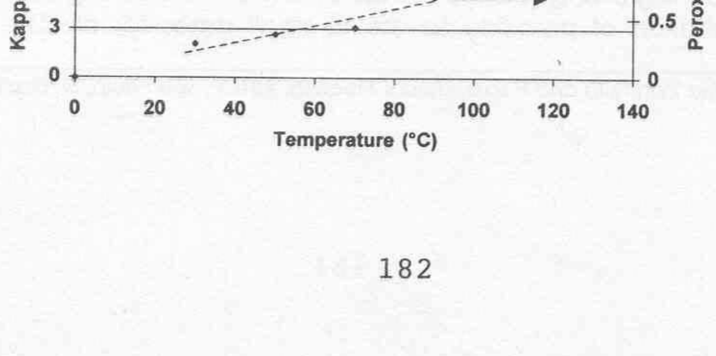
A new peroxide bleaching process has been developed which is designed to use existing equipment in the mill with minor additions of pumps, mixers, and small reaction tubes. The process, introduced by Paprican and IMPCO (2,3), is denoted as high temperature peroxide (P_{HT}). The process consists of two steps: first; applying peroxide under conditions of high temperature (~110°C) and moderate pressure for a short period of time (10-20 minutes) followed by atmospheric retention in an existing bleach tower, illustrated in figure 1. This technology enables minimal use of peroxide and capital to achieve significant delignification and brightening for a TCF bleaching line, for a full TCF mill, or an ECF/TCF swing mill.

Figure 1: P_{HT} Stage (Upflow/ Downflow)



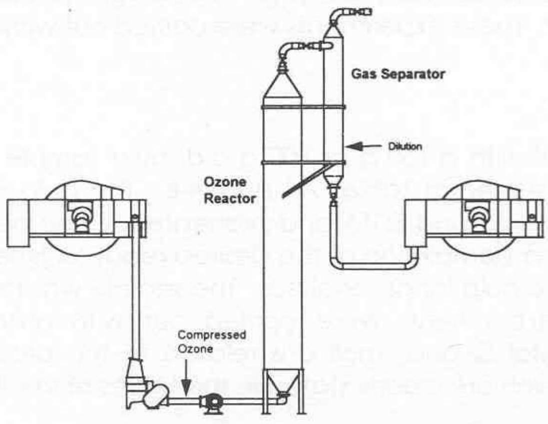
The advantage of using high temperature peroxide was first presented by Paprican (2). Various applications of the technology have been further described in the literature (3,8). The following graph from Paprican's work illustrates the advantages of increased operating temperature in the peroxide stage.

Figure 2: Temperature Impact on Peroxide Kinetics (2)



The application of ozone bleaching to the production of TCF pulps has been widely published. Either high or medium consistency ozone bleaching is viable, and the selection of the technology should be based on a detailed capital and operating cost for the installation(9). The conversion of an existing fiberline will generally favor implementation of a medium consistency ozone stage, since the addition of a press for the high consistency stage is unnecessary. A typical medium consistency ozone bleaching stage is shown in Figure 3 below.

Figure 3: Medium Consistency Ozone Bleaching Stage



This study aims to apply this understanding to mill implementation of ozone and peroxide in existing bleach plants, using conventionally cooked softwood kraft pulps, bleached to a brightness level in the mid- to high 80's ISO. Another study, implementing only peroxide as an active bleaching chemical has been previously been presented (10), but the production of high quality pulps is limited when the kappa is about 28-30.

EXPERIMENTAL

➢*Oxygen Delignification (O)*

The oxygen delignification was carried out with 150 g o.d. pulp samples under the conditions described in Tables A-I and A-II. The experiments were carried out in a 20-L stainless steel rotating reactor equipped with four 2-L individual cells, which allowed for four simultaneous delignifications. Each cell is equipped with thermometer, manometer and valves for injection and relief of gases. The desired charges of sodium hydroxide and magnesium sulfate were added and manually mixed with the pulp in a polyethylene bag. The initial pH of the mixture was taken and the samples preheated to the desired temperature in a microwave oven. The samples were placed in the reactor cells already preheated to the desired temperature. A certain amount of time (about 20 min) was required in order for the temperature to equilibrate and then oxygen was injected into each cell to reach the desired reaction pressure. After the pre-established time elapsed, the reactor pressure was released, the pulp was discharged into a screening box of 120 mesh, and 300 ml of liquor was squeezed out from the pulp for pH determination. Then, the sample was washed with excess tap water. These experiments were carried out with two repetitions.

➢*High Temperature Peroxide (P_{HT})*

The high temperature peroxide (P_{HT}) process was carried out with a 75 g o.d. pulp sample in the same reactor described for oxygen delignification, under the conditions described in Tables A-I and A-II. However, glass cells of 7 mm thickness (75 g o.d. pulp capacity) were used inside the stainless steel vessels in order to prevent peroxide losses via surface catalysis. Chemicals were added and manually mixed with the pulp in a polyethylene bag. The initial pH of the mixture was taken and the sample preheated to the desired temperature in a microwave oven. Then, the sample was placed in a glass cell, which was capped with muslin cloth, and the glass cell placed in the reactor cell already preheated to the desired temperature. The cell was closed and purged with N_2. A certain amount of time (about 10 min) was allowed, under a N_2 atmosphere, in order for the temperature to equilibrate and then the oxygen was injected in the cell at the desired reaction pressure. At the end of 15 minutes the pressure was discharged and the pulp was kept in the reactor for an extra 120 min under the same conditions. The sample was then discharged into a screening box of 120 mesh and 200mL of liquor was squeezed out from the pulp for pH and residual peroxide analyses. Following, the pulp sample was washed with excess distilled water. These experiments were carried out with 4 repetitions.

➢*Chelation (q or Q)*

Chelation was carried out with a 150 g or 300 g o.d. pulp sample in a polyethylene bag under the conditions presented in Tables A-I and A-II. The pulp sample was thoroughly mixed with water, sulfuric acid and EDTA and preheated to the desired temperature in a microwave oven. After the completion of the desired reaction time, about 40 mL of liquor was squeezed out from the pulp for pH analyses. The sample was then washed with excess distilled water. These experiments were carried out with only one repetition. The difference between capital Q and small q is related to the process conditions used in these chelation stages which are clearly stated in the tables of results.

➢*Ozone (Z)*

Ozonation was performed on previously acidified pulp sample under the conditions presented in Table A-I. The sample was acidified to pH 2.5 with 4N H_2SO_4 at 3.5% consistency, kept at room temperature for 5 min and then dewatered to a consistency of about 37%. The pulp was then fluffed in a variable speed fluffer and the consistency was determined (40-45%). Immediately after, ozonation was carried out on a 25 g o.d. pulp sample in a 3-L glass flask adapted in a well-sealed rotary evaporator. Air was evacuated from the system prior to ozone injection. A stream of ozone of known concentration was injected into the rotating flask for an amount of time sufficient to give the desired dosage of ozone on o.d. pulp basis. At the same time, the ozone not reacted with the pulp was collected in a 5% KI solution and the residual concentration determined. The ozone consumed by the pulp was calculated as the difference between applied and residual ozone. At the end of the reaction, the ozone treated pulp was immediately chelated at pH around 6.0 and then washed. These experiments were carried out with 8 repetitions.

➢*Analytic Methods*

Kappa No.: TAPPI T236 om-85
Viscosity: TAPPI T230 om-82
Brightness: CPPA C5
Reversion: 1 hour at 105±3°C and 0% RH
Pulp Metals: Atomic absorption CG7000 spectrophotometer after wet ashing of pulp according to CPPA standard.
Final Pulp: Thorough washing and neutralized to pH 5.5-5.6 with sodium sulfite.
Chemical Dose: kg of reagent/metric ton of oven dry pulp.

Brightness:
Brightness Pad: CPPA C5
Brightness Development: TAPPI T-525 om-86

Table A-I: Stage Operating Conditions for Pulp A & C (Brazilian Kraft Softwood)

	O_{30}	O_{45}	q	Q	P_{HT}
Consistency, %	12	5	12	12	12
Temperature, °C	90	90	60	90	110/98
Time, minutes	30	5	30	20+40	15+120
pH			~6		
Pressure, kPa (psi)	650 (95)	650 (95)	-	500→0 (70-0)	500/0 (70/0)
DTPA, kg/mt	-	-	2	-	1.5
$MgSO_4$, kg/mt	5	5	-	5	5

Table A-II: Stage Operating Conditions for Pulp B (North American West Coast Kraft Softwood)

	O_{20}/EO	O_{45}	Q (ph ~6)	P	P_{HT}
Consistency, %	10	10	4	10	10
Temperature, °C	100	100	60-80	80	110/98
Time, minutes	45	55	15	90	20+90
Pressure, kPa (psi)	345 (50)	585 (85)	-	-	500/0 (70/0)
NaOH, kg/mt	10	40	-	16-25	20-30
DTPA, kg/mt	-	-	3 EDTA	0	0-2
$MgSO_4$, kg/mt	-	-	-	2.5	2.5

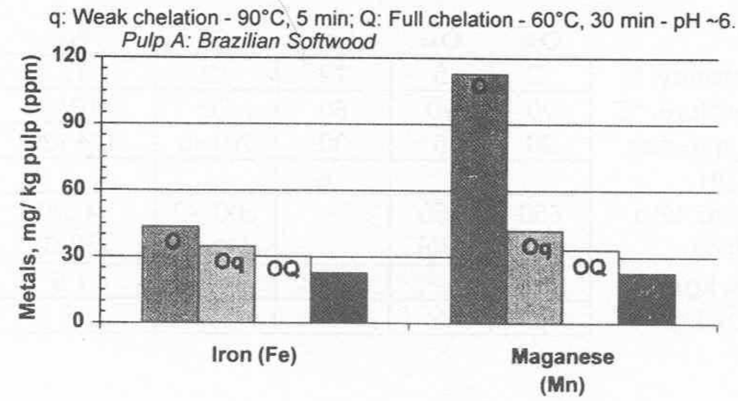
TABLE A-III: Pulp Samples

Pulp	Source	Kappa	Viscosity (cP)	Brightnes s (% ISO)
A	Brazilian Softwood	28.4	37.0	26.5%
B	North American West Coast Softwood	29.5	37.0	24.9%
C	Brazilian Softwood	25.6	35.9	27.8%

➢ ***Metals Contents***

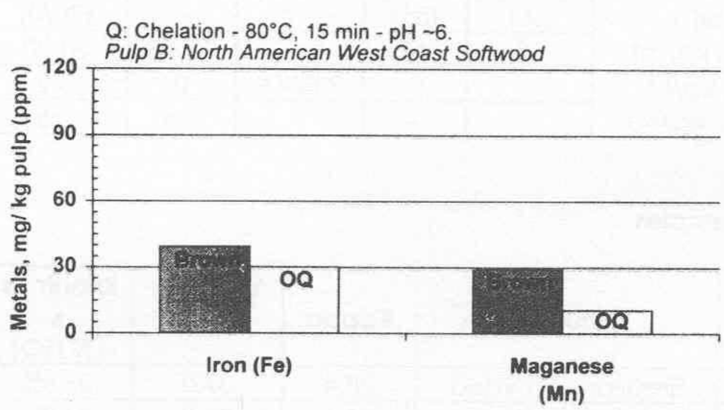
The metals content of pulps A & B are illustrated by figures 4 and 5. Pulp A, the Brazilian kraft softwood, began with an extremely high Mn content, >130 ppm, and even multiple chelation steps could not bring the level below 20 ppm. The incoming metals profile of pulp C was similar to Pulp A, so the metals removal on this sample was not studied in detail.

Figure 4: Pulp A Metals



Pulp B, the North American West Coast kraft softwood, was only tested with a single chelation step. It is possible that further chelation may have improved the final brightness response of this pulp. Although the Mn level was lower for pulp B, the brightness response curve was not as steep as pulp A. After chelation Mg was added back to the pulp in the form of $MgSO_4$, as specified in table A. After Mg addition the resulting Mg/Mn entering the P stage averaged 45 for pulp A and 57 for pulp B.

Figure 5: Pulp B Metals



RESULTS AND DISCUSSION

Results from three industrial softwood kraft pulps are presented in this study, and is broken into three areas of concentration:

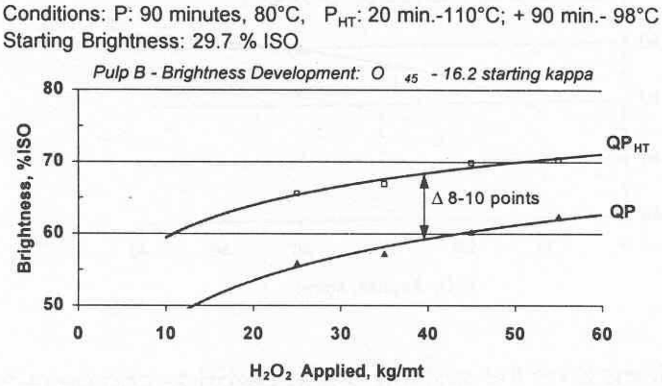
- Brightness Development
- Kappa Reduction
- Strength Properties

➢***Brightness Development***

Figures 6 to 10 illustrate the factors that affect brightness development.

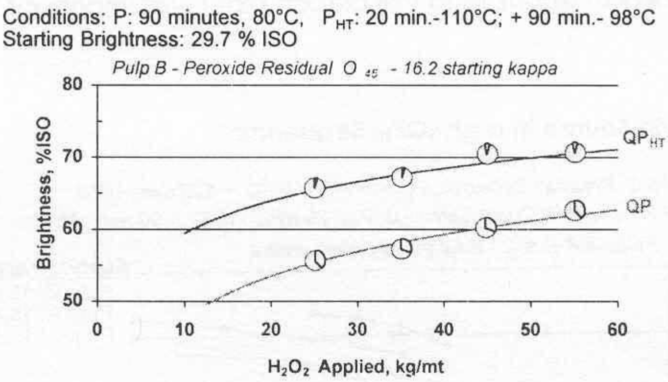
It is important to first understand the performance of the high temperature peroxide stage compared to a conventional atmospheric peroxide stage. Figure 6 shows the brightness development of a conventional (P) and a high temperature (P_{HT}) peroxide stage when they are preceded by a chelation step. At the brightness level of 60% ISO, the P_{HT} option provided a 75% reduction in the required peroxide charge. In both cases the P stage is preceded by a chelation step that reduced the Manganese content to about 10 ppm.

Figure 6: QP vs QP_{HT}



The key reason for the higher brightness development is the increased consumption of peroxide. Figure 7 shows the residual peroxide levels for the same curves presented in the previous figure. Typically the QP option maintained a 30-40% residual for the 90 minute P stage at 80°C. A longer retention time in this position would have likely led to a reduced residual and some further improvements in brightness. For this particular situation, the mill did not have a larger tower to use without a major investment in capital.

Figure 7: Peroxide Residual

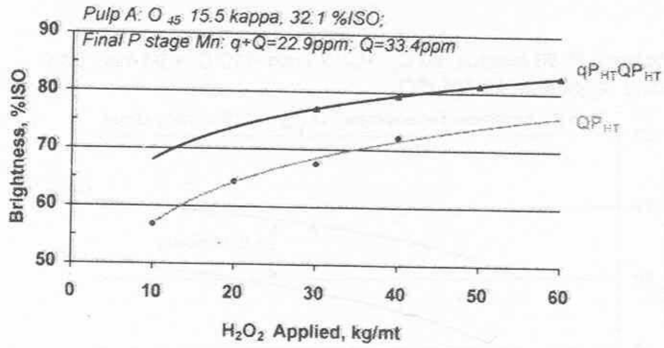


The addition of a 15 minute pressurized upflow tube run at 110°C, as a P_{HT} stage, reduced the peroxide residual to 5-10% resulting in the brightness gains shown, as well as a reduction in the final bleached kappa number.

The impact of splitting the peroxide charge over two stages is significant, as illustrated by figure 8. The addition of peroxide in two stages with an interstage chelation step improved the efficiency and further increased the pulp brightness ceiling by about 8% ISO, over a single P_{HT} stage application.

Figure 8: Split Peroxide Application

Pulp A: Brazilian Softwood, P_{HT}: 15 min.-110°C; + 120 min.- 98°C; 1[ST]stage 15 kg/t

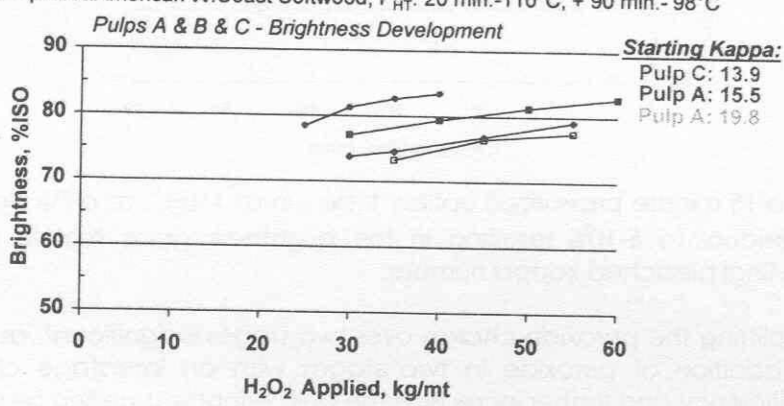


At the 70% ISO brightness level the splitting of the peroxide charge reduced the peroxide requirement by nearly 70%. The two stage P_{HT} approach also enabled a low 80's brightness target with 40 kg/mt of H_2O_2 applied, when preceded by an oxygen delignification step. The amount of peroxide to the first P stage was also examined. The first P_{HT} stage shown had a 15 kg/mt application rate. Further increasing the first P_{HT} charge to 25 kg/mt H_2O_2 provided no additional gains in efficiency.

The brightness response of three different pulps at four different kappa numbers entering the bleach plant are shown in Figure 9, for the $qP_{HT}QP_{HT}$ sequence. It is clearly shown that there is a direct relationship between the incoming kappa number and the brightness development. A kappa of about 15 to the bleach plant was important to exceed an 80% ISO brightness.

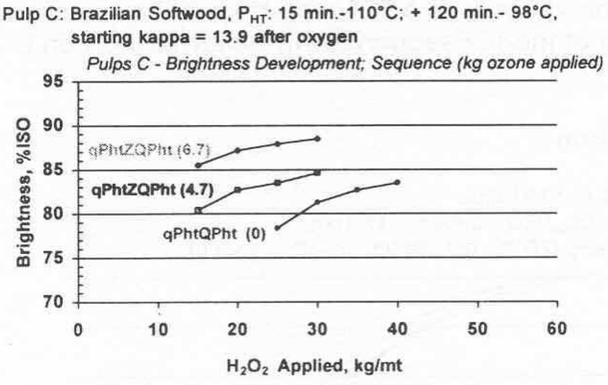
Figure 9: Impact of Pulp Source in a $qP_{HT}QP_{HT}$ Sequence

Pulp A and C: Brazilian Softwood, P_{HT}: 15 min.-110°C; + 120 min.- 98°C
Pulp B: N.American W.Coast Softwood, P_{HT}: 20 min.-110°C; + 90 min.- 98°C



The use of ozone in the sequence dramatically impacts the brightness development, and allows the ability to produce high brightness pulps in TCF sequences economically. Figure 10 below illustrates the brightness development as a function of peroxide applied in the $qP_{HT}QP_{HT}$ sequence previously plotted in figure 9, compared to the same basic sequence but adding a small charge of ozone (4.7 or 6.7 kg $O3$/t) between the two peroxide stages, in a $qP_{HT}(ZQ)P_{HT}$ sequence. The laboratory simulation for ozone bleaching was performed by the high consistency method. Sufficient work has been completed to understand the relationship for both medium and high consistency systems.

Figure 10: Impact of Ozone Use in a $qP_{HT}(ZQ)P_{HT}$ Sequence



➤*Kappa Reduction*

Figures 11 and 12 illustrate the kappa reduction across TCF bleaching sequences on conventionally bleached softwood kraft pulp at various kappa numbers to the bleach plant.

It is typical that softwood kraft pulps made using only oxygen and peroxide have a relatively high bleached pulp kappa number. A final kappa number of about 5 is not unusual, and is supported by the data shown in Figure 11 below. It can also be noted that the final kappa number of the pulp is affected by the kappa number entering the bleach plant.

Figure 11: Kappa Reduction in the $qP_{HT}QP_{HT}$ Sequence

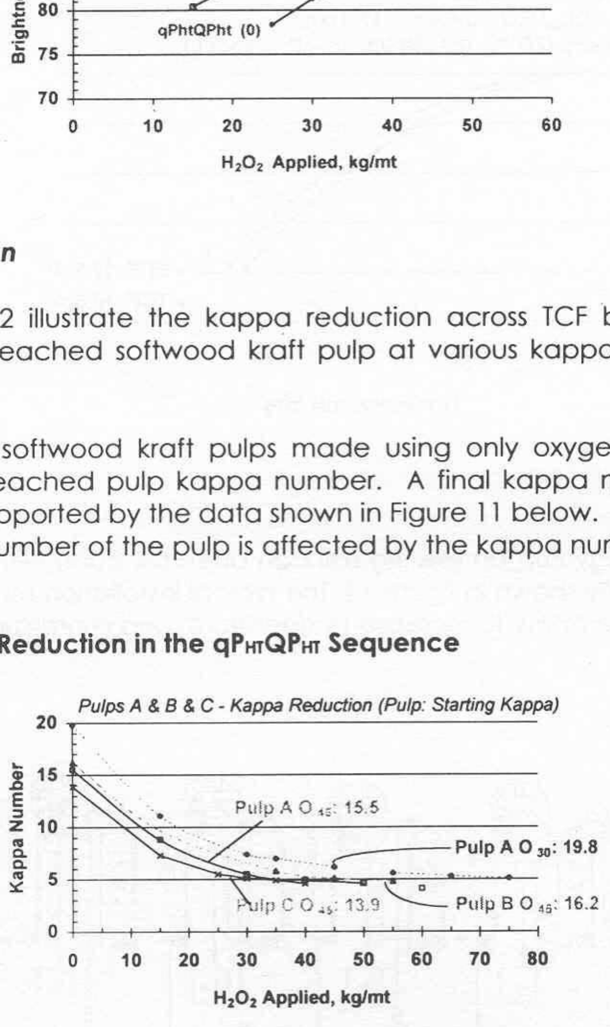
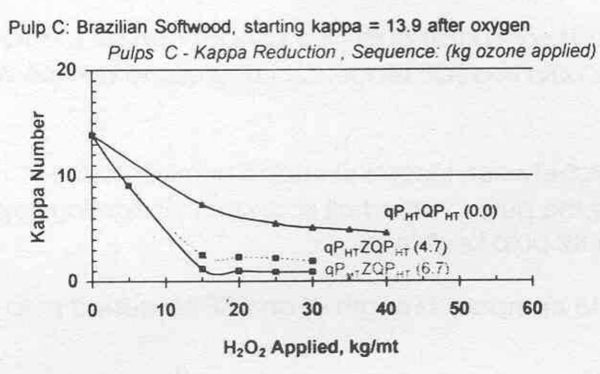


Figure 12 illustrates the strong effect of the use of ozone (a very strong delignifying reagent) in the TCF sequence. The final bleached kappa number when using ozone is similar to that achieved with conventional or ECF bleaching sequences.

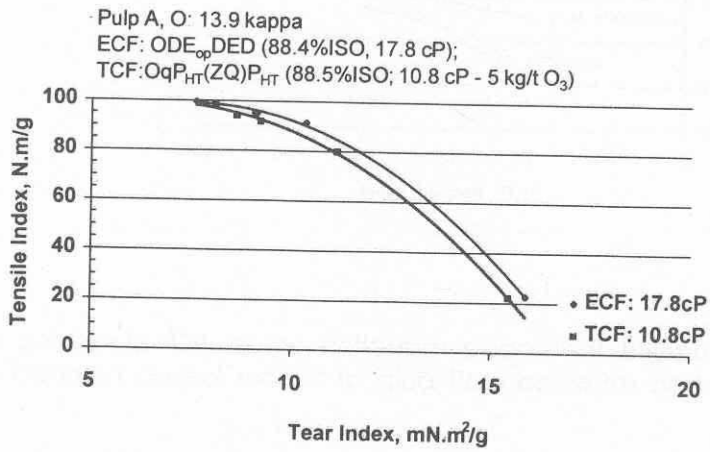
Figure 12: Impact of Ozone use in the $qP_{HT}(ZQ)P_{HT}$ Sequence



➢*Strength Properties*

The correlation between the viscosity of a TCF pulp does not correlate to that of an ECF pulp. Typically the viscosity of the TCF sequence will be lower than an ECF sequence with similar strength properties.

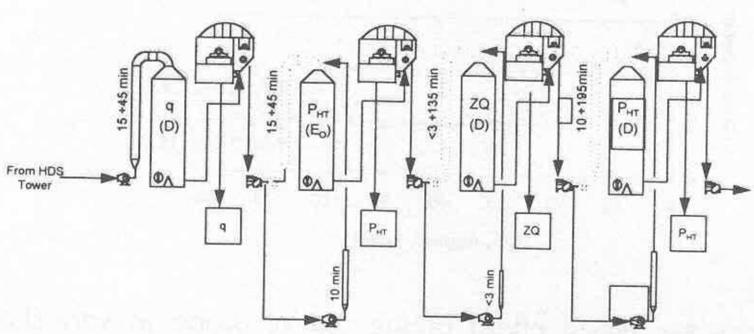
Figure 13: Strength Comparison



➢*Mill Retrofit*

The retrofit of P_{HT} technology into an existing mill can often be done with minimal impact on capital, as schematically shown in figure 14. The typical installation may just require the addition of new mixers, the ability to increase temperature, and a pressurized upflow tube with pressure release.

Figure 14: Mill Retrofit



CONCLUSIONS

- A conventionally cooked softwood kraft pulp (>25 kappa) can be bleached to 80+% ISO brightness in the sequence $qP_{HT}QP_{HT}$ using only peroxide as an active bleaching agent.

- A conventionally cooked softwood kraft pulp (>25 kappa) can be bleached to a high strength 88+% ISO brightness pulp in a TCF sequence using ozone and peroxide in the sequence $qP_{HT}(ZQ)P_{HT}$.

- There is a strong correlation between incoming kappa number to the TCF bleach plant and the brightness ceiling of the pulp. Very small changes in incoming kappa number can lead to significantly higher final pulp brightness.

- Viscosity can not be used to compare strength of an ECF bleached pulp to TCF.

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