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REFINER PEROXIDE BLEACHING

by

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A thesis submitted to the Department of
Paper Science and Engineering
in partial fulfilment of the
requirements for the degree of
Bachelor of Paper Engineering

Western Michigan University
Kalamazoo, Michigan
December, 1984

Dedicated
in memory
to
Aunt Lilian
and
Uncle Walter

This thesis by Sharon E. Perkins
is accepted in its present form
by the Department of Paper Science
and Engineering
as satisfying the thesis requirements
for the degree of
Bachelor of Paper Engineering

Approved by the Director of the Department

Date

Approved by the Research Supervisor

Date

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THESIS PROPOSAL

Thermomechanical pulping is a high yield, low cost operation. Current mill bleaching methods maintain the high yield but incur high capital costs. Dithionite bleaching is limited to a maximum brightness gain of 8 to 9 points while peroxide is capable of up to 15 points brightness gain.

The following research work was done in an attempt to achieve the same brightness increase given by tower peroxide bleaching using a reduced capital cost method. Considerable work has previously been done using the refining zone for this purpose, but a number of problems have yet to be overcome.

The most serious of these problems were silicate depositions on the refiner plates and less than adequate brightness gains. The possibility of two-stage (refiner-peroxide followed by dithionite) has also not been adequately investigated.

ABSTRACT

Refiner peroxide bleaching trials were carried out at the Abitibi-Price Research pilot plant using a Sunds-Defibrator CD300 pilot-scale refiner. Results show that, at the pilot scale, blowline addition of bleach liquor gives better brightness gains than addition in the refining zone. Using this technique, brightness gains equivalent to tower bleaching can be obtained when the bleaching parameters are properly controlled. The most important factors were post-refiner retention time and temperature, and the alkali charge in the bleach liquor. These three factors were shown to be highly interdependent. Refining pressure (temperature) was shown to have little effect on brightness gain in this system but did effect both the bleached and unbleached brightness of the TMP. As in tower bleaching, it was found that chelation of metal ions is essential if maximum bleaching efficiency is to be achieved. Refiner blowline bleaching had no effect on pulp strength other than that expected from peroxide bleaching under more standard conditions. A mathematical model of peroxide bleaching was also developed with the intended use of calculating the required bleaching parameters for a mill system.

Other experiments showed that refiner dithionite (hydrosulphite) bleaching holds promise but that the best overall system might be refiner blowline peroxide bleaching followed by dithionite bleaching in a second stage. Computer modelling of this two-stage system and a cost analysis of the results showed that as much as a 30% reduction of chemical cost can be achieved if two-stage bleaching is used instead of peroxide bleaching alone.

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INTRODUCTION

A. Wood Chemistry

The chemical composition of wood is approximately 50% carbon, 6% hydrogen and 44% oxygen with less than 1% other elements, mostly nitrogen(1). These elements are built up into four classes of wood components; cellulose, the hemicelluloses, lignin, and the extractives.

i. Cellulose, is a polysaccharide with a weight-average degree of polymerization between 10,000 and 17,000. It is built from anhydroglucose units connected to each other by (1-4)-glucosidic linkages(2,3).

The molecules are arranged into small building units called fibrils which have a complex and poorly understood structure(4). The cellulose fibrils are the main structural elements of wood fibres.

Cellulose cannot be solubilized in water, dilute acids or alkalis at room temperature. It can be dissolved using cuprimonium hydroxide, some salt solutions and some strong acids(5).

ii. Hemicelluloses, also polysaccharides, have a degree of polymerization of 100-200(6). There are three major types; the xylans, the mannans and the galatans(7). Hemicelluloses, unlike cellulose, are branched non-crystalline polymers which can sometimes be extracted from wood using dilute alkali or boiling water(8). Although they are part of the fibre matrix no hemi-cellulose structural elements have as yet been discovered.

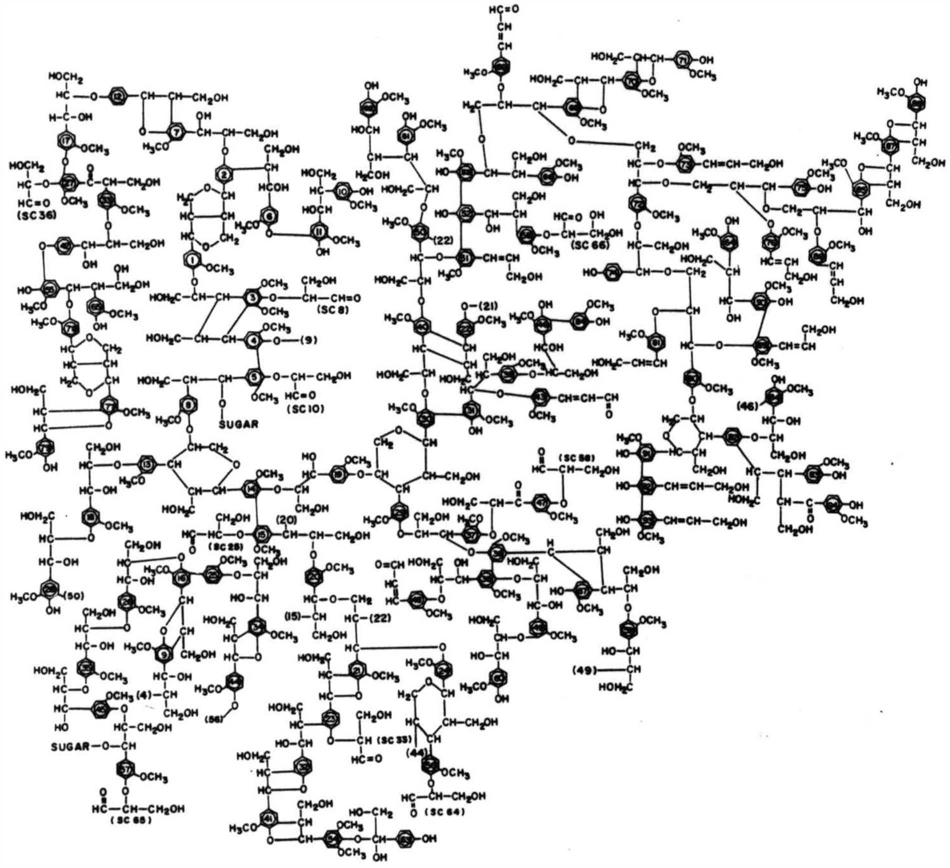


Figure 1. Glasser and Glasser's 1981 Structure of Softwood Lignin

iii. Lignin is an aromatic polymer built from phenylpropane units(9). Its highly cross-linked structure results from carbon-carbon, carbon-oxygen bonds through the α, β, γ, 2, 3, 4, and 5 positions of the phenylpropane units(10). These units are built up in a complex way to form a structure similar to the one proposed by Glasser and Glasser(11).

Due to the large natural variations occurring between different species, the problem of isolating lignin from wood in an unchanged form, and the intrinsic complexity of the lignin macromolecule, the exact chemical structure remains unknown.

iv. The wood extractives are non-structural low molecular mass organic compounds which are soluble in water or organic solvents. These compounds include polyphenols, fatty acids and resins(12).

Based on extractive free dry wood, softwoods are (on the average) made up of 43% cellulose, 28% hemicellulose and 29% lignin. Hardwoods contain 43% cellulose, 35% hemicellulose and 22% lignin(1).

B. Softwoods

Softwoods, are made up to a large extent by tracheids. The tracheids are supporting elements that also conduct water(13).

About 95% of softwood xylum is built from tracheids while the remainder is mostly ray (parenchyma) cells. These cells run radially through the tree(14). A diagram of a softwood cube is presented in Figure #2.

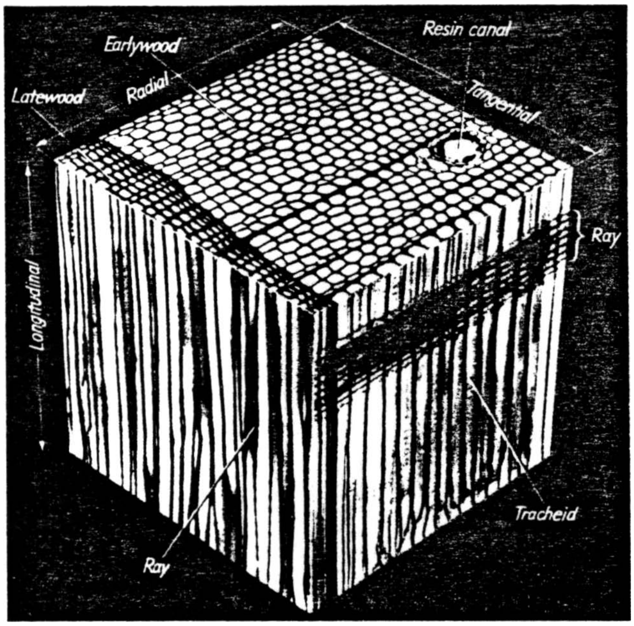


Figure 2. Softwood Cube

C. Tracheid Structure

As shown in Figure #3(15), the tracheid structure consists of the lumen (or centre of the cell) secondary wall (by far the most dominant layer), primary wall and middle lamella at the boundary between fibres. The secondary wall is subdivided into further layers (S_1, S_2, S_3)(16).

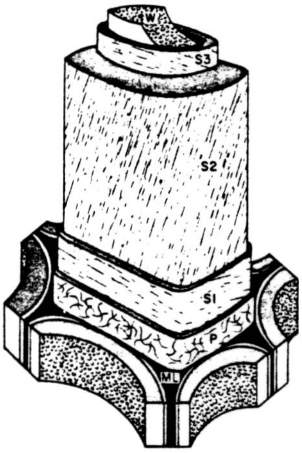


Figure 3. Diagram of a Tracheid

D. Lignin Distribution

Figure #4 shows a UV photomicrograph of a black spruce tracheid cell wall (lignin absorbs UV light while carbohydrates are transparent) showing the lignin distribution.

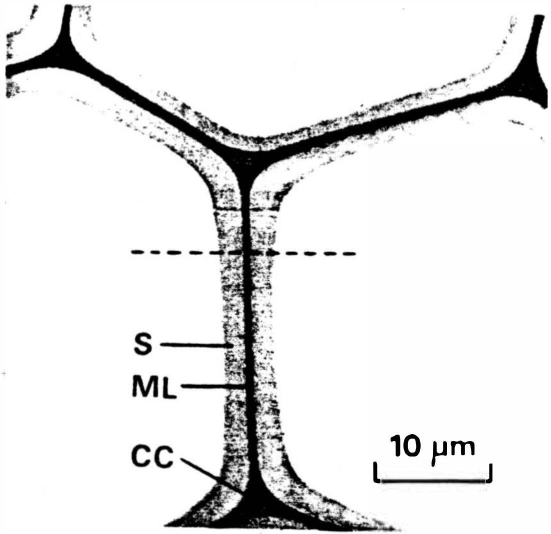


Figure 4. UV Photomicrograph of a Black Spruce Tracheid Cell Wall

Such observations have shown that lignin occurs in the secondary wall of the fibre as well as in the middle lamella. Although the concentration of lignin in the middle lamella (80%) is much higher than the concentration of lignin in the secondary wall (20%), the majority of softwood lignin is actually found in the secondary wall due to the much larger proportion of secondary wall material. For black spruce about 77% of the total lignin exists in the secondary wall whereas only 23% is in the middle lamella. Whiting(17) has shown that, for the reactions studied, secondary wall lignin is more reactive than middle lamella lignin. Douek(18) has shown that the majority of the colour in extractive free douglas fir wood originates in the lignin, thus indicating that this is the wood component which must be brightened during non-delignifying bleaching. However, no work has been done to show whether, during non-delignifying bleaching, there is a difference in reactivity between middle lamella lignin and secondary wall lignin.

E. Hydrogen Peroxide Bleaching

The bleaching of wood fibres is considered to be a process that destroys, alters or solubilizes the lignin, coloured organic matters, and other undesirable residues. Bleaching of mechanical pulp requires that the majority of the original components remain in the wood in order to maintain a high yield including the 25-30% that makes up the lignin fraction.

(Chemical pulps having significantly lower yields after bleaching, have very little of the lignin remaining). To avoid delignification and maintain high yields for mechanical pulps, the favoured bleaching chemicals are sodium dithionite and hydrogen peroxide(9). Hydrogen peroxide bleaching is an oxidative reaction that results in modification of the lignin macromolecule reportedly through cleavage of carbon-carbon bonds associated with the alpha carbonyl functionalities(20). Coloured chromophoric groups such as alpha-carbonyls, conjugated carbonyls and certain conjugated ethylenic groupings are reported to be converted to colourless functions such as organic acids(20,21,22).

Hydrogen peroxide dissociates in the following way:

$$H_20_2 \rightleftharpoons H^+ + H0_2^-; \qquad \text{pka } 11.01 \ 60^0C^{(23)}$$

The equilibrium concentration of $H0_2^-$ increases with increasing pH(24).

There is also a decomposition reaction that increases with increased alkalinity and increased concentration of heavy metal ions(25).

$$2\,H_2O_2 \longrightarrow O_2 + 2H_2O$$

The perhydroxyl ion HO_2^- is considered to be the active species involved in hydrogen peroxide bleaching(26). Its rate of decomposition is increased with increased temperature(24).

F. Dithionite Bleaching

Dithionite (hydrosulphite) bleaching is non-delignifying and involves the reduction of coloured chromophoric groups such as quinoid structures to hydroquinones and alpha/beta unsaturated aldehydes and some ketones to alcohols(20,27). The light absorption in the visible region is reduced due to this decrease in conjugation within the molecule(28).

The reaction involves the $S_2O_4^=$ anion. Because this is a reducing reaction, air entrainment should be minimized to avoid the production of bisulphite through reaction with oxygen(20).

$$2\,Na_2S_2O_4 + O_2 + 2H_2O \longrightarrow 4\,NaHSO_3$$

G. Hydrogen Peroxide Bleach Liquor

In hydrogen peroxide bleaching, certain other chemicals are required to obtain the maximum effect. These chemicals go together to produce a bleach "liquor" which contains sodium silicate, magnesium sulphate, and sodium hydroxide as well as hydrogen peroxide.

In peroxide brightening, the sodium silicate enhances the brightness reponse. The mechanism of the reaction has not been well studied but some authors have attributed its value through action as a detergent, penetrant, buffer and stabilizer (30). However it seems quite clear that silicate has two distinct functions: it stabilizes the peroxide against decomposition and it improves peroxide's chemical ability to brighten wood.

Sodium silicate reacts with magnesium ions (usually obtained as magnesium sulphate or epsom salts) to form a magnesium silicate precipitate. The precipitate stabilizes the peroxide liquor against decomposition during storage (31,32,33). Sodium silicate also has a film forming characteristic that provides a protective glass coating for pipes and tanks, avoiding metal contamination of the pulp.

Many silicate replacements have been tested but all have proven inferior either from a utility or a cost point of view, or both(34). The common level of silicate application is 4 to 5% sodium silicate solution (41.6^{0} Be, 11.5% NaOH) based on O.D. pulp(35).

The bleach liquor contains sodium hydroxide to raise the pH and force the equilibrium towards the production of perhydroxyl ions. However if the pH is too high decomposition increases so that the total alkalinity, represented by sodium hydroxide and sodium silicate, of the bleach liquor must be carefully controlled(36).

Hydrogen peroxide is the active bleaching component of the bleach liquor. With increasing peroxide dosages the bleaching response of the pulp will increase. The brightness gain increases rapidly at lower peroxide dosages, but as the peroxide concentration is increased the brightness response levels off(37).

When the bleaching reaction is considered complete there will still be a residual amount of peroxide and alkali remaining on the pulp(35,38). To stop any further reactions and to bring the pulp pH down to normal papermaking values, the residual alkali is neutralized with sulphur dioxide to a final pH of 5 to 6. The SO_2 consumes the residual peroxide and is itself coverted to sulphuric acid. The SO_2 is said also to decolourize certain organic components of the pulp(36).

H. Factors Affecting Peroxide Bleaching

The efficiency of peroxide bleaching is affected by pulp consistency, pH, retention time, temperature, wood species and quality as well as the stability of the peroxide (28).

i) Consistency

Increasing the consistency of peroxide bleaching increases the rate of bleaching and the extent of bleaching (19). This increase is limited by problems of pulp handling and mixing of chemicals with the pulp so that the highest consistency currently used is about 25%.

ii) pH

The optimum pH for peroxide brightening depends on such factors as peroxide dosage, reaction temperature, and reaction time. Under normal conditions the pH at the start of the bleaching reaction is about 10.5. During the reaction the formation of acidic products from the lignin and hemicelluloses, as well as the consumption of alkali in both brightening and non-brightening reactions lowers the pH to a value of about 8.5

(under optimum conditions)[28]. As mentioned earlier, increasing the pH favours the formation of the perhydroxyl ion, the active bleaching species. However if the pH is too high, detrimental reactions such as peroxide decomposition and lignin darkening begin to predominate, resulting in lower brightness gains.

iii) Temperature

The peroxide bleaching reaction is usually carried out at 55°C for two hours at 10-12% consistency. At higher temperatures the time for brightening is decreased but so is the bleaching efficiency[28].

iv) Metal ions

The decomposition rate of hydrogen peroxide is increased drastically by the presence of heavy metal ions, especially manganese. In order to minimize this effect the metal ion concentration may be reduced using a chelating agent. Chelating agents form soluble complexes with the metal. Pentasodium diethylenetriaminepentaacetate (DTPA) is commonly used for this purpose[41].

I. Factors Affecting Dithionite Bleaching

Several factors affect dithionite bleaching including: dithionite dosage, consistency, pH, time and temperature, among others (28).

i) Dithionite dosage

Above 1% dithionite based on oven dry pulp the brightness gain levels off and eventually decreases. There are a number of reactions involved in dithionite bleaching and the reason for a maximum brightening effect at a concentration of 1% is fairly complex. It is an unstable compound which at high concentrations has a faster rate of decomposition than brightening (28).

ii) Consistency

At low consistencies the dilution factor reduces the chemical-fibre contact while at high consistencies the reactive hydrosulphite is difficult to mix evenly for homogeneous brightening. Bleaching is generally carried out at 4% consistency (28) although recently some new equipment has allowed work on dithionite bleaching at medium consistencies (10-15%) (42).

iii) pH

At pH values below 5, dithionite decomposes quickly to thiosulphate, reducing bleaching efficiency (43). At pH values about about 6.5 it is not an effective reducing agent for lignin. Thus dithionite bleaching is carried out in the pH range of 5 to 6.5.

iv) Reaction

Normal reaction conditions for dithionite bleaching are 60 to 70°C for 1 to 2h, although temperatures up to 90°C can be used without any loss in brightening efficiency (44). At this high temperature, 95% of the brightening reaction is complete in the first 10 to 20 minutes (44).

J. Two Stage Bleaching

Hydrogen peroxide bleaching is more expensive than dithionite bleaching but is capable of reaching higher brighteness targets. In combination, even higher brightness gains are possible. Since dithionite-reduced organic groups can be reoxidized by peroxide, peroxide bleaching is the first step of a two stage system. The average gain for hemlock, spruce and/or balsam fir is 7-9 points when using sodium dithionite while peroxide will normally give at least 15 points. Effective two stage bleaching can give 20 points increase in brightness or lower brightness gains at a reduced chemical cost (28).

K. Conventional Peroxide Bleaching

A continuous peroxide tower bleaching system is shown in Figure 5. The pulp is chelated and then washed to remove the chelated metal ion. The consistency is increased in the thickener which is followed by a mixer to introduce the bleach liquor. The system shown uses a multi-head pump to regulate the quantity of each component used. A computer controlled system monitors the incoming pulp brightness using a sensor at the top of the tower. The computer uses this data to adjust the pump accordingly. The bleach tower itself can be as large as 20 m high by 6m in diameter. Upon exiting the bleach tower the pH is reduced to about 5.5 using an in-line mixer and sulphurous acid.

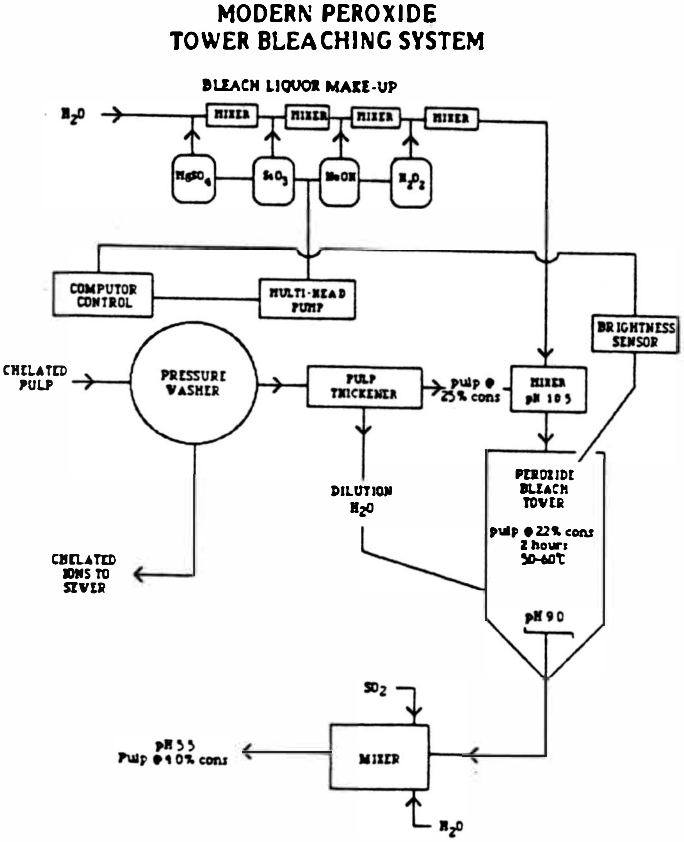


Figure 5. Continuous Tower Peroxide Bleach Plant

L. Dithionite Bleaching

With dithionite bleaching there is also the need for some type of holding vessel to allow one to two hours of retention. Air entrainment must be minimized to avoid decomposition of the dithionite. For maximum brightness gains the pulp consistency, pH, temperature, and retention time should be carefully controlled (36).

M. Refiner Peroxide Bleaching

Peroxide bleaching is most commonly carried out in a tower operation providing controlled conditions and a significant brightness gain (up to 15 points). Refiner bleaching has been investigated by a number of authors (45-48) in an attempt to avoid the initial cost of tower equipment and installation, and to take advantage of the high consistency and excellent mixing present in the refining zone.

i) Bleach Liquor Addition

In order to take full advantage of the bleaching chemicals the addition point must be carefully considered. Three alternatives are possible (45).

a) Addition to the wood before fibre separation.
b) Addition into the refiner during fibre separation.
c) Addition after fibre separation.

Akerlund(45) reported maximum efficiency of the bleaching chemicals was obtained when addition took place in the first stage pressurized refiner, between the disks but not immediately in the eye of the refiner. He reasoned that when the peroxide was added at the eye, the blowback of the generated steam removed some of the liquor, but when added just after the pressure maximum, through channels normally used for dilution water, the bleach liquor was carried through with the pulp.

Addition of the bleach liquor into the refiner casing as well as the refiner blow-line have also been studied(46). Other work includes the addition of bleach liquor onto pre-pressed chips in the expansion chamber, prior to refining(47). Other results indicate that the optimum point of addition is after the initial pressurized refining stage. Although blow-line mixing was poor, the second stage refiners would achieve a uniform final product in normal operations(47).

Akerlund(48) et al has established a patent for refiner peroxide bleaching, (aka. Defibrator Bleaching) claiming addition of sodium silicate along with a sequestering agent prior to refining followed by peroxide addition during refining results in a good bleaching efficiency. Investigations of refiner bleaching have also been carried out on non-woody plants such as Kenaf.

The two methods include i) pre soaking of field dried roselle in bleach liquor before initial refining and ii) application of liquor prior to the second stage refining(49).

ii) Conditions

The refining zone provides intensive turbulence for effective mixing of the (freshly exposed) wood fibres with the bleach liquor(45). The high temperatures between the refining disks results in a fast reaction rate while the short retention time avoids excessive peroxide degradation(50).

A comparison of unoptimized refining casing bleach liquor addition against blow-line bleach liquor addition indicated that while both methods produced inferior results to tower bleaching, the blow-line bleaching results were promising. In the trials the temperature of the refiner casing was 135°-155°C while the temperature of the blow-line just after bleach addition was 100°C. It was considered that peroxide decomposition was the problem at the higher temperatures(46).

Retention times for the pulp after bleach addition were varied for each system (some 15-30 minutes(45), others 2 hours(51)). It appears that the individual experimental conditions stipulate the amount of time required to reach optimum brightness.

iii) Chemical Requirements

Optimization experiments for the various types of peroxide bleaching are often overlooked. Three observations were pointed out when working with refiner bleaching (45):

1. The alkalinity at low peroxide levels must be carefully controlled but is less crucial for higher peroxide charges.

2. An overcharge of alkalinity will rapidly deteriorate the brightness to levels even lower than the original unbleached brightness.

3. For higher brightness gains the silicate dosage is of extreme importance.

iv) Advantages and Disadvantages

The main advantage of refiner peroxide bleaching is the large capital savings over that of a tower operation. The bleaching response is excellent and the fibre strength characteristics are improved (50). Refining energy has been noted to decrease by as much as 15% during peroxide refiner bleaching (45).

Refiner bleaching is apparently more sensitive to the quality of the wood used and can result in a fluctuation of brightness gained(51). One serious condition found during full scale operation was that expected brightnesses were rarely reached(45).

One of the most severe drawbacks to peroxide bleaching from a production standpoint is the formation of silicate deposits on the refiner plates during refiner peroxide bleaching(52). Silicate replacements have been investigated to avoid their problem but have proven inadequate for achieving the optimum bleaching response(53).

Metal ion contamination found naturally in the wood species as well as from the equipment surfaces creates serious bleachability problems stemming from peroxide decomposition. Chelating agents can be added in the refiner with the bleach liquor but the results are less than adequate(54).

v) Refiner Dithionite Bleaching

The lack of air in a pressurized refiner improves the efficiency of dithionite bleaching. The high temperatures and high consistencies create a fast reaction with good bleach chemical penetration. One drawback is that the refiner must be resistant to corrosion(55).

This type of refiner bleaching has obtained far less notoriety than peroxide refiner bleaching, and the claims are not specific.

EXPERIMENTAL DESIGN

The purpose of this study was to investigate the variables involved in hydrogen peroxide bleaching in the blow-line of a thermomechanical pulping system. In order to determine the effectiveness of the pilot plant trials, the spruce refiner pulps were bleached in the laboratory to simulate conventional tower bleaching. The results from "tower" bleaching could then be compared to refiner bleaching.

The experimentaion was carried out in stages, each stage contributing to the next, in order to determine the actual effect of each parameter on the entire system.

Stage I

1 - Laboratory Hydrogen Peroxide Bleaching
    a) Vary NaOH level
    b) Vary Silicate level
2 - Laboratory Dithionite Bleaching

Stage II

1 - Bleach liquor addition
    a) refining zone
    b) post refining zone (blow-line)
2 - Refining pressure variations

Stage III

1 - Bleach Liquor Optimization (at several peroxide dosages)
    - a) Silicate level
    - b) NaOH level

2 - Effect of retention time and temperature on bleached pulps.

Stage IV

1 - Chelating Agent
    - a) added in bleach
    - b) added at some point in the system
    - c) added to the chips

Stage V

1 - Dithionite Bleaching
    - a) before refiner
    - b) in blow-line

2 - Lab dithionite bleaching on blow-line bleached pulps.

Stage VI

1 - Computer Modelling of Peroxide Bleaching

2 - Computer Modelling of Two Stage Peroxide-Dithionite Bleaching

EXPERIMENTAL PROCEDURE

A. MATERIALS:

I WOOD SPECIES

The wood species used for all laboratory work and pilot plant trials was black spruce (picea mariana) obtained from Abitibi-Price Woodlands in Thunder Bay, Ontario, Canada. The trees were cut to five foot lengths on site during the week of May 14 to 18, 1984 and were received at Abitibi-Price Reseach on May 24, 1984 where they were peeled, chipped and screened.

II CHEMICALS

The following chemicals used in the bleaching experiments:

Hydrogen Peroxide (50% H_2O_2, obtained from CIL Inc. and Dupont Inc.)

Sodium Hydroxide (reagent grade)
Sodium Silicate (Product "N" obtained from National Silicates Inc.)

Magnesium Sulphate ($MgSO_4 \cdot 7H_2O$, reagent grade)
Sodium Dithionite (Virwite 10 obtained from Virchem Inc.)

B. LABORATORY BLEACHING:

I. PEROXIDE

A standard laboratory peroxide bleaching procedure was used in order to simulate tower bleaching for comparison to refiner bleaching. The "standard" bleach liquor was formulated as follows, adding the components in the order given:

0.05% $MgSO_4 \cdot 7H_2O$ (epsom salts)
5.0% sodium silicate (41.6° Be)
2.5% total alkali
2.5% H_2O_2

Other bleach liquor formulations were also used to investigate tower bleaching at different peroxide dosages.

The standard procedure is outlined below:

i. A predetermined amount of pulp, at 13.5% consistency, was placed in a polyethylene bag and suspended in a 50°C hot water bath for 30 min.

ii. The required amount of bleach liquor was added and the pulp mixed by hand. This resulted in a bleaching consistency of 12%.

iii. The sample was retained in a 50^{0}C hot water bath for 2 h.

iv. The sample was removed from the hot bath and drained under vacuum of all excess liquid, keeping the filtrate for residual testing if desired.

v. The bleached pulp was diluted with distilled water and mixed thoroughly while the pH was adjusted to 4.5 - 5.5 by addition of sulphurous acid (SO_2 water).

iv. The pulp was again drained and stored at 4^{0}C until needed.

II. DITHIONITE (HYDROSULPHITE)

The procedure for laboratory dithionite bleaching is described below:

i. The desired amount of pulp was mixed thoroughly at a consistency of 3% with hot deionized water (60^{0}C).

ii. The slurry was deaerated under a vacuum and stirred under a nitrogen blanket.

iii. With continuous mixing the desired amount of a 1% solution of sodium hydrosulphite (Virwite 10) was added.

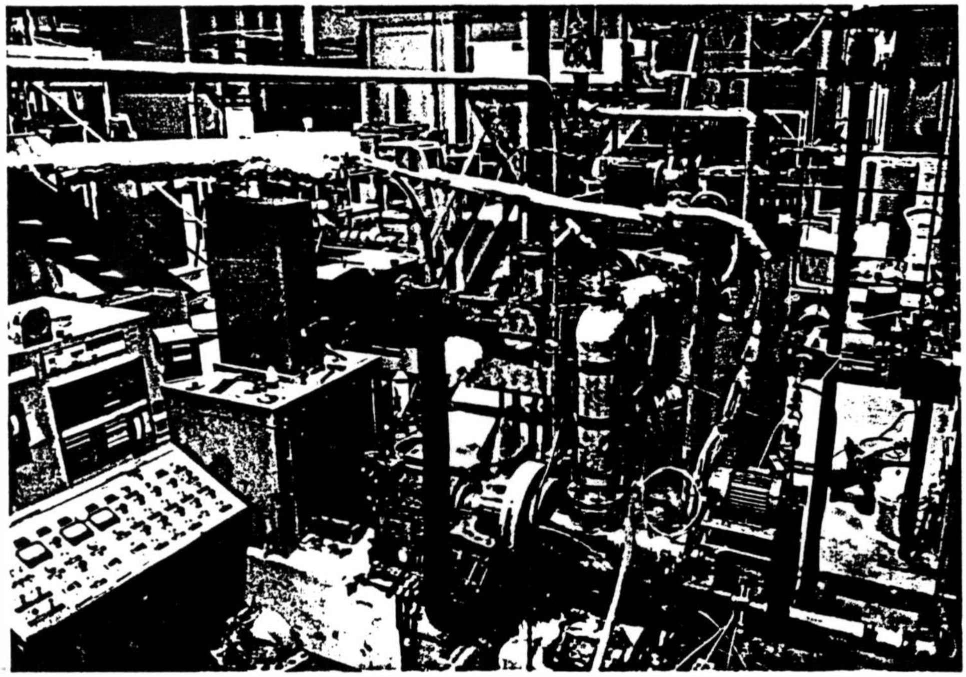
iv. The container was sealed and retained at 65^{0}C for 90 minutes.

v. After bleaching, the pulp was diluted, stirred and drained and then stored at 4^{0}C until needed.

C. PILOT PLANT OPERATIONS

1) SUNDS DEFIBRATOR (CD300)

A Sunds Defibrator 300 mm conical-disk refining system was used for the bleaching study. A photograph of the pilot plant is shown below.



The operating conditions for the system were those shown in Table I, unless indicated otherwise.

TABLE I

CD300 OPERATING PARAMETERS

1. Infeed Hoppper	Pre-steam for 10 min.
2. Hopper Plug Screw Feed	Crush chips at 420 kPa
3. Impregnator	Water added at 210 kPa
4. Digester	3 to 4 min. at 210 kPa
5. Refiner Load	2200 kW·h/ODT (110 HPD/ODT)
6. Plate Clearance	Disk...0.40 to 0.45 mm Conical...0.20 to 0.24 mm
7. Thruput	800g/min
8. Pulp Consistency	25% exiting blowline
9. Pulp Temperature	75^{0}C exiting blowline
10. Residence Time	3s in blowline

II. CD300 FLOW DESCRIPTION

The chips are initially added to the infeed hopper and presteamed. Between the hopper and the digester the chips travel through a plug screw where severe compression occurs. The chips swell when released into the pressurized digester. At this point liquids may be added for excellent absorption. A series of screws carry the chips from the digester to the refiner where defibration takes place. The blowline allows the pulp to travel from the refiner casing to an atmospheric cyclone discharge.

III. ADDITION POINTS

Points of liquid addition include the impregnator, the screwfeed between the digester and the refiner, the refining zone and the blow-line.

IV. METHOD OF LIQUID ADDITION

The liquid, primarily bleach liquor, was added using a laboratory metering pump (FMI Model RP-D). The pump injected the bleach liquor directly into the blow-line on the "outlet" side of the refiner. A 'T' valve was used to connect two sample bottles to the pump. A schematic of the liquid addition system is shown in Figure 1. Having two sample bottles allowed rapid change from one bleach liquor to the next.

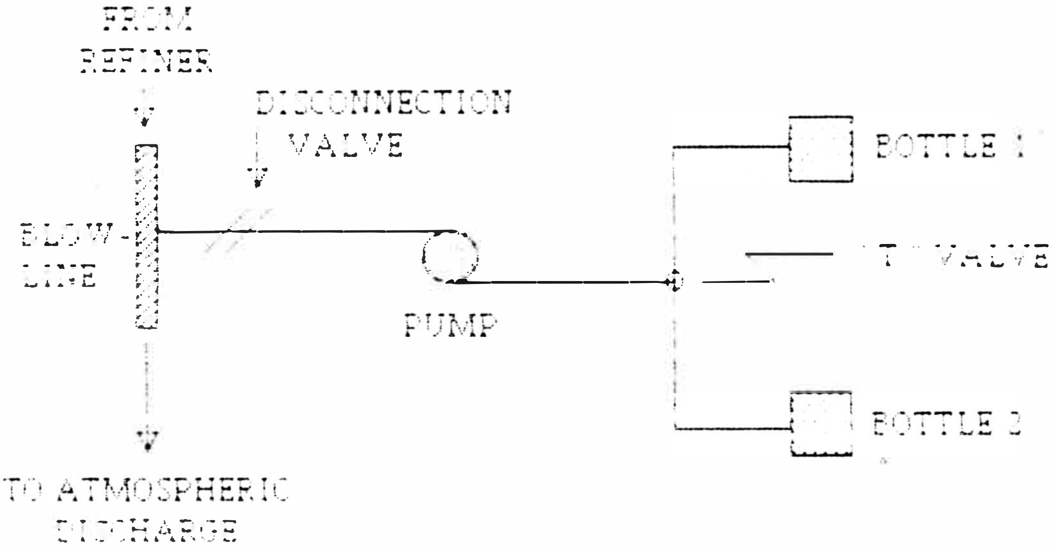


Figure 1. Bleach Liquor Addition System

V. SAMPLING

The refined pulp was collected at the mouth of the atmospheric discharge cyclone using a large polyethylene bag. The pulp was collected for one minute in order to check the throughput of the refiner. From this bag smaller samples were removed for the required treatment.

D. PULP TREATMENT

I. RETENTION

Pulps to be retained for any length of time at a given temperature were sealed in a polyethylene bag. The elevated temperatures were maintained using controlled temperature water baths, with the bags put directly in the water.

II. SOURING

The hydrogen peroxide bleaching reaction was quenched by dilution of the pulp followed by vigorous mixing with a lightening mixer while adding sulphurous acid to reduce the pH to 5.5.

E. BRIGHTNESS MEASUREMENTS

I. BRIGHTNESS PADS

Standard 3g. brightness pads were made using a buchner funnel and qualitative filter papers. The pads were dried in a controlled temperature and humidity room for 24 h.

II. ELREPHO MEASUREMENTS

The instrument used to measure the % brightness was the Elrepho. The standard CPPA method was followed (CPPA Method E.1).

RESULTS AND DISCUSSION

1. Bleach Liquor Point of Addition:

Because of the reported problems with silicate precipitation on the refiner plates during "refiner-bleaching" it was decided that a useful alternative might be to bleach in the blowline of the refiner.

TABLE I

Effect of Point of Bleach Liquor Injection

(1.6% H_2O_2, 0.05% $MgSO_4$, 2.1% T.A.)

	Brightness Gain (%)
Refiner	5.3
Blowline	6.3

The data presented in Table I shows that blowline bleaching enables a slightly higher brightening response than refining-zone bleaching. As well, during bleach liquor addition to the refining zone, the CD300 refiner load tended to be more unstable producing a non-uniform pulp of poor quality. Thus adding the bleach liquor in the refiner blowline eliminates the possibility of silicate deposition on the refiner plates, stabilizes refiner load, and gives a better bleaching response. For these reasons all subsequent pilot plant trials were done with liquor addition in the blowline (unless otherwise mentioned).

2. Alkalinity Optimization:

Of the chemical factors which influence peroxide bleaching, alkalinity is perhaps the most important. For each peroxide dosage there is a corresponding optimum alkalinity at which the best brightening will occur. Total alkalinity optimization was carried out for a range of peroxide dosages. (The "total alkali" dosage arises from the NaOH added directly to the liquor and from the NaOH present in the silicate).

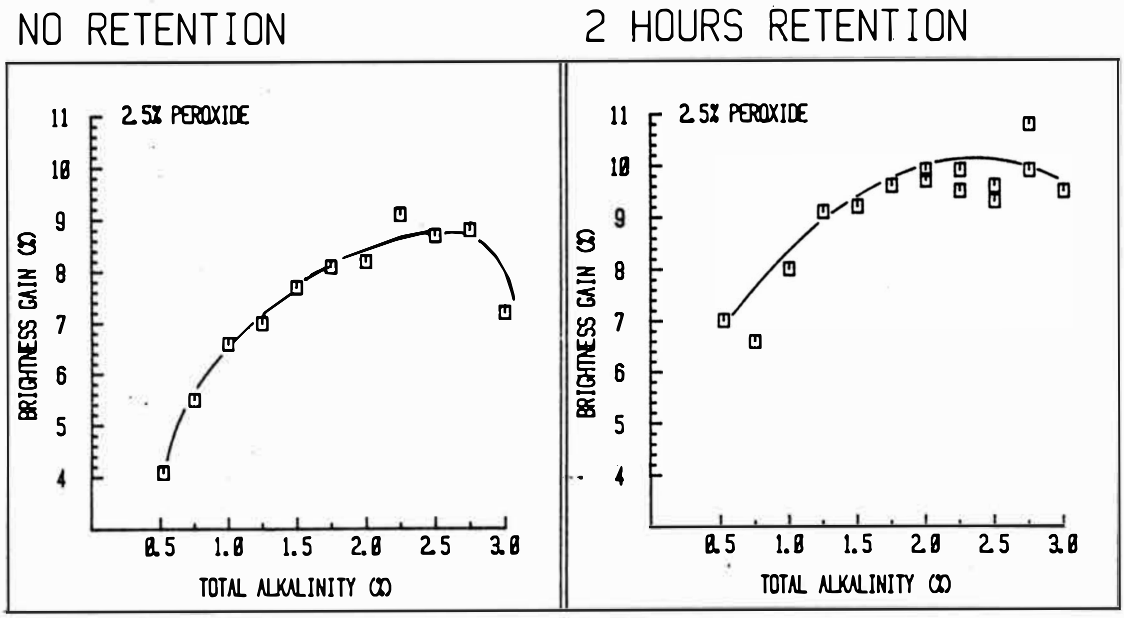


Figure 1. Brightness gain against total alkalinity for 2.5% peroxide with no post-refiner retention and with 2h retention. The 'NO RETENTION' plot actually represents a total retention time before souring of 1.5 min.

Figure 1 shows the results obtained by varying the alkalinity between 0.5% and 3% for a 2.5% peroxide dosage (0.5% $MgSO_4$ and 5% SiO_3 were also used). Note that there is an obvious maximum in each of the two curves presented. Thus having either too little or too much alkali is detrimental to the bleaching response. As well, the maximum for the two curves can be seen to occur at different alkalinities (about 2.6% total alkalinity for pulp soured immediately after blowline bleaching and about 2.25% total alkalinity for pulp held at $50^{o}C$ for 2h after emergence from the blowline). Thus the optimum alkalinity dosage is dependant not only on the peroxide dosage but also on the post-refining treatment conditions. The dependence of optimum total alkalinity on both peroxide dosage and post-refiner retention is shown in Figure 2 where the optimum alkalinity has been determined at five different peroxide dosages. A few points should be noted from the data. First the relationship between optimum total alkalinity and peroxide dosage is not linear. Thus the ratio between total alkalinity and peroxide in a bleach liquor must change each time a new peroxide dosage is used. Secondly, for all peroxide dosages a higher alkalinity is required when no post-refiner retention is used thus demonstrating that post refiner treatment conditions must be established before the systems' optimum alkalinity can be determined.

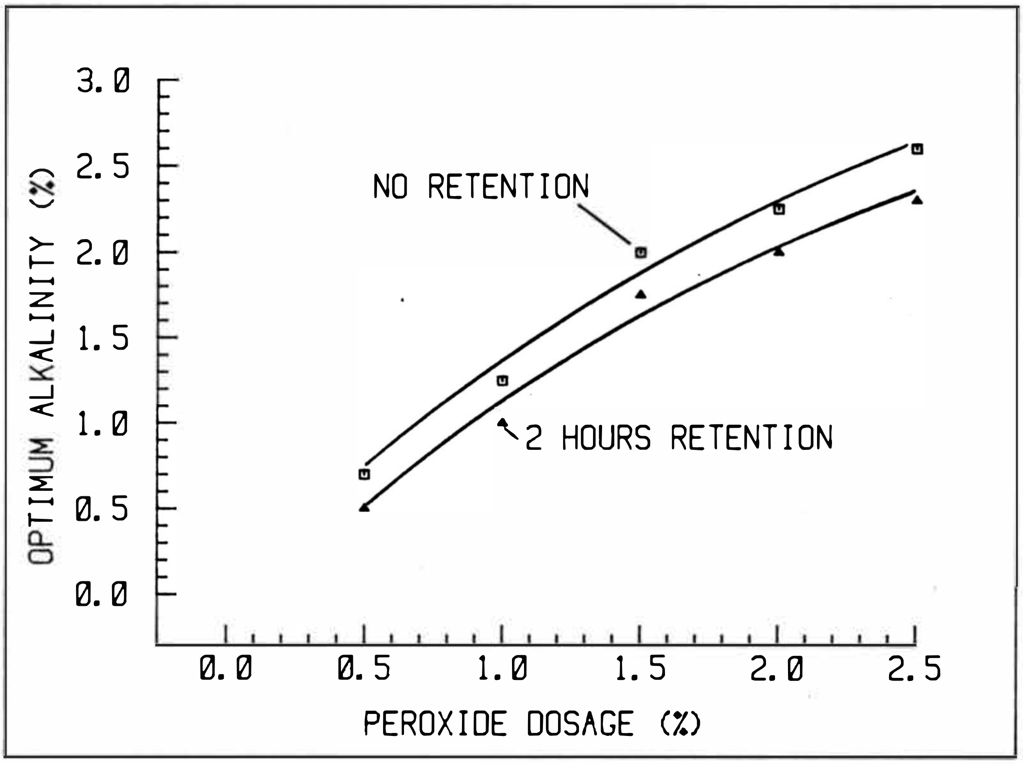


Figure 2. Optimum alkalinity against peroxide dosage with no post-refiner retention and with 2h retention at 50°C.

3. The Effect of Sodium Silicate:

The effect of sodium silicate dosage was tested using a bleach liquor containing 0.5% H_2O_2 , 0.05% $MgSO_4$ and 1.3% T.A. (total alkalinity) and varying the silicate level from 0 to 10%. The brightness gains for the respective silicate dosages can be seen in Figure 3. Below 2% SiO_3 the bleached brightness is lower than the unbleached brightness. Above this level the brightness gain improves up to four or five percent silicate, at

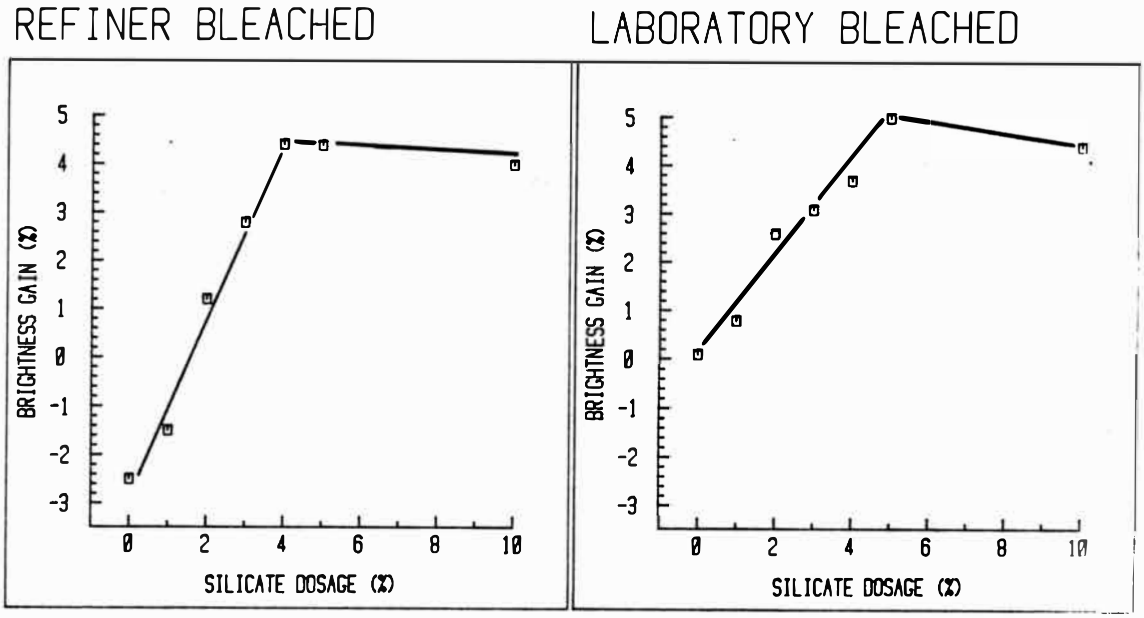


Figure 3. Brightness gain against silicate dosage for blow-line bleached pulp and laboratory bleached pulp.

which time it levels off. There is no benefit in increasing the silicate level above 4 to 5%. Similar results are shown for pulps bleached in the laboratory. The results in Figure 3 show conclusively that silicate is an essential part of refiner-blowline peroxide bleaching. It is not possible to reduce the silicate dosage below the normal 4 to 5% level without seriously affecting brightness gain. This suggests only two possible solutions to the silicate deposition problem. First, the silicate could be replaced by some other chemical. Unfortunately no other chemical is known which can duplicate the benefits of silicate. Second, the bleach liquor could be added immediately after refining, thus preventing contact of silicate with the refiner plates; i.e. blowline bleaching. The second is at present the best alternative. (Note: after about 12h of peroxide blowline bleaching, no silicate deposit could be detected in the blowline of the equipment used for this project).

Based on the data presented in Figure 3, 5% sodium silicate based on oven dry wood, was used in all subsequent bleaching experiments.

4. Retention Times for Bleached Pulps:

A 1.5% peroxide bleach liquor was made up at three alkalinity levels, and pulp was blowline bleached with the liquor. The treated pulp was then retained in a 50°C water bath for time intervals up to 2h. Figure 4 shows the brightness gains for each alkalinity at different retention times. It is evident that the optimum time is dependent on the alkalinity of the samples. At the lower alkalinity the time to reach maximum brightness is at least 2h while the 2.0% alkalinity sample reached the maximum brightness gain in less than one hour. As well the maximum brightness gain is different for each alkalinity level. Thus there is a strong interdependence of optimum alkalinity and retention time, which have a combined effect on brightness gain. For a particular mill process it would be necessary to optimize

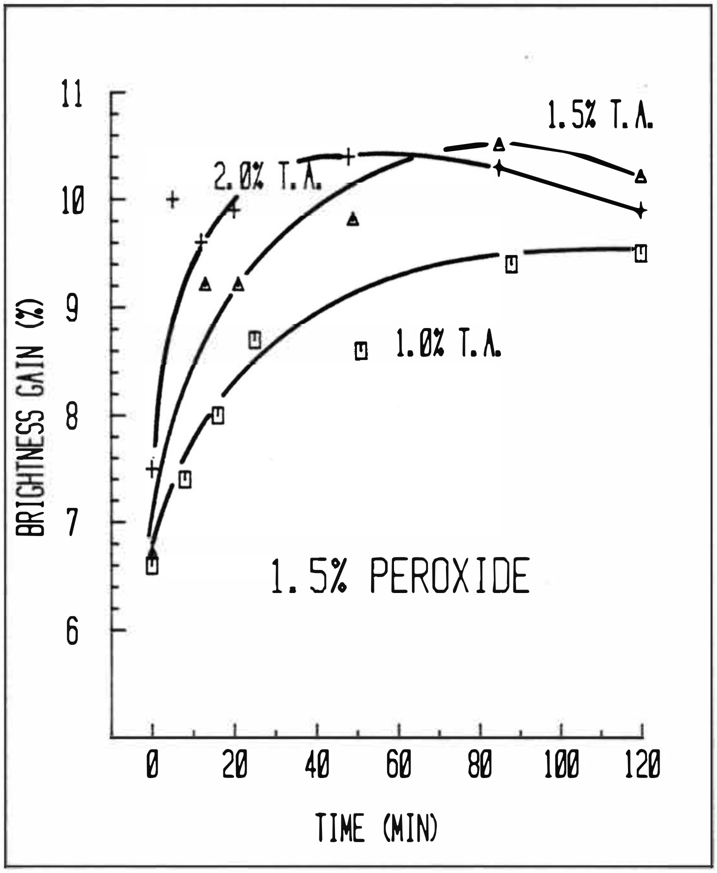


Figure 4. Brightness gain against post-refiner retention time for pulp bleached with 1.5% peroxide and at different alkalinities.

the alkalinity not only for the peroxide dosage but also for the retention time as well.

5. Refiner Pressure:

Refiner bleaching trials were carried out at three different pressures, 180 kPa, 210 kPa and 240 kPa (25, 30 and 35 psi respectively).

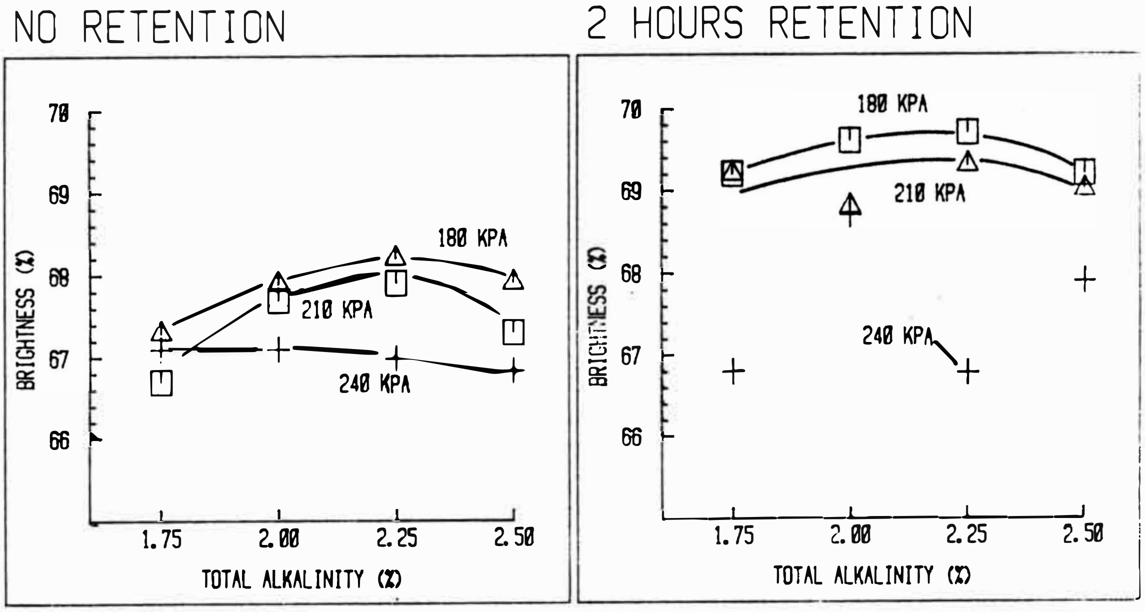


Figure 5. Brightness Against Total Alkalinity for Blowline Bleached Pulps Refined at Different Pressures

Figure 5 shows bleached brightnesses for various alkalinities (2% peroxide) sampled at each of the designated pressures. The data shows that lower refining pressures give higher final bleached brightnesses. However, the unbleached brightness values are also higher at lower pressures (57.6, 56.9 and 55.8% for 180, 210 and 240 kPa respectively). Thus when brightness gains are examined (Figure 6) the results are about the same (within experimental error) at each pressure. This can be easily explained.

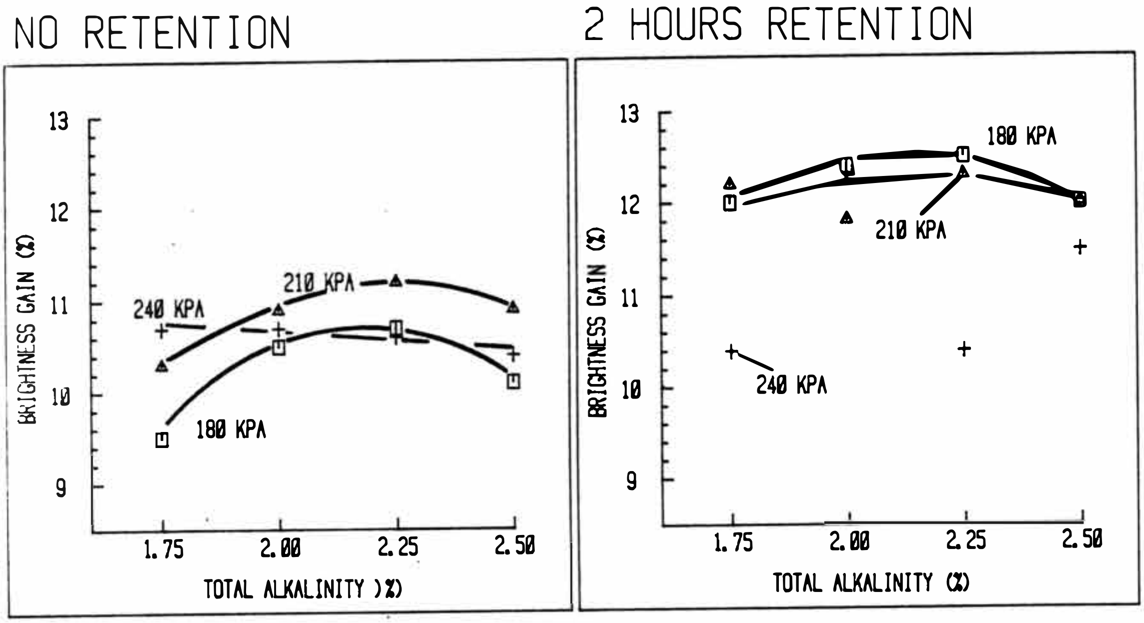


Figure 6. Brightness Gain Against Total Alkalinity for Blowline Bleached Pulps Refined at Different Pressures

At higher refining pressure, the temperature is higher and hence the brightness of the unbleached pulp is lower. However, in blowline bleaching, the residence time after liquor addition is very small (three seconds) after which the temperature quickly drops to about 75^{0}C. As well the temperature in the blowline is probably very close to 100^{0}C irrespective of refining pressures since the blowline is at close to atmospheric pressure . Thus, although refining pressure has a strong effect on both bleached and unbleached brightnesses, its effect on brightness gain is small (at least for this system).

Since operating the CD300 at 180 kPa caused poor pulp quality because of difficulties experienced in stabilizing the load, the remaining pilot trials were run at 210 kPa (30 psi).

6. Chelation of Metal Ions:

The Black Spruce chips used for the trials had a high manganese content as shown in Table 2.

TABLE 2
Metal ion contents in mg·kg^{-1} (ppm)

	Al	Cu	Fe	Mn
Untreated Pulp	9.8	7.5	15.1	100.2

Manganese is known to strongly interfere with peroxide bleaching causing lowering of brightness gains. Manganese can easily be sequestered with a chelating agent such as DTPA (pentasodium diethylenetriaminepentaacetate). However recent work has shown that the ions need not only to be sequestered but also to be washed from the pulp and removed(40). In conventional pulp systems this is a simple process since it is defibrated pulp which is chelated. However in refiner bleaching the chelation must be done on chips. This involves three steps: penetration of the chips by the DTPA, chelation of the metal ions, and subsequent removal of the chelated ions from the chips. The second step, chelation, is very fast but the rates of the other two steps have not been studied. For these experiments crushed chips which had been fed through a plug screw feeder were used (Figure 7).

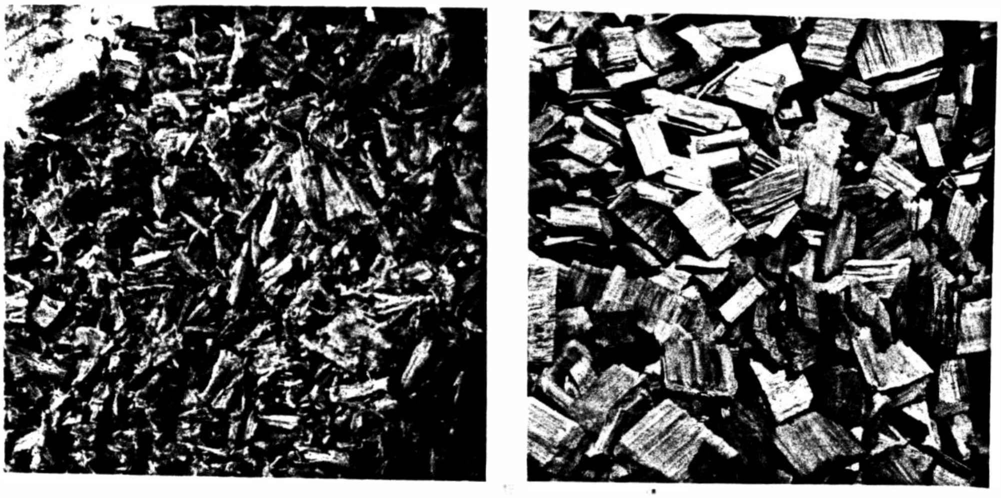


Figure 7. Photographs of Plug Screw Fed Chips (left) and Normal Chips (right).

These chips are highly fractured in the fibre direction improving the speed of penetration. When these chips were treated with DTPA and then washed the manganese content was reduced as in Table 3.

TABLE 3

Chelation of Crushed Black Spruce Chips

DTPA (%)	Soaking Time (h)	Number of Washing Steps	Metal Analysis (PPM) Al	Cu	Fe	Mn
0	0		9.8	7.5	15.1	100.2
0.5	23	1	28.0	3.9	16.4	29.5
0.5	54	2	7.7	2.6	8.1	6.0
0.5*	66	4	7.1	3.1	15.6	19.6

*Experiment done in pilot plant

For the pilot plant trial, approximately 30 kg of chips were soaked for 66 h then washed 4 times. The analysis of these chips showed a reduction in the manganese content, but it was not quite as large as for the small batch done for 54 hours. This may have been a result of an inability to agitate the large amount of chips in the pilot trial. The pulp brightness of these chips after bleaching, was far superior to any other method of DTPA application in the pilot plant study. The various applications and the corresponding brightness gains are shown in Table 4. Note that a 15.4 point brightness gain was achieved when chelated chips were blow-line bleached.

TABLE 4

Use of DTPA in Refiner Bleaching

DTPA ADDITION (0.5%)	BLEACH LIQUOR ADDITION	BRIGHTNESS GAIN (%)
Blowline	Blowline	12.1
Refiner Plates	Blowline	13.6
Impregnator	Refiner Plates	9.2
Impregnator	Blowline	12.3
Screwfeed	Blowline	13.8
Pilot Plant Chelation (0.5% DTPA) followed by washing	Blowline	15.4

7. Strength Analyses:

The data presented so far indicates that post refiner retention of bleached pulp is necessary for maximum brightness gains. However, the common practice after refining is to dilute the pulp immediately with agitation (latency removal). This allows the pulp fibres to straighten from their highly curled state after refining. Retention of the pulp at high consistencies for extended periods and for long times might affect pulp strengths. Experiments were done to investigate the possibility. Table 5 shows the dry and wet properties of refiner blowline bleached and unbleached pulps retained at different temperatures and for different times after refining.

All treatments indicate an improvement in strength over the unbleached pulp. The density increased along with burst index, wet and dry tensile stress and breaking length. The tear index was approximately the same for all samples. The shive count was down for the bleached samles, especially the diluted sample held at 65oC for one hour at 0.3% consistency simulating retention in a latency chest. All the other samples were held at the refining consistency, about 21%. As hoped, none of these treatments adversely affected pulp strength, in fact some small improvements were obtained.

8. Refiner Bleaching vs. Tower Bleaching:

Samples of the CD300 refiner pulp were bleached in the laboratory to simulate tower peroxide bleaching. The brightness gains (against peroxide dosage) for both lab bleaching and refiner blowline bleaching are shown in Figure 8. The results are effectively the same for both types of bleaching. The correlation between the two is also shown in Figure 8 by plotting the brightness gain obtained by refiner bleaching against laboratory brightness gains at the same peroxide dosages on the same pulp samples. It must be remembered, however, that blowline bleaching brightness gains are equivalent to tower gains only when post-refiner retention at reasonably low temperatures is used.

TABLE 5
Physical Properties

	Unbleached	Soured Immediately	2h 50°C	0.5h 100°	0.3% Consistency 1 h 65°C
CSF	107	110	117	118	107
Wet Strength:					
Stress (N/cm)	0.94	1.14	1.06	1.11	1.08
Shive Count(%)	0.20	0.13	0.11	0.15	0.07
Dry Strength:					
Density (g/cm)	0.32	0.37	0.35	0.36	0.37
Burst Index (MN/kg)	1.12	1.38	1.29	1.37	1.27
Tear Index ($N{\cdot}m^2/kg$)	5.77	6.10	5.70	6.00	5.60
Tensile Stress N/cm	15.7	17.9	17.1	18.2	17.6
Breaking Length (m)	2650	3000	2780	3000	2950
Brightness %	56.3	68.1	70.1	68.6	68.6
Brightness Gain(%)		11.8	13.8	12.3	12.3

Bleach Liquor

2.5% H202
2.5% T.A.
5% SiO_3
0.05% $MgSO_4$

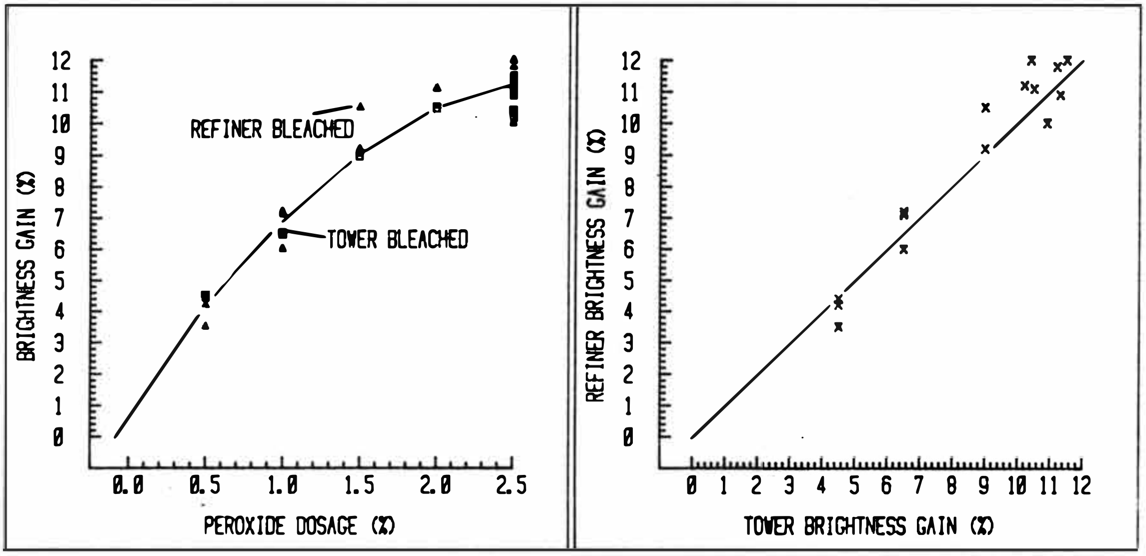


Figure 8. Left: Brightness Gain Against Peroxide Dosage for Both Blowline Bleached and Laboratory Bleached TMP

Right: Refiner Blow-line Brightness Gain (2h post refiner retetention at 50^{O}C) against Laboratory Brightness Gain

9. Second Stage Dithionite Bleaching:

One of the potential applications of refiner peroxide bleaching is in so-called "two stage" bleaching. In a conventional two stage system tower peroxide bleaching is followed by bleaching with dithionite in a second tower. The brightness gains are higher than those possible with either system on its own, but the capital costs are usually considered to be too high. However, if the peroxide bleaching could be done in a refiner, the capital costs would be reduced. This might be particularly valuable in the newsprint industry where the maximum brightness gain achievable with dithionite is only about 6-8 points in most mills. As newsprint brightness targets increase the limiting brightness gains available from dithionite may become a serious problem.

In these experiments pulp was bleached with peroxide in the refiner while the dithionite stage was carried out in the lab. The bleachability of refiner peroxide bleached pulp decreases as the hydrosulphite (Virwite 10) dosage increases (Figure 9).

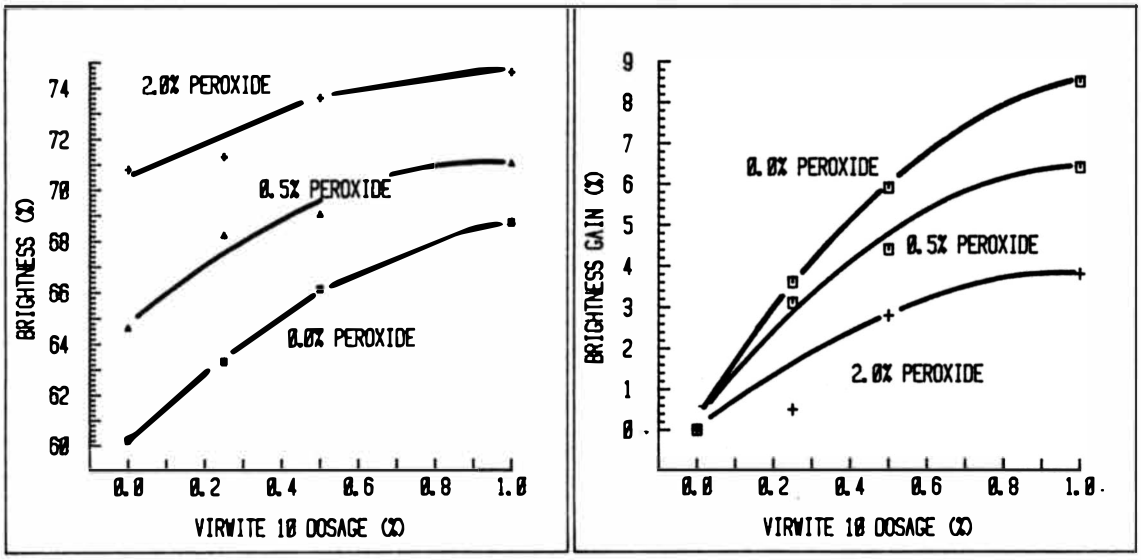


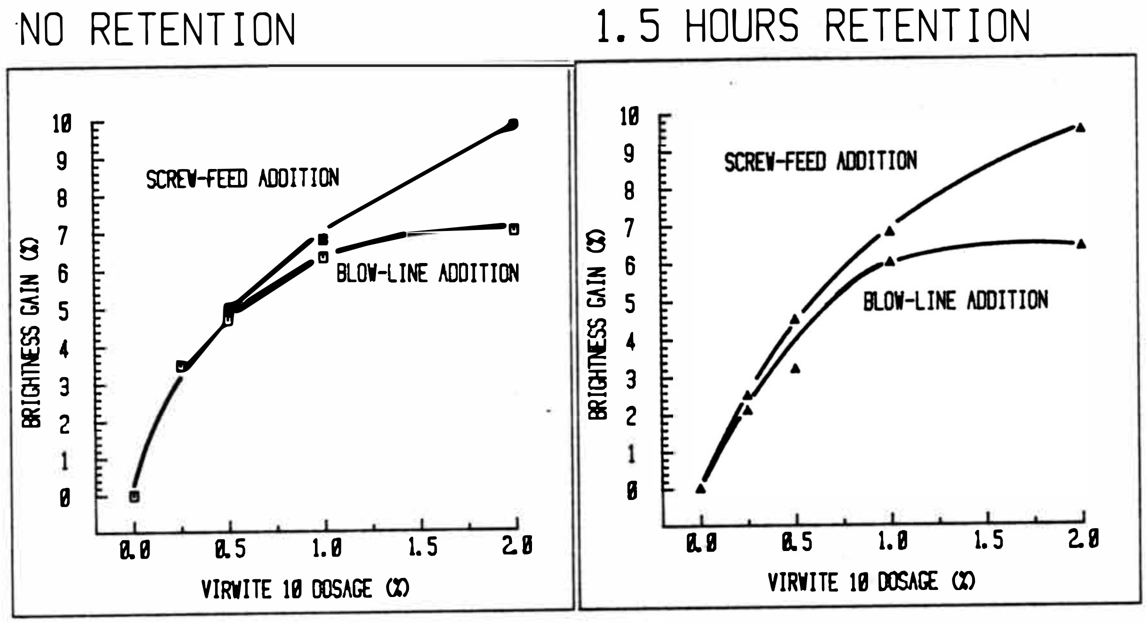
Figure 9. Left: Brightness Against Virwite 10 Dosage for TMP Previously Bleached with 0%, 0.5% and 2.0% Peroxide. Right: Brightness Gain Against Virwite 10 Dosage for TMP Previously Bleached with 0%, 0.5% and 2.0% Peroxide

This data shows the effect of a second stage dithionite laboratory bleaching on refiner bleached and unbleached pulps. The left hand graph shows dithionite bleaching of three pulp samples, one unbleached with peroxide, one bleached with 0.5% peroxide, and another bleached with 2% peroxide in the refiner. It can be seen that bleaching with Virwite increases the pulp brightness above that achieved in the first peroxide stage. The right hand graph shows only the brightness gain achieved on dithionite bleaching which is beyond that already achieved by the peroxide. This plot makes it obvious that increasing the brightness with peroxide unfortunately decreases the brightness gain possible with the second stage.

The effect of this interrelation on the economics of two stage against one stage bleaching will be considered in a later section.

10. Dithionite Refiner Bleaching

Although peroxide refiner bleaching was the primary area of investigation in this work, it was decided that dithionite bleaching in the blowline might also give some interesting results. The results, (Figure 10) indicate good brightness increases are possible; up to 10 points. However the efficiency of brightening was not as good, with 6.5 points at 1% Virwite being achieved compared to laboratory brightness gains of 8.5


NO RETENTION

1.5 HOURS RETENTION

Figure 10. Brightness Gain Against Virwite 10 Dosage for Refiner Dithionite Bleached TMP.

points at the same dosage level. However a few other interesting observations were also made. First there was no benefit on retaining the pulp for 1.5h at 65°C after exiting the refiner. Thus post-refiner retention might not be required, unlike refiner peroxide bleaching. The reaction of dithionite with wood at these temperatures is obviously, therefore, very rapid. Secondly, adding the dithionite to the screw-feeder prior to refining gave better results than blowline bleaching. This is presumably because of the slightly longer retention time at high temperatures and/or better mixing in the refining zone. Thirdly, the brightness gain increased as the dithionite dosage increased, all the way up to 2% dithionite. In a good tower system there should be no additional brightness gain above 1% dithionite. Since in the refiner system levelling off did not occur at 1%, it must be presumed that the bleaching was not carried out efficiently. This may be explained by entrainment of air in the pulp, since oxygen reacts with dithionite, destroying its ability to brighten wood. If air entrainment could be prevented it is possible that the 10 point brightness gain could be achieved at much lower dithionite dosages. There is obviously need of more work in this area.

11. Computer Modelling of Bleaching Reactions:

The data presented thus far for peroxide bleaching has shown that complicated interrelations between temperature, retention time and total alkalinity exist and that these factors combine (among others) to influence brightness gain. No one set of best conditions could be established since each factor not only affected brightness gain but also would affect the cost of building a refiner bleaching system as well as the results achieved. In order to better understand these relationships, computer modelling of the effects of these factors on brightness gain was attempted.

Laboratory peroxide bleaching experiments were done at temperatures ranging from 25^{0}C to 95^{0}C. All experiments were done at a constant peroxide dosage of 2%. The first set of experiments kept the retention times constant and varied the alkalinities. For each temperature the optimum alkalinity was chosen. The second set of experiments involved taking the optimum alkalinity for each temperature and varying the retention times.

Using three variables, (time, temperature and alkalinity) the information was stored in a computer along with the corresponding brightness gains.

The Marquardt[56] algorithm for least-squares estimation of nonlinear parameters was used. In this method a starting equation of proper "form" must be provided to the computer. (The form is the dependance of a given variable on the function, i.e. if the brightness changes as the log of retention time changes, then the initial form of the equation must be a "log-form" such as $f(x) = A \log x\cdot$ where $f(x)$ is the function, A is the coefficient to be determined by the computer, and x is the variable; time).

The starting form of the equation used in this work was:

$$B = A_1 + A_2 \cdot X_1 + A_3 \cdot X_1^2 + A_4 \cdot \log(X_2) + A_5 \cdot (\log(X_2))^2$$
$$+ A_6 \cdot (X_3) + A_2 \cdot (X_3)^2 + A_8 \cdot X_1 \cdot X_3 + A_9 \cdot X_3 \cdot \log(X_2) + A_{10} \cdot X_1 \cdot \log(X_2)$$

where:

B = brightness gain

A_n = coefficient to be determined by computer

X_1 = retention time (h)

X_2 = temperature (^oC)

X_3 = total alkalinity (%)

The program ran through seven iterations and resulted in a correlation coefficient of 0.946 (See Appendix 1 for examples of computer printouts). The equation which was arrived at by the computer is given below:

$$B = 21.2 + 0.449X_1 - 0.00233X_1^2 + 17.1 \log X_2 - 2.24 (\log X_2)^2 +$$
$$16.7X_3 - 2.14X_3^2 - 0.128X_1 \cdot X_3 - 4.46X_3 \cdot \log X_3 - 0.126 X_1 \cdot \log X_2$$

The original data can be reentered into the equation so that the difference between the measured brightness gain and the calculated brightness gain (known as residuals) can be seen.

The residuals are shown in Appendix 1 indicating very close correlation between actual brightness and the calculated brightness. The advantage of this equation is that it can be used to simulate experiments <u>within</u> the range of experimental conditions used for data. (Simulated experiments at conditions outside this range may be interesting but the results have a high degree of uncertainty). For example, a useful question might be: what are the best results obtainable under any conditions and what are these conditions.

This can be solved quite simply by taking the partial derivatives of the equation ($\partial B/\partial x_1$; $\partial B/\partial x_2$; $\partial B/\partial x_3$) and setting each to zero. When the first derivative equals zero the equation must be either a maximum or a minimum (in this case, a maximum is the only result possible).

The three derivatives are:

$$\partial B/\partial x_1 = 0.499-0.00466x_1 - 0.128x_3 - 0.126 \log x_2 = 0$$

$$\partial B/\partial x_2 = 17.1 - 4.48 \log x_2 - 4.46 x_3 - 0.126 x_1 = 0$$

$$\partial B/\partial x_3 = 16.7 - 4.28x_3 - 0.128x_1 - 4.46 \log x_2$$

Thus there are three simultaneous equations with three variables and the equations can be solved. On solution the equation predicts that the maximum brightness gain possible (using this pulp sample and 2% peroxide) is 11.2 points with the following reaction conditions: temperature = 13.5°C, time = 16.8 h; and total alkalinity = 2.22%. The equation can also be used to measure the maximum brightness gain possible at a given temperature. If the temperature is set constant at a value of say 100°C, the master equation derivates to give two equations with two variables. On solving, maximum brightness gain possible is only 7.3 points. In likewise manner the equation can be used to predict several trends:

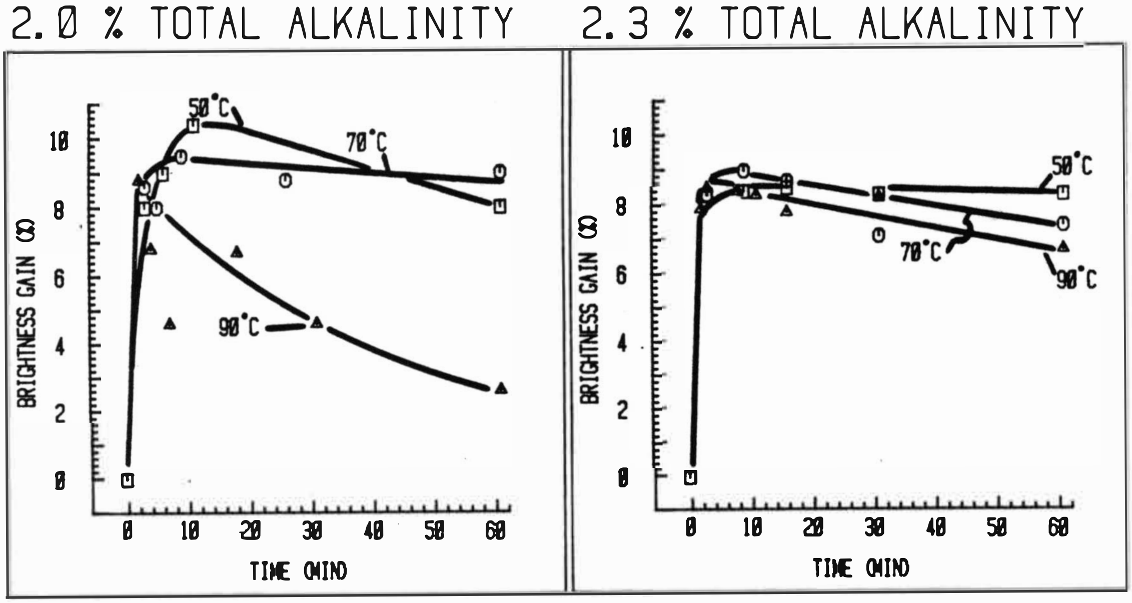
i) With increased temperatures the maximum obtainable brightness decreases.
ii) Increased temperatures require lower alkalinities.
iii) The optimum total alkalinity is inversely proportional to retention time.
iv) Retention times extended beyond what is actually needed will cause a brightness loss.
v) Time, temperature and alkalinity are interrelated, as shown by the cross terms.

These predictions had been observed qualitatively in the previous experiments. As well they were within the limits of the experimental data. Other predictions can be made beyond the limits of the data that show interesting trends. One such prediction is that good brightness gains could be achieved at low temperatures (25^{o}C) and high alkalinities (4%) for short retention times (5 min). More laboratory work needs to be done to determine whether this extrapolated prediction is indeed correct. However the results do point to new and interesting possibilities.

A further use of the equation is that it can be used for quantitative estimations in designing a bleaching system. Once the required brightness gain is established, the equation can predict the amount of retention required, the temperature and the alkalinity. Since reduction in retention time by increasing temperature must be balanced against reduction in brightness gain at higher temperatures, the equation can be used to determine which compromise is best for each situation. However, more experiments under "mill conditions" are needed to improve the usefulness of the model.

12. Retention Time:

The results presented thus far have shown a definite need for post-refiner retention of blow-line bleached pulp (see Figure 4). However the effect was not properly quantified. Therefore further, more closely controlled experiments were conducted to establish a more accurate measure of the amount of time required. The computer model demonstrated that, at least for long retention times, lower temperatures result in higher brightness gains. However, computer calculations at very short retention times give unexpected predictions of high brightness gains if the conditions are properly controlled. Figure 11 shows the effect of post-refiner retention for short periods of time at different alkalinities and temperatures. This data shows that up to 10 points brightness gain can be achieved within 10 minutes by lowering the pulp temperature after refining to 50°C and by choosing the proper alkalinity. (This compares to about 10.5 to 11 points achieved with 2h retention; see Figure 8).


2.0 % TOTAL ALKALINITY

2.3 % TOTAL ALKALINITY

Figure 11: Brightness gain against post refiner retention time for Pulp Bleached with 2.0% Proxide and Held at Different Temperatures.

13. Computer Analysis of Two Stage Bleaching Economics:

The computer modelling technique discussed in the previous section can also be used in the study of two stage bleaching.

The data used in Figure 4 can be used in a Marquardt algorithm to obtain an equation which describes the interrelation of peroxide and dithionite bleaching. Using this technique the following equation was obtained:

$$B = 45.4 \log(x_1 + 1) + 26.4 \log(x_2 + 1) - 2.18 \cdot x_1 \cdot x_2 - 5.26 \cdot x_1 - 1.25 \cdot x_2$$

where:

B = brightness gain

x_1 = peroxide dosage (%)

x_2 = dithionite dosage (%)

When the data from Figure 4 is fitted to this equation the correlation coefficient is 0.99.

The equation can be used to estimate the relative chemical costs of single stage and two stage bleaching in the following way. Suppose a target brightness gain is chosen, say 8 points. The equation gives a number of possible combinations of peroxide and dithionite dosages which will give this brightness (e.g. 0.92% peroxide + 0.0% dithionite; 0.6% peroxide + 0.25% dithionite; 0.4% peroxide + 0.49% dithionite; etc). If the chemical costs involved in bleaching with equal dosages of peroxide and dithionite were the same, the lowest cost would occur when the sum of peroxide dosage plus dithionite dosage was minimized. However this is not the case. Peroxide bleaching involves costs for the purchase of hydrogen peroxide, sodium hydroxide and sodium silicate, ignoring the cost of DTPA, $MgSO_4$ and SO_2. (The cost of $MgSO_4$ is very small compared to peroxide costs and both DTPA and SO_2 would be used in essentially the same amounts in either one-stage or two-stage bleaching). Dithionite bleaching involves only the purchase of a dithionite bleaching chemical such as Virwite 10. Bleaching 1T of pulp at a 1% dosage of peroxide costs about $13.60 for hydrogen peroxide, $1.70 for sodium hydroxide and $1.80 for sodium silicate; a total of $17.10. The bleaching of 1T of pulp at a 1% dosage of dithionite costs about $11.60 for Virwite 10. Therefore at an equal dosage level the cost of dithionite bleach chemicals is only about 0.7 times the cost of peroxide bleach chemicals. Therefore in computing what dosage of peroxide and dithionite is the most chemically cost efficient for reaching the target brightness, the dithionite dosage must be multiplied by a factor of 0.7 to compensate for the cost differences.

Figure 12 shows the results of such a calculation. Graphs are presented in which the peroxide dosage, plus 0.7 times the dithionite dosage required to reach a given brightness, is plotted against the peroxide dosage (left) and the dithionite dosage (right). There is obviously a minimum in each of these curves shown corresponding to the optimum amounts of peroxide and dithionite needed to obtain the target brightness gain. In Figure 12 (left) the optimum dithionite dosage for a given brightness gain is plotted against the corresponding optimum peroxide dosage. The curve is non-linear showing the importance of proper experimental optimization for each brightness gain. Figure 13 (right) shows the chemical cost advantage of two-stage bleaching over bleaching with either peroxide or dithionite. For large brightness gains, the cost advantage is significant; up to 30%. (Some large newsprint mills spent up to $1.5 million per year for dithionite. This would be reduced by about 20% to 30% or $300,000 to $450,000 per year).

Thus, potentially, one of the best applications of refiner blowline peroxide bleaching may be in the production of newsprint where refiner bleaching could be done as a first step, followed by dithionite bleaching which already is in place in most newsprint mills. The process would be even more useful should newsprint brightness requirements be increased in the future.

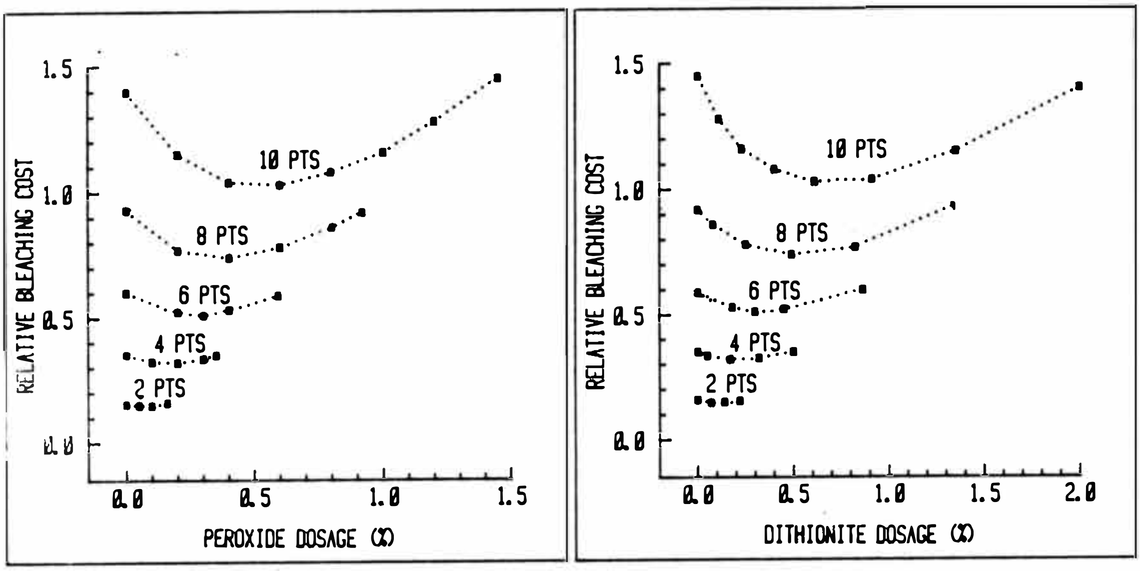


Figure 12. Relative Bleaching Cost Against Peroxide Dosage (left) and Dithionite Dosage (right).

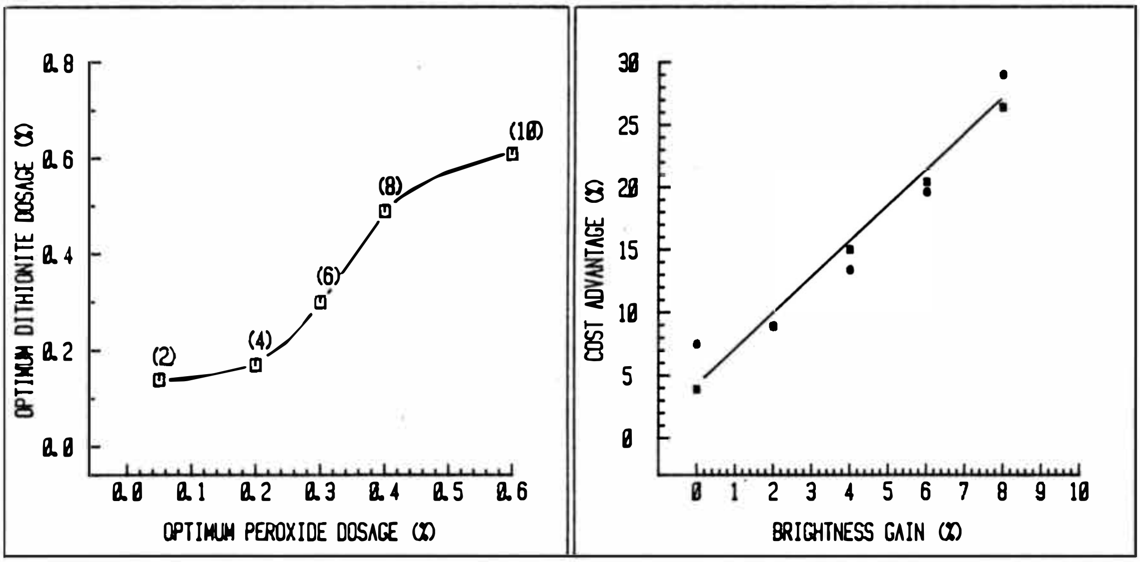


Figure 13. Left: Optimum Dithionite Dosage Against Optimum Peroxide Dosage Required to Produce the Target Brightness Gains (in brackets).
Right: Cost Advantage of Two Stage Bleaching Against Brightness Gain in Peroxide Bleaching (squares) and Dithionite Bleaching (circles).

APPENDIX

Sample Computer Printout

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ABITIBI-PRICE RESEARCH CENTRE - STATISTICAL PACKAGE(NON-LINEAR LEAST SQUARES - MARQUARDT METHOD)



DEBUG LEVEL = 1       MAXIMUN ITERATIONS =     50      CONVERGENCE CRITERIA =  0.100E-04

EQUATION =  1

 PERKINS' BRIGHTNESS EQUATION

              X(J)=DATA(IBASEX(J)+I)
              FUNCTN=A(1)+A(2)*X(1)+A(3)*X(1)**2+A(4)*ALOG10(X(2))
              1 +A(5)*(ALOG10(X(2)))**2+A(6)*X(3)
              2 +A(7)*X(3)**2+A(8)*X(1)**2*X(3)**2
              3 +A(9)*X(3)*ALOG10(X(2))+A(10)*X(1)*ALOG10*(X(2))


VARIABLE      DESCRIPTI ON

    4         BRIGHTNESS GAIN
    2         TEMP  (C)
    1         TIME  (H)
    3         T. A.

STARTING VALUES

                       1         2         3         4         5         6         7         8         9        10
COEFFICIENTS =  0.100E+01 0.100E+01 0.100E+01 0.100E+01 0.100E+01 0.100E+01 0.100E+01 0.100E+01 0.100E+01 0.100E+0

                       1         2         3         4         5         6         7         8         9        10
COEFFICIENTS =  0.142E+04-0.293E+02 0.127E+00-0.198E+04 0.833E+02 0.201E+02-0.138E+03 0.273E-01 0.600E+03 0.143E+0
STAND. DEV.  =  0.895E+05 0.114E+04 0.759E+01 0.726E+05 0.112E+05 0.333E+05 0.912E+04 0.890E+00 0.228E+05 0.577E+03


TOTAL SUM OF SQUARES       =  0.446E+03
RESIDUAL SUM OF SQUARES    =  0.377E+11
CORRELATION COEFFICIENT    =  0.000E+00

DEGREES OF FREEDOM     =     47
NUMBER OF POINTS       =     57
NUMBER OF ITERATIONS   =      1



                       1         2         3         4         5         6         7         8         9        10
COEFFICIENTS =  0.453E+03-0.412E+01 0.460E-01-0.560E+03-0.252E+01-0.259E+02-0.228E+02 0.530E-02-0.163E+03-0.364E+01
STAND. DEV.  =  0.330E+03 0.628E+01 0.357E-01 0.389E+03 0.251E+02 0.138E+03 0.370E+02 0.407E-02 0.116E+03 0.272E+01

TOTAL SUM OF SQUARES       =  0.446E+03
RESIDUAL SUM OF SQUARES    =  0.339E+06
CORRELATION COEFFICIENT    =  0.880E+00
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DEGREES OF FREEDOM    =    47
NUMBER OF POINTS      =    57
NUMBER OF ITERATIONS  =     2

                          1          2          3          4          5          6          7          8          9         10
COEFFICIENTS =   0.155E+02-0.270E+00 0.141E-02-0.157E+02-0.220E+01 0.631E+01-0.200E+01 0.369E-04 0.513E+01 0.905E-01
STAND. DEV.  =   0.708E+02 0.135E+01 0.747E-02 0.834E+02 0.651E+01 0.270E+02 0.721E+01 0.656E-03 0.248E+02 0.573E+00

TOTAL SUM OF SQUARES        =  0.446E+03
RESIDUAL SUM OF SQUARES     =  0.116E+05
CORRELATION COEFFICIENT     =  0.000E+00

DEGREES OF FREEDOM    =    47
NUMBER OF POINTS      =    57
NUMBER OF ITERATIONS  =     3

                          1          2          3          4          5          6          7          8          9         10
COEFFICIENTS = -0.452E+01 0.121E+00-0.557E-03 0.826E+01-0.213E+01 0.837E+01-0.125E+01-0.193E-03-0.183E+01-0.661E-01
STAND. DEV.  =  0.145E+01 0.850E-01 0.468E-03 0.524E+01 0.402E+00 0.167E+01 0.447E+00 0.537E-04 0.156E+01 0.360E-01

TOTAL SUM OF SQUARES        =  0.446E+03
RESIDUAL SUM OF SQUARES     =  0.440E+02
CORRELATION COEFFICIENT     =  0.901E+00

DEGREES OF FREEDOM    =    47
NUMBER OF POINTS      =    57
NUMBER OF ITERATIONS  =     4

                          1          2          3          4          5          6          7          8          9         10
COEFFICIENTS = -0.460E+01 0.122E+00-0.565E-03 0.836E+01-0.213E+01 0.838E+01-0.124E+01-0.194E-03-0.186E+01-0.668E-01
STAND. DEV.  =  0.318E+01 0.809E-01 0.335E-03 0.375E+01 0.287E+00 0.120E+01 0.319E+00 0.384E-04 0.111E+01 0.257E-01

TOTAL SUM OF SQUARES        =  0.446E+03
RESIDUAL SUM OF SQUARES     =  0.225E+02
CORRELATION COEFFICIENT     =  0.950E+00

DEGREES OF FREEDOM    =    47
NUMBER OF POINTS      =    57
NUMBER OF ITERATIONS  =     5

                          1          2          3          4          5          6          7          8          9         10
COEFFICIENTS = -0.460E+01 0.122E+00-0.565E-03 0.836E+01-0.213E+01 0.838E+01-0.124E+01-0.194E-03-0.186E+01-0.668E-01
STAND. DEV.  =  0.318E+01 0.808E-01 0.335E-03 0.375E+01 0.287E+00 0.120E+01 0.320E+00 0.384E-04 0.111E+01 0.257E-01

TOTAL SUM OF SQUARES        =  0.446E+03
RESIDUAL SUM OF SQUARES     =  0.225E-02
CORRELATION COEFFICIENT     =  0.950E+00

DEGREES OF FREEDOM    =    47
NUMBER OF POINTS      =    57
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 TOTAL SUM OF SQUARES     =  0.446E+03
 RESIDUAL SUM OF SQUARES  =  0.225E+02
 CORRELATION COEFFICIENT  =  0.950E+00

 DEGREES OF FREEDOM     =     47
 NUMBER OF POINTS       =     57
 NUMBER OF ITERATIONS   =      6

                         1          2          3          4          5          6          7          8          9         10
 COEFFICIENTS = -0.460E+01 0.122E+00-0.565E-03 0.836E+01-0.213E+01 0.838E+01-0.124E+01-0.194E-03-0.186E+01-0.668E-01
 STAND. DEV.  =  0.319E+01 0.608E-01 0.335E-03 0.375E+01 0.287E+00 0.120E+01 0.320E+00 0.384E-04 0.111E+01 0.257E-01

 TOTAL SUM OF SQUARES     =  0.446E+03
 RESIDUAL SUM OF SQUARES  =  0.225E+02
 CORRELATION COEFFICIENT  =  0.950E+00

 DEGREES OF FREEDOM     =     47
 NUMBER OF POINTS       =     57
 NUMBER OF ITERATIONS   =      7

                         1          2          3          4          5          6          7          8          9         10
 COEFFICIENTS = -0.460E+01 0.122E+00-0.565E-03 0.836E+01-0.213E+01 0.838E+01-0.124E+01-0.194E-03-0.186E+01-0.668E-01
 STAND. DEV.  =  0.220E+01 0.421E-01 0.232E-03 0.260E+01 0.198E+00 0.827E+00 0.221E+00 0.266E-04 0.770E+00 0.178E-01

 TOTAL SUM OF SQUARES     =  0.446E+03
 RESIDUAL SUM OF SQUARES  =  0.225E+02
 CORRELATION COEFFICIENT  =  0.950E+00

 DEGREES OF FREEDOM     =     47
 NUMBER OF POINTS       =     57
 NUMBER OF ITERATIONS   =      7
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SUGGESTIONS FOR FURTHER RESEARCH

Blowline bleaching has been thoroughly investigated on a pilot plant scale and, at this level, appears to be a feasible method of TMP bleaching.

The method needs to be extended to mill scale work. Further considerations must also be given to the individual optimization of alkalinity for the time and temperature available in mill refiners. In particular the possibility of high alkalinity, low retention time bleaching needs to be studied.

Second stage hydrosulphite bleaching following full scale blowline bleaching should be more fully investigated to better establish the practicality of such a system at the mill scale.

Whole chip chelation was found beneficial but the method was time consuming and expensive. A practical method for production applications should be developed.

Further work with the computer modelling would provide data that may help to determine if this type of empirical analysis actually applies to full scale conditions. It may also provide valuable insights into the kinetics of pulp bleaching.