Optimization of peroxide bleaching systems

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ABSTRACT *Process simulation was used to optimize peroxide bleaching systems including those with one and two stages with various recirculation strategies for bleaching mechanical pulps. When bleaching spruce to a high brightness of 80% ISO, savings of $6.50–7.00/o.d. metric ton of pulp can be made by installing a two-stage process compared to a one-stage process. All peroxide should be charged in the second stage, and peroxide filtrate is recycled to the first stage. Medium consistency in the first tower and high consistency in the second tower are recommended.*

KEYWORDS
Consistency
Bleaching
Process simulation
Pulping

In recent years, there has been an increasing interest in the use of mechanical pulps as a result of low investment and production costs. Chemically treated mechanical pulps (CTMP) and chemimechanical pulp (CMP) have been introduced into markets where previously only chemical pulps were used. CTMP has been found suitable for products such as fluff, tissue, paperboard, newsprint, and fine printing and writing papers.

Bleaching of these high-quality mechanical pulps to high brightness, over 80% ISO, is costly because of the high price of hydrogen peroxide. The bleach plant must be carefully designed to efficiently utilize the charged peroxide by recycling residual peroxide in a strategic fashion.

Using process simulation, we studied various bleaching systems, including one- and two-stage processes, with the results supported by laboratory and mill-scale data. The process simulation was performed on a personal computer using the general energy and materials balance system (GEMS) modular simulation software (*1*).

The optimization was carried out for Scandinavian spruce thermomechanical pulps (TMP), but it can be applied to any other wood species, if the kinetics and stoichiometry of the bleaching are known.

Mathematical models

Kinetics

The GEMS process simulation system we used includes a recently developed mathematical model for peroxide bleaching of mechanical pulps (*2*). The computer model is based on empirical kinetics developed by Moldenius (*3*):

$$dC_k/dt = k\,(H_2O_2)^{0.67}\,(OH^-)^{0.23}C_k^{2.2} \quad (1)$$

where

(H_2O_2) = $(H_2O_2) + (OOH^-)$
= sum of undissociated and dissociated peroxide, moles/L

(OH^-) = hydroxide ion concentration, moles/L

C_k = light absorption coefficient at 457 nm, m^2/kg

t = bleaching time, min

k = rate constant
= $A \times \exp(-E/RT)$

A = pre-exponential factor

E = activation energy, J/mole

R = gas constant, (J/mole)/K°

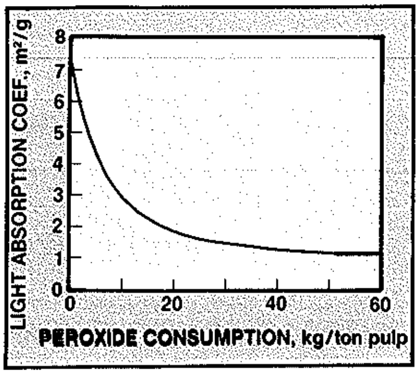
T = temperature, K°.

The computer model predicts brightness, residual peroxide, and alkali from the process variables: temperature, chemical charge, residence time in the tower, and pulp consistency during bleaching. Parameters in the model can be tuned to predict bleach response for different wood species with different bleachabilities.

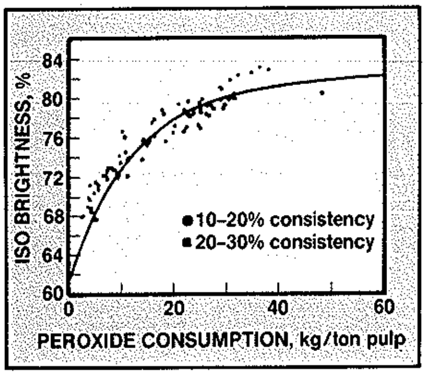
Stoichiometry

In addition to the kinetic relationship, the stoichiometry for the bleaching

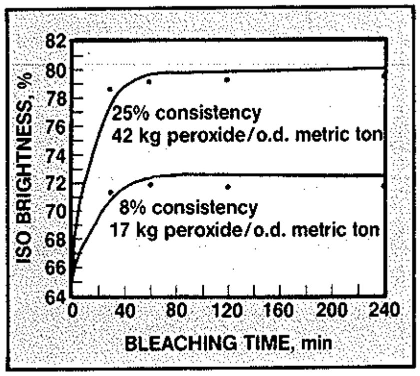
1. Bleaching stoichiometry: light absorption coefficient vs. peroxide consumption



2. Bleaching stoichiometry: model calculations for laboratory bleachings at optimum pH (about pH 11) and temperatures below 70°C



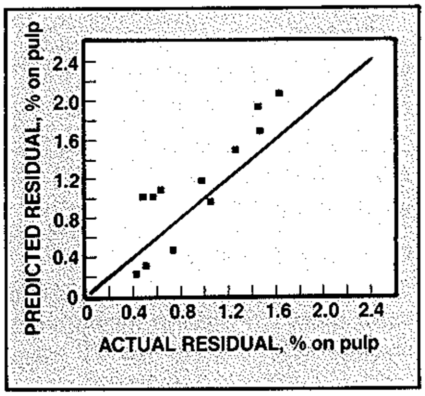
3. Model predictions, with the points showing laboratory data (65°C)



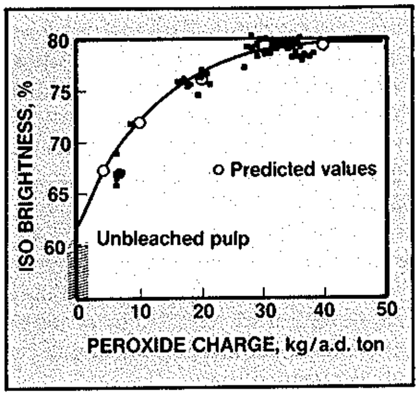
I. Laboratory bleaching trials at 65° and 80° C

Temp., °C	Brightness, % ISO	Peroxide consumption, kg/o.d. metric ton
65	75.8	18.4
80	75.0	20.4

4. Peroxide residuals, predicted vs. actual



5. Predicted vs. actual values of peroxide charge and brightness for the Ostrand mill



reaction must be known. The bleaching stoichiometry describes how much peroxide is consumed by the pulp to eliminate a certain amount of chromophores—or to reach a certain brightness.

Figure 1 shows the stoichiometric curve included in the computer model. Light absorption coefficient is predicted from the kinetic and stoichiometric relationships. Brightness is then calculated from the light absorption and light scattering coefficients using the Kubelka-Munch theory.

Figure 2 shows the stoichiometric relationship as brightness vs. consumed peroxide at a light scattering coefficient of 55 m^2/g. The curve represents the model, and the points are data from laboratory bleachings of Scandinavian spruce TMP. The laboratory bleachings are performed at temperatures below 70°C and at optimum pH. Peroxide charge is in the range 5-50 kg/o.d. metric tons of pulp. The pulps are thoroughly washed and chelated with DTPA prior to bleaching.

Figure 2 shows that the stoichiometry is independent of pulp consistency and peroxide charge. Stoichiometry has been shown to be independent of bleaching temperature up to 70°C (*4*).

Laboratory experiments with TMP show that a higher brightness can be reached when bleaching at 60-70°C compared to 80°C (**Table I**). Bleaching at 80°C also consumes more peroxide as a result of decomposition reactions.

Unfortunately, peroxide is not only consumed in reactions that eliminate chromophores. A number of factors promote side reactions, such as decomposition reactions and other peroxide-consuming reactions. Darkening reactions will also affect the peroxide consumption to a set brightness for a certain pulp. These factors are as follows:

1. Carry-over of organic substances from the refining stage to the bleach plant (*5*)
2. Increased peroxide decomposition due to catalysis by heavy metals (*5*)
3. Increased decomposition due to high temperature
4. Alkaline darkening caused by excess alkali charge.

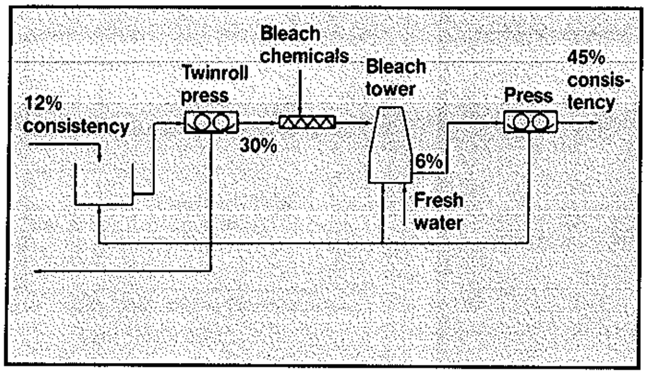
Bleaching at a lower pH than the optimum gives a more favorable stoichiometry (*4*) but results in a lower final brightness. Lachenal *et al.* have shown that pretreatment with chlorine will give a more favorable bleaching stoichiometry (*6*).

Model tuning and verification

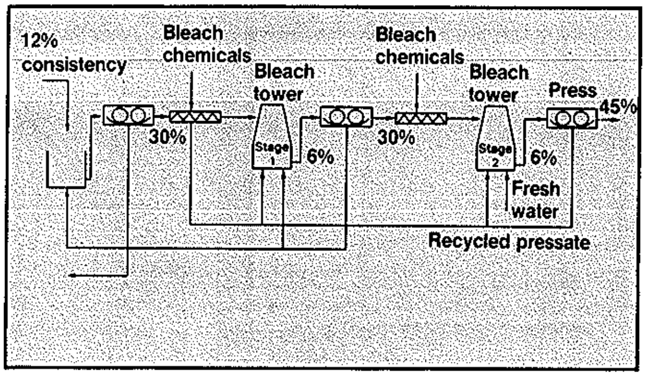
The first task was to tune the peroxide bleaching model to laboratory and mill data. **Figure 3** shows brightness vs. bleaching time for laboratory bleachings. The data points represent the laboratory data, while the curves represent model predictions at different bleaching conditions. The temperature was 65°C, and the alkalinity was at optimum pH at the start of the reaction.

Figure 4 shows peroxide residuals predicted by the model vs. residuals measured in laboratory experiments

6. One-stage bleaching process



7. Two-stage bleaching process



under various bleaching conditions.

Figure 5 shows process data for the SCA Ostrand mill. This mill is bleaching CTMP at medium consistency with thorough washing and recirculation of the peroxide pressate (*5*). Each point represents a daily average during two months of operation. The process was simulated at mill conditions, and the predicted brightness is represented by the circles in Fig. 5.

By using the proposed stoichiometric equation in the design of single- and multiple-stage bleach plants, we have assumed that:

1. The bleaching is performed at optimum pH and temperature to reach maximum brightness
2. The pulp is clean and well chelated
3. The amount of peroxide consumed to reach a set brightness is independent of whether the bleaching is performed in one or two stages.

Differences in peroxide charge to reach a certain brightness can therefore be referred to differences in the process and not to differences in the chemistry of the process.

The established model can now be used to predict brightness in more complex systems including two stages and various recirculation strategies. **Figures 6 and 7** show process flow diagrams for the one- and two-stage systems we compared in this study.

Optimization

The goal of this optimization is to minimize peroxide cost to reach a target brightness by finding optimum set points for the following variables:

1. Pulp consistency in Stage 1
2. Pulp consistency in Stage 2
3. Residence time in Stage 1 and Stage 2
4. Peroxide charge in Stage 1
5. Peroxide charge in Stage 2.

The alkalinity is assumed to be optimum (approx. pH 11), and the temperature is 65°C.

One-stage process

Common bleaching processes are high consistency (25–30%) or medium consistency (12–15%). In the MC case, peroxide pressate may be recycled as dilution water to the bleach tower to increase the concentration of peroxide in the tower. In both cases, the pulp is pressed to 30% consistency before the chemicals are added, to minimize carry-over of organic material from the refining stage. A pulp consistency of 30% into the bleach plant also makes it possible to recycle a large volume of peroxide-containing white water in the MC case. Recycling of peroxide filtrate is valuable, especially when the peroxide charge is high and the peroxide residuals are correspondingly high.

The chemicals are added in a medium- or high-consistency mixer before the pulp enters the bleach tower. In the bottom of the bleach tower, the pulp is diluted to 6% consistency with fresh water and recycled water and is pressed to 45% consistency before it leaves the bleach plant. A press with 45% consistency discharge is commonly used in systems where the pulp is flash dried after bleaching.

Two-stage process

The two-stage process is shown in Fig. 7. As in the one-stage system, the pulp is pressed to 30% consistency prior to bleaching. Bleaching chemicals can be charged in one or both stages, and the pulp consistency may be medium or high in both stages. After each stage, the pulp is diluted with peroxide pressate before pressing. Between the stages, the pulp is pressed to 30% consistency; after the second stage, it is pressed to 45% consistency, as in the one-stage system.

Fresh water is added in the bottom of the second tower to wash out extractives and other dissolved components. This rinsing decreases the amount of peroxide leaving with the pulp but also increases the volume of peroxide-containing white water in the bleach plant.

Results and discussion

In comparing the one-stage systems, we found that the high-consistency process requires a lower peroxide charge to reach 80% brightness. The computer model also indicated that the benefits of a high-consistency process increase with increasing brightness target.

Optimum conditions for a two-stage bleaching process

Here, we will consider the high-consistency process to be the optimum one-stage process.

With medium consistency (MC) in Stage 1 and high consistency (HC) in Stage 2, the simulation gave us a high concentration of bleaching chemicals at the end of the bleaching process, where the chromophores are most difficult to bleach. This process also gives us an opportunity to recycle

II. Composition of commercial papers

Process	Peroxide, kg/o.d. metric ton Stage 1	Stage 2	Brightness, % ISO
MC-HC	0	30	79.6
MC-HC	15	15	79.2
MC-MC	0	30	79.3
MC-MC	15	15	78.9
HC-HC	0	30	79.1
HC-HC	15	15	79.2

III. Prices of bleaching chemicals

Chemical	Price, $/kg	Charge, kg/o.d. metric ton
Hydrogen peroxide (100%)	0.95	. . .
Sodium hydroxide (100%)	0.15	25
Sodium silicate (54 Be)	0.15	35
Na_5-DTPA (39% active content)	0.95	3

IV. Chemical cost for one- and two-stage bleaching systems

Process	Consistency, %	Time, min	Peroxide charge, kg/ o.d. metric ton	Chemical cost, $/o.d. metric ton
One-stage MC	15	120	48	57.45
One-stage HC	25	120	40	49.85
Two-stage MC-HC	15-25	60-120	33	43.20

V. Bleaching conditions for laboratory trials

	One stage	Two stages Stage 1	Stage 2
Peroxide charge, kg/o.d. metric ton	42[a]	7[b]	35[b]
Initial pH	10.8	10.6	10.9
Temperature, °C	65	65	65
Pulp consistency, %	25	15	25

[a]This simulates a one-stage system with 40 kg/o.d. metric ton peroxide charge (2 kg/o.d. metric ton are recirculated).
[b]This simulates a two-stage system with 33 kg/o.d. metric ton peroxide charge, including recirculation.

peroxide residuals from Stage 2 to Stage 1, which would not be possible in a system with two high-consistency towers.

With all peroxide charged in Stage 2, residuals will be 25-50% of charged peroxide, and a considerable amount of peroxide can be recycled to Stage 1. This way of charging also results in a higher chemical concentration in the bleaching liquor and a stronger impetus for the bleaching reaction at the end of the bleaching. **Table II** compares final brightness for different ways of charging the peroxide in the two towers.

A higher brightness is reached when all peroxide is charged in the second tower for the MC-HC and MC-MC systems. Since no peroxide can be recycled in the HC-HC system, the same brightness is reached whether all peroxide is charged in Stage 2 or the peroxide charge is divided between the two stages.

Total residence time cannot be optimized, since this would result in unrealistically large bleach towers under the simulated conditions. However, the optimization tells us that the residence time in the towers should be ratioed to the actual chemical charge in the towers.

Economic comparison

We compared the economics of a high-consistency, one-stage process with the economics of the proposed two-stage process. Prices of bleaching chemicals used are listed in **Table III.** The prices are from the North American west coast in December 1986.

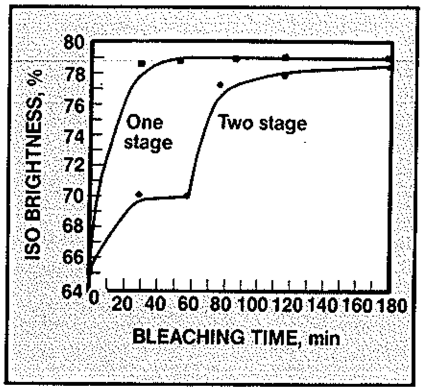
Table IV shows the chemical costs for the two processes when bleaching Scandinavian spruce TMP to 80% brightness. These calculations predict savings of approximately $6.65/o.d. metric ton of pulp in favor of the two-stage process. For a mill producing 300 o.d. metric tons/day, the savings in chemical cost will be $700,000/year.

The two-stage process will yield not only a brighter pulp but also a cleaner pulp. The pre-bleaching tower will act as a washing stage and will decrease extractives content and COD carry-over to the final bleaching stage.

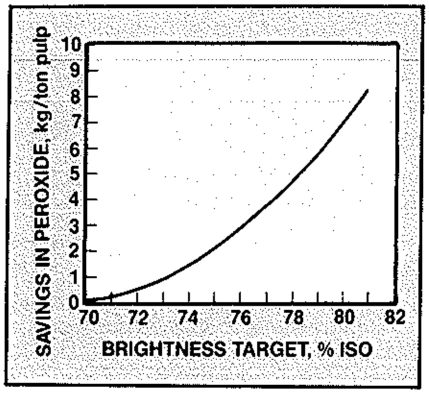
The results from the computer simulation of the one- and two-stage process were also checked in the laboratory. Pulps were bleached under the simulated conditions with peroxide charges estimated by the peroxide balance including recycled peroxide. The bleaching conditions for the laboratory trials are shown in **Table V.** The one-stage laboratory bleaching simulates a high-consistency, one-stage bleach plant with a peroxide charge of 40 kg peroxide /o.d. metric tons pulp, while the two-stage laboratory bleaching trial simulates a two-stage bleach plant where the actual peroxide charge is 33 kg/o.d. metric tons in the second bleaching tower. Brightness vs. bleaching time for the laboratory trials is shown in **Fig.** 8. Both trials give a final brightness of 79% ISO—that is, the trials confirm that savings of approximately $6.65/o.d. metric tons (7 kg peroxide/o.d. metric ton) can be had when bleaching to high brightness.

The peroxide savings for the two-stage system will decrease as the brightness target decreases. **Figure 9**

8. Model predictions and laboratory data points for both one- and two-stage bleaching to the same brightness



9. Savings in peroxide using two-stage bleaching as a function of target brightness



shows predicted savings in peroxide vs. target brightness, when the optimized two-stage system is compared to the best one-stage system. This curve shows that when bleaching to high brightness, a two-stage process should be chosen. When the brightness target is lower, a one-stage process may be sufficient. Peroxide residuals are reduced at lower peroxide charge, and little can be gained by recirculating peroxide.

The selection between a one- and a two-stage process should be based on the real savings, which are peroxide cost savings minus additional capital costs. The additional costs include the tower for pre-bleaching, the press, the pump, and the chemical mixer. However, these costs depend on several factors: interest rate, installed capacity, installation cost, etc. Each case must be considered individually.

Conclusions

When bleaching to high brightness (80% ISO), a two-stage process can save $6.50–7.00/o.d. metric ton of pulp over the best one-stage process.

The optimized two-stage bleaching system is a high-consistency process with pre-bleaching at medium consistency. All peroxide is charged in the second bleach tower and is recycled to the first tower.

When the brightness target is lower, 70–75% ISO, a one-stage process may be sufficient.

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