

Dynamic modeling of pressurized peroxide stages with application to full bleach plant simulation

BARRY MALMBERG AND LOU EDWARDS

ABSTRACT: The dynamic model of a pressurized peroxide stage described here predicts brightness progression and the consumption of bleaching chemicals against time. The paper outlines the mathematical components of the model, validates the model through available laboratory bleaching studies, and illustrates how mills might apply the model to optimize chemical charges to meet brightness targets.

Application: Mills can apply this model to help optimize chemical application to meet brightness and viscosity targets.

Environmental regulations concerning chlorinated phenolics and absorbable organic halides (AOX) discharge and environmental and economic pressure to reduce water usage have created a demand for alternative bleaching methods to traditional chlorine (C) and chlorine dioxide (D) bleaching.

Current U.S. Environmental Protection Agency (EPA) regulations have focused upon reducing chlorine-based pollutants in mill effluent streams, with more stringent regulations being proposed [1]. Strict environmental regulations in Europe have placed pressure upon mills to convert to totally chlorine free (TCF) bleaching sequences. Increased water recycling at kraft mills employing C/D bleaching sequences will increase the concentrations of chloride recycled to the kraft recovery area, which can pose significant kraft recovery boiler plugging risks and corrosion problems [2].

The most attractive bleaching and delignification option to C/D bleaching sequences is the use of hydrogen peroxide bleaching coupled with oxygen delignification. Conventional hydrogen peroxide bleaching of kraft pulp occurs in the temperature range of 80°C to 95°C. Pressurized hydrogen peroxide bleaching allows the bleaching reaction to occur at temperatures greater than

100°C, accelerating the chromophore removal reactions. The aim of this work is to develop a quantitative mathematical model for pressurized peroxide bleaching of kraft pulp for use in mill optimization and systems studies of pulp brightness, chemical consumption, and pulp strength. The mathematical model is integrated into a commercial process simulation program (WinGEMS) for complete bleach plant simulation. Comprehensive information of the model is detailed elsewhere [3].

MODEL

For our model, we assume that the overall peroxide dynamics are chemical reaction-limited and the system is locally homogenous. Experimental evidence indicates film diffusion of active bleaching chemicals to the fiber surface [4] and intrafiber mass transfer [5] are not limiting factors in the overall peroxide dynamics. We estimated ion diffusivity in the fiber wall from conductivity calculations for pulp suspensions and were able to predict equilibration times for ions between the bulk liquor and fiber wall within minutes [6]. This further indicates that diffusion of active bleaching chemicals to the fiber surface is not the limiting factor in overall peroxide bleaching rate.

Kinetics

The rate of bleaching in the first few minutes is very fast compared to later rates. Overall, different lignin fragments may be more easily brightened or removed than others, creating a spectrum of reaction rates. In previous modeling studies, researchers have used multiple, parallel kinetic expressions, dividing the bleaching progress into “fast” and “slow” reaction stages [7,8]. They have also resorted to a high order dependency in pulp lignin concentration in the kinetic expressions [8,9]. The arbitrary division between “fast” and “slow” stages creates extra model parameters to be fitted to experimental data, and still does not adequately represent the gradual transition between “fast” and “slow” reaction regimes.

The high order dependency in pulp species concentration limits applicability of a model to narrow regions within the parameterized data set. The current model uses a concentration-dependent rate constant to better represent the entire bleaching time course. This approach has been adopted earlier in comprehensive modeling of chlorine and chlorine dioxide bleaching [10] and has proven successful in representation of mill bleaching behavior [11]. The use of a concentration-dependent

BLEACHING

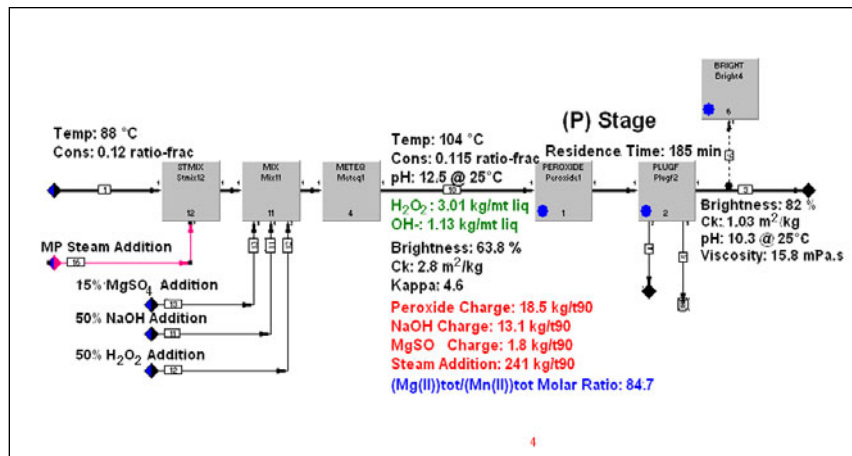
rate constant allows us to reproduce experimental results with a minimal number of parameters. It also allows us to use the same model over a wide range of incoming lignin concentrations, increasing its applicability.

Transition metals (particularly manganese, copper, and iron) catalytically decompose hydrogen peroxide in alkaline solution, leading to a reduction of overall efficiency for peroxide bleaching. The rate expressions proposed by Jakubíková et al. for the peroxide decomposition due to manganese and copper have been integrated into the model [12]. Iron is also an important transition metal for decomposition of hydrogen peroxide, but its catalytic effect is currently not included in the model.

The effect of iron on the decomposition of hydrogen peroxide is complicated due to the differences in decomposition effects between pulp-free systems and systems where pulp is present [13]. It has been concluded by the author (Malmberg) that base catalyzed decomposition of hydrogen peroxide does not contribute significantly to the overall peroxide decomposition in peroxide bleaching of kraft pulps [3]. The primary contributors to peroxide consumption in pulp bleaching systems are reactions with the pulp and catalytic decomposition due to transition metals.

The effect of oxygen concentration is neglected because its effect is small. Koukkari [14] and Stevens [4] studied pressurizing the reaction vessel with nitrogen versus oxygen. They found no significant difference in reaction kinetics between the two pressurizing gases. The primary influence of increased oxygen pressure is to enable higher reaction temperature, which has a marked influence upon the rate of the brightening reaction.

The system is assumed to be a pseudo-homogenous system, with chemical reactions at the fiber-liquor interface being the rate-limiting step. We used a fifth and sixth order Runge-Kutta-Verner method (DIVPRK subroutine in the IMSL libraries) [15] to solve the set of or-



1. WinGEMS schematic of the dynamic pressurized peroxide model.

dinary differential equations. The model is fully integrated in the commercial process simulation program, WinGEMS.

Equilibrium

The primary bleaching agent in peroxide bleaching is the perhydroxyl anion (HO₂) [16,17]. Other agents, such as free radicals and nascent oxygen, have also been proposed as possible bleaching agents, but are not likely to be the dominant bleaching compound [18]. The pK_b of the peroxide disassociation reaction is 1.5 [19] at 100 °C (pK_w = 12.0 @ 100 °C), so strongly alkaline conditions are required for effective use of hydrogen peroxide in bleaching applications. The peroxide disassociation equilibrium is necessary to determine the amount of perhydroxyl anions available for bleaching and for its role in base-catalyzed and transition metal-induced peroxide decomposition. Teder and Tormund determined the value of K_b as a function of temperature and ionic strength. We extrapolated their results [19] for use in the current model. The effect of ionic strength on the bleaching system can be accounted for exclusively through the change in K_b [20].

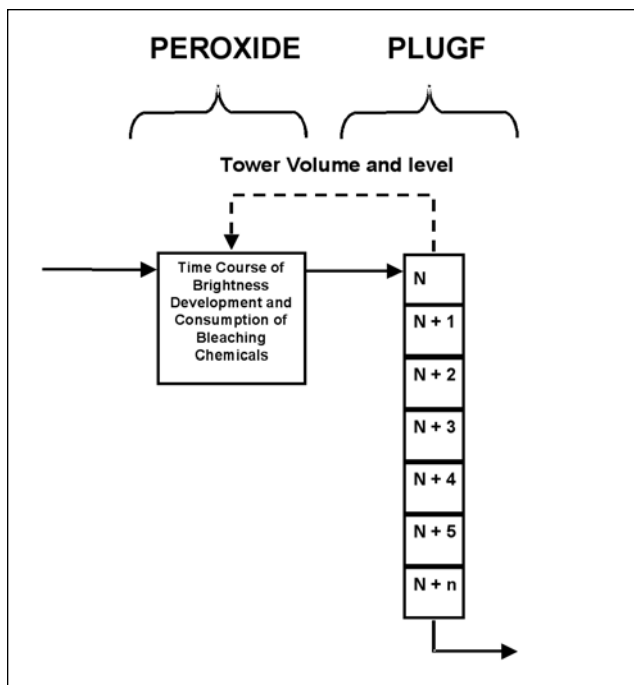
Magnesium-manganese ratio

In the presence of pulp or anionic polymer, magnesium can co-precipitate (as a solid solution) with catalytically active transition metals such as manganese and iron, preventing these metals from catalytically decomposing hydrogen

peroxide [21,22]. Lidén and Öhman used the solid solution concept to provide a unified theory for explaining the protective role of magnesium and silicate during peroxide bleaching [22].

Brown and Abbot studied the influence of magnesium on manganese-induced peroxide decomposition in the presence and absence of chelated thermomechanical pulp (TMP) [23]. The addition of magnesium sulfate (MgSO₄) accelerated the peroxide decomposition reaction in the absence of pulp fibers. The rate of decomposition was suppressed in the system containing pulp. These results support the theory that magnesium forms co-precipitates with manganese and iron when anionic functional groups are present. It offers a thermodynamic explanation for the effectiveness of the empirical Mg:Mn ratio of 30 used in bleaching conditions. It also explains why magnesium is not effective in protecting against copper-catalyzed peroxide decomposition [24] and helps explain various other mill observations.

Studies of solid solution formation of Mn_(x)Mg_(1-x)(OH)₂(s) [25] and surface precipitation of magnesium carbonate (MgCO₃[s]) and manganese carbonate (MnCO₃[s]) [26] in alkaline aqueous solution at conditions relevant to the bleach plant used a SOLGASWATER-based model [27] for the thermodynamic analyses. We integrated thermodynamic data presented by Wiklund et



2. Schematic of kinetic and hydrodynamic model.

al. [25,26] for the hydroxide and carbonate species into a comprehensive thermodynamic model for metals distributions in bleach plants [3,28], to calculate the free concentration of Mn(II) in bleach plant liquors. The WinGEMS module, MetEQ, calculates the equilibrium composition of a multicomponent, multiphase aqueous system. It is based on the Gibbs free energy minimization program SOLGASWATER [27]. The free Mn(II) concentration is used as an input into the peroxide decomposition model due to the catalytic action of manganese. **Figure 1** shows the WinGEMS schematic of the peroxide bleaching system.

Hydrodynamics

The plug flow approximation is used to represent tower hydrodynamics. Even though this is not strictly the case, a plug flow representation is adequate for mill decision and scheduling applications and is satisfactory for high-consistency towers. The density of the fiber-liquor solution is assumed to be constant throughout the tower. The pulp and liquor are assumed to have the same residence time; i.e. channeling does not exist. The tower is assumed to be isothermal; i.e. no heat is lost and the heat generated from the bleaching reactions is negligible, though the structure is in place within the model code to add these additional terms.

Analysis of available tracer data in the literature show that bleach towers operating at 10% or greater consistency will exhibit at least 90% plug flow behavior [29]. Our analysis done with the dispersed plug flow model showed negligible differences in light absorption coefficient decrease and hydrogen peroxide consumption compared to the plug flow case.

Combined kinetic-hydrodynamic model

We combined the kinetic model with the hydrodynamic plug flow model for complete dynamic representation of a pressurized peroxide stage. The kinetic model (peroxide) receives the tower volume and operating level from the plug flow module and calculates end-points that are sent to the plug flow module. The plug flow module (PLUGF) calculates the delay associated with the tower residence time. Schematically, this is shown in **Fig. 2**. With this approach, the modular nature of WinGEMS is maintained and a complete peroxide tower module can be constructed by implementing compound blocks.

Model parameterization

Stevens' [4] experimental data were the primary source for parameter optimization. In a series of experiments, light absorption data were measured as a function of initial hydrogen peroxide concentration, initial pH, and temperature. Simultaneous optimization of equation parameters with experimental data as a function of peroxide concentration

Initial		At Equilibrium		pH	
[NaOH]	[H ₂ O ₂]	[OH ⁻]	[HO ₂ ⁻]	@ 25°C	@ 90°C
0.057	0.1	0.018	0.04	12.25	10.5
0.037	0.05	0.018	0.02	12.25	10.5

I. A solution with the same initial pH, but with different perhydroxyl anion concentrations.

Initial		At Equilibrium		pH	
[NaOH]	[H ₂ O ₂]	[OH ⁻]	[HO ₂ ⁻]	@ 25°C	@ 90°C
0.057	0.1	0.018	0.04	12.25	10.5
0.069	0.075	0.030	0.04	12.47	10.72

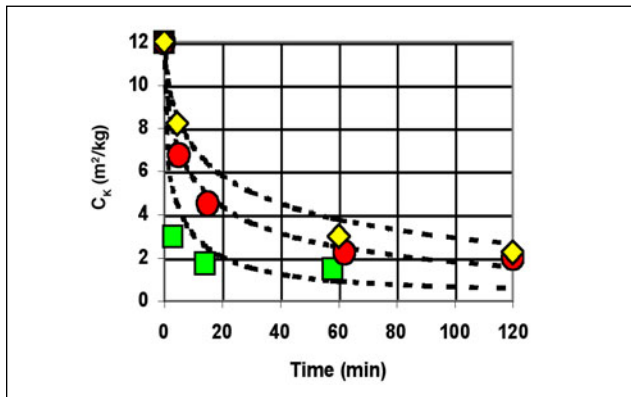
II. A solution with the different initial pH, but with the same perhydroxyl anion concentrations.

and pH is required because different combinations of sodium hydroxide and hydrogen peroxide can produce the same amount of perhydroxyl anion. **Table I** demonstrates one case where two solutions that produce the same equilibrium pH have a two-fold difference in perhydroxyl concentration. **Table II** demonstrates a case where two solutions have the same concentration of perhydroxyl anions and have different starting conditions and a different equilibrium pH.

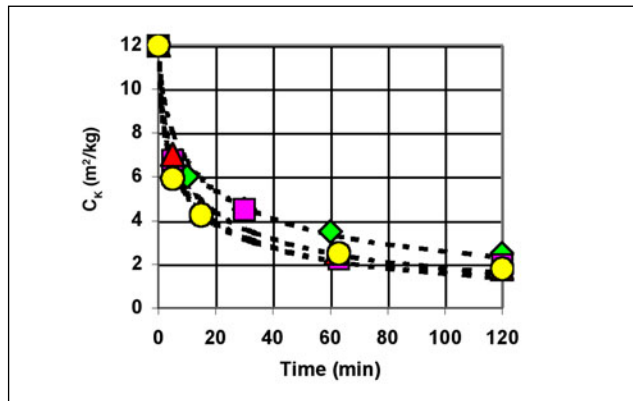
MODEL VALIDATION WITH LABORATORY RESULTS

We parameterized the current model with laboratory data from three types of pulps: white pine [4], birch [32], and eucalyptus [34]. Minimal model tuning is required to predict the time-dependent behavior between the various pulp types.

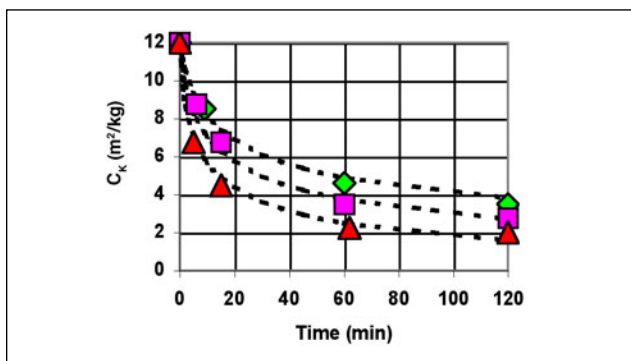
BLEACHING



3. Effect of temperature upon the reduction of light absorption coefficient at 457 nm, initial $[H_2O_2]_T = 0.098$ mol/L, initial pH of 10.5 at T, diamonds = T of 80°C, circles = T of 90°C, squares = T of 110°C.



4. Effect of initial pH upon the reduction of light absorption coefficient at 457 nm, initial $[H_2O_2]_T = 0.098$ mol/L, T = 90°C, diamonds = initial pH of 10.0 at T, squares = initial pH of 10.5 at T, triangles = initial pH of 11.0 at T, circles = initial pH of 11.5 at T.

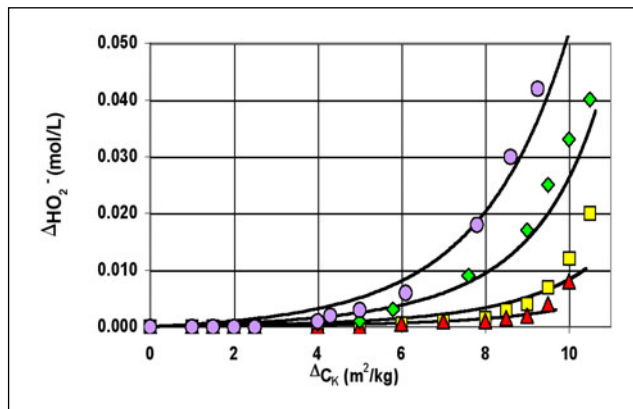


5. Effect of initial hydrogen peroxide concentration upon the reduction of light absorption coefficient at 457 nm, initial pH = 10.5 at 90°C, T = 90°C, diamonds = initial $[H_2O_2]_T$ of 0.0163 mol/L, squares = initial $[H_2O_2]_T$ of 0.033 mol/L, triangles = initial $[H_2O_2]_T$ of 0.098 mol/L.

White Pine

Figures 3-5 present results showing the reduction of light absorption coefficient vs. time as a function of initial hydrogen peroxide concentration, initial pH, and temperature respectively. All lines are model predictions and all symbols are experimental data from the peroxide bleaching of oxygen delignified kraft pine pulp from Stevens [4]. Reported initial pulp conditions were kappa number = 13.3, lignin content = 0.02 g lignin/g pulp, brightness = 37.4%, and CED viscosity = 22.8 cP.

Historically, kinetic studies have focused upon brightening kinetics while using an algebraic relationship to calculate the reaction stoichiometry. Limitations of using an algebraic stoichiometric relationship to predict consumption of bleaching chemicals are that all effects consuming peroxide are lumped together, preventing isolation and elucidation of bleaching and decomposition effects. Separation of peroxide consumption due to base-catalyzed peroxide decomposition



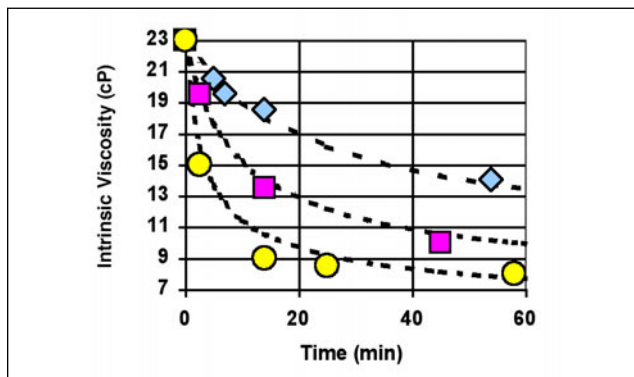
6. Stoichiometry of hydrogen peroxide bleaching, T = 90°C, triangles = initial pH of 10.0 at T, squares = initial pH of 10.5 at T, diamonds = initial pH of 11.0 at T, circles = initial pH of 11.5 at T.

and bleaching allows other decomposition effects such as peroxide decomposition due to transition metals to logically be incorporated into the model structure.

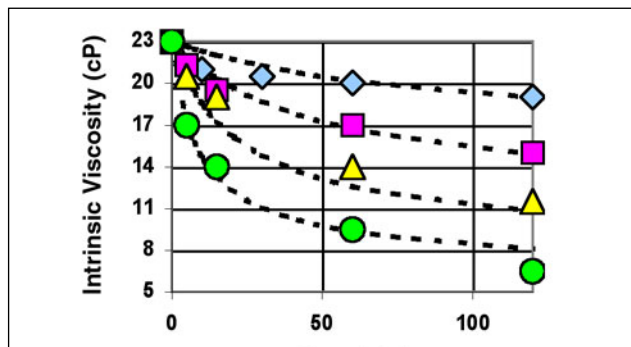
The reaction stoichiometry can be calculated by summing all kinetic expressions for the consumption of peroxide:

- base-catalyzed peroxide decomposition,
- peroxide consumption reactions with pulp,
- copper induced peroxide decomposition, and
- manganese-induced peroxide decomposition.

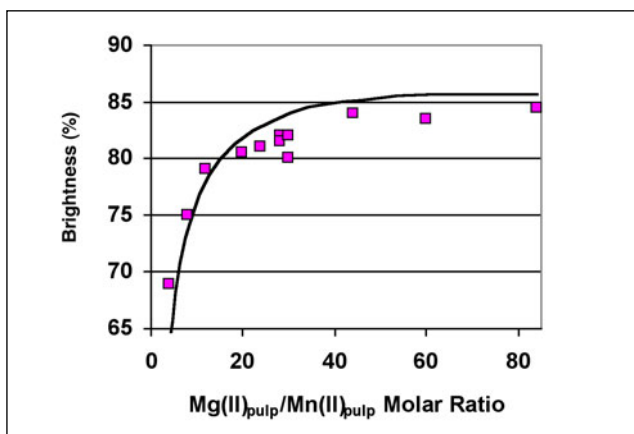
The results are compared to the traditional presentation of chemical consumption versus change in chromophore removal (**Fig. 6**). We analyzed available rate data for base catalyzed decomposition of hydrogen peroxide and determined that homogeneous catalysis most likely contributed significantly to the attributed base-catalyzed decomposition rates reported by Stevens [4]. By assuming that the sodium hydroxide is contaminated with a small concentration of manganese



7. Effect of initial pH upon pulp strength, 0.098 mol/L $[H_2O_2]$, 110°C, initial kappa = 13; dotted lines are model results, diamonds = pH, 10.0, squares = pH, 10.5, triangles = pH, 11.0, circles = pH, 11.5.



8. Effect of initial pH upon pulp strength, 0.098 mol/L $[H_2O_2]$, 90°C, initial kappa = 13; dotted lines are model results, diamonds = pH, 10.0, squares = pH, 10.5, triangles = pH, 11.0, circles = pH, 11.5.



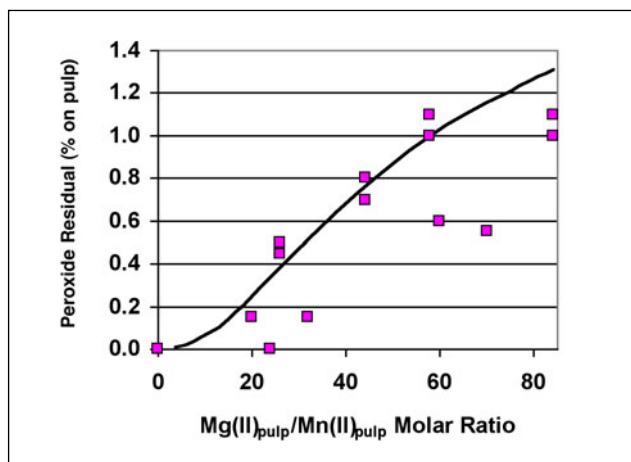
9. Effect of Mg:Mn molar ratio on final brightness for a PO stage; squares = experimental results from Lindeberg [32], solid line = model results.

(3×10^5 mol%), we were able to closely reproduce Stevens' stoichiometric data (Fig. 6).

Carbohydrate degradation for white pine

Hydroxide, hydrogen peroxide, and decomposition products can react with cellulose, resulting in loss of pulp strength, an important output pulp parameter. A zero order dependence in cellulose for the degradation reaction has been previously reported in studies of oxygen delignification [30, 31]. The number of carbohydrate bonds are essentially unchanged during the progression of the bleaching reaction so the zero order dependence with respect to the concentration of cellulose chain units is expected.

Olm and Teder [30] studied the kinetics of oxygen delignification and found that carbohydrate degradation behaves much like delignification, i.e. a transition from a rapid reaction rate during the first few minutes to a slower rate as the reaction proceeds and noted that the transition occurred simultaneously for the carbohydrate and lignin reactions. **Figures 7 and 8** com-



10. Effect of Mg:Mn molar ratio on final peroxide residual for a PO stage; squares = experimental results from Lindeberg [32], solid line = model results.

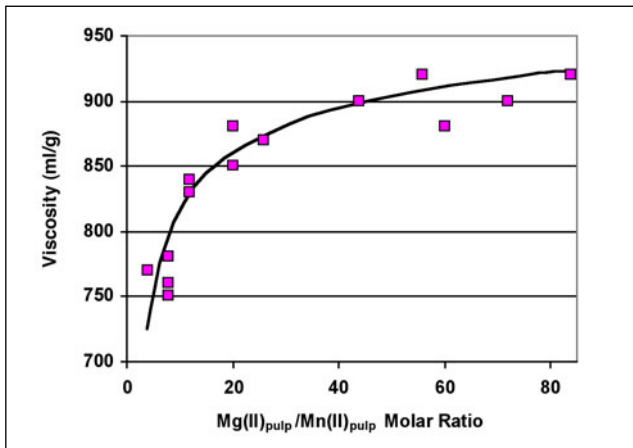
pare model results with experimental results from Stevens [4]. The selectivity of peroxide bleaching can be quantified as the ratio between the brightening rate and carbohydrate degradation rate, providing a useful optimization parameter.

Birch

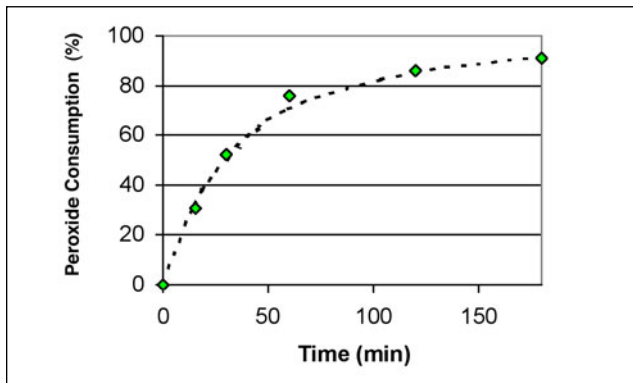
Lindeberg studied the effect of varying the Mg/Mn molar ratio on the bleaching response of birch [32]. **Figures 9-11** compare experimental results to model predictions. The following process conditions are valid for Figs. 9-11: temperature = 90°C, consistency = 10%, retention time = 240 min, hydrogen peroxide charge 25 kg/ton pulp, sodium hydroxide charge 16 kg/ton pulp, initial brightness, 51.6% ISO, and initial viscosity 976 mL/g.

The likely chemical species for carbohydrate degradation are hydroxyl and oxyl radicals [33]. Gierer et. al proposed a superoxide-driven Fenton mechanism for the generation of hydroxyl radicals under conditions prevalent in peroxide bleaching [33]. From the proposed mechanism, the hydroxyl

BLEACHING



11. Effect of Mg:Mn molar ratio on final pulp viscosity for a PO stage; squares = experimental results from Lindeberg [32], solid line = model results.

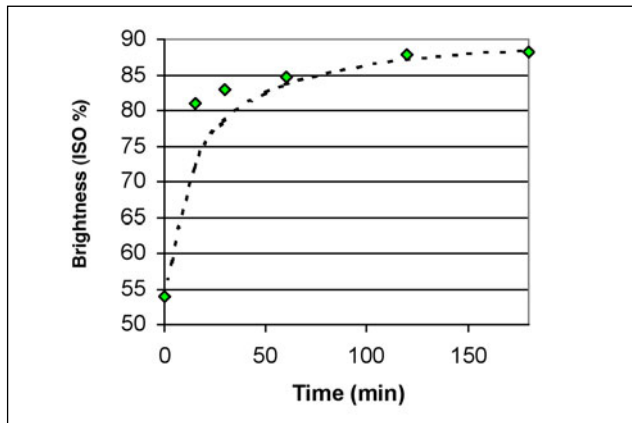


13. Peroxide consumption vs. time for the pressurized peroxide bleaching of eucalyptus; diamonds = experimental results from Barna et al. [34], dotted line = model results.

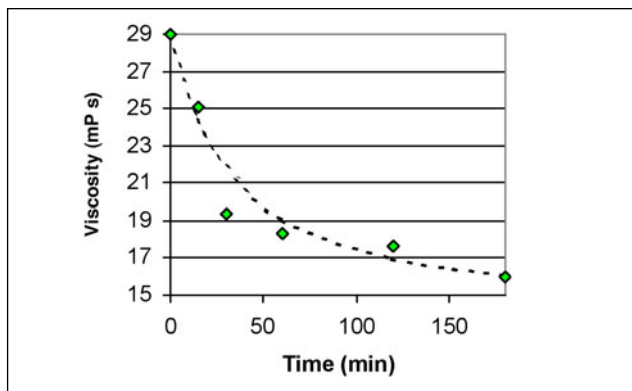
generation rate should be dependent upon the free concentration of transition metal involved in the catalytic Fenton reaction, which is clearly shown in Fig. 11. The results show that the equilibrium magnesium/manganese solid solution model coupled with a kinetic expression for the manganese induced catalytic decomposition of hydrogen peroxide can effectively predict the effect of Mg(II)/Mn(II) molar ratio upon the final brightness, peroxide residual, and viscosity loss.

Eucalyptus

Barna et al. examined the bleachability of eucalyptus with pressurized peroxide bleaching [34]. Industrial eucalyptus kraft oxygen delignified pulp was used and the reactor conditions are: 10% consistency; temperature = 110°C; reactor pressure = 500 kPa; 2.5% H₂O₂, 1.5% NaOH, and 0.05% Mg. **Figures 12-14** compare experimental results to model predictions for brightness gain, peroxide consumption, and strength loss, respectively. The dynamic response of bright-



12. Brightness progression vs. time for the pressurized peroxide bleaching of eucalyptus; diamonds = experimental results from Barna et al. [34], dotted line = model results.



14. Strength loss vs. time for the pressurized peroxide bleaching of eucalyptus; diamonds = experimental results from Barna et al. [34], dotted line = model results.

ness progression, peroxide consumption, and strength loss are well predicted by the model.

MILL RESULTS

The model has been applied to data from a North American totally chlorine free (TCF) mill with a bleaching sequence of QEopP₁P₂(P). The mill bleaches a mixture of redwood, spruce, and Douglas fir. Real-time operating data were used to calculate optimized chemical charges to the pressurized peroxide stage to produce a target product brightness.

Mill data pretreatment

A standard exponential filter is applied to the input brightness measurements to attenuate the noisy signal, **Equation (1)** (symbols are defined in the nomenclature section). Application of Equation (1) to the incoming brightness and light absorption coefficient of the pressurized peroxide tower is shown in **Fig. 15**. Conversion between light absorption co-

Manipulated Variables	Constraints		
H ₂ O ₂ charge (kg/ton ₉₀) ¹	≤	50	≥ 5
NaOH charge (kg/ton ₉₀) ²	≤	50	≥ 5
MgSO ₄ charge (kg/ton ₉₀)	≤	12	≥ 0
Temperature (°C)	≤	80	≥ 120

¹Based upon kg of actual peroxide, 50% peroxide solution is applied.

²Based upon kg of actual alkali, 50% solution of sodium hydroxide is applied.

III. Manipulated variables and constraints.

Costs	\$/kg
H ₂ O ₂	1.01
NaOH	0.35
MgSO ₄	0.53
MP Steam ¹	0.0065
Credits	
H ₂ O ₂ Residual	1.01

¹Medium pressure saturated steam, 1135 kPa, 185.5°C.

IV. Chemical costs used in the optimization.

	\$/day	%Change relative to TCF Mill Data
TCF Mill Data	7364	—
83.5 % ISO Target Brightness	7908	6.9 %
83.0 % ISO Target Brightness	7431	0.9 %

V. Case cost index.

efficient (used in the kinetic model) and brightness values is achieved via a modified Kubelka-Munk equation [3].

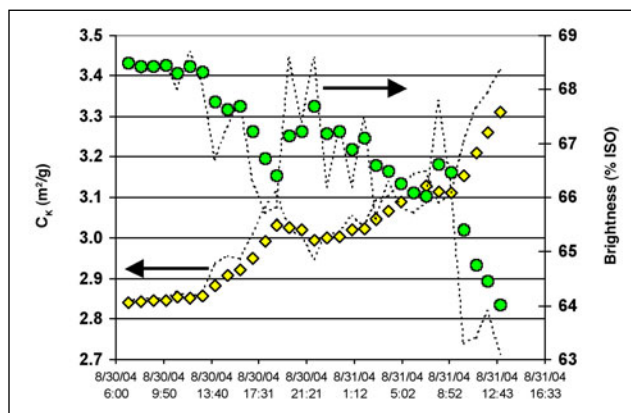
$$Y_n = aY_{n-1} + (1 - a)X_n$$

Equation (1)

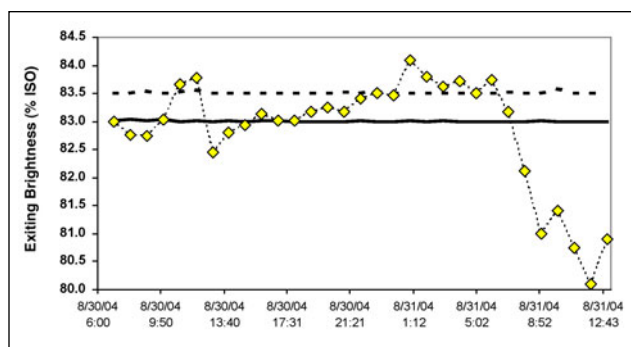
From the filtered results, the incoming brightness steadily decreases (Fig. 15), eventually causing a decrease in exit brightness. Manipulating the control variables can compensate for the lower incoming brightness.

Chemical charge optimization

WinGEMS versions 5.0 and greater have a model optimization toolkit that employs the standard solver module within Excel. Manipulated variables (**Table III**) are optimized to achieve a user-defined brightness target, subject to a cost function. In this case, strength targets are not included in the optimization because the mill produces bleached market pulp for tissue and strength properties are not critical. Chemical costs used in the optimization are given in **Table IV**. Full credit is given in the optimization for peroxide residual because it is recycled to the P₁ stage. Oxygen is not included in



15. Effect of input signal filtering (using $t_f = 2$); dotted lines = original input data, circles = filtered brightness values, diamonds = filtered light absorption coefficient values.



16. Exiting brightness vs. time; diamonds = filtered TCF mill data, thick solid line = target brightness of 83.0% ISO (optimized), thick dotted line = target brightness of 83.5% ISO (optimized).

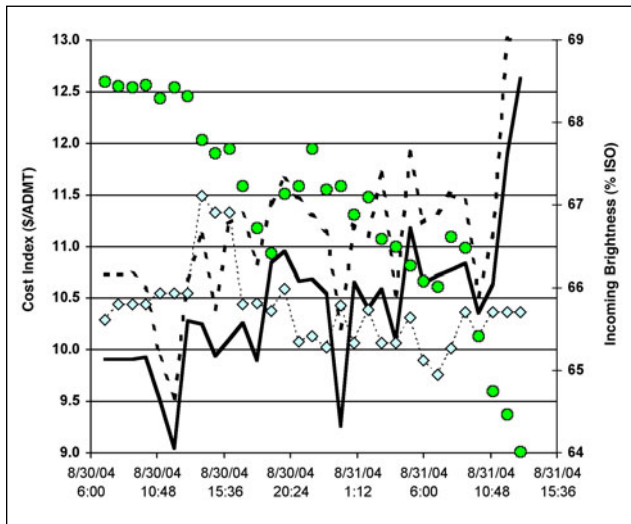
the cost function because of its low cost.

Optimized model results for two target brightness settings (83.0% ISO and 83.5% ISO) were calculated and compared to TCF mill data for a 28-hour time frame (8/30/04, 7:00 a.m. - 8/31/04, 11:00 a.m.). The mill usually tries to produce 83.0% ISO brightness product. **Figure 16** displays the output brightness results for the three cases. The decrease in incoming brightness shown in Fig. 15 eventually causes the degradation in exiting brightness shown in Fig. 16.

Table V shows a chemical cost index for the three cases. The model results have a slightly higher cost index than the TCF run because the exiting brightness is maintained at a target brightness vs. the degradation in brightness in the TCF case (Fig. 16).

The incoming brightness produces the majority of variability in exiting brightness. In the TCF run, degradation in incoming brightness eventually caused the lowered exiting brightness because chemical charges did not increase accordingly. The optimization model calculates optimal chemical charges at each time step to maintain a target brightness.

BLEACHING



17. The effect of incoming brightness on the chemical charge cost index; circles = filtered incoming brightness, diamonds = TCF mill chemical charge data, thick solid line = model results, target brightness 83.0% ISO, thick dotted line = model results target brightness 83.5% ISO.

cal charges at each time step to maintain a target brightness. Variability in production rate, incoming brightness, stock temperature, and peroxide and alkali residual entering the pressurized peroxide tower are considered in the optimization. **Figure 17** shows the cost index versus time for the three cases. In the optimization cases, the cost index increases over time because the increase chemical charges are compensating for the decreasing incoming brightness.

CONCLUSIONS

We created a mathematical model for the dynamic behavior of pressurized peroxide bleaching of kraft pulp. The mathematical model can be used to test different control strategies and can be used by mills for scheduling. The model can be applied online to reduce product variability, maintain quality parameters, and minimize chemical costs given a target brightness. **TJ**

NOMENCLATURE

Symbol	Description	Units
C_K	Light absorption coefficient at 457 nm	m^2/kg
$C_{K_{00}}$	Floor level light absorption coefficient at 457 nm	m^2/kg
C_{K_0}	Initial light absorption coefficient at 457 nm	m^2/kg
$k_{0,x}$	Frequency factor for reaction x	
E_{Ax}	Activation energy for reaction x	kJ/mol
$[HO_2^-]$	Perhydroxyl anion	mol/l
b	Structural constant	mol/l
K_C	Reaction intermediate equilibrium constant	
t	Time	min
R	Molar gas constant, 8.314 472 [35]	$J \cdot mol^{-1} \cdot K^{-1}$

B	Brightness	% ISO
a	$\hat{O}_F / (\hat{O}_F + T)$	unit-less
$\hat{O}_F$	Filter time constant	hours
T	Discrete time step	hours
X_n	Noisy input at time step n	hours
Y_n	Filtered output at time step n	hours
Y_{n-1}	Filtered output at time step $n-1$	hours

ACKNOWLEDGEMENTS

A portion of this work was funded by MISTRA, the Swedish "Foundation for Strategic Environmental Research" as part of the "Ecocyclic Pulp Mill" research program. The authors would like to acknowledge Stockton Pacific for use of their mill results.

Submitted: February 14, 2005

Revised: March 2, 2006

Accepted: March 3, 2006

LITERATURE CITED

1. U.S. Environmental Protection Agency, 40 CFR parts 63 and 430, "National Emission Standards for Hazardous Air Pollutants for Source Category: Pulp and Paper Production; Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards: Pulp, Paper, and Paperboard Category; Correction," *Federal Register* 42238-42240, August 7, 1998.
2. Backman, R., Hupa, M., and Uppstu, E., *Tappi J.* 70(6): 123(1987).
3. Malmberg, B., "Development and application of general process simulation tools within the pulp and paper industry," Ph.D. dissertation, University of Idaho, Moscow, Idaho, USA, 2005.
4. Stevens, J.A., "Fundamental aspects of hydrogen peroxide bleaching of kraft pulp in ECF and TCF bleaching sequences," Ph.D. thesis, Georgia Institute of Technology, Atlanta, Georgia, USA, 1998.
5. Hsu, J., "Mass transfer and kinetics in oxygen delignification of wood pulp," Ph.D. thesis, Georgia Institute of Technology, Atlanta, 1988.
6. Been, J., and Oloman, C., *J. Pulp Paper Sci.* 21(3): J80(1995).
7. Teder, A. and Tormund, A., *AIChE Symposium Series* 76(200): 133(1980).
8. Hsu, C. and Hsieh, J., *AIChE J.* 34(1): 116(1988).
9. Axegård, P., Moldenius, S., and Olm, L., *Svensk Papperstid.* 82(5): 131(1979).
10. Gu, Y. and Edwards, L., *TAPPI J.* 2(7): 3(2003).
11. Gu, Y. and Edwards, L., *TAPPI J.* 2(6): 19(2003).
12. Jakubíková A., D'Aveni, A., Coupeau, S., et al., *Cell. Chem. Tech.* 34(3-4): 341(2000).
13. Brown, D. and Abbot, J., *J. Wood Chem. Tech.* 15(1): 85(1995).
14. Koukari, P. and Salminen, J., *J. Pulp Paper Sci.* 26(12): 441(2000).
15. IMSL software libraries, Visual Numerics, Inc., Houston, Texas, USA, 1997.
16. Gellerstedt, G. and Agnemo, R., The reactions of lignin with alkaline hydrogen peroxide, part III, the oxidation of conjugated carbonyl structures, *Acta Chem. Scand.* B34: 275(1980).
17. Spiro, M. and Griffith, W., *Textile Chem. Color.* 29(11): 12(1997).
18. Hobbs, G. and Abbot, J., *J. Wood Chem. Tech.* 14(2): 195(1994).
19. Teder, A. and Tormund, D., The equilibrium between hydrogen peroxide and the peroxide ion – a matter of importance in peroxide bleaching, *Svensk Papperstid.* 83(4): 106(1980).
20. Moldenius, S. and Sjögren, B., *J. Wood Chem. Tech.* 2(4): 447(1982).
21. Lidén, J., Wiklund L., and Öhman, L.-O., *SPCI 2002 Conference Proceedings*, Stockholm, Sweden, pp. 193-196.

BLEACHING

22. Lidén, J. and Öhman, L.-O., *J. Pulp Paper Sci.* 24: 269(1998).
23. Brown, D. and Abbot, J., *J. Wood Chem. Tech.* 15(1): 85(1995).
24. Lidén, J. and Öhman, L.O., *J. Pulp Paper Sci.* 23(5): J193(1997).
25. Wiklund, L., Öhman, L., and Lidén, J., *Nordic Pulp Paper Res. J.* 16(3): 240(2001).
26. Wiklund, L., Öhman, L., and Lidén, J., *Nordic Pulp Paper Res. J.* 16(4): 339(2001).
27. Eriksson, G., *Analytica Chimica Acta*, 112: 375(1979).
28. Gu, Y., Malmberg, B., and Edwards, L., *TAPPI J.* 3(1): 26(2004).
29. Wang, R., Tessier, P., and Bennington, C., *AIChE Journal*, 41(12): 2603(1995).
30. Olm, L. and Teder, A., *Tappi*, 62(12): 43(1979).
31. Germgård, U., Teder, A., and Tormund, D., *Proceedings of the 1985 TAPPI Pulping Conference*, TAPPI PRESS, Atlanta, Georgia, USA, pp. 529-536.
32. Lindeberg, O., Improvement of the chelating stage in a TCF sequence when closing up the bleach plant, Proceedings of the 1994 International Pulp Bleaching Conference, [Add publisher (CPPA or TAPPI?) and city/location of publisher; then delete paper title] pp. 21-28, 1994.
33. Gierer, J., Reitberger, T., Yang, E., et al., *J. Wood Chem. Tech.* 21(4): 313(2001).
34. Barna, J., Colodette, J., Salvador, E., et al., *Proceedings of the 1996 TAPPI Pulping Conference*, TAPPI PRESS, Atlanta, pp. 949-956.
35. Mohr, P. and Taylor, B., CODATA Recommended Values of the Fundamental Physical Constants: 1998, National Institute of Standards and Technology, Gaithersburg, MD, 1998.

INSIGHTS FROM THE AUTHORS

Pressurized peroxide bleaching is an attractive TCF bleaching method that will likely gain more prominence in the future. Models for pressurized peroxide bleaching can help mills optimize the bleaching performance of this process.

Our work synthesizes a number of ideas from previous researchers for bleach stage modeling for complete bleach stage representation. The most difficult aspect of this re-



Malmberg



Edwards

search was the general lack of complete, well-controlled pressurized peroxide bleaching studies in the literature that could be used for model validation. The most interesting aspect of the work was applying the model in the mill setting. Based on our work, we believe mills can apply this model to help optimize chemical application to meet brightness and viscosity targets. This model should be applied at other mills using pressurized peroxide bleaching for optimization purposes.

Malmberg and Edwards conducted this research at the University of Idaho, Department of Chemical Engineering, Moscow, Idaho, USA. Malmberg now works at NCASI as a senior research engineer; email Edwards at jkidd@uidaho.edu; email Malmberg at BMalmberg@wcr-ncasi.org.

rheology

pigments

coating

additives

2007 TAPPI Coating and Graphic Arts Conference

April 22-25, 2007 • Hyatt Regency Miami
Miami, Florida

This year's TAPPI Coating Conference is a dedicated, standalone focusing on overcoming the challenges and providing practical solutions for professionals in coating, printing, and graphic arts fields.

The 2007 Coating and Graphic Arts Conference features:

- » A superb, peer-reviewed technical program
- » Concentrated tutorials on additives and rheology
- » A state-of-the-industry presentation from Pöyry
- » An Exhibit and Supplier Showcase highlighting the newest technologies, products, and services
- » An extraordinary opportunity for learning and networking with peers and suppliers

Course participants are invited to attend the Conference Welcome and Keynote, Exhibit, and CIG Lunch & Learn activities.

Registrants for the Course and Conference Package can also attend conference sessions on Wednesday, April 25. Details are online at www.tappi.org/07COMAT.

For more information, visit www.tappi.org/07COAT or call 1.866.850.0999

TAPPI
people resources solutions®

Special Training Event
Coating Materials: Pigments, Binders and Additives Course
April 22-24, 2007
Hyatt Regency Miami

CS↑miami Coating Solutions↑International