Virtual bleach plants, Part 3: Caustic extraction and peroxide bleaching models

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ABSTRACT: This paper presents a kinetic model for caustic extraction and peroxide bleaching. A reaction network has been proposed for chemical reactions among pulp components and bleaching chemicals. We use a set of kinetic equations to describe the reaction rate for each reaction in the network. Laboratory data serve to identify model parameters.

Combining this model with other models in this series of papers, a "virtual bleach plant" (VBP) can be built in simulation. This "virtual bleach plant" can serve as an engineering tool to test various process options and to optimize bleach plants, e.g., evaluating COD carryover impacts on bleaching chemical consumption. It can also be used as a full bleach plant software sensor for advanced process control.

Application: The modeling approach described here can help address complicated mill operation and process improvement issues.

Caustic extraction is an essential stage in pulp bleaching. Due to environmental and economical reasons, oxygen and/or peroxide reinforcement in extraction stages are becoming common practice in the industry. In order to achieve the lowest chemical cost, it is necessary to choose the right combination of caustic, oxygen, and peroxide. It is quite difficult to optimize the chemical charges among all the bleaching stages in a bleach plant, such as using peroxide in the extraction stage to reduce ClO_2 usage.

Virtual bleach plants (VBP) provide a process simulation tool to evaluate mill process alternatives and optimize operating conditions. Part 1 of our VBP reports [1] presents two bleach plant simulations that demonstrate the practical use of VBP. Part 1 also describes the general modeling and simulation concept of VBP. Part 2 of VBP [2] describes a unified ClO_2 and Cl_2 bleaching model that is used in Part 1. We developed the unified bleaching model from a new modeling approach based on a reaction network. In Part 3, we apply this modeling approach to caustic extraction and peroxide bleaching. The kinetic parameters are identified using laboratory bleaching data from the literature. We used these bleaching models in the mill ECF case studies shown in Part 1 of VBP [1]. A totally chlorine free (TCF) bleach plant simulation is shown in this paper.

MODEL STRUCTURE

Oxygen and hydrogen peroxide are widely used in modern bleach plants. For various totally-chlorine-free (TCF) processes, hydrogen peroxide is used as the major bleaching chemical. **Table I** shows the proposed bleaching reaction network and **Table II** defines the symbols used in Table I. We developed the reaction network to describe the kinetic behavior of bleaching; it is not intended to represent the bleaching mechanisms.

Table I describes three groups of reactions, each based on one bleaching chemical (caustic, peroxide, or oxygen). The oxygen reactions are only proposed for the oxygen effect in Eop stage. The proposed reactions, reactions 31-33, produce an early delignification effect caused by oxygen reinforcement. When oxidized lignin, X2(p), and chlorine substituted lignin, D(p), are dissolved or converted into other species through various reactions, the effect of oxygen reinforcement diminishes. The actual reactions between oxygen and wood components are certainly more complex. However, the proposed oxygen reactions are enough to represent the major oxygen effect in the Eop stage. If more oxygen reactions are included in the reaction network, a kinetic model can be developed for oxygen delignification.

Caustic extraction reactions

Reactions 1-16 in Table I represent the reactions among caustic and wood components. We chose these reactions to model the most widely used caustic bleaching stages, such as E_1, E_2, Eop, and P.

The model represents the effect of previous bleaching stages on caustic reactions through the initial species ratios in the caustic extraction. Lignin from kraft cooking, A(p), is the initial lignin state. Oxygen delignified pulp contains oxidized lignin, X1(p) and X2(p). ClO_2 pre-treated pulp also contains oxidized lignin and some chlorine substituted lignin, B(p). The major lignin in Cl_2 pre-treated is lignin with three substituted chlorine atoms, D(p).

Reactions 1-5 are major reactions for oxygen delignified pulp and ClO_2 pre-treated pulp. Reactions 8 and 11 are also involved with ClO_2 pre-treated pulp, although B(p) concentration is very low. Reactions 6, 7, 9, 10, 14, and 15 are only involved with Cl_2 pre-treated pulp. Reactions 12 and 13 are included to adjust caustic consumption, yield loss, and COD generation in bleaching liquor. Reactions 14-16 are mainly for the prediction of chlorine content in dissolved lignin (i.e. AOX). If we remove Cl_2, we can significantly simplify the model.

No reaction is included in the model to reflect the pH change caused by neutralization. In our current simulation, we base the caustic consumption from pH change on a general equilibrium calculation that we published earlier [3].

Peroxide bleaching reactions

The proposed reactions for peroxide as a bleaching chemical in Table I are intended to model not only the effect of peroxide in caustic extraction, but also peroxide-based TCF bleaching.

The actual bleaching chemical used in the reaction network (Table I) for hydrogen peroxide is the perhydroxyl radical ($\bullet OOH^-$). The concentration of $\bullet OOH^-$ is determined by the equilibrium reaction, Reaction 17 in Table I. The equilibrium constant for Reaction 17 is as follows [4]:

CAUSTIC BLEACHING REACTIONS	
X2(p) + (m)OH^- → X2(a)	(1)
X1(p) + (m)OH^- → X1(a)	(2)
A(p) + (m)OH^- → A(a)	(3)
X2(p) + (m)OH^- → X1(p)	(4)
X1(p) + (m)OH^- → A(p)	(5)
D(p) + (m)OH^- → D(a)	(6)
C(p) + (m)OH^- → C(a)	(7)
B(p) + (m)OH^- → B(a)	(8)
D(p) + (m)OH^- → C(p)	(9)
C(p) + (m)OH^- → B(p)	(10)
B(p) + (m)OH^- → A(p)	(11)
E(p) + (m)OH^- → E(a)	(12)
H(p) + (m)OH^- → H(a)	(13)
D(a) + (m)OH^- → C(a)	(14)
C(a) + (m)OH^- → B(a)	(15)
B(a) + (m)OH^- → A(a)	(16)
PEROXIDE BLEACHING REACTIONS	
$H_2O_2 + OH^- \Leftrightarrow OOH^- + H_2O$ (equilibrium)	(17)
A(p) + (m)OOH^- → A(a)	(18)
X1(p) + (m)OOH^- → X1(a)	(19)
X2(p) + (m)OOH^- → X2(a)	(20)
A(p) + (m)OOH^- → X1(p)	(21)
X1(p) + (m)OOH^- → X2(p)	(22)
X2(p) + (m)OOH^- → X3(p)	(23)
E(p) + (m)OOH^- → E(a)	(24)
H(p) + (m)OOH^- → H(a)	(25)
$OOH^- \rightarrow H_2O$ (self-decomposition)	(26)
OOH^- + (Metals) → H_2O (metals decomposition)	(27)
coL(a) + (m)OOH^- → W(a)	(28)
coE(a) + (m)OOH^- → W(a)	(29)
coH(a) + (m)OOH^- → W(a)	(30)
OXYGEN BLEACHING REACTIONS	
X2(p) + (m)O_2 → X3(p)	(31)
X2(p) + (m)O_2 → W(a)	(32)
D(p) + (m)O_2 → D(a)	(33)

I. Reaction network for the caustic extraction and peroxide bleaching model.

PULP SPECIES, (p)	
A(p)	Lignin from Kraft cooking
B(p)	A(p) with one chlorine substitution
C(p)	A(p) with two chlorine substitution
D(p)	A(p) with three chlorine substitution
X1(p)	A(p) oxidized once
X2(p)	A(p) oxidized twice
X3(p)	A(p) oxidized three times
E(p)	Extractives
H(p)	Hemicellulose
m	Stoichiometric coefficient (varies from reaction to reaction)
AQUEOUS SPECIES, (a)	
A(a)	Dissolved A(p)
B(a)	Dissolved B(p)
C(a)	Dissolved C(p)
D(a)	Dissolved D(p)
X1(a)	Dissolved X1(p)
X2(a)	Dissolved X2(p)
L(a)	A(a)+B(a)+C(a)+D(a)+ X1(a)+X2(a)
E(a)	Dissolved E(p)
H(a)	Dissolved H(p)
coL(a)	Carryover dissolved lignins
coE(a)	Carryover dissolved extractives
coH(a)	Carryover carbohydrates
W(a)	Dissolved wood solids

II. Species definitions for Table I.

$$pK_b = \log_{10}\frac{[\cdot OOH^-]}{[OH^-][H_2O_2]} = \frac{1330}{T} - 2.13 + 0.15\sqrt{[Na^+]} \quad (1)$$

The impact of pH on peroxide bleaching is reflected through Reaction 17.

Reactions 18-20 in Table I represent the delignification effect from peroxide. Reactions 21-23 represent oxidation by peroxide. In the model, oxidized lignin has different contributions to kappa number. For example, X3(p) has no contribution to kappa number. Reactions 24 and 25 are mainly intended to better predict pulp yield loss and bleaching liquor COD content. Reactions 28-30 are included to represent COD carryover effect. In the model, COD carryover causes peroxide consumption and results in less peroxide available for delignification and lignin oxidation.

Peroxide decomposition in mill conditions is not well understood. In the model, we divide the decomposition into two parts: peroxide self-decomposition (Reaction 26) and decomposition related to transition metals (Reaction 27). The rate of Reaction 26 is described as follows [5]:

$$r = 1.8\times10^{11}\exp\left(-\frac{6.0\times10^4}{RT}\right)(5.72\times10^{-5} + 9.04\log_{10}[OH^-]) \quad (2)$$

The impact of transition metals on peroxide decomposition is complex [4, 5]. Not enough mill measurements are available to validate or estimate peroxide decomposition under mill conditions. When better data are available, the impact of metals on peroxide decomposition can be added through Reaction 27. However, the current model is only good for processes where transition metals are under control. For caustic extraction stages after a ClO_2 or Cl_2 stage, adequate washing can remove almost all transition metals in pulp [7]. However, transition metals in TCF processes need careful management [7].

Reaction rate equations

The reaction rate for each reaction in Table I is summarized by the following kinetic equations:

$$r = k[S_{PA}]^a[BC]^b \quad (3)$$

$$k = k_{temp}k_{conc} \quad (4)$$

$$k_{temp} = A_T e^{-E/RT} \quad (5)$$

$$k_{conc} = A_C e^{-\Delta[S_p]/([S_p]_i C_k RT)} \quad (6)$$

See nomenclature for definitions and Part 2 of this series [2] for more details.

Lignin content, brightness, absorption coefficient and kappa relationships

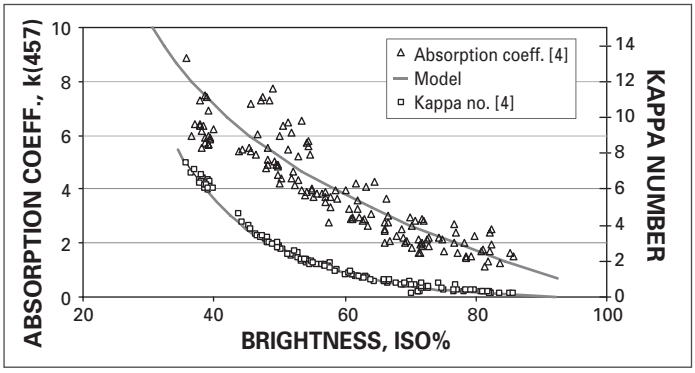
We used various chemical components, such as lignin, in the models. However, the direct measurements in the pulp and paper industry are "combined effects" variables, such as kappa and brightness. In VBP models, the following relationships are used. Lignin content is calculated from kappa number according to the following equation:

$$L_P = \frac{1.53 kappa}{196}\frac{C_{PS}}{1-C_{PS}} \quad (7)$$

Eq. 8 relates brightness to absorption coefficients:

$$\frac{B}{100} = 1 + \left(\frac{k_{457}}{5.0}\right) - \sqrt{1.7\left(\frac{k_{457}}{5.0}\right) + \left(\left(\frac{k_{457}}{5.0}\right)\right)^2} \quad (8)$$

We based Eq. 8 on an equation in the literature [8]. The scattering coefficient—the number 5.0 in Eq. 8—is determined from data shown in **Fig. 1** [4]. We also adjusted the number 1.7 in Eq. 8 from a value of 2.0. Kappa is related to absorption coefficient by the following empirical equation:



1. Relationships among brightness, absorption coefficient and kappa number [4].

$$kappa = 6.0\exp(0.45\ln(k_{457})) \quad (9)$$

Figure 1 compares the relationships among laboratory measurements [4]. The measurements are from kraft cooked, oxygen delignified pulp with 80% Douglas fir and 20% redwood. Brooks then bleached the mill pulp (kappa 13.5) in the laboratory using peroxide and caustic. It is possible that the relationships are dependent on wood species and process specifics.

RESULTS AND DISCUSSIONS

Caustic extraction

The kinetic data (**Figs. 2, 3, and 4**) used to identify the caustic reaction parameters are from the literature [9]. All the data are from a single sample of softwood kraft pulp with kappa 29.5 and bleached in the laboratory using Cl_2 and caustic at 0.4% pulp consistency.

Figure 2 shows the time and initial kappa effects on caustic delignification of Cl_2 pre-treated softwood pulp at 60°C, pH = 11 (constant), and chlorine changes of 0.15, 0.20, and 0.25 times the brown kappa. The delignification process has a typical fast phase and slow phase. The measurements show approximately 25% delignification at 20 min and initial kappa has almost no impact (24.3% for initial kappa 18, 25.2% for kappa 13, and 26.9% for kappa 10.3). Figure 2 also shows the model predictions. Different from previous kinetic models, the current model predicts that initial kappa does not affect the degree of delignification. At 20 min, model predicted delignification is 26%, and 28.6% at 30 min. Although residence time is always beneficial for delignification during caustic extraction, its impact becomes less and less.

Figure 3 shows the effects of pH on caustic delignification (T = 80°C, chlorine change of 0.2 times the brown kappa). Higher pH always results in faster delignification and lower "floor" kappa. Figure 3 shows no "floor" kappa for $pH_{25°C}$ = 12.5. Due to cost, it is not practical to use extremely high pH during caustic extraction. Also, high pH may cause loss of pulp strength. An optimum caustic charge may be found through work like this.

Temperature is another adjustable operating variable during caustic extraction. (Figure 4: pH = 11 and chlorine change of 0.2 times the brown kappa.) Just like the pH effect, higher temperature always results in faster delignification. Although bleaching towers have no limitation on temperature, the extraction stage washers do limit extraction temperature. It is difficult to operate drum washers at vat temperatures higher than 90°C. The current model represents the temperature effect on caustic delignification very well.

CAUSTIC REACTIONS [1]

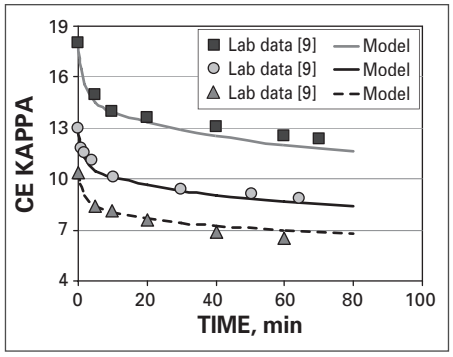
Reaction	m	a	b	k_{conc} [2]	$A_T A_C$	E J/mol.K	Ck
(1)	0.20	1	1	1	2.00E+06	3.00E+04	—
(2)	0.25	1	1	1	9.52E+03	3.00E+04	—
(3)	0.25	1	1	1	7.94E+02	3.00E+04	—
(4)	1	1	1	1	3.34E+03	1.50E+04	—
(5)	1	1	1	1	1.68E+02	1.50E+04	—
(6)	0.1	1	1	1	1.76E+05	3.00E+04	—
(7)	0.1	1	1	1	1.76E+05	3.00E+04	—
(8)	0.1	1	1	1	9.52E+03	3.00E+04	—
(9)	1	1	1	1	3.34E+03	1.50E+04	—
(10)	1	1	1	1	3.34E+03	1.50E+04	—
(11)	1	1	1	1	1.68E+02	1.50E+04	—
(12)	1	1	1	1	3.86E+02	2.50E+04	—
(13)	1	1	1	1	3.86E+01	2.50E+04	—
(14)[3]	1	1	1	1	0.00E+00	2.50E+04	—
(15)[3]	1	1	1	1	0.00E+00	2.50E+04	—
(16)[3]	1	1	1	1	0.00E+00	2.50E+04	—
PEROXIDE REACTIONS [1]							
(17)	(see Eq. 1 for equilibrium constant)						
(18)	2	1	1	—	1.20E+06	6.00E+04	1
(19)	2	1	1	—	4.60E+08	6.00E+04	1
(20)	2	1	1	—	4.60E+08	6.00E+04	1
(21)	2	1	1	—	3.20E+08	6.00E+04	1
(22)	2	1	1	—	4.60E+08	6.00E+04	1
(23)	2	1	1	—	4.60E+08	6.00E+04	1
(24)	1	1	1	1	(see Eq.2)		
(25)	1	1	1	1	(not included)		
(26)	1	1	1	1	1.20E+04	6.00E+04	—
(27)	1	1	1	1	1.20E+04	6.00E+04	—
(28)[4]	1	1	1	1	2.00E+09	6.00E+04	—
(29)[4]	1	1	1	1	2.00E+09	6.00E+04	—
(30)[4]	1	1	1	1	2.00E+09	6.00E+04	—
OXYGEN REACTIONS							
(31)[5]	5	1	1	1	1.20E+11	6.00E+04	—
(32)[5]	5	1	1	1	8.60E+10	6.00E+04	—
(33)[5]	1	1	1	1	1.20E+11	6.00E+04	—

[1] See nomeclature for parameter description. [2] k_{conc} = 1, no concentraction correction is included (see Eq. 4). [3] Have not been identified yet (no data). [4] Estimated from mill data, need better laboratory data. [5] Estimated from existing models.

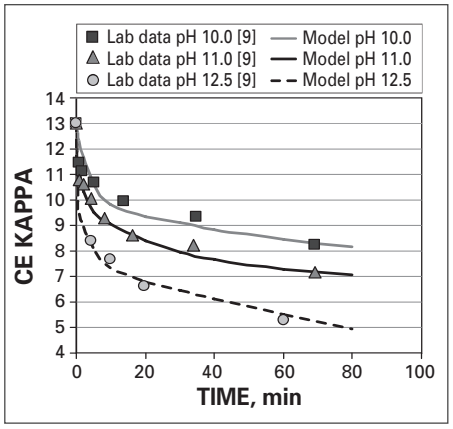
III. Summary of predictive bleaching model parameters.

Table III lists all model parameters used in the calculations for Figs. 2-4. These parameters should be considered as pulp dependent. Wood species and process details used from cooking to extraction affect the delignification in caustic extraction. However, very limited information is available. We suggest that only an "overall" tuning (to keep the relative rate ratios for each reaction unchanged) be performed when the proposed model is applied to a specific mill process.

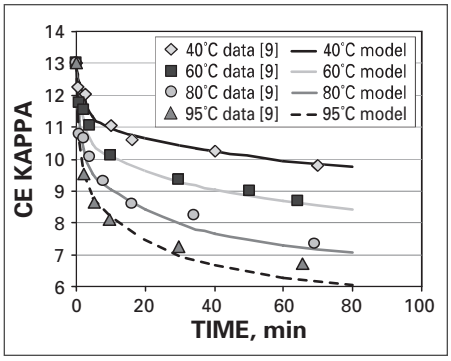
After the caustic model parameters were identified using the data from chlorine pre-treated pulp (Table III), the model



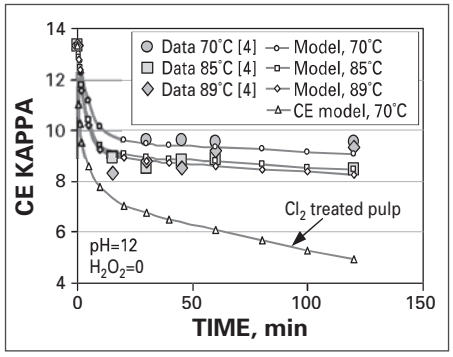
2. Caustic delignification of Cl_2 treated pulp [9].



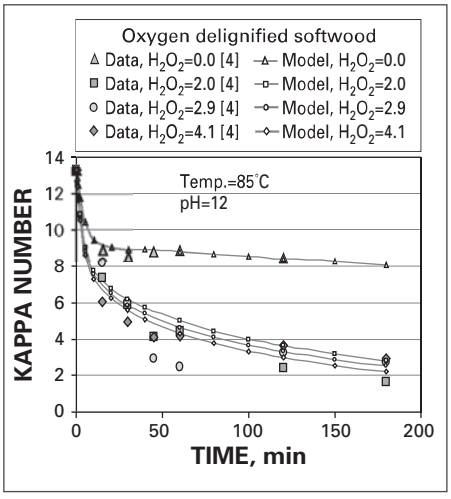
3. Effect of pH $_{25\,°C}$ on caustic delignification of Cl_2 treated pulp [9].



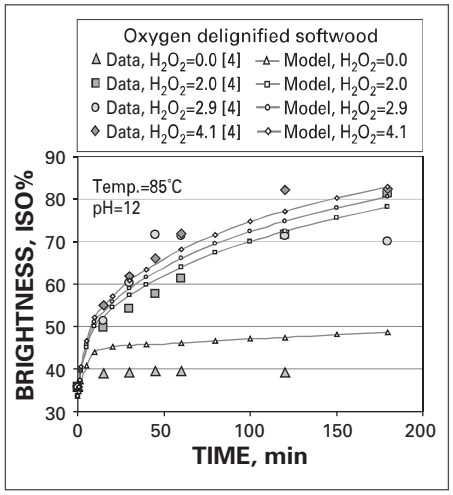
4. Effect of temperature on caustic delignification of Cl_2 treated pulp [9].



5. Caustic delignification of oxygen delignified and chlorinated pulp [4].



6. Effect of peroxide concentration on kappa reduction [4].



7. Effect of peroxide concentration on brightness [4].

was applied to oxygen delignified pulp. Figure 5 shows that the model parameters identified from chlorine pre-treated pulp also apply to oxygen delignified pulp. Figure 5 also shows that chlorine pre-treated pulp is more easily delignified during caustic extraction than oxygen delignified pulp. In the model, the difference is caused by the initial lignin species. For chlorine pre-treated pulp, the major lignin species remaining in the pulp are lignin with two or three chlorine substitution, D(p) and C(p) in Tables I and II. For oxygen delignified pulp, the major lignin species remaining in the pulp are oxidized lignin, X2(p) and X1(p) in Tables I and II.

Peroxide delignification and bleaching

The reaction network in Table I suggests that additional reactions occur when peroxide is used during bleaching while the reactions involving caustic as a bleaching chemical are still happening. The actual reaction species used in the model for peroxide is $\bullet OOH^-$ which is formed according to following equilibrium reaction:

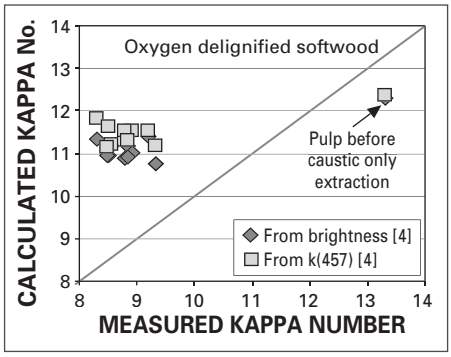
$$H_2O_2 + OH^- <==> \bullet OOH^- + H_2O$$

The equilibrium constant is dependent on temperature and ion strength (Eq. 1).

The model parameters for peroxide were identified from another set of laboratory peroxide bleaching data [4]. Mill kraft cooked, oxygen delignified pulp with 80% Douglas fir and 20% redwood, kappa 13.5, was laboratory bleached by peroxide at various temperatures, pH and peroxide concentrations. During the experiments, Brooks maintained peroxide concentrations and pH at constant levels by continuously adding peroxide and caustic. Brooks also kept temperatures constant. During model identification for peroxide bleaching, model parameters for simultaneous caustic delignification are calculated according to the results from the above section for caustic delignification occurring with no peroxide present.

Figure 6 shows the effect of peroxide concentration on delignification. As expected, the existence of peroxide in caustic solution increases the delignification rate and final kappa reduction while caustic alone is still able to achieve significant kappa reduction. However, the difference between H_2O_2 concentration at 2.0 g/L and 4.1 g/L is very small. Figure 7 shows the brightness gains for the same experiments as those in Fig. 6. Peroxide resulted in much higher brightness gain than caustic alone.

The comparison of model calculation with the measurements in Figs. 6 and 7 shows that the model can describe the effect of peroxide delignification and brightness very well. However, the model predicts too high brightness gain for caustic extraction without peroxide while the delignification from caustic only is well predicted. Figure 8 shows that for caustic only extraction, kappa numbers calculated from brightness and



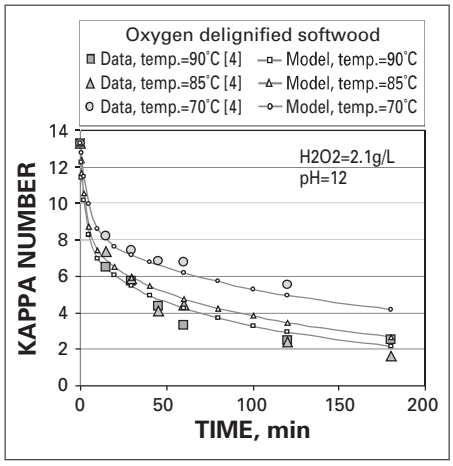
8. Brightness reversion during caustic extraction [4].

absorption measurements (Eqs. 8 and 9) are higher than actual kappa measurements. The fact that the brightness gain was lower than the contribution from lignin removal during caustic extraction suggests there was brightness reversion during caustic extraction.

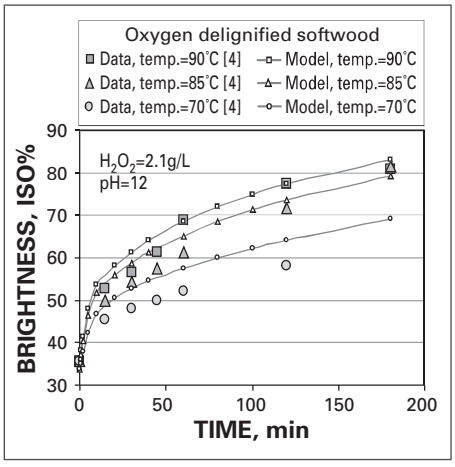
Different from mill operations, the peroxide bleaching experiments in Figs. 6 and 7 kept peroxide concentrations constant by continuous addition of peroxide. In order to avoid brightness reversion during mill operation, enough peroxide has to be charged initially to maintain some peroxide residual at the end of the bleaching stage. However, high peroxide residual does not help bleaching very much.

Figures 9 and **10** show the temperature effect on peroxide delignification and brightness. Similar to caustic extraction, higher temperature always results in faster delignification, lower final kappa number and higher brightness. Compared with ClO_2 bleaching, peroxide bleaching has more difficulty reaching high brightness. Although it is possible for peroxide bleaching to get higher brightness through high peroxide and caustic application (**Figs. 7 and 11**), chemical cost makes this kind of practice impossible. High temperature is a more practical way to get more and faster reaction between peroxide and lignin components. A pressured bleaching tower is needed to achieve temperature higher than 100°C. The current model has not been tested for temperature higher than 95°C. Fundamentally, the model is sound to simulate pressured peroxide bleaching.

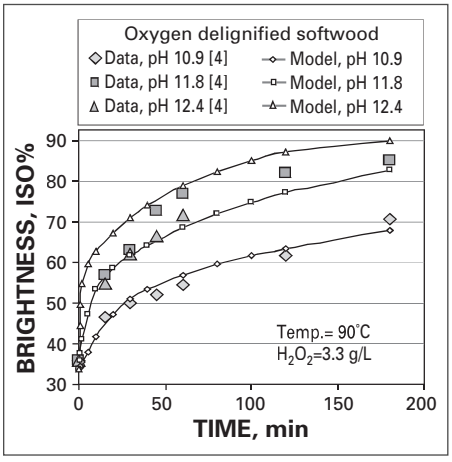
Figure 11 shows the pH effect of peroxide bleaching. Higher pH always results in higher brightness gain.



9. Temperature effect on kappa reduction during peroxide bleaching [4].



10. Temperature effect on brightness gain during peroxide bleaching [4].

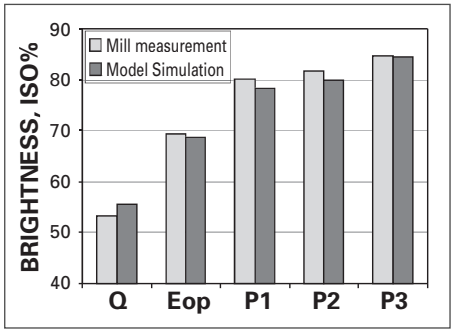


11. pH effect on brightness during peroxide bleaching [4].

However, brightness gain is still only one factor considered in choosing an optimum pH. In the model, OH^- concentration is not directly used in the rate equations related to peroxide (Reactions 18-30). The pH effect in peroxide bleaching results from the change of $\bullet OOH^-$ concentration through the equilibrium among H_2O_2, OH^-, and $\bullet OOH^-$ (Reaction 17).

TCF BLEACH PLANT SIMULATION

The Samoa Pacific mill bleach plant was converted from OCEDED into $OQEopP_1P_2P_3$ in 1994 [10]. Mill water was applied to P_3 and Q washers. Q washer filtrate was purged for metals control. Alkaline filtrates were used counter-currently from P_3 to Eop. Eop filtrate was used on No. 2 post oxygen washer. There is an O_2 surge tower between No. 2 post oxygen washer and Q tower. The peroxide residual in Eop filtrate has a bleaching effect in the O_2 surge tower.



12. Samoa Pacific mill $OQEopP_1P_2P_3$ bleach plant brightness simulation.

Figure 12 shows the averages of mill hourly brightness from October 15-21, 1995. Post-oxygen kappa was 9.4, which also is used for the initial kappa in the bleach plant simulation. Model predicted brightness for O_2 surge tower discharge is 55.6% and no measurement is available. Model predicted brightness is compared with mill measurements in Fig. 12. The model matches mill measurements very well. The proposed model is practical for process engineering and analysis.

FUTURE WORK

Modeling and process simulation can effectively consolidate knowledge and measurements currently scattered in the literature and other resources. The current VBP models mainly focus on the prediction of delignification, brightness and bleaching chemical consumption. More details can be attached into this mainframe of bleaching models. For example:

- Pulp strength
- Dirt in bleached pulp
- Characteristics of bleaching liquor, such as COD, AOX, etc.
- Other concerns for mill operations, such as VOC and oxalate generation (scale).

More detailed mill simulation and carefully designed mill measurements can help to demonstrate and expand the capacity of process simulation to address mill process issues. Similar to VBP, our research group also has developed VOC air emissions [11] and metals equilibrium models [7]. A single process simulation that contains all these predictive models can provide a powerful tool to understand current mill operations and provide suggestions on economical process improvements.

CONCLUSIONS

We developed bleaching models for caustic extraction and peroxide bleaching. The models predict the effects of bleaching time, initial kappa, bleaching chemical concentrations, temperature, and pH. After integration into process simulators, these models have been applied to simulate mill caustic related bleaching stages, such as E_1, E_2, and Eop [1]. The models also simulate peroxide bleaching stages in TCF processes. Combined with the unified ClO_2 and Cl_2 bleaching model [2], virtual bleach plant models are able to simulate most modern bleach plants in the industry.

The bleaching models are divided into two layers: the reaction network (Table I) and the kinetic expression for each reaction (Eqs. 3-6). With simplified bleaching chemistry, the reaction network is mainly proposed to describe issues related to bleach plant operation. The model parameters are identified from laboratory bleaching kinetic data. This modeling approach has successfully consolidated our bleaching chemistry knowledge, laboratory data, and mill measurements to address complicated mill operation and process improvement issues. **TJ**

NOMENCLATURE

a = Exponent for non-bleaching chemical concentrations
A_C = Pre-exponential constant for the concentration effect
A_T = Pre-exponential constant for temperature effect
b = Exponent for bleaching chemical concentrations
B = Pulp brightness, ISO%
$[BC]$ = Bleaching chemical concentration, mol/L
C_k = Model parameter for the concentration effect
C_{PS} = Pulp consistency, mass fraction
E = Activation energy, J/mol.K
$[H_2O_2]$ = Peroxide concentration, mol/L
kappa = Kappa number
k = Rate constant
k_{457} = Absorption coefficient at 457 nm
k_{conc} = Rate constant with concentration effect
k_{temp} = Rate constant with temperature effect
L_P = Lignin concentration, mol/L
$[Na^+]$ = Na^+ concentration, mol/L
$[OH^-]$ = OH^- concentration, mol/L
pK_b = Equilibrium constant for Reaction 17
r = Reaction rate, mol/min.
R = General gas constant, mol.K/J
$[S_{PA}]$ = Concentration of pulp or aqueous species, mol/L
$[S_P]_i$ = Initial concentration of pulp species, mol/L
T = Temperature, K
$\Delta[S_P]$ = Concentration change of pulp species, mol/L

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