Virtual bleach plants, Part 2: Unified ClO_2 and Cl_2 bleaching model

YONGXIANG GU AND LOU EDWARDS

ABSTRACT: This paper presents a unified kinetic model for chlorine dioxide and elemental chlorine bleaching. Derived from bleaching chemistry, reaction networks have been proposed to consolidate the information from bleaching mechanism studies. The purpose of this model is to represent mill bleaching stages for process improvements and operations. The model provides much more information than traditional bleaching kinetic models. However, this model is not for understanding basic bleaching mechanisms. We used various laboratory bleaching data to identify model parameters and validate the model.

Combining this model with other models in this series of papers, a "virtual bleach plant" (VBP) can be built for simulation. Mills can use this "virtual bleach plant" 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 VBP can help mills better evaluate economic, environmental, and product quality issues.

The U.S. pulp industry is shifting to elemental chlorine free (ECF) bleaching. Pulp mills that are still using Cl_2 will need process improvements. Engineers and operators in these mills will have a learning process to operate ECF bleach plants. Process modeling can facilitate this transition process by evaluating process alternatives and operating conditions using simulation instead of costly mill trials. In Part 1 of this series [1], Case B demonstrates how virtual bleach plant (VBP) simulation is helping a mill optimize its chemical charges.

Chlorine dioxide and chlorine bleaching are characterized by complex pulp chlorine chemistry. The following two equilibrium reactions serve to determine the reactive species in the chlorine-water system [2]:

$$Cl_2 + H_2O \Leftrightarrow HOCL + HCl \qquad (1)$$

$$HOCL \Leftrightarrow H^+ + OCl^- \qquad (2)$$

Therefore, the actual reactive species in Cl_2 bleaching can be molecular chlorine (Cl_2), hypochlorous acid (HOCl), and hypochlorite (OCl^-). The most important factor that affects the distribution of these chlorine species is pH. Because molecular chlorine (Cl_2) and HOCl behave differently during bleaching, we must include molecular Cl_2 and HOCl as active bleaching chemicals (instead of total Cl_2) in the model. The distribution of these chlorine species can be computed from the equilibrium of Reactions 1 and 2.

When ClO_2 reacts with unbleached pulp, chlorite (ClO_2^-) and hypochlorous acid (HOCl) are generated [3,4]. Chloride (Cl^-), ClO_2^-, and ClO_3^- are detected in ClO_2 bleaching filtrate [5]. Because HOCl exists, ClO_2 bleaching is chemically connected to Cl_2 bleaching through Reaction 1, which is an equilibrium reaction. A unified ClO_2 and Cl_2 bleaching model is required to understand ClO_2 bleaching.

UNIFIED ClO_2 AND Cl_2 BLEACHING MODEL

Conventional bleaching kinetics correlate kappa number (brightness) with bleaching chemical concentrations and temperature. Quite often, different equations describe kappa and bleaching chemicals, i.e., there is no defined stoichiometric relationship between kappa change and chemical consumption. The research on bleaching mechanisms has shown that many reactions are involved in bleaching. However, it is not practical to model bleaching according to bleaching mechanisms for the purpose of mill bleach plant simulation.

Another approach to model bleaching is to represent bleaching by rate controlling steps and modeling each step by conventional power law kinetics. Ni, et al. [6] developed a chlorine bleaching model with three reactions in series. However, the model is still limited to predicting kappa and chlorine concentration. Saltin, et al. [7] used a similar approach to model chlorination and caustic extraction.

In this paper, we develop a bleaching model to simulate mill bleach plants for mill operation and process engineering. The model is not limited to predicting kappa/brightness and bleaching chemical concentration. Other issues related to mill processes, such as the impact of carryover COD on chemical consumption, are also included. The model uses a network of bleaching reactions. We summarize or simplify some of the reactions in the network from available mechanisms. Other reactions are included to address specific issues, such as COD prediction. We developed kinetic equations for each reaction and identified kinetic parameters from laboratory kinetic data.

ClO_2 bleaching reaction network

Table I is the proposed reaction network for chlorine dioxide bleaching. **Table II** defines the symbols used in Tables I and III. Earlier research showed that ClO_2 is stable in bleached pulp slurry at bleaching conditions [5]. Therefore, there is no direct ClO_2 decomposition reaction. Based on experimental demonstrations, the reaction of ClO_2 with unbleached pulp generates HOCl [4]. Chlorite and chlorate can be found in bleaching filtrates [5]. Reactions 1-3 represent the reactions between ClO_2 and lignin. Lignin is dissolved through Reaction 1. Lignin also is oxidized once and twice through Reactions 2 and 3. Dissolved lignin, chlorite, chloride, HOCl, and methanol are generated during ClO_2 bleaching. Methanol generation is of interest for VOC air emissions [8].

Reactions 4 and 5 in Table I are included to predict yield loss and dissolved organics generation in bleaching filtrate. Filtrate COD is calculated from dissolved organics. Although there are not enough

LIGNIN DISSOLUTION AND OXIDATION REACTIONS

$$A(p) + (m+Me)ClO_2 \rightarrow A(a) + (Me)CH_3OH + (m)Cl^- + (m)H^+ \quad (1)$$

$$A(p) + (m)ClO_2 \rightarrow X1(p) + (0.5m)ClO_2^- + (0.125m)HOCl + (0.375m)Cl^- + (0.875m)H^+ \quad (2)$$

$$X1(p) + (m+Me)ClO2 \rightarrow X2(p) + 0.5(m+Me)HOCl + 0.5(m+Me)ClO_2^- + (Me)CH_3OH + 0.5(m+Me)H^+ \quad (3)$$

NON-LIGNIN PULP SPECIES REACTIONS

$$E(p) + (m)ClO_2 \rightarrow E(a) + (m)Cl^- + (m)H^+ \quad (4)$$

$$H(p) + (m)ClO_2 \rightarrow H(a) + (m)Cl^- + (m)H^+ \quad (5)$$

$$Par(p) + (m)ClO_2 \rightarrow W(a) + (m)Cl^- + (m)H^+ \quad (6)$$

DISSOLVED ORGANICS REACTIONS

$$L(a) + (m)ClO_2 \rightarrow W(a) + (m)Cl^- + (m)H^+ \quad (7)$$

$$coL(a) + (m)ClO_2 \rightarrow W(a) + (m)Cl^- + (m)H^+ \quad (8)$$

$$coE(a) + (m)ClO_2 \rightarrow W(a) + (m)Cl^- + (m)H^+ \quad (9)$$

$$coH(a) + (m)ClO_2 \rightarrow W(a) + (m)Cl^- + (m)H^+ \quad (10)$$

CHLORITE REACTIONS

$$5ClO_2^- + 4H^+ \rightarrow 4ClO_2 + Cl^- + 2H_2O \quad (11)$$

$$ClO_2^- + 4H^+ \rightarrow Cl^- + 2H_2O \quad (12)$$

$$ClO_2^- + HOCl \rightarrow ClO_3^- + Cl^- + H^+ \quad (13)$$

EQUILIBRIUM REACTIONS

$$Cl_2 + H_2O \Leftrightarrow HOCl + H^+ + Cl^- \quad (14)$$

$$HOIC \Leftrightarrow OCl^- + H^+ \quad (15)$$

I. Reaction network for chlorine dioxide bleaching.

data to determine parameters related to Reaction 4, the model has the potential to address issues in which extractives are the major concern, such as pitch deposits. Reaction 6 predicts pulp cleanliness. It has a different kinetic pattern from delignification [9]. Similarly, pulp properties, such as pulp strength, and other by-products can be included in the model by adding related reactions into the reaction network. The model is expandable without changing the model structure and existing predictions.

Recent laboratory bleaching studies [10] have shown that splitting ClO_2 charge and washing can achieve more delignification at the same ClO_2 total charge. Dissolved lignin from ClO_2 bleaching is consuming ClO_2 during ClO_2 bleaching. Reaction 7 models this phenomenon. We have assumed that all dissolved lignin species behave the same with regard to ClO_2 consumption in the aqueous phase.

	PULP SPECIES		AQUEOUS SPECIES
A(p)	Lignin from Kraft cooking	A(a)	Dissolved A(p)
B(p)	A(p) with one chlorine substitution	B(a)	Dissolved B(p)
C(p)	A(p) with two chlorine substitutions	C(a)	Dissolved C(p)
D(p)	A(p) with three chlorine substitutions	D(a)	Dissolved D(p)
X1(p)	A(p) oxidized once	X1(a)	Dissolved X1(p)
X2(p)	A(p) oxidized twice	X2(a)	Dissolved X2(p)
E(p)	Extractives	L(a)	A(a)+B(a)+C(a)+D(a)+ X1(a)+X2(a)
H(p)	Hemicellulose	E(a)	Dissolved E(p)
Par(p)	Particle (dirt) in pulp	H(a)	Dissolved H(p)
—	—	coL(a)	Carryover dissolved lignins
—	—	coE(a)	Carryover dissolved extractives
m	Stoichiometric coefficient	coH(a)	Carryover carbohydrates
Me	Number 0f -OCH_3 per lignin	W(a)	Dissolved wood solids

II. Species definitions for Tables I and III.

COD carryover affects ClO_2 bleaching in the D_0 stage [11]. Reactions 8-10 represent COD carryover impact. Carryover dissolved organics are broken down into dissolved lignin, extractives, and carbohydrates. These dissolved organics consume ClO_2 according to these reactions. In other words, less ClO_2 is available for pulp bleaching due to the existence of dissolved organics carryover.

Chlorine dioxide is generated from chlorite at acid conditions (see Reaction 11) [5]. Chlorite also can be decomposed into chloride at acid conditions (Reaction 12). Chlorate is formed from chlorite and HOCl through Reaction 13.

The two equilibrium reactions (Reactions 14 and 15) for the chlorine-water system are also included in the model. Depending on pH, chlorine species can be Cl_2, HOCl, or OCl^-. Because HOCl is generated from the reactions between pulp lignin and ClO_2 [4], molecular Cl_2 can exist in ClO_2 bleaching through the equilibrium reactions, depending on the bleaching conditions. Because the concentrations of HOCl and Cl_2 in ClO_2 bleaching are very low and are consumed rapidly, no HOCl and Cl_2 are detected in bleaching filtrates. However, understanding the chemistry connection between ClO_2 and Cl_2 bleaching makes our model better. For example, the chloride impact on ClO_2 [12] can be explained through the shift of these chlorine species in these equilibrium reactions. In our model, AOX generated during ClO_2 bleaching is through Cl_2 or HOCl (see **Table III** for Cl_2 bleaching reaction network). No chlorine substitution on lignin is included for ClO_2 bleaching.

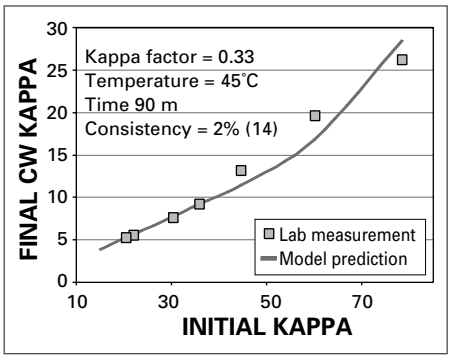
Cl_2 bleaching reaction network

Similar to the ClO_2 bleaching, we propose a Cl_2 bleaching reaction network (Table III). Pulp lignin is dissolved according to Reactions 21-23 in Table III. Chlorine substitution on pulp lignin is shown as Reactions 24-26. Chlorine substitution also occurs in the aqueous phase as Reactions 34 and 35. Cl_2 attacks non-lignin species according to Reactions 29 and 30. The major purpose of including Reactions 29 and 30 is for yield loss and COD generation predictions. Reactions 31-33 model the impact of COD carryover.

Reactions 27 and 28 represent the interaction of Cl_2 and ClO_2 through pulp lignin species. Studies confirm that the charge sequence and interval variously affect the delignification of Cl_2 and ClO_2 bleaching (D/C, C/D or CD stage) [2]. The ClO_2 reaction network (Table I) suggests that ClO_2 does not react with lignins that have chlorine substitution [B(p), C(p), and D(p)]. However, Cl_2 reacts with lignin oxidized by ClO_2 in Table III [X_1(p) and X_2(p)]. Therefore, more lignin is removed in the D/C stage than in the CD or C/D stage. Because the relative ratios of pulp lignin species are significantly changed during the initial stage (the first minute), the small charge time difference makes a big difference on the lignin ratios, and therefore, on the results of the whole bleaching stage. Table III suggests that no chlorine substitution occurs on oxidized lignin [X_1(p) and X_2(p)]. Therefore, a D/C stage generates less AOX than

corresponding CD and C/D stages.

Due to the equilibrium reactions (Eqs. 14 and 15 in Table I), the actual chlorine species in Cl_2 and water system can be Cl_2, HOCl, and OCl^-. Similar reactions have been included with HOCl or OCl^- as actual bleaching chemicals. Thus, the proposed bleaching model can be adapted to hypchlorite and hypochlorous acid bleaching.



1. Impact of initial kappa on final kappa for Cl_2 bleaching.

Reaction rate equations

The reaction rate for each reaction in Tables I and III is modeled by conventional power law kinetic equations. The reaction rate is expressed as:

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

in which, $[S_{Pi}]$ is pulp or aqueous species concentration, $[BC]$ is bleaching chemical concentration, a and b are model parameters, and k is the reaction rate constant. In the model, we treat the pulp as a pseudo-homogenous solution.

The rate constant, k, is divided into two parts:

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

in which, k_{temp} reflects the temperature effect and k_{conc} reflects the effect of pulp species concentration. We use Ahrenius' equation for k_{temp}:

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

Different from conventional rate constant equations, a concentration effect is included as k_{conc}:

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

In Eq. 6, A_C is a constant, $\Delta[S_P]$ is concentration change of related pulp species, $[S_P]_i$ is initial pulp species concentration, and C_k is a model parameter to reflect the concentration effect on the rate constant.

It is a common phenomenon in bleaching that delignification divides into a fast phase and a slow phase. One possible explanation to this phenomenon is that different lignin fragments have different reaction rates. Easily dissolved lignin fragments are removed at a fast rate in the early stage, hard-to-dissolve lignin fragments remain. "Fast lignin" and "slow lignin" have been proposed in cooking kinetic models [13]. However, real wood lignin species are more complicated. The transition of fast delignification into slow delignification is gradual. Although several pulp lignin species have been included in the current models (Table II) they are still not enough to reflect the true complexity of lignin. Eq. 6 serves to consider the reaction rate difference without including more detailed lignin species. The parameter C_k in Equation 6 reflects the molecular structure difference on reaction rates.

LIGNIN DISSOLUTION AND CHLORINE SUBSTITUTION REACTIONS

$$A(p) + (m+Me)Cl_2 \rightarrow A(a) + (Me)CH_3OH + 2(m+Me)Cl^- + 2(m+Me)H^+ \quad (21)$$

$$B(p) + (m+Me)Cl_2 \rightarrow B(a) + (Me)CH_3OH + 2(m+Me)Cl^- + 2(m+Me)H^+ \quad (22)$$

$$C(p) + (m+Me)Cl_2 \rightarrow C(a) + (Me)CH_3OH + 2(m+Me)Cl^- + 2(m+Me)H^+ \quad (23)$$

$$A(p) + (m)Cl_2 \rightarrow B(p) + 2(m)H^+ \quad (24)$$

$$B(p) + (m)Cl_2 \rightarrow C(p) + 2(m)H^+ \quad (25)$$

$$C(p) + (m)Cl_2 \rightarrow D(p) + 2(m)H^+ \quad (26)$$

ClO_2 OXIDIZED LIGNIN REACTIONS

$$X1(p) + (m+Me)Cl_2 \rightarrow X1(a) + (Me)CH_3OH + 2(m+Me)Cl^- + 2(m+Me)H^+ \quad (27)$$

$$X2(p) + (m+Me)Cl_2 \rightarrow X2(a) + (Me)CH_3OH + 2(m+Me)Cl^- + 2(m+Me)H^+ \quad (28)$$

NON-LIGNIN PULP SPECIES REACTIONS

$$E(p) + (m)Cl_2 \rightarrow E(a) + 2(m)Cl^- \quad (29)$$

$$H(p) + (m)Cl_2 \rightarrow H(a) + 2(m)Cl^- \quad (30)$$

DISSOLVED ORGANICS REACTIONS

$$coL(a) + (m)Cl_2 \rightarrow W(a) + 2(m)Cl^- \quad (31)$$

$$coE(a) + (m)Cl_2 \rightarrow W(a) + 2(m)Cl^- \quad (32)$$

$$coH(a) + (m)Cl_2 \rightarrow W(a) + 2(m)Cl^- \quad (33)$$

$$A(a) + (m)Cl_2 \rightarrow B(a) + 2(m)Cl^- \quad (34)$$

$$B(a) + (m)Cl_2 \rightarrow C(a) + 2(m)Cl^- \quad (35)$$

III. Reaction network for chlorine bleaching.

Without considering its possible implication on molecular structure, Eq. 6 is a better equation to fit delignification curves. It avoids the arbitrary division of lignin into "fast lignin" and "slow lignin." It describes fast and slow delignification without high powers on pulp species concentrations and predicts initial kappa impact on delignification (**Fig. 1**) much better than the kinetic equations with pulp species concentrations raised to high powers.

VALIDATION OF BLEACHING MODELS

In order to calculate delignification rates, all the kinetic parameters in Eqs. 3-6 and for all reactions in Tables I and III have to be determined. Because many reactions are competing for the same bleaching chemicals and the others are connected through various pulp or aqueous species, it is difficult to determine these model parameters. The following separation and simplifications are used during model parameter identification:

1. Separate Cl_2 bleaching from ClO_2 bleaching. Because no ClO_2 is involved in Cl_2 bleaching, Cl_2 related parameters are determined from the measurements of Cl_2 bleaching.
2. Acidic chlorite decomposition rates are determined from experimental measurements.
3. ClO_2 bleaching reactions are determined from the measurements of ClO_2 bleaching when parameters related to Cl_2, HOCl, and ClO^- are fixed according to Cl_2 bleaching.
4. An overall tuning factor for all reaction rates is used to tune Cl_2 bleaching rate parameters for HOCl or OCl^- bleaching.
5. Measurements from clean pulp bleaching are used to determine bleaching related reactions. Then, carryover related reactions are determined from the bleaching measurements with initial dissolved organics.

CLO_2 BLEACHING[1], TABLE I

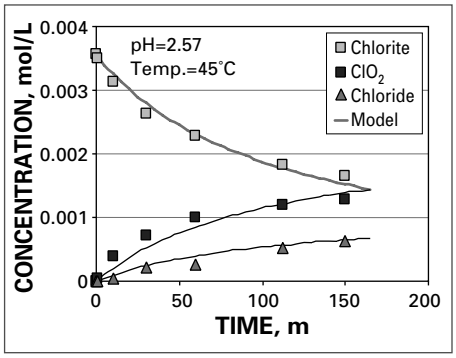
Reaction	m	a	b	k_{conc}[3]	A_TA_C	E, J/mol.K	C_k
(1)[2]	1	1	1	—	7.27E+07	2.50E+04	0.45
(2)	1	1	1	—	5.28E+07	2.50E+04	1.00
(3)[2]	1	1	1	1	8.00E+05	2.50E+04	—
(4)	1	1	1	1	7.00E+06	2.50E+04	—
(5)	1	1	1	1	7.24E+04	2.50E+04	—
(6)	1	1	1	1	3.86E+05	3.50E+04	—
(7)	1	1	1	1	7.27E+06	2.50E+04	—
(8)	1	1	1	1	3.64E+07	2.50E+04	—
(9)	1	1	1	1	3.50E+06	2.50E+04	—
(10)	1	1	1	1	3.62E+04	2.50E+04	—
(11)[4]	—	1	1	1	4.29E+10	5.50E+04	—
(12)[4]	—	2	0.5	1	7.51E+09	5.50E+04	—
(13)[4]	—	2	0.5	1	3.69E+13	6.50E+04	—
(14)	(Equilibrium constant, K = 3.94E-4)						
(15)	(Equilibrium constant, K = 5.60E-8)						

CL_2 BLEACHING[1], TABLE III

Reaction	m	a	b	k_{conc}[3]	A_TA_C	E, J/mol.K	C_k
(21)[2]	1	1	1	—	9.50E+09	4.00E+04	0.564
(22)[2]	1	1	1	1	7.50E+07	4.00E+04	—
(23)[2]	1	1	1	—	2.30E+11	6.25E+04	—
(24)	0.5	1	1	—	1.65E+10	4.00E+04	0.403
(25)	0.5	1	1	1	4.85E+08	4.00E+04	—
(26)	0.5	1	1	1	2.88E+09	5.00E+04	—
(27)[2]	1	1	1	1	2.00E+13	5.60E+04	—
(28)[2]	1	1	1	1	2.00E+13	5.60E+04	—
(29)	1	1	1	1	2.00E+05	2.50E+04	—
(30)	1	1	1	1	2.00E+05	2.50E+04	—
(31)	1	1	1	1	4.75E+09	2.50E+04	—
(32)	1	1	1	1	1.00E+05	2.50E+04	—
(33)	1	1	1	1	1.00E+05	2.50E+04	—
(34)	0.5	1	1	1	3.03E+08	4.00E+04	—
(35)	0.5	1	1	1	6.03E+07	4.00E+04	—

(1) See nomeclature for parameter description. (2) Me = 0.45 for ClO_2 ; Me = 0.85 for Cl_2. (3) k_{conc} = 1, no concentraction correction is included (see Eq. 6). (4) Parameter a is for ClO_2^- and parameter b is for H^+ or HOCl.

IV. Summary of predictive bleaching model parameters.



2. Acidic decomposition of chlorite [5].

6. Stoichiometric coefficients for bleaching chemicals are determined by matching kappa reductions and bleaching chemical consumptions simultaneously.
7. Equilibrium constants are from the literature.

Acidic decomposition of chlorite

There is a good amount of published information about acidic chlorite decomposition through Reaction 11 in Table I. However, available experimental measurements of acid chlorite decomposition [5] have shown that more chloride is found than that generated from Reaction 11. Therefore, Reaction 12 in Table I is used to balance chloride generation. The relative reaction rate of Reactions 11 and 12 is determined through matching experimentally measured ClO_2^-, ClO_2, and Cl^- concentrations. **Figure 2** compares laboratory measurements with model prediction. **Table IV** lists the model parameters for Reactions 11 and 12 in Table I.

Cl_2 bleaching

Figure 3 shows typical kappa reduction and Cl_2 consumption for Cl_2 bleaching. During the initial half minute, 65% of delignification in Cl_2 bleaching is achieved with 50% of the Cl_2 consumed. Within 5 min, 80% delignification is achieved and 65% Cl_2 is consumed. Methanol is generated rapidly during the initial bleaching. Available Cl_2 delignification mechanism research suggests that the methoxyl group has to be removed from lignin fragments before the fragment can be removed from pulp by chlorine. Therefore, *Me* in Reactions 21-23 is the same as average number of methoxyl groups per lignin fragment (0.85 is used for the specific species in Fig. 3).

Figure 4 shows that chlorine substitution on pulp lignin is very rapid at the beginning of bleaching. In Fig. 4, the chlorine content in lignin is expressed as the numbers of chlorine atoms on each lignin fragment (molar ratio of Cl/C_9). Chlorine substitution is represented by Reactions 24-26 in Table III. Therefore, kinetic parameters related to Reactions 24-26 are determined to match the measurements of chlorine content in pulp lignin.

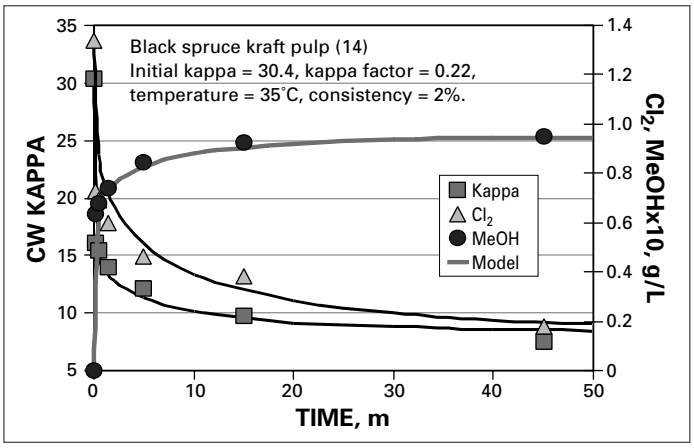
The effect of pulp lignin concentration on delignification rate has been included in matching kappa reduction in Fig. 3. Related kinetic parameters are a in Eq. 3 and C_k in Eq. 6. In this kinetic model, all pulp species are first order (i.e., a = 1) for all pulp species (Table IV). Further examination of pulp lignin effect on delignification has been done through bleaching data with different initial kappa numbers. Figure 1 compares model predicted final kappa numbers and laboratory measurements for chlorine bleaching. The model not only predicts intermediate kappa during chlorine bleaching (Fig. 3), but also final kappa numbers (CW kappa) for a wide range of initial kappa numbers (Fig. 1).

The effect of temperature on bleaching—the parameters in Eq. 5—has been determined through fitting bleaching data measured for temperatures of 25°C and 45°C. Table IV shows the results. Not enough information is available to determine the activation energy for each reaction. Therefore, we use a single activation energy for each reaction group.

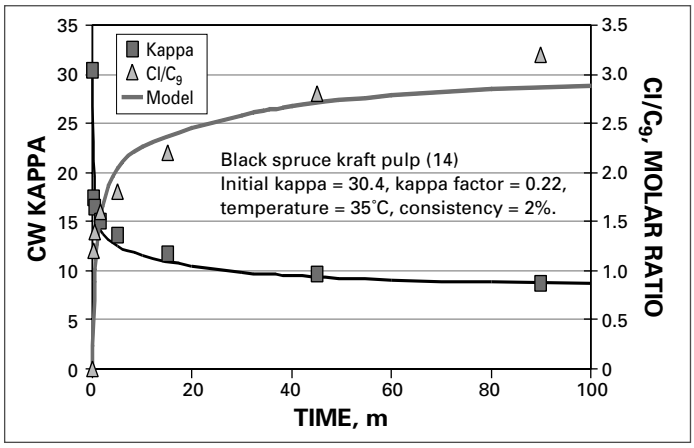
ClO_2 bleaching

Chlorine species in ClO_2 laboratory bleaching filtrates have been analyzed carefully [5]. ClO_2, ClO_3^-, ClO_2^-, and Cl^- are found in the filtrate. Some chlorine shows up in dissolved organics and on pulp also. In the filtrate, no HOCl, OCl^-, or Cl_2 were detected, which suggests that these chlorine species are consumed rapidly during ClO_2 bleaching. **Figure 5** shows the changes of chlorate, chlorite and AOX during ClO_2 bleaching.

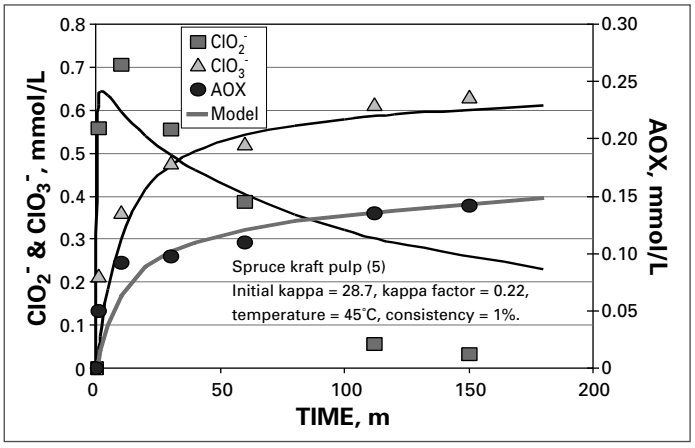
We base the generation rate of HOCl—Reactions 2 and 3 in Table I—on fitting bleaching data shown in Fig. 5 and **Fig. 6**. The model matches overall kappa reduction and ClO_2 consumption, as well as ClO_2^- generation, AOX generation, and chlorine substitution on pulp lignin.



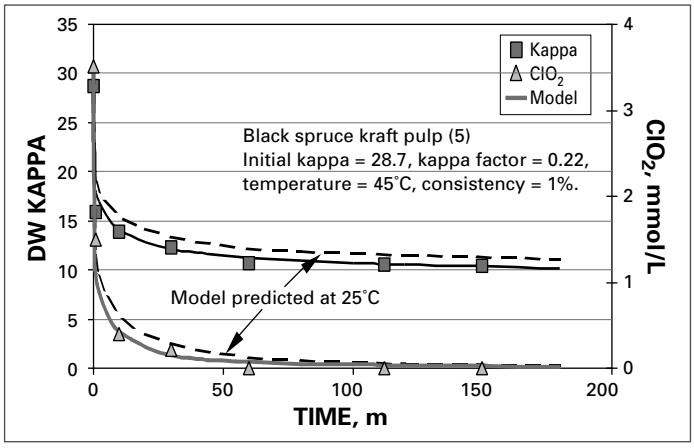
3. Delignification and Cl_2 consumption during Cl_2 bleaching.



4. Chlorine content in pulp lignin during Cl_2 bleaching.



5. Chlorine species in ClO_2 bleaching filtrate.



6. Kappa reduction and ClO_2 consumption for ClO_2 bleaching.

Although chlorine substitution on pulp and dissolved lignin is not included in the ClO_2 bleaching model (Table I), the chlorine substitution reactions in Cl_2 bleaching (Table III) are connected to ClO_2 bleaching through HOCl-Cl_2-water equilibrium. In this model, the AOX generation and chlorine substitution on pulp during ClO_2 bleaching are predicted from the Cl_2 bleaching model (Table III), while Reactions 2 and 3 in the ClO_2 bleaching model control the HOCl generation rate.

Temperature effect on ClO_2 bleaching is determined using data gathered for 25°C and 45°C. Table IV lists the model parameters for ClO_2 bleaching. Although the activation energy for each reaction is high, the effect of temperature on final kappa is very limited. For example, a 20°C increase in bleaching temperature only results in a 1.0 final kappa reduction. However, ClO_2 is consumed faster at high temperature.

Although the current bleaching model is based on Cl_2 or ClO_2 only bleaching, the model can be applied to bleaching by a Cl_2 and ClO_2 mixture. The model has been applied for mill C/D stage simulation [1]. Because HOCl and OCl^- have been included in the model as active bleaching chemicals, the model can also be applied to hypochlorous acid bleaching and hypochlorite bleaching, although model parameters would need further tuning.

CONCLUSIONS

We have developed a unified chlorine dioxide and elemental chlorine predictive bleaching kinetic model. The model predicts the effects of chemical applications, temperature, residence time and initial kappa on bleaching. The model also predicts the generation of various species in bleaching filtrates, such as dissolved lignin, carbonate, methanol, oxalate, and chlorine species. Combined with process simulators, we have successfully applied the model to mill bleach plant simulations [1].

The model is divided into two layers. On the top, it is the reaction networks (Tables I and III). On the bottom, it is the kinetic expression (Eqs. 3-6), for each reaction in the reaction networks. We developed the reaction networks according to our understanding of bleaching chemistry and the purposes of our model. We identified the kinetic parameters through various separate laboratory measurements. Adding a concentration term in the reaction rate constant expression (Eq. 6) is a big help to model fast and slow delignification. It is demonstrated that this model approach is able to handle complicated issues without oversimplification. On the current model frame, more predictions, such as pulp strength, can be added. **TJ**

NOMENCLATURE

- a = Power to non-bleaching chemicals
- A_C = Pre-exponential constant for the concentration effect, mol/min.
- A_T = Pre-exponential constant for temperature effect, mol/min.
- b = Power to bleaching chemicals
- [BC] = Bleaching chemical concentration, mol/l
- C_k = Model parameter for the

concentration effect
E = Activation energy, J/mol.K
k = rate constant, mol/min.
k_{conc} = rate constant with concentration effect, mol/min.
k_{temp} = rate constant with temperature effect, mol/min.
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

LITERATURE CITED

1. Gu, Y.X., and Edwards, L.L., *TAPPI J.*, 2(6): 19(2003).
2. Dence, C.W., and Reeve, D.W., *Pulp Bleaching—Principles and Practice*, TAPPI PRESS, Atlanta, Georgia, USA, 1996.
3. Ni, Y., and van Heiningen, A.R.P., *Nordic Pulp Paper J.*, 8(4): 350(1993).
4. Ni, Y., "A Fundamental Study of Chlorine Dioxide Bleaching of Kraft Pulp," Ph.D. Dissertation, McGill University, July 1992.
5. Ni, Y., Kubes, G.J., and van Heiningen, A.R.P., *Nordic Pulp Paper J.*, 7(4): 200(1992).
6. Ni, Y., Kubes, G.J., and van Heiningen, A.R.P., *J. Pulp Paper Sci.*, 21(1): J30(1995).
7. Stalin, G.E., "Kraft Pulp Bleaching: Kinetic Models of Conventional Systems and Laboratory Investigation of Chlorine Free Sequences," Ph.D. Dissertation, University of Idaho, September 1993.
8. Gu, Y.X., Edwards, L.L., Zhu, J.Y., and Chai, X.S., *TAPPI J.*, 84(4): 62(2001).
9. Axegard, P., *Svensk Papperstidn.*, 83(10): 284(1980).
10. Chirat, C., Lachenal, D.D., and Mortha, G., *Proceedings of the 2000 TAPPI Pulping/Process & Product Quality Conference*, TAPPI PRESS, Atlanta.
11. Pikka, O., Vehmaa, J., Alastalo, J., and Gullichsen, J., *Proceedings of the 2000 TAPPI Pulping/Process & Product Quality Conference*, TAPPI PRESS, Atlanta.
12. Gemgard, U., and Teder, A., CPPA Trans. Tech. Sect. 6(2): TR31(1980).
13. Edwards, L.L., and Norberg, S., *Tappi J.*, 56(1):108(1973).
14. Ni, Y., Kubes, G.J., and van Heiningen, A.R.P., *J. Pulp Paper Sci.*, 16(1): 13(1990).

Received: October 5, 2002
Accepted: March 5, 2002

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the July *Solutions! for People, Processes and Paper* magazine (Vol. 86 No. 7)

INSIGHTS FROM THE AUTHORS

The industry needs tools to help evaluate mill bleach plant alternatives. Part 2 of this series begins to fill in the details of the models used for the mill applications in Part 1.

Bleaching chemistry is very complex, so for this model we had to develop the "reaction network" approximation. This paper shows more details of the reaction network for ClO_2 and Cl_2.

From this research series, it is clear that simulation can address real mill issues (e.g., alternative filtrate configurations). Mills can use VBP to help evaluate economic, environmental, and product quality issues. Elemental chlorine free (ECF) conversion options, in particular, can be evaluated using VBP.

Our next step is to apply the VBP to more mill cases so it can be improved.

Gu and Edwards are with the Department of Chemical Engineering, University of Idaho, Moscow, ID 83843, USA. Email Edwards at jkidd@uidaho.edu


Gu


Edwards