Kinetic models for all chlorine dioxide and extraction stages in full ECF bleaching sequences of softwoods and hardwoods

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ABSTRACT: We present new and improved semi-empirical mathematical models for all the chlorine dioxide stages and extraction stages (including oxygen and/or peroxide reinforced) in a full elemental chlorine free (ECF) bleaching sequence. The models predict variations of kappa number, pH, brightness, and bleaching chemical consumption at each step of multistage ECF bleaching sequences. Our aims were to improve the kinetic and stoichiometric equations involved in the chlorine dioxide stages [D_o, D_1, D_2] for their predictability for different kinds of softwood and hardwood pulps and to model the extraction stages with or without oxygen and/or hydrogen peroxide reinforcement [E, (EO), (EOP), (EP)]. The predicted results fit very closely to a wide range of laboratory and literature data, and the predictability was extended to a greater variety of pulps (softwoods and hardwood pulps, kraft or other alkaline pulps).

Application: Our study provides information that will help in the application of kinetic models to the design of new mills or improvements to existing pulp bleaching processes.

Even with extensively developed semi-empirical mathematical modelling of ECF bleaching sequences, tougher environmental regulations, increasing chemical costs, and tighter customer demand call for accurate and robust kinetic models that can be used to optimize process and control of bleach plants.

The chemistry of chlorine dioxide bleaching has been extensively investigated during the past 20–30 years. A number of investigators have proposed the static as well as dynamic behavior of various parts of the bleach plant. In one approach, which based the modelling on the chemical reactions network in each stage, each bleaching stage was represented by rate controlling steps and modelled by conventional power law kinetics. Kinetic equations for each reaction were developed and kinetic parameters were identified from laboratory kinetic data for chlorine dioxide and extraction stages [1–3]. However, such models were exceedingly complex and not practical.

A more practical approach, on which most literature is based, combined chemical kinetics and mass transfer to develop simple semi-empirical models. A simulation model for pulp bleaching was based on multiphase modelling and microscale phenomena [4]. Extensive kinetic studies [5–7] showed that the rate of delignification with chlorine dioxide is fifth order with respect to kappa number. Although this model was extremely sensitive to initial kappa number values, it was not a realistic representation of delignification kinetics. That model was further improved by other researchers [8] to predict the dependence of ClO_2 consumption with respect to the decrease in kappa number. The variation in pH incorporated the effect of carboxyl groups and phenolic groups present in the pulp. Though the models were simpler and more accurate, they had some important drawbacks. They combined D_o with E_1 stage and D_1 stage with E_2 stage, thus rendering them unable to incorporate the addition of peroxide or oxygen in E stages. The use of only one single kinetic equation in each stage made the models too specific and inflexible. Also, the empirical fit between kappa number after D_oE_1 stage and Kubelka-Munk, K_{457}, parameter (light absorption coefficient at 457 nm) at the beginning of D_1 stage—the relation between kappa number (lignin content) and brightness (pulp color)—needed to be changed depending on the kind of pulp. More recently, some equations for softwood pulp were reviewed [8–10] to account for these shortcomings.

We discuss in detail all the kinetic and stoichiometric equations involved in the chlorine dioxide stages [D_o, D_1, D_2] and extraction stages [E, (EO), (EOP), (EP)]. Our aims were to improve some equations used in the former simulators [8–9, 11] to improve their predictability for different kinds of softwood and hardwood pulps and to model the extraction stages with or without oxygen and/or hydrogen peroxide reinforcement [E, (EO), (EOP), (EP)]. By identifying key governing parameters, we were able to propose new comprehensive empirical models that are simpler, more accurate, applicable to a broader range of process conditions, and easily adjustable (if required) with different kinds of wood species. We developed mathematical models for each pulp processing unit and linked them together to create a generic bleaching stage in a simulator for ECF process using the platform Visual Studio 2005 (Visual Basic for interface and C++ for simulations, the differential equations were solved by finite-difference combined with explicit Euler method).

MODELING OF ClO_2 STAGES

D_O stage

We made several observations after investigating the effect of kappa factor and temperature for the pulps at different kappa numbers. First, the chlorine dioxide delignification reaction seems to be a combination of a very fast reaction followed by a slow one, which can be related to the concept of fast- and slow-reacting lignin. An asymptote for both kappa number and brightness is linked to what is known as floor lignin, and a similar approach was followed earlier [12] to model the kinetics for the kraft CE sequence that was later adapted to D_o stage from C stage [11]. Second, the degree of delignification increases with increasing kappa factor and decreasing unbleached kappa number. Third, the reaction was faster at 50°C than at 40°C, and the chlorine dioxide consumption with respect to kappa number decrease was found to be dependent on temperature, initial kappa number, and initial ClO_2 charge.

The rate of the fast and slow lignin removal is given by Eqs. 1–5:

$$R_f = -\frac{dK_f}{dt} = k_f * [ClO_2] * K_f \quad (1)$$

$$R_s = -\frac{dK_s}{dt} = k_s * [ClO_2] * K_s \quad (2)$$

where the reaction rate constants, k_f and k_s are expressed as:

$$k_f = 2.6 * 10^{14} * \exp(-\tfrac{68010}{RT}) \quad (3)$$

$$k_s = 22.47 * \exp(-\tfrac{2079}{RT}) \quad (4)$$

(softwood)

$$k_s = 22.47 * \exp(-\tfrac{1247}{RT}) \quad (5)$$

(hardwood)

with $[ClO_2]$ being the concentration of chlorine dioxide expressed as active chlorine (mol/L), K_f and K_s, the content of fast and slow reacting lignin each expressed as the kappa number. The total kappa number is then $K = K_f + K_s + K_\infty$, where, K_∞ is the floor level or unreactive lignin. The initial values of the fast and slow kappa numbers K_{fo} and K_{so} are given by Eqs. 6–7:

$$K_{fo} = 0.30\ K_o \text{ and } K_{so} = 0.50\ K_o \quad (6)$$

(softwood)

$$K_{fo} = 0.36\ K_o \text{ and } K_{so} = 0.44\ K_o \quad (7)$$

(hardwood)

where K_o is initial kappa number of the pulp.

The value of activation energy for the fast kinetic phase is 68 kJ/mol. The corresponding value for the slow kinetic phase is about 2 kJ/mol. The higher value of activation energy for the fast kinetic phase implies that during this phase, ClO_2 reacts with the free phenolic groups present in the easily extractable lignin. In contrast, the lower value of activation energy for the slow kinetic phase implies that during this phase, slow diffusion of degradation products through the fiber matrix takes place in addition to the slow oxidation by ClO_2 of the double bonds and nonphenolic units present in the structure of residual lignin preoxidized by ClO_2. This was not accounted for in earlier studies [8, 11].

The stoichiometric relationship between chlorine dioxide consumption and decrease in kappa number is given by Eq. 8:

$$\frac{d(\Delta ClO_2)}{dK} = \ell\,[H^+]^{-0.04} K^{-1.4} \quad (8)$$

where K is kappa number at any time, $[H^+]$ is hydrogen ions concentration in mol/L, and ΔClO_2 is the molar consumption of ClO_2. Also, ℓ is the function of initial kappa number (K_o), initial ClO_2 charge (ClO_{2o}), and temperature (T), which was earlier developed for softwoods [10] and has similar structure for hardwoods given in Eqs. 9–10:

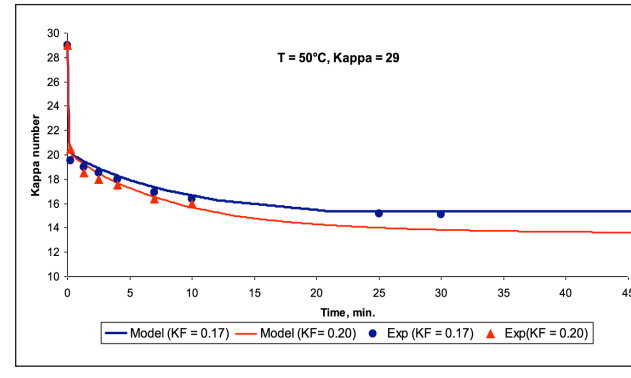
$$\ell = 0.0958 * \exp(734.4/T) * (0.209 * ClO_{2o}^2 - 2.0757 * ClO_{2o} + 10.269) * (-0.006337 * K_o + 0.0005023 * K_o^2) \quad (9)$$

(softwood)

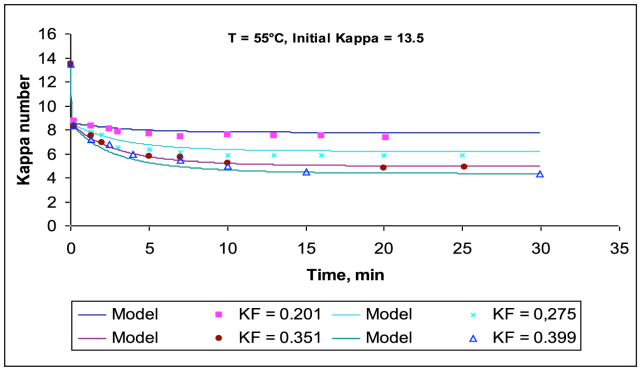
$$\ell = 0.3832 * \exp(314.8/T) * (0.0048 * ClO_{2o}^2 - 0.0731 * ClO_{2o} + 1.3855) * (0.0335 * K_o - 0.0002 * K_o^2 \quad (10)$$

(hardwood)

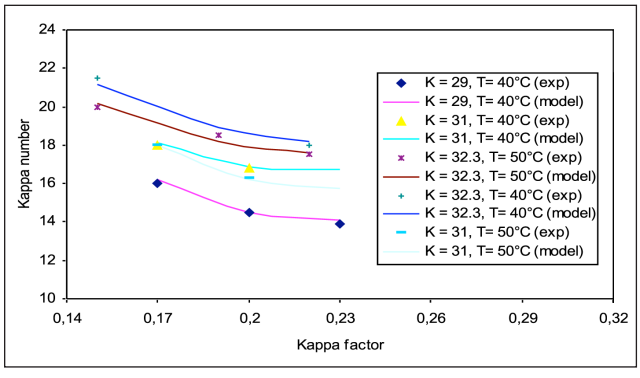
This dependency of coefficient on initial ClO_2 charge better explains the similar observations in recent works [13]. It is also established that the chlorine dioxide consumption with respect to kappa number decrease was also dependent on temperature. **Figures 1** and **2** illustrate decrease of kappa number of a softwood (K = 29) and a hardwood (K = 13.5) taken from literature [14–15] versus time at different kappa factors. It is clear that the chlorine dioxide delignification reaction seems to be a combination of a very fast reaction followed by a slow one. The models proposed earlier [5–9] represented this as fifth order with respect to kappa number, which was not a realistic representation of delignifica-



1. Kappa number with respect to time in D_o stage for a softwood pulp (model validation with literature data [14]).



2. Kappa number with respect to time in Do stage for a hardwood pulp (model validation with literature data [15]).



3. Final kappa number at different initial kappa factors and temperatures used for softwood pulp (model validation with literature data [14]).

tion kinetics. Moreover, those models predicted results only for softwoods after an E stage instead of that after a D_o stage. Tessier and Savoie [14, 15] modeled the slow phase of delignification kinetics without representing the fast phase with a rate equation. Further, no detailed effects of pH, temperature, ClO_2 consumption, and other bleaching parameters were accounted for and the parameters need to be adjusted for a particular set of conditions. Wang and others [12] adapted the C stage models [11] to represent slow phase and fast phase by separate equations. However, the equations were not developed in detail. For example, the ClO_2 consumption with decrease in kappa number was taken linear contrary to results presented later in other studies [8–10, 13], along with the representation of fast and slow phase with same apparent activation energies and the effect of buffering capacity of ionisable groups in pulp while predicting pH. The improved models in our study not only account for all these aspects but also represent the robustness by fitting to a variety of literature data as well as experimental data generated during this research.

The model also fit closely, just as in Fig. 1, to the data for the decrease of kappa number with respect to time at different kappa factors and temperatures for the softwoods (K = 29, 31, 32.3) from same literature source [14]. **Figure 3** summarizes the final kappa number for these softwoods with different initial kappa number at different ClO_2 charges applied and at different temperatures. It is clear that more delignification is achieved at higher temperatures. The model appears to fit well to the experimental data.

Second (D_1) and third (D_2) ClO_2 bleaching stages

The kinetic models in literature [6, 7] were improved for D_1 and D_2 stages. The model is given in Eqs. 11–13 as follows:

$$R_D = -\frac{dK_D}{dt} = k_D * [ClO_2]^{0.5}[H^+]^{-0.3}[K_D - K_{D\infty}]^m \quad (11)$$

$$k_D = A_1 * \left(\frac{1}{K_{D_o}^2} + A_2\right) * \exp\left(-\frac{E_a}{RT}\right) \quad (12)$$

$$\frac{dClO_2}{dK_D} = \frac{A_3}{K_D^n} \quad (13)$$

where, K_D is the chromophore content of the pulp expressed as the light absorption coefficient at 457nm, $K_{D\infty}$ is the floor light absorption coefficient (~0.1 m²/kg), $[ClO_2]$ is the molar concentration of ClO_2, $[H^+]$ is the hydrogen ions concentration in mol/L, E_a is the activation energy (~59 kJ/mol), and K_{Do} is the initial light absorption coefficient. The constants A_1 and A_2 are dependent on the type of prebleaching. $A_1 = 0.145\times10^{10}$, $A_2 = -0.435\times10^{-3}$, $A_3 = 0.393$ and n=1 and m=3 are the values published for D_1 stage [7].

However, two parameters—the constant factor relating chlorine consumption with change in light absorption coefficient and the order (m) of light absorption coefficient in the kinetic equation—had to be adjusted to fit a large set of data coming from softwoods and hardwoods. We found that for the case of D_1 stage, m=1 and A_3 is given in Eqs. 14 and 15:

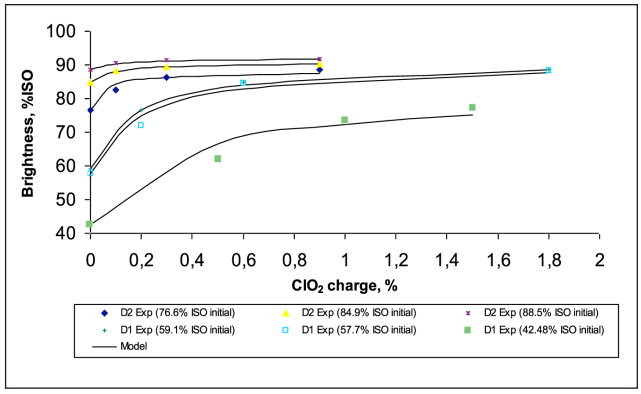
For input brightness <54 %ISO:

$$A_3 = 0.03 * [c]^2 - 0.085 * [c] + 0.095 \quad (14)$$

For input brightness >54 %ISO:

$$A_3 = 0.0424 * [c] + 0.0101 \quad (15)$$

where, [c] is the initial chlorine dioxide charge in D_1 stage expressed as $\%ClO_2$. When the pulp entering D_1 stage had low brightness level (<54% ISO, generally unbleached softwood pulps), the brightening response at low application levels of ClO_2 was observed to be slower than that for the pulp entering D_1 stage with higher brightness (>54% ISO, generally hardwoods and oxygen delignified pulps). This can be related to the fact that pulp with higher lignin content (higher kappa number) and thus lower brightness after first extraction stage is initially difficult to bleach. **Figure 4** illustrates this observation by comparing two pulps entering D_1 stage, one with brightness of 57.7% ISO and the other with brightness of 42.5% ISO. The higher-brightness pulp (57.7% ISO) has a quicker brightening development than the lower-brightness pulp (42.5% ISO) at lower ClO_2 charges. This tendency was not ac-



4. Comparison of experimental and model brightness for D_1 stage and D_2 stages (model validation with literature data [16] on hardwood pulp and experimental data on softwood pulp).

counted for in coefficients proposed earlier [8], mainly due to limited validation of models, especially for unbleached softwood kraft pulp. The model with improved coefficients were validated by our laboratory data for several wood species and thus, in present form, fits well for unbleached or oxygen delignified softwoods and hardwoods.

We also found that the behavior of the pulp in the D_2 stage depends on the brightness of the pulp entering the stage in several important respects. In modeling the D_2 stage, we adopted an approach that was slightly different from that used for the D_1 stage. As stated earlier, the brightness of the pulp emerging from a bleaching stage depends on both the state of the entering pulp and the amount of chemical applied in the stage. We adjusted the two coefficients described earlier. For stage D_2, $A_1 = 0.234\times10^9$ and n = 2.5. A_2 and A_3 are expressed in Eqs. 16 and 17 as functions of the conditions in the E_2 stage:

$$A_2 = B_1 * [OH^-]^{0.1} [t_r]^{0.3} * \exp(-\frac{E_{a1}}{RT}) \quad (16)$$

$$A_3 = B_2 * [OH^-]^{-0.08} * \exp(-\frac{E_{a2}}{RT}) \quad (17)$$

Here $[OH^-]$, t_r and T are the alkalinity, retention time, and temperature of the E_2 stage. The constants B_1 and B_2 were estimated to be 9.1×10^{12} and $(0.1004* \ln(K_{Do}) + 0.2358)$ by fitting the model to experimental data. The values of E_{a1} = 15 kJ/mol and E_{a2} = -8 kJ/mol which is in agreement with literature [11]. In Fig. 4, the results after fitting, with new coefficients, are compared with the corresponding literature [16] data for high brightness extracted hardwood pulp and that with the experimental data generated during current study for a low brightness extracted softwood pulp. The brightness values for the fitted model agreed with the experimental as well as literature data. For D_2 stage, there was a slight deviation observed for lower initial brightness, but under experimental error.

On the basis of electroneutrality of the medium given by Eq. 18, a general equation was derived to predict the pH variation of the medium for all ClO_2 stages. The buffering capacity of ionizable groups in pulp was predicted using Eq. 19:

$$[H^+] + [\text{cations}] = [OH^-] + [\text{Ph-O}^-] + [RCOO^-] + [\text{anions}] \quad (18)$$

$$c_{Ph} \times \frac{K_{Ph}}{1+K_{Ph}} + c_{carb} \times \frac{K_{carb}}{1+K_{carb}} + \frac{K_w}{[H^+]} + h \times \Delta[ClO_2] - \sum_j z_j C^{z_j+} + \sum_i z_i C^{z_i-} - [H^+] = 0 \quad (19)$$

where $[H^+]$ is hydrogen ions concentration in mol/L, [cations] $= \Sigma z_j C^{zj+}$ is the sum of concentration of cationic species in mol/L with z as ionic charge of j^{th} cationic species, $[OH^-]$ is hydroxyl ions concentration in mol/L, $[\text{Ph-O}^-]$ is the concentration of ionized free phenolic groups in pulp in mol/L, $[RCOO^-]$ is the concentration of ionized carboxyl groups in pulp in mol/L, [anions] is the sum of concentration of anionic species like carbonates, hydrogen carbonates, etc. as major buffering species in the liquor in mol/L, ΔClO_2 is the molar consumption of ClO_2, c_{carb} and c_{Pb} are the carboxyl and phenolic content in the pulp in mol/L, K_{carb} and K_{Pb} are the dissociation constant of carboxyl and phenolic content, and h is the stoichiometric coefficient with the values of 0.6 for D_o stage and 0.7 for D_1 and D_2 stages.

MODELING OF FIRST EXTRACTION STAGES

E and (EO) stages

The models for E and (EO) extraction stages were based on the same concept of fast and slow lignin removal, similar to kinetics earlier developed for CE sequence [12] and later adapted by other researchers [11] for DE sequence. The rate of the extraction reactions in E stage is expressed in Eqs. 20–23:

$$R_{Ef} = -\frac{dK_{Ef}}{dt} = k_{Ef} * [OH^-]^{0.2} * K_{Ef} \quad (20)$$

$$k_{Ef} = 6.85*10^6 * \exp(-\frac{39000}{RT}) * f \quad (21)$$

$$R_{Es} = -\frac{dK_{Es}}{dt} = k_{Es} * [OH^-]^{0.05} * K_{Es} \quad (22)$$

$$k_{Es} = 0.0165 * \exp(-\frac{2000}{RT}) * f \quad (23)$$

where, f is the kappa factor used in D_o stage, $[OH^-]$ is hydroxyl ion concentration (mol/L), and k_{Ef} and k_{Es} are the rate constants of the fast and slow reactions, respectively. We found that the initial ratio calculation for fast and slow kappa numbers was dependent on the initial chlorine dioxide charge used in D_o stage. To represent this behavior, kappa factor used in D_o stage was chosen as a parameter. The equation to calculate the initial ratio of slow and fast kappa numbers earlier proposed in literature [11,12] was modified as in Eqs. 24:

$$\frac{K_{Efo}}{K_{Eso}} = 27200 * (-13.604 * f^2 + 7.8719 * f - 0.1266) * \exp(-\frac{28001}{RT}) * [OH^-]^{0.25} \quad (24)$$

The rate of the reactions in fast phase for (EO) stage was found to be same as that in E stage. However, the rate of the reactions in slow phase for (EO) stage was found to follow a second order with respect to kappa number. Also, the rate constants of the slow reactions, k_{Es}, for (EO) depend on the oxygen pressure, as in Eqs. 25 and 26:

$$R_{Es} = -\frac{dK_{Es}}{dt} = k_{Es} * [OH^-]^{0.05} * K_{Es}^2 \quad (25)$$

$$k_{Es} = F(P) * \exp(-\tfrac{37274}{RT}) * f \quad (26)$$

where, P is pressure in bar and F(P) is an empirical function given in Eqs. 27 and 28:

0 < P(bar)≤ 2.4

$$F(P) = 4748.67 * P^{(0.4717 - \frac{171.28}{RT})} \quad (27)$$

2.4 < P(bar)≤ 5

$$F(P) = 2.3308 * P^{(8.7071 - \frac{3162}{RT})} * \exp(\tfrac{2667}{RT}) \quad (28)$$

Figures 5, **6**, and **7** illustrate experimental values taken from literature [13, 17–19] of final kappa numbers at different initial ClO_2 charges in D_o stage, different extraction stage pH, different temperatures, different O_2 pressures, and different initial kappa numbers used for E and (EO) stages. The model predictions appear to be excellent and within experimental error for a wide range of process conditions.

(EP) and (EOP) stages

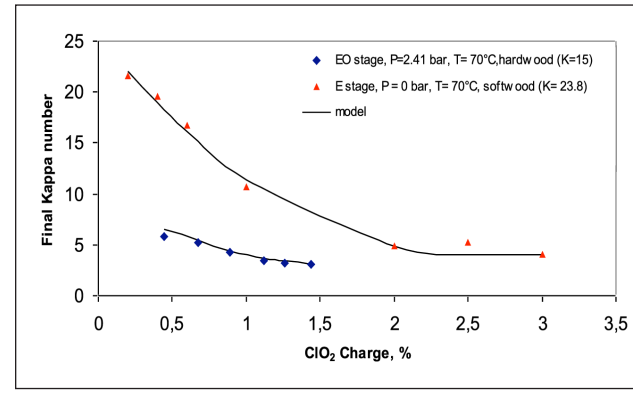
We also developed a semi-empirical model to predict the reduction of kappa number, brightness, pH, and chemical consumption in (EOP) and (EP) stages. The model was based on the measurements of H_2O_2 and NaOH consumption and kappa number during the bleaching reaction. The rate of decomposition of H_2O_2 was modelled according to Eqs. 29 and 30:

$$R_{[H_2O_2]_{tot}} = -\frac{d[H_2O_2]_{tot}}{dt} = k_{H_2O_2 tot} * [H_2O_2]_{tot} \quad (29)$$

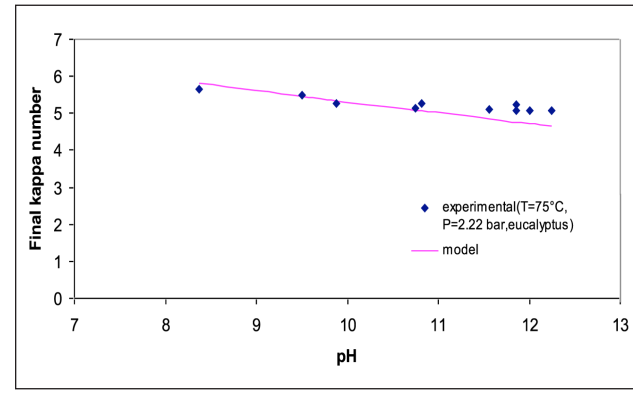
$$k_{H_2O_2 tot} = 1600 * \exp(-\tfrac{4650}{RT}) \quad (30)$$

Figure 8 shows that the rate of decomposition of H_2O_2 was found to be independent of pressure when total pressure was varied between 1 and 10 bars. The order of the decomposition reaction was found to be 1, which is in agreement with the literature [20, 21]. This model refers primarily to base-catalyzed decomposition of peroxide and is valid under mild interference from transition metal ions.

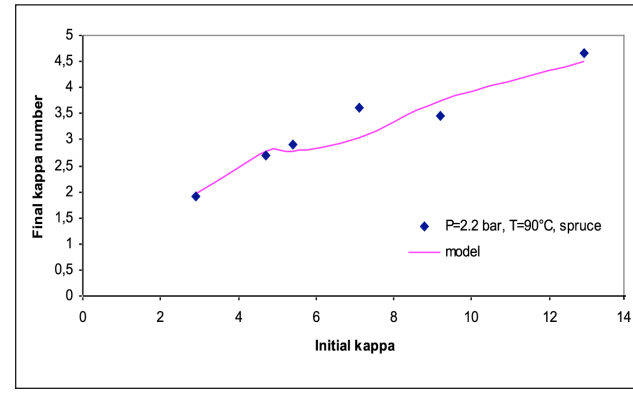
Figure 9 shows the comparison of experimental data taken from literature [22] and model results for the temperature 95°C and 110°C. With increasing temperature, the rate of consumption of H_2O_2 and NaOH increases and the pH of the solution decreases. Also, as bleaching results, improved brightness and a lower kappa value are reached with less retention time. At any constant temperature the pressure has no effect on the rate of the peroxide decomposition nor is there any notorious effect of pressure on the rates of the chemical consumption in the bleaching reactions. A slightly increased kappa number reduction and more evidently improved brightness are achieved with increasing pressure at constant temperature. Contrary to E and (EO) stages, where



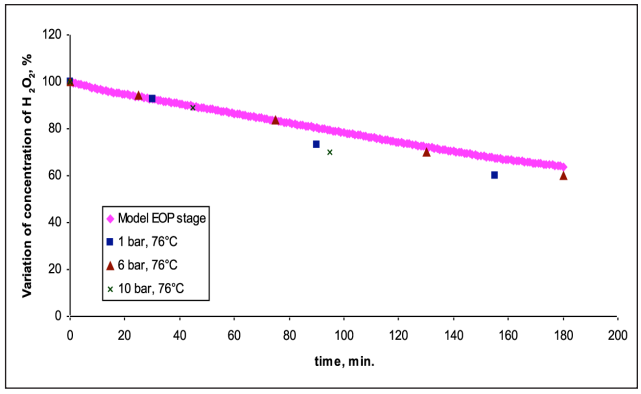
5. E and (EO) stage kappa number at different ClO_2 charges used in D_o stage (model validation with literature data [13, 19]).



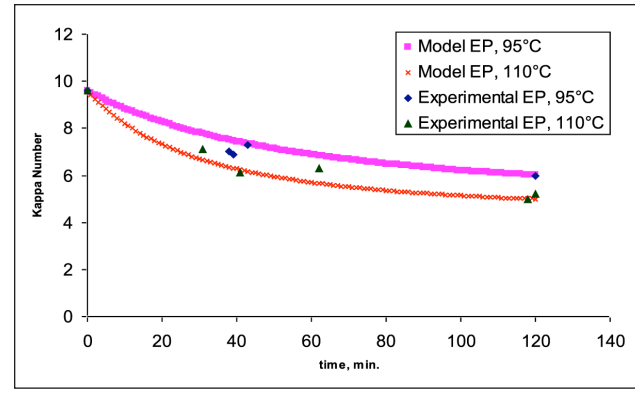
6. Final (EO) stage kappa number at different pH in (EO) stage (model validation with literature data [17]).



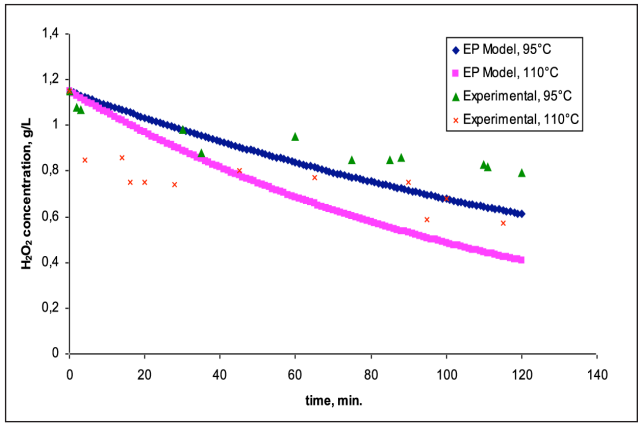
7. Final (EO) stage kappa number at different kappa number after D_o stage (model validation with literature data [18]).



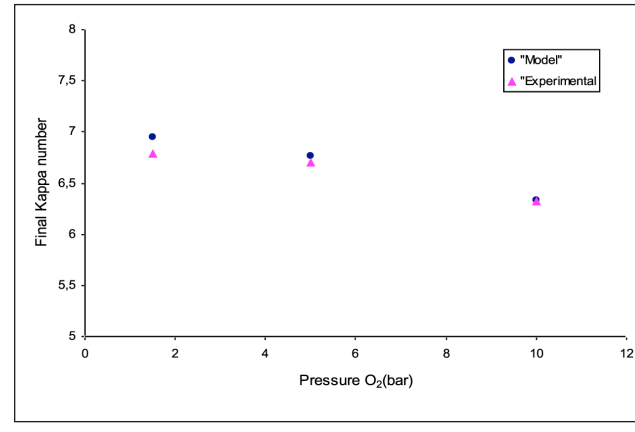
8. Variation of concentration of H_2O_2 with time at 76°C and different pressures (model validation with literature data [21]).



10. Variation of kappa with time at 95°C and 110°C for initial kappa of 9.6 (model validation with literature data [22]).



9. Variation of concentration of H_2O_2 with time at 95°C and 110°C (model validation with literature data [21]).



11. Comparison of final kappa number at different O_2 pressure for initial kappa number of 12, T=95°C (model validation with literature data [21]).

the primary reactive species is OH^- ions, the additional presence of highly reactive HOO^- ions leads to no distinction being made between fast and slow phases of kappa number reduction. A single equation was developed describing the reduction of kappa number with respect to time. This is in agreement with recent studies [23, 24] demonstrating that diffusion of active bleaching chemicals is not the limiting factor in overall peroxide bleaching rate and the division between fast and slow phases does not adequately represent the gradual transition between fast and slow reactions regimes during peroxide stages.

However, the exponent of kappa number was found to be dependent on O_2 pressure. The proposed model for variation of kappa number with respect to time, as in Eqs. 31 and 32, is:

$$\frac{dK}{dt} = -k_{EP,EOP} * K^a [H_2O_2]^b [OH^-]^c \quad (31)$$

$$k_{EP,EOP} = 0.55 * \exp(13.67 - \frac{7740}{RT}) \quad (32)$$

where, a = F(P) = 0.0007 * P^2 + 0.004 * P + 2.1625, b = 1.8, c = 0.2, P is O_2 pressure in bar. For the (EP) stage, F(P) = 2.1625. The experimental data [21, 22] and respective fitted curves from the model for the initial kappa no. of 9.6 at the temperatures of 95°C and 110°C are shown in **Figures 10** and **11**.

Correlations relating kappa number to brightness

Kappa number is related to absorption coefficient by an empirical function (Eq. 33) and the Kubelka-Munk equation is used to convert light absorption coefficient values to brightness (Eq. 34):

$$\frac{k}{s} = f(K) \quad (33)$$

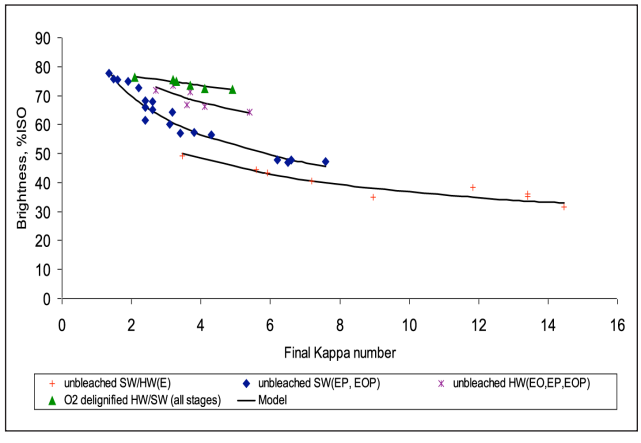
$$\frac{B}{100} = 1 + \frac{k}{s} - \sqrt{2 * \frac{k}{s} + \left(\frac{k}{s}\right)^2} \quad (34)$$

where, f(K) is an empirical function relating kappa number and light absorption coefficient, B denotes the percent reflectance of the pulp sheet in the blue light region at a wavelength of 457 nm (i.e., brightness) and s is the light scattering coef-

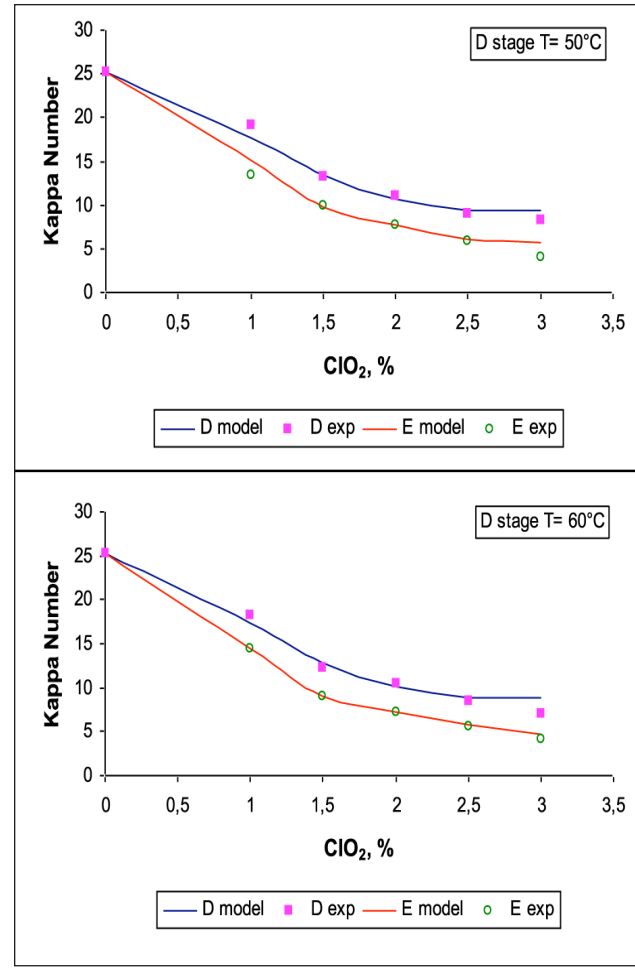
ficient measured at the same wavelength. The relation between k/s and kappa number varies according to the nature of wood (softwood/hardwood), type of pulp (unbleached/oxygen delignified), and the type of extraction stage. However, it follows Eq. 35:

$$\frac{k}{s} = a_1 * K^2 + a_2 * K + a_3 \qquad (35)$$

Table I summarizes the values of the coefficients a_1, a_2, and a_3 for different cases. **Figure 12** shows a typical comparison of laboratory data and model predictions. It is clear that in the case of unbleached softwood pulp, peroxide has an important effect in brightness development contrary to unbleached hardwood pulps in which significant gain in brightness can be obtained both by the presence of O_2 and H_2O_2 in first extraction stage. Oxygen delignified pulps behave differently from unbleached pulp in the way that brightness follows the same trend without respect to the stages,



12. Comparison of experimental and model brightness for unbleached/O_2 delignified pulps.



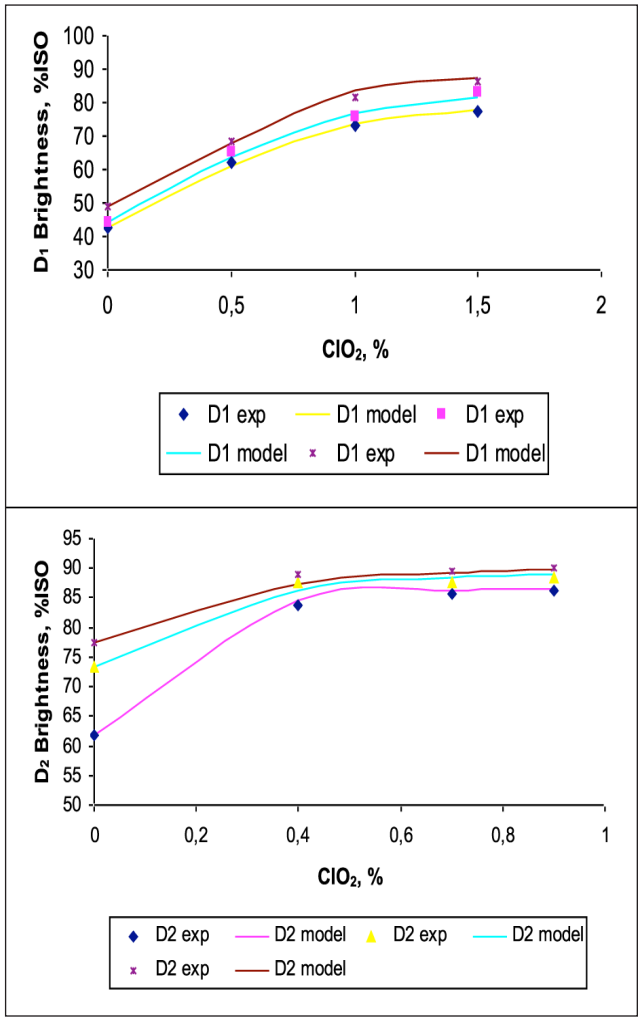
13. Experimental and model results for D_o and E_1 stages at two D_o stage temperatures.

Pulp type	Wood	Extraction stage	a_1	a_2	a_3
unbleached	softwood	E, (EO)	-0.0014	0.0646	0.0415
unbleached	softwood	(EP), (EOP)	-0.0014	0.0594	-0.0478
unbleached	hardwood	E	-0.0014	0.0646	0.0415
unbleached	hardwood	(EO), (EP), (EOP)	-0.0014	0.0301	-0.0207
O_2 delignified	softwood/hardwood	E, (EO), (EP), (EOP)	0.0003	0.0047	0.0243

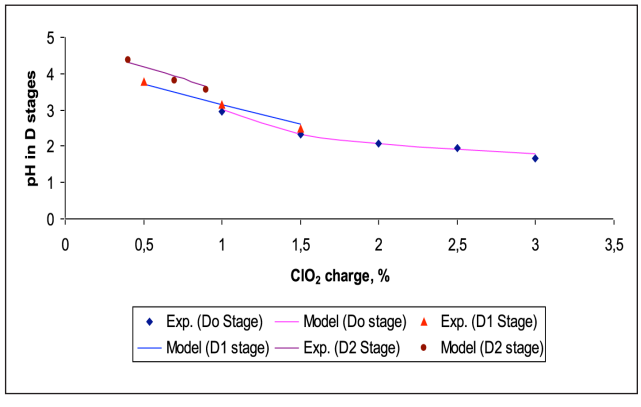
I. Coefficients for relation between k/s and kappa number for different cases.

	D_o	E_1	D_1	E_2	D_2
kappa factor	0.1–0.31	–	0.05–0.156	–	0.042–0.094
ClO_2,%	1.0–3.0	–	0.5–1.5	–	0.4–0.9
Temperature, °C	50, 60	70	70	70	70
NaOH,%	–	2%	–	1%	–
pH	1.68–2.93	11.8–12.2	2.0–4.0	12.2	3–4.5
Consistency, %	10	10	10	10	10
Time, min.	60	60	150	60	180
Initial brightness, %ISO	25.2	varying	42.48, 44.34, 49.12	varying	61.86, 73.26, 77.37

II. Conditions used during experimental study on $D_oE_1D_1E_2D_2$ sequence.



14. Experimental and model results for D_1 and D_2 stages at different initial brightness.



15. Comparison of experimental and model pH for D_o, D_1 and D_2 stages.

solely depending on the final value of kappa number exiting from a particular prebleaching stage.

EXPERIMENTAL

An industrial softwood pine kraft pulp (Tembec-Tarascon, France) with an initial kappa number of 25.2 and an initial brightness of 25.2 ISO was used as raw material. The pulp was sampled after the post kraft pulping washer and was subjected to further washing in the laboratory before bleaching. The study used a conventional ECF bleaching sequence, D_o-$E_1D_1E_2D_2$, solely for models validation. The bleaching stages were performed at 10% consistency in polyethylene bags introduced in a temperature-controlled water bath.

Table II summarizes the conditions used in each bleaching stage. Pure aqueous ClO_2 solutions were prepared by acidification of saturated aqueous $NaClO_2$ with 4N sulphuric acid and ClO_2 gas absorption in pure refreshed water. The prepared ClO_2 solution did not contain any dissolved molecular chlorine. The concentrations of residual mineral chlorinated species (chlorine dioxide, chlorite, chlorate and the sum of hypochlorite and molecular chlorine) were measured on a filtrate sample of bleaching liquor using iodometric titrations [25]. Pulp kappa number was determined according to the NF ISO 302-1981 test method. ISO brightness was determined according to the T452 om-87 TAPPI test method by a Color Touch DATA COLOR instrument. **Figures 13–15** illustrate the results predicted by models as compared with the experimental data generated. Again, the predicted results from the model were found to fit very well to the experimental results.

CONCLUSIONS

We presented the models for all the chlorine dioxide stages [D_o, D_1, D_2] and extraction stages [E, (EO), (EOP), (EP)]. The models predict variations of kappa number, pH, brightness, and bleaching chemical consumption at each step of multistage ECF bleaching sequences. A wide range of laboratory data and literature data was used to validate the models. The results predicted fit very closely to the laboratory and literature bleaching data, and the predictability was extended to a greater variety of pulps (softwood and hardwood pulps, kraft, or other alkaline pulps). Further, the models we developed were for each pulp bleaching stage that can be linked together to create a generic ECF bleaching sequence in a simulator and can be a useful application tool for prediction, decision, diagnosis, process regulation, process optimization, or education. **TJ**

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NOMENCLATURE

a = exponent in Eq. 31, dimensionless
a_1= constant in Eq. 35, dimensionless
a_2= constant in Eq. 35, dimensionless
a_3= constant in Eq. 35, dimensionless

A_1 = constant in Eq.12, $kg^2 \cdot m^{-4} \cdot min^{-1} \cdot mol^{-2} \cdot L^{0.2}$
A_2 = constant in Eq.12, kg^2/m^4
A_3 = constant in Eq.13, m^{2n}/kg^{n-1}
[anions] = the sum of concentration of anionic species, mol/L
b = exponent in Eq. 31, dimensionless
B = the percent reflectance of the pulp sheet in the blue light region at a wavelength of 457 nm, % ISO
B_1 = constant in Eq.16, $kg^2 \cdot m^{-4} \cdot min^{-0.3} \cdot mol^{-0.1} \cdot L^{0.1}$
B_2 = constant in Eq.17, $kg^{1-n} \cdot m^{2n} \cdot mol^{0.08} \cdot L^{-0.08}$
c = exponent in Eq. 31, dimensionless
[c] = initial chlorine dioxide charge in D_1 stage in Eq.14 and 15, $\%ClO_2$
c_{carb} = the carboxyl content in the pulp, mol/L
c_{Pb} = the phenolic content in the pulp, mol/L
[cations] = the sum of concentration of cationic species, mol/L
ClO_{2o} = the initial concentration of chlorine dioxide, % active Cl
[ClO_2] = the concentration of chlorine dioxide expressed as active chlorine, mol/L
ΔClO_2 = the molar consumption of ClO_2, mol/L
E_a = the activation energy of bleaching reaction, kJ/mol
E_{a1} = the activation energy in Eq. 16, kJ/mol
E_{a2} = the activation energy in Eq.17, kJ/mol
f = the kappa factor used in D_o stage, dimensionless
h = the stoichiometric coefficient in Eq. 19, dimensionless
[H^+] = hydrogen ions concentration, mol/L
k = the light absorption coefficient measured at a wavelength of 457nm, m^2/kg
k_{Ef} = the rate constant of the fast lignin removal in extraction stage, $L^{0.2} \cdot mol^{-0.2} \cdot min^{-1}$
$k_{EP,EOP}$ = the rate constant of lignin removal in EP or EOP stage, $L^2 \cdot mol^{-2} \cdot min^{-1}$
k_{Es} = the rate constant of the slow lignin removal in extraction stage, $L^{0.05} \cdot mol^{-0.05} \cdot min^{-1}$
k_f = the rate constant of the fast lignin removal in D_o stage, $L \cdot mol^{-1} \cdot min^{-1}$
$k_{H2O2tot}$ = the rate constant of decomposition of H_2O_2, min^{-1}
k_s = the rate constant of the slow lignin removal in D_o stage, $L \cdot mol^{-1} \cdot min^{-1}$
K = kappa number, mL 0.1N $KMnO_4$/g fibre
K_{carb} = the dissociation constant of carboxyl content, L/mol
K_D = the chromophore content of the pulp expressed as the light absorption coefficient at 457nm, m^2/kg
K_{Do} = the initial light absorption coefficient, m^2/kg
$K_{D\infty}$ = the floor light absorption coefficient, m^2/kg
K_{Ef} = the content of fast reacting lignin in extraction stage expressed as the kappa number
K_{Efo} = the content of initial fast reacting lignin in extraction stage expressed as the kappa number
K_{Es} = the content of slow reacting lignin in extraction stage expressed as the kappa number
K_{Eso} = the content of initial slow reacting lignin in extraction stage expressed as the kappa number
K_f = the content of fast reacting lignin in D_o stage expressed as the kappa number
K_{fo} = the content of initial fast reacting lignin in D_o stage expressed as the kappa number
K_o = initial value of kappa number in D_o stage
K_{Pb} = the dissociation constant of phenolic content, L/mol
K_s = the content of slow reacting lignin in D_o stage expressed as the kappa number
K_{so} = the content of initial slow reacting lignin in D_o stage expressed as the kappa number
K_∞ = the floor level or unreactive lignin in D_o stage expressed as the kappa number
ℓ = the stoichiometric coefficient, dimensionless
m = exponent in Eq.11, dimensionless
n = exponent in Eq.13, dimensionless
[OH^-] = the hydroxyl ions concentration, mol/L
P = pressure, bar
[Ph-O^-] = the concentration of ionized free phenolic groups in pulp, mol/L
R = universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
[$RCOO^-$] = the concentration of ionized carboxyl groups in pulp, mol/L
R_D = the rate of light absorption coefficient decrease in a brightening reaction, $m^2 \cdot kg^{-1} \cdot min^{-1}$
R_{Ef} = the rate of the fast lignin removal in extraction stage, min^{-1}
R_{Es} = the rate of the slow lignin removal in extraction stage, min^{-1}
R_f = the rate of the fast lignin removal in D_o stage, min^{-1}
$R_{[H2O2]tot}$ = the rate of decomposition of H_2O_2, $L^{-1} \cdot mol \cdot min^{-1}$
R_s = the rate of the slow lignin removal in D_o stage, min^{-1}
s = the light scattering coefficient measured at a wavelength of 457nm, m^2/kg
t_r = the retention time of the E_2 stage, min
T = temperature, °K
z_i = ionic charge of i^{th} anionic species, dimensionless
z_j = ionic charge of j^{th} cationic species, dimensionless

LITERATURE CITED

1. Ni, Y., Kubes, G. J., and Van Heiningen, A. R. P., *J. Pulp Paper Sci.*, 21(1): J30(1995).
2. Saltin, G. E., "Kraft pulp bleaching: Kinetic models of conventional systems and laboratory investigation of chlorine free sequences," Ph.D. dissertation, University of Idaho, Moscow, Idaho, U.S.A., September 1993.
3. Gu, Y. X., and Edwards, L. L., "Virtual bleach plants, Part 2: Unified ClO_2 and Cl_2 bleaching model," *TAPPI J.*, 2(7): 3(2003).
4. Kuitunen, S., Tarvo, V., Lehtimaa, T., and Aittamma, J., "Fundamental modelling of pulp bleaching", *13th ISWFPC Conference Proceedings*, APPiTA, Auckland, New Zealand, pp. 257–264, (2005).
5. Germgad, U., Teder, A., and Tormund, D., *Trans. of Tech. Sect.*, 6(2): TR31(1980).
6. Teder, A., and Tormund, D., *Trans. Tech. Sect.*, 3(2): TR41(1977).
7. Tedter, A., and Tormund, D., *AIChE Symposium Series*, 200(76): 133(1980).
8. Mortha, G., Lachenal, D., and Chirat, C., "Modeling multistage chlo-

rine dioxide bleaching," *11th ISWPC Conference Proceedings, Vol. III*, Nice, France, pp. 447–451, (2001).

9. Mortha, G., Lachenal, D., and Chirat, C., "Predicting the results of ClO2 bleaching by modelling", *Proceedings of the PAPTAC 86th Annual Meeting*, Montreal, Quebec, Canada, (2000).
10. Jain, S., Mortha, G., Bénattar, N., and Calais, C., "Critical assessment on modelling of elemental chlorine free bleaching sequence", *14th ISWFPC Conference Proceedings*, paper 172 Tappsa, Kloof, Durban, South Africa, (2007).
11. Wang, R. X., Tessier, P. J. C., and Bennington, C. P. J., *AIChE J.*, 41(12): 2603(1995).
12. Axegård, P., 82(12): 361(1979).
13. Bénattar, N., "Contribution à l'étude du blanchiment des pâtes papetières obtenues par des procédés sans soufre", Ph.D. thesis, Grenoble INP– AGORA, Grenoble, France (2005).
14. Savoie, M., and Tessier, P., *TAPPI J.*, 80(6): 145(1997).
15. Tessier, P., and Savoie, M., *TAPPI J.*, 83(6): 139(2000).
16. McDonough, T. J., Rawat, N., and Krishnagopalan, G. A., *Appita J.*, 57(5): 381(2004).
17. Basta, J., Wane, G., Meulier, L., Herstadt-Svard, S., Birath, L., and Fujiwara, N., "New aspects of ECF bleaching on Eucalyptus pulps", *Proceedings of the 28th Annual Pulp and Paper Meeting*, ABTCP, Sao Paulo, Brazil, pp. 115–133, (1995).
18. Reeve, D. W., and Weisher, K. M., *TAPPI J.*, 82(10): 136(1999).
19. Bjorklund, M., Germgard, U., and Basta, J., *Appita J.*, 57(3): 234(2004).
20. Stevens, J. A., and Hsieh, J. S., "Dynamic modelling of hydrogen peroxide decomposition in pressurized peroxide bleaching", TAPPI proceedings, International Pulp Bleaching Conference, Atlanta, GA, USA. Tappi Press, pp. 589–593, (1996).
21. Koukkari, P., and Salminen, J. "Thermochemistry and reaction kinetics of PO-bleaching," *9th ISWFPC Conference Proceedings*, Montreal, Quebec, Canada, pp. 501–505, (1997).
22. Koukkari, P., and Salminen, J. "Thermochemical modelling of PO-bleaching," International Pulp Bleaching Conference Proceedings, Book 2, KCL Finnish Pulp and Paper Research Institute, Tyvaskyla, Finland, pp. 527–531, (1998).
23. Wiklund, L., Ohman, L., and Liden, J., *Nordic Pulp Paper Res. J.*, 16(4): 339(2001).
24. Malmberg, B., and Edwards, L., *TAPPI J.*, 6(2): 9(2007).
25. Wartiovaara, I., *Paperi ja Puu– paper och Tra*, 9: 534(1982).

INSIGHTS FROM THE AUTHORS

This work fits into our area of research at Grenoble-INP and represents a significant improvement in modelling over earlier studies. Our biggest challenge was to gather all information and fit it into the context of a large volume of existing work and data. We occasionally encountered results that were unexpected. The next step is to refine and extend modelling to ECF and TCF processes or dynamic mill modelling and include energy balances.

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