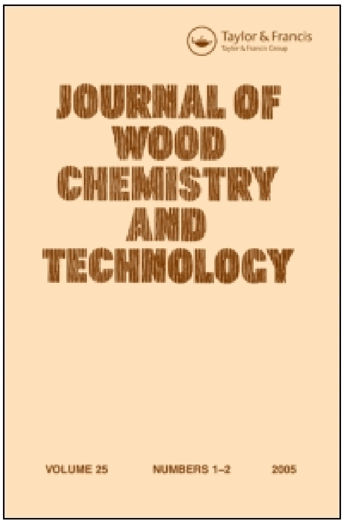

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Huan Wang[a]; Zhibin He[a]; Yonghao Ni[a]
[a] Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, NB, Canada

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A Kinetic Model of the Magnesium Hydroxide–Based Peroxide Bleaching Process of a TMP

Huan Wang, Zhibin He, and Yonghao Ni
Limerick Pulp and Paper Centre, University of New Brunswick,
Fredericton, NB, Canada

Abstract: In this study, a kinetic model of the magnesium hydroxide–based peroxide bleaching was developed. A thermo-mechanical pulp (TMP) was used to determine how the bleaching rate is affected by the peroxide and alkali concentrations, and temperature at a high pulp consistency (30% pulp consistency). The model was based on the rate of chromophore elimination characterized by the decrease in the light absorption coefficient of bleached pulp at 457 nm, C_k. The reaction rate of chromophore destruction proceeds via a very fast phase initially, followed by a second phase, which is much slower and approaches asymptotically a "floor level" of chromophore concentration.

The rate equation is:

$$\frac{dC_k}{dt} = k\ [H_2O_2]^{1.3}[OH^-]^{0.14}(C_k - C_{kf})^{2.7}$$

$$k = 2.25 \times 10^6\ e^{-61800/RT}$$

The term of $C_k - C_{kf}$ represents reactive chromophores available in the pulp. C_{kf} was determined as 3.04 m^2/kg, which corresponds to a brightness of 79.6% ISO.

Keywords: Brightness development, kinetics, magnesium hydroxide, mechanical pulp, peroxide bleaching, thermo-mechanical pulp

Address correspondence to Yonghao Ni, Limerick Pulp and Paper Centre, University of New Brunswick, P. O. Box 6900, Fredericton, NB, E3B 6C2, Canada. E-mail: yonghao@unb.ca

INTRODUCTION

As the application of bleached mechanical pulp in different paper grades continues to increase in the paper industry and the market demand on pulp brightness continues to rise, the mechanical pulping industry becomes more and more dependent on peroxide bleaching for brightness improvement. Hydrogen peroxide, which has been applied in the industry for a long time, is still the dominant chemical for bleaching of mechanical pulps.

Hydrogen peroxide bleaching is usually carried out under alkaline conditions to achieve significant brightening effect. Sodium hydroxide is usually used as the alkali source. Such a process is characterized by an efficient brightness development; however, due to its strong alkalinity, in particular at the initial phase of the process, significant amounts of organics from pulp fibers are dissolved into the bleaching filtrate resulting in pulp yield loss, and the formation of anionic trash, to be carried into the papermaking process.[1,2] Also, a strong alkalinity may lead to extensive hydrogen peroxide decomposition in cases whereby poor chelation and/or metal management occurs.[3,4] Another concern is alkali darkening, that is, the formation of new chromophores in the course of bleaching due to the strong alkaline condition.[5–7]

Some recent studies have shown that the substitution of magnesium hydroxide ($Mg(OH)_2$) for caustic soda (NaOH) in peroxide bleaching of mechanical pulp can result in many beneficial effects, such as less anionic trash formation, lower COD load of the effluent, higher bleaching yield and better optical properties of the bleached pulp,[8–17] as well as decreased oxalate-related scaling problem in the bleach plant.[18,19] Although the reaction rate of the $Mg(OH)_2$-based process is slower than the NaOH-based process, it can be compensated for by a longer reaction time and/or a higher bleaching temperature.[14] A number of mills in North America have implemented the technology.

There have been many kinetic investigations in the literature regarding peroxide bleaching of mechanical pulps.[20–26] All are related to the traditional NaOH-based peroxide bleaching process. The kinetic model of the $Mg(OH)_2$-based peroxide bleaching has not been reported. The strong alkalinity in the NaOH-based peroxide process can cause excessive dissolution of lignin and hemicellulose, resulting in increased COD load of the effluent and decreased pulp yield. In addition, the high alkalinity of the process leads to the formation of a significant amount of anionic trash, which is carried over to the wet-end of the paper machine and interferes with chemicals used in the papermaking process, leading to increased polymer/additive cost, reduced drainage and decreased product quality. Using weak alkalis, such as magnesium hydroxide, is a solution to these problems.

The purpose of this study was to develop a kinetic model to describe the brightness development under various bleaching conditions of the $Mg(OH)_2$-based process by following a similar approach reported before.[27] The bleaching rate (dC_k/dt) is defined as the chromophore elimination per unit time. The chromophore concentration was estimated by the Kubelka-Munk light absorption coefficient at 457 nm, k_{457}, and denoted as C_k.

EXPERIMENTAL

Raw Material

The spruce unchelated mill TMP pulp samples were received from a mill in Eastern Canada. Chemicals used in the experiments were reagent grades except Na_2SiO_3 and $Mg(OH)_2$, which were industrial grades from National Silicate and Martin Marietta Magnesia specialty, respectively.

Chelation

The unchelated TMP pulp with 10% consistency was received directly from the unbleached pulp storage tower. A lab chelation was performed under the conditions of 60°C, 30 min, 0.4% DTPA on o.d. pulp. Subsequently, the pulp slurry was filtrated in a Buchner funnel with a 200-mesh screen, the filtrate was recycled once to go through the fibre mat to collect the fines. The pulp mat was then pressed to a 30% consistency, and it was stored in sample bags in a refrigerator and ready to be used for pulp bleaching.

Peroxide Bleaching

The peroxide bleaching experiments were conducted in plastic bags using the following conditions: 6 grams of oven dry pulp, 30% pulp consistency, 0.8% $Mg(OH)_2$, 0.5% DTPA (diethylenetriaminepentaacetic acid), 3.5%H_2O_2. The required amount of DTPA and magnesium hydroxide were added to the pulp first, which was in a plastic bag. After a thorough mixing, the bag, with its contents, was placed into a temperature bath for one minute. Then, the required amount of hydrogen peroxide was added to the bag. Again, a thorough mixing was provided. The plastic bag was sealed and placed into a water bath for the desired retention time.

At the completion of the bleaching time, the pulp sample was cooled down to room temperature immediately with cold running water, and some bleaching liquor was pressed from the pulp sample. The bleaching liquor was immediately used for determining the pH and residual peroxide. The concentration of hydrogen peroxide was determined iodometrically.

The bleached pulp sample was then dispersed into a 2% pulp slurry with deionized water, and its pH adjust to 5.0 with sulphurous acid, and then handsheets were prepared in accordance with the CPPA standard C.5(1996). Deionized water was used on all occasions.

In order to obtain the light scattering coefficient (s) and light absorption coefficient (k), the sheet brightness was measured following the CPPA standard E.1 (1996), and the k/s was calculated from the Kubelka-Munk equations.

Data Analysis

We used the so-called differential method[23,28] for the establishment of the rate expression. To determine the rate constant and the reaction orders in the proposed bleaching rate equation, a series of bleaching experiments were carried out with fixed initial conditions (consistency, chemical dosages) at a constant temperature but with various reaction times to obtain experimental data on the relationships of C_k-t, $[H_2O_2]$-t, and $[OH^-]$-t. Mathematical expressions were then obtained from the experimental data by regression. The reaction rate (dC_k/dt) at any time (t) in the bleaching process can then be calculated by differentiating the mathematical expression of the C_k-t relations. With the data on C_k-t, $[H_2O_2]$-t, $[OH^-]$-t, and (dC_k/dt)-t, the best-fit values of the rate constant (k) and the reaction order variables (a, b, and n) in the proposed rate equation can be calculated on a computer using Maple. The bleaching experiments were then repeated at different temperatures, and the same data analysis procedures were repeated to obtain the estimated values for k, a, b, and n for the given temperature. The activation energy (E_a) was determined according to the Arrhenius law.

RESULTS AND DISCUSSION

Figure 1 shows the time-dependent change of brightness during the bleaching process at three temperature levels. Similar to the conventional sodium hydroxide–based peroxide bleaching process, the magnesium hydroxide–based peroxide process can be characterized by very fast reactions at the beginning, and slows down significantly as the reaction progresses. As bleaching reaction continues, the brightness approaches asymptotically a “floor level.” The apparent limit to brightness may be associated with the properties of the pulp itself, which is the presence of unreactive chromophoric structure in the pulp, and responsible for the formation of so-called ‘floor-level’ chromophores, C_{kf}.[27] The brightness ceiling for a single peroxide stage is 79.6% ISO, which was obtained at 80°C with peroxide charge of 12%, magnesium hydroxide charge of 1.5%, and DTPA charge of 0.8% for 8 hours.

The kinetic model has a general expression:

$$-\frac{dC_k}{dt} = k[H_2O_2]^a[OH^-]^b(C_k - C_{kf})^n \tag{1}$$

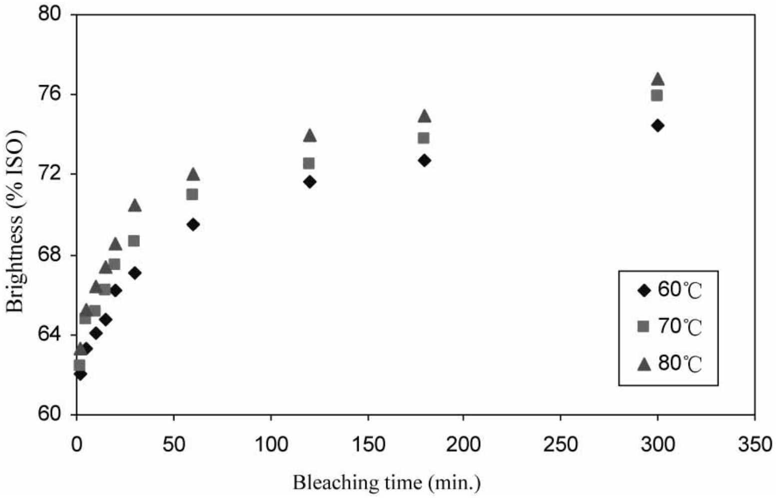

Figure 1. Brightness development of the peroxide bleaching process at different temperatures.

C_k = the concentration of chromophores, estimated by the light absorption coefficient at 457 nm
k = reaction rate constant
t = reaction time
a, b, n = orders of reaction

There are four variables of the kinetic model, that is, reaction rate k and reaction orders with respect to peroxide, alkali and light absorption coefficient.

As indicated in Eq. (1), the chromophore concentration is described by the absorption coefficient determined at 457 nm, C_k. Earlier kinetic studies have shown that C_k is proportional to the concentration of chromophore in pulp, and is thus more suitable than the brightness, which is affected by both the light absorption coefficient and the light scattering coefficient.[27] Therefore, the absorption coefficient was used to describe the chromophore concentration, instead of brightness. The absorption coefficient at 457 nm, C_k, can be determined from the pulp brightness, and the reflectance of a paper sheet with a basis weight of W_0 over a black background, R_0, from the Kubelka-Munk equations.[27]

Effect of Temperature

In order to examine the effect of temperature on the rate of chromophore removal, we plotted the absorption coefficient at 457 nm as a function of time, for temperatures of 60, 70, 80°C, shown in Figure 2. As expected, the rate of chromophore elimination increases as the temperature increases.

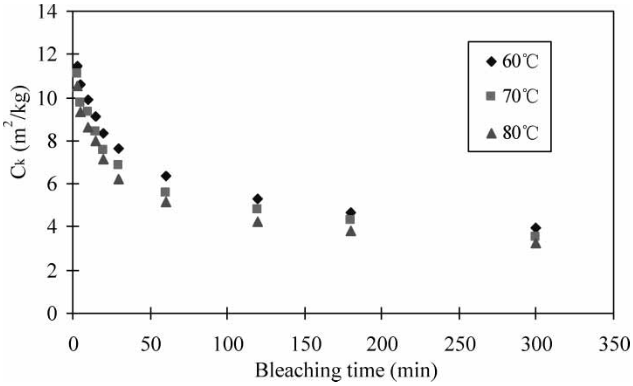

Figure 2. The decrease of light absorption coefficient during the bleaching process.

Effect of Peroxide and Alkali Concentration

The separate effects of peroxide and alkali can not be obtained directly by the differential method.[23] By estimating the reaction rate in a C_k–time plot and the peroxide and alkali concentrations at that time, a kinetic equation can be calculated. Figure 3 shows the decrease in peroxide concentration during the bleaching, and the pH profiles were shown in Figure 4. In each case, the pH increased slightly during the first phrase (the first 15 minutes). Subsequently the pH decreased significantly from 15 minutes to 300 minutes. This is different from the pH development of the NaOH-based peroxide bleaching process, whereby the pH decreases at all time as the reaction continues.[22] This can be explained by the fact that $Mg(OH)_2$ is a weaker alkali and the majority of the charged magnesium hydroxide are present as particles in the pulp fibre for the first 15 minutes, subsequently it is dissolved in the filtrate.

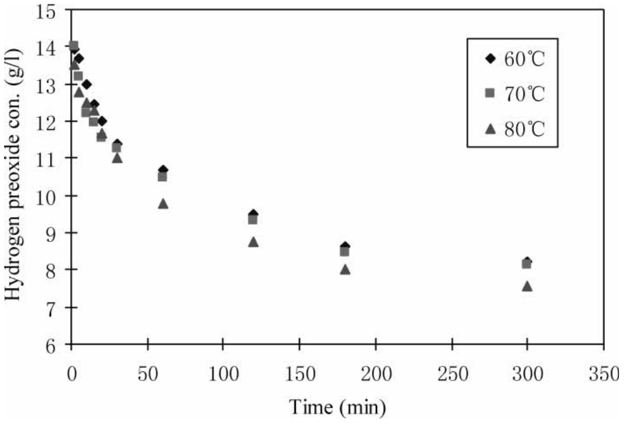

Figure 3. The decrease of peroxide concentration during the bleaching process.

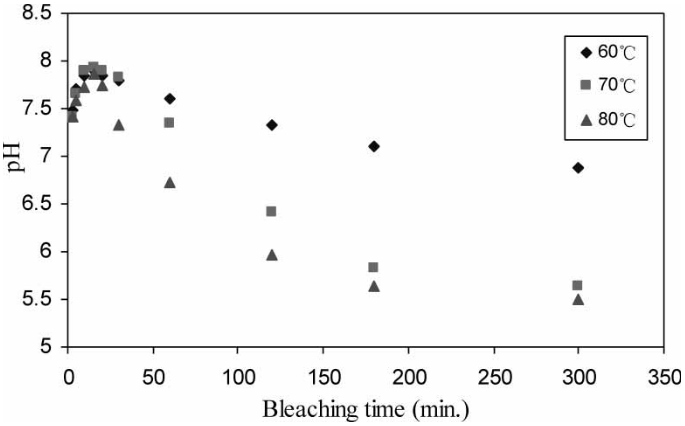

Figure 4. The pH profiles at different temperatures.

Final Model

With the determination of chromophore concentration C_k and the measurement of hydrogen peroxide concentration and pH during peroxide bleaching, it is possible to determine the rate constants of Eq. (1) by an optimization technique.

A computer program was used to obtain the reaction order for each reactant.[29] The activation energy (E_a) for the reaction can be obtained from the Arrhenius plot, as shown in Figure 5. The final rate equation is:

$$-\frac{dC_k}{dt} = k[H_2O_2]^{1.3}[OH^-]^{0.14}(C_k - C_{kf})^{2.7}$$
$$k = 2.25 \times 10^6\ e^{-61800/RT} \quad (2)$$

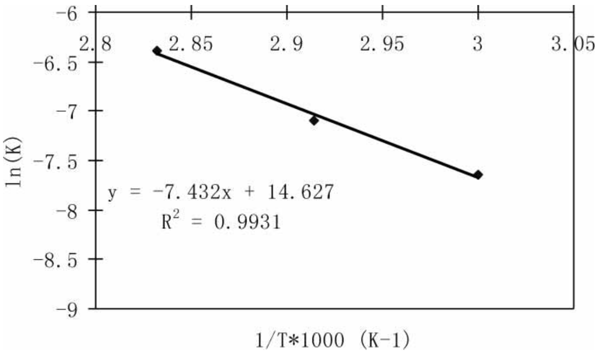

Figure 5. Arrhenius plot of the rate constant.

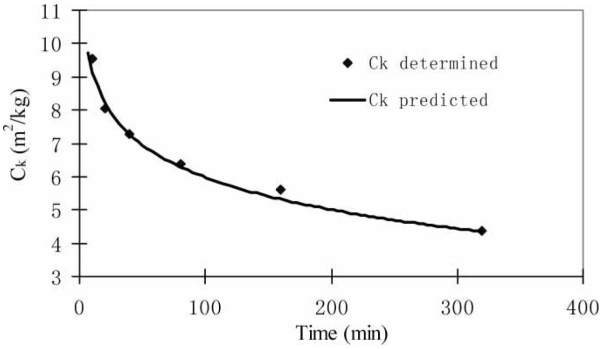

Figure 6. Comparison of experimentally determined and predicted light absorption coefficients, I. (The bleaching conditions were 1.0% $Mg(OH)_2$, 0.5% DTPA, 3.5% H_2O_2, and 70°C).

Confirmation of the Model

Finally, with the present kinetic model, we can predict the development of chromophore destruction during the $Mg(OH)_2$-based peroxide bleaching. Figure 6 shows the results of the absorption coefficients predicted based on Eq. (2) versus those determined experimentally. The bleaching conditions were 1.0% $Mg(OH)_2$, 0.5% DTPA, 3.5% H_2O_2 (based on o.d. pulp) and 70°C. These conditions were to simulate those used in the mill, which was allowed to produce about 75% ISO. It is evident that the model predictions follow the experimental data.

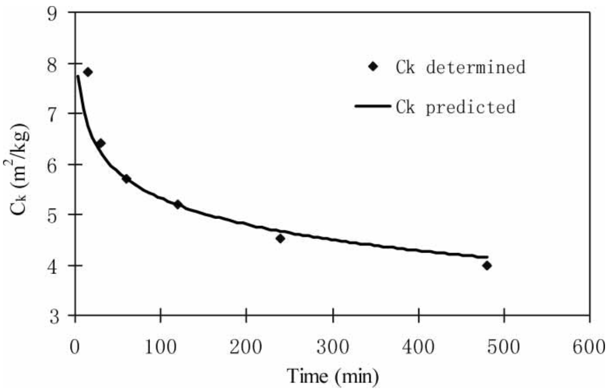

Figure 7. Comparison of experimentally determined and predicted light absorption coefficients, II. (The bleaching conditions were 1.0% $Mg(OH)_2$, 0.5% DTPA, 6.0% H_2O_2, and 70°C).

Another experimental run was conducted to confirm the model. The conditions were 1.0% $Mg(OH)_2$, 0.5% DTPA, 6.0% H_2O_2 (based on o.d. pulp), and 70°C. The results are shown in Figure 7. Based on these results, one can conclude that the developed rate equation accurately predicts the rate of chromophore elimination during the $Mg(OH)_2$-based peroxide bleaching of TMP pulp.

CONCLUSIONS

The kinetic model of the magnesium hydroxide–based peroxide bleaching was developed based on the rate of chromophore elimination characterized by the decrease in the light absorption coefficient. The chromophore destruction proceeds rapidly in the initial phase, followed by a much slower reaction during which a "floor-level" chromophore concentration is approached asymptotically. The inclusion of C_{kf}, the "floor-level" chromophore concentration in the kinetic equation, is to reflect the fact that not all of the chromophoric groups can be destroyed during the hydrogen peroxide bleaching stage.

The reaction orders were determined based on the differential method. The rate of the chromophore elimination can be expressed as:

$$-\frac{dC_k}{dt} = k[H_2O_2]^{1.3}[OH^-]^{0.14}(C_k - C_{kf})^{2.7}$$

$$k = 2.25 \times 10^6\ e^{-61800/RT} \tag{2}$$

Where $C_k - C_{kf}$ is the reactive chromophores available in the pulp, C_{kf} is determined as 3.04 m^2/kg, which corresponds to a brightness of 79.6% ISO.

The Arrhenius' activation energy was 61.8 $kJ \cdot mol^{-1}$. It should be point out that the kinetic model may be valid only for conditions resembling those used in its determination. Finally, it was shown that the kinetic equation can accurately predict the experimental results.

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