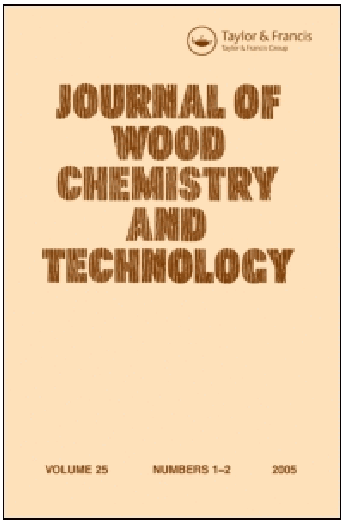

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KINETIC MODELS FOR HYDROGEN PEROXIDE BLEACHING OF MECHANICAL PULPS

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ABSTRACT

Several commercial thermomechanical pulps and stone groundwood pulps were bleached to determine how the bleaching rate is affected by peroxide and alkali concentration, pulp consistency and temperature. The bleaching rate seems to be determined by the balance between the bleaching action of peroxide anion (HO_2^-) and color formation by alkali (OH^-). At a given peroxide concentration, increased alkalinity increased the bleaching rate due to the formation of peroxide anion, up to a given alkali concentration above which a further increase led to a decrease in reaction rate. This is probably due to the fact that at high alkalinity, pOH < 2.5, an increase in hydroxide ion concentration gives only a slight increase in the peroxide anion concentration, at lower alkalinity, the increase in peroxide anion concentration is approximately proportional to that of the hydroxide ion.

The bleaching rate (dC_k/dt) at 15% pulp consistency could be expressed by the kinetic equation

$$-dC_k/dt = k\left[H_2O_2\right]_{tot}^{0.67}\left[OH^-\right]^{0.23} C_k^{2.2}$$

where C_k is the light absorption coefficient at 457 nm. The reaction orders were dependent on the method of investigation. The Arrhenius' activation energy was about 45 kJ mol^{-1}.

INTRODUCTION

Peroxide bleaching is today mostly manually controlled. The charges of bleaching chemicals are regulated principally by taking into consideration the production of pulp and the final brightness. When a change in brightness occurs as a consequence of some disturbance such as altered pulp consistency or quality of wood, there is a considerable lapse of time before detection and before a correction can be made. The bleaching time is 1-2 hours and another half hour is usually required for determination of the final brightness. This can result in a waste of bleaching chemicals and an uneven brightness of level of the bleaching pulp. For an optimization and automatic control of the bleaching process it is advantageous to know how the rate of chromophore elimination is affected by temperature and the concentration of alkali and peroxide, and what chemicals are required to achieve a certain brightness gain. This basic information, transformed into a mathematical form, can then be used for computer simulation or in a computerized control of the bleaching process.

The purpose of this study was to find a kinetic model and also to study whether parameters other than alkali, peroxide, pulp consistency and temperature affect the rate of chromophore elimination in either thermomechanical pulp or stone groundwood. Several kinetic models were discussed and two bleaching and evaluation techniques were used. Results from preliminary work have been published earlier[1].

KINETIC MODELS

For a kinetic study there are two primary methods of investigation to choose from.

The first is the "Constant Conditions Method" in which the concentrations of active chemicals, peroxide and alkali are held constant throughout the bleaching. This condition is maintained by adding chemicals, in the present case peroxide and alkali, to a very low pulp consistency slurry, as they are consumed. The advantage of this method is that it is easy to isolate the effect of each variable. The conditions also resemble the technique commonly used for bleaching chromophore model compounds[2]. This make a comparison between bleaching of pulp and bleaching of chromophore model compounds easy. It is also a well-established technique for kinetic investigations of pulp bleaching and thus facilitates the comparison with the kinetics of other processes[3,4]. The disadvantage is the divergence from the mill conditions. This is especially pronounced in the case of pulp consistency and the chemical concentration profiles during the bleaching.

In the "Differential Method", the bleaching conditions resemble a mill bleaching, i.e. the bleaching chemicals are charged to the pulp at the start, and the concentration of peroxide and alkali then decrease as the bleaching proceeds. The advantages and disadvantages of the Differential Method are quite contrary to those of the Constant Conditions Method, but the mill-resembling "Differential Method" is the most adequate form for use in practice.

Both the Constant Conditions Method and the Differential Method were used in this study. The two methods led to slightly different kinetic models which are discussed below.

The bleaching rate ($-dC_k/dt$) is defined as the chromophore elimination per unit time. The chromophore content can be estimated by the Kubelka-Munk light absorption coefficient at 457 nm, k_{457}, and denoted C_k.

The fundamental property, light absorption coefficient, is more appropriate than reflectivity (brightness) to characterize the pulp with respect to color content. This is due to the fact that the reflectivity of paper depends on both the chemical composition color and the physical structure of the paper.

To be able to use the kinetic equation in practice, the measurable forms of the chemical reagents must be represented in the equation. In peroxide bleaching, these are hydrogen peroxide, $[H_2O_2]_{tot}$ and alkalinity, $[OH^-]$. The bleaching may be expressed by the mathematical model in Equation 1.

$$-dC_k/dt = k \left[H_2O_2\right]_{tot}^{a} \left[OH^-\right]^{b} C_k^{n} \qquad [1]$$

where a, b, n = reactions orders,

k = rate constant, and

$$\left[H_2O_2\right]_{tot} = \left[H_2O_2\right] + \left[HO_2^-\right]$$

RESULTS AND DISCUSSION

Constant Condition Method

Effect of reaction time

The decrease in the light absorption coefficient with bleaching time was initially very rapid but later became increasingly slower. The form of this curve (Fig. 1) is a measure to the reaction order n in Equation 1. A reaction order of 4.8 was found to approximately fit the experimental data. The technique to determine n was described previously[5]. Different pulps showed some dispersion around the mean value 4.8 as reported in Table 1.

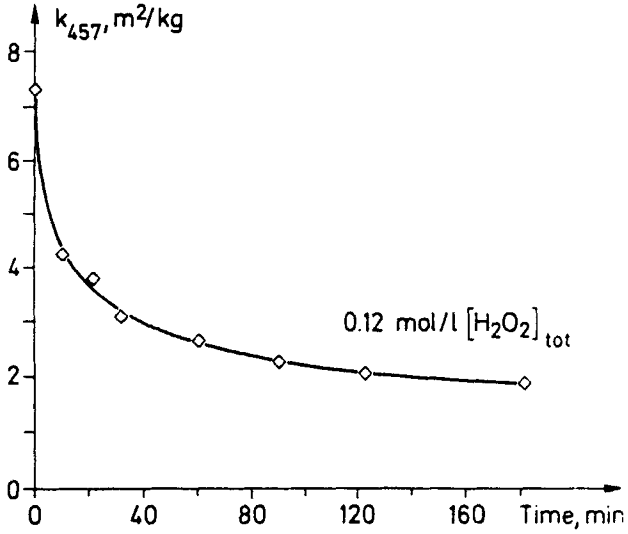

FIGURE 1. The light absorption coefficient versus bleaching time pOH 3, 0.12 mol H_2O_2/l, 60°C.

TABLE 1

Reaction Orders Determined for Thermomechanical Pulps (T) and Stone Groundwood Pulps (SGW) by the Constant Conditions Method.

Pulp	Reaction orders, Equation 1			Activation Energy (kJ/mol)	Rate constant, k $(m^2/kg)^{-3.8}$ $(mol/l)^{-1.45}$ $(min)^{-1}$ 60°C
	a	b	n		
SGW-1	1.0 (0.2)	0.38 (0.08)	5 (0.2)	68 (15)	0.028
SGW-2	1.0 (0.1)	0.44 (0.01)	5 (0.5)	43 (4)	0.023
SGW-3	-	-	4.5 (1.0)	50 (4)	-
T-1	1.0 (0.5)	0.43 (0.06)	5 (0.5)	47 (5)	0.022
T-2	1.0 (0.2)	0.73 (0.16)	4.5 (1.0)	44 (7)	0.016
T-3	1.0 (0.1)	0.48 (0.08)	4.5 (1.0)	-	-

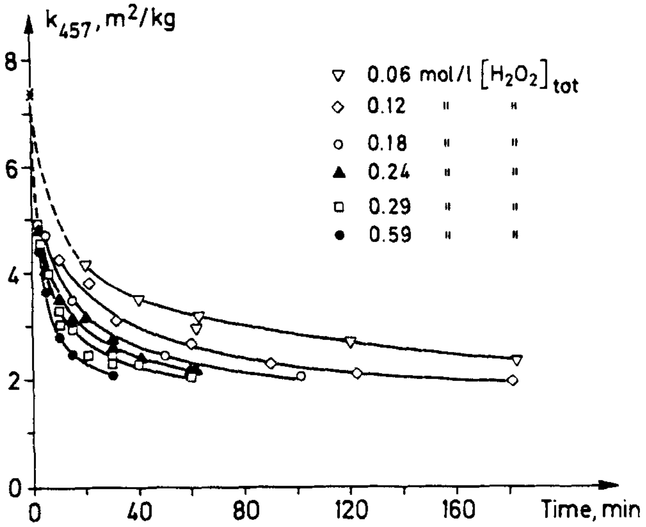

FIGURE 2. The light absorption coefficient versus bleaching time at different peroxide concentrations. pOH 3, 60°C. Constant conditions.

The dispersion in reaction order for each pulp is expressed in Table 2 as the range between the highest and lowest estimated values.

A reaction order of 4.8 is of course not an ordinary reaction order related to some simple reaction mechanism. It must be interpreted merely as an empirical reaction order which describes a fast initial phase and a slow final phase[5]. The bleaching effect is probably the combination of many simultaneous reactions, i.e. the bleaching of different chromophores with different bleaching rates and the creation of others through the action of alkali and peroxide.

Effect of total peroxide concentration

The bleaching rate increased, as expected, with increasing peroxide concentration (Fig. 2). At a constant (pOH = $-\log [OH^-]$), the bleaching rate was directly proportional to the total concentration of peroxide for both TMP and SGW pulps. Thus, the value of a in Equation 1 is approximately 1.0.

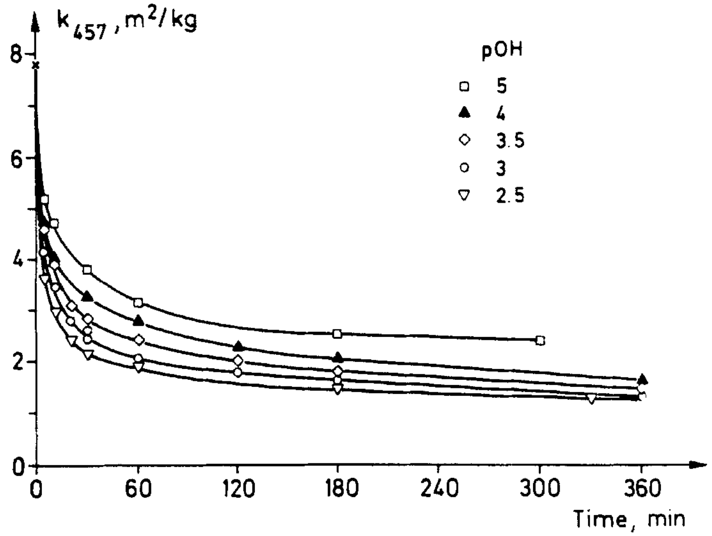

FIGURE 3. The light absorption coefficient versus bleaching time at different pOH levels
0.176 mol H_2O_2/l, 60°C. Constant conditions.

Effect of alkali concentration

The bleaching rate increased with increasing alkali concentration in the range pOH 5-2.5 (Fig. 3). The reaction order with respect to alkali (b, Equation 1) is approximately 0.45 in this range. Thus, the final kinetic model for this pOH range is

$$-dC_k/dt = k \left[H_2O_2\right]_{tot}^{1.0} \left[OH^-\right]^{0.45} C_k^{4.8} \qquad [2]$$

A further increase in alkalinity led, to a pronounced decrease of the bleaching rate (Fig. 4).

The maximum in the bleaching rate at pOH 2.5 is probably due to a balance between the bleaching reactions of peroxide and chromophore creation by alkali and peroxide.

Figure 5 shows the increase in the light absorption coefficient due to reactions with alkali in the absence of peroxide. This creation of chromophores probably also takes place during peroxide

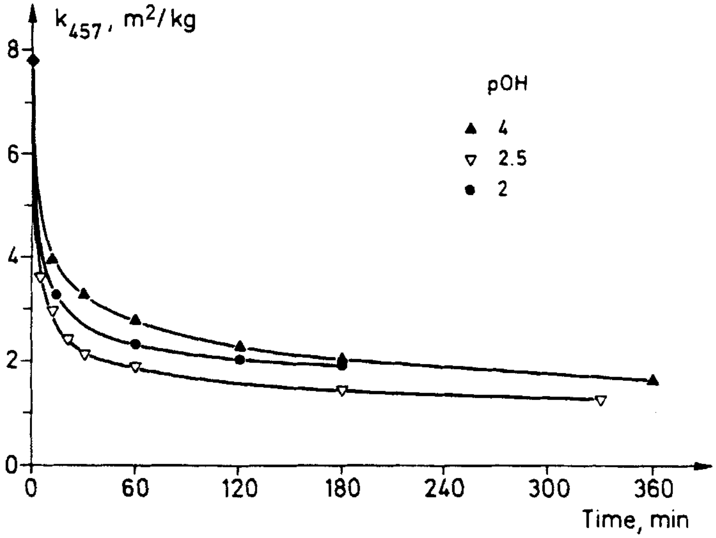

FIGURE 4. The light absorption coefficient versus bleaching time at different pOH levels.
0.176 mol H_2O_2/l, 60°C. Constant conditions.

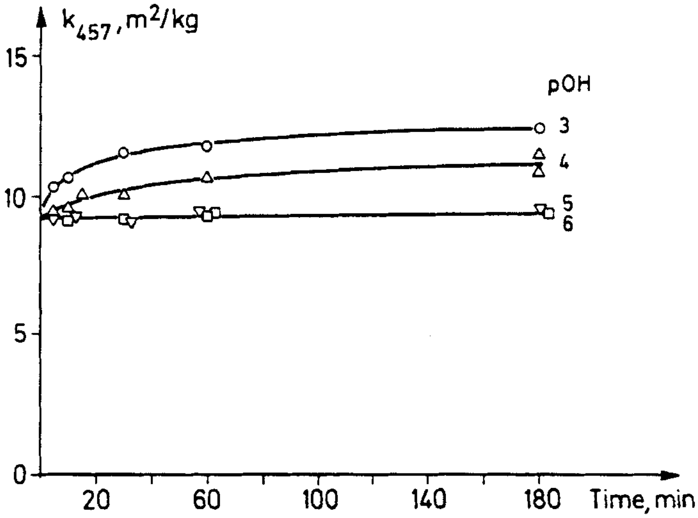

FIGURE 5. The light absorption coefficient versus alkali treatment time at different pOH levels, 60°C. Constant conditions.

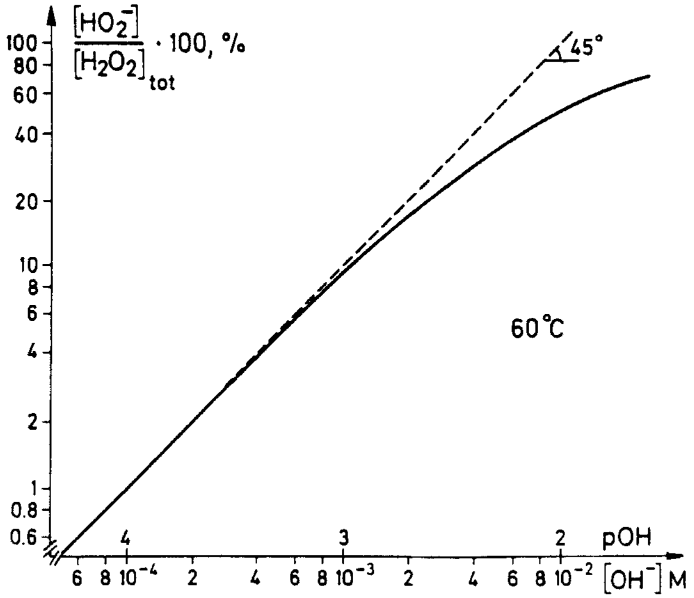

FIGURE 6. The degree of peroxide dissociation versus hydroxyl ion concentration. 60°C.

bleaching, but the alkali-created chromophores are then partly eliminated by peroxide so the net effect is a chromophore elimination. The point at which increased alkalinity starts to decrease the bleaching rate may be interpreted as the point at which the hydroxyl ion concentration is increased more than the peroxide anion concentration.

Effect of peroxide anion concentration

The bleaching action of peroxide is primarily due to the peroxide anion $[HO_2^-]$[6,7]. Alkali addition increases the peroxide anion concentration according to the following equilibrium.

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O \qquad [3]$$

In Figure 6 the degree of peroxide dissociation is shown versus alkalinity at 60°C with $pK_b = 2$[8]. In the range pOH 4-3, there is an approximate proportionality between peroxide anion and hydroxide ion. At lower pOH (higher alkalinity), the hydroxide ion concentration increases more than the hydrogen peroxide anion concentration. The maximum in the bleaching rate is thus probably due to the fact that above a certain alkali level the alkaline chromophore-creating reactions start to prevail over the bleaching reactions.

If bleaching was accomplished solely by the peroxide anion, i.e. the bleaching rate was proportional to the peroxide anion concentration, the rate equation would have the form:

$$-dC_k/dt = k\,[HO_2^-]^{1}\,C_k^{4.8} \qquad [4]$$

The peroxide anion concentration can be expressed as

$$\left[HO_2^-\right] = \frac{\left[H_2O_2\right]tot \cdot \left[OH^-\right]}{K_b + \left[OH^-\right]} \qquad [5]$$

Combining Equations 4 and 5 gives:

$$-\frac{dC_k}{dt} = k\left[H_2O_2\right]tot \cdot \frac{\left[OH^-\right]}{K_b + \left[OH^-\right]} \cdot C_k^{4.8} \qquad [6]$$

According to Equation 6 the bleaching rate would be directly portional to the hydroxide concentration, i.e. a reaction order of 1.0, if $[HO^-] << K_b$ such that the $[OH^-]$ in the denominator can be neglected. At higher hydroxide concentrations, $[OH^-]$ would be significant in both the denominator and the numerator. Since the reaction order with respect to alkali was 0.45 in the pOH range 6-2.5, the bleaching rate is not determined solely by the peroxide anion, but is also affected by the hydroxide concentration.

The effect of peroxide anion on the bleaching rate is dependent on hydroxide concentration as shown in Figure 7. When the peroxide anion concentration was increased by adding

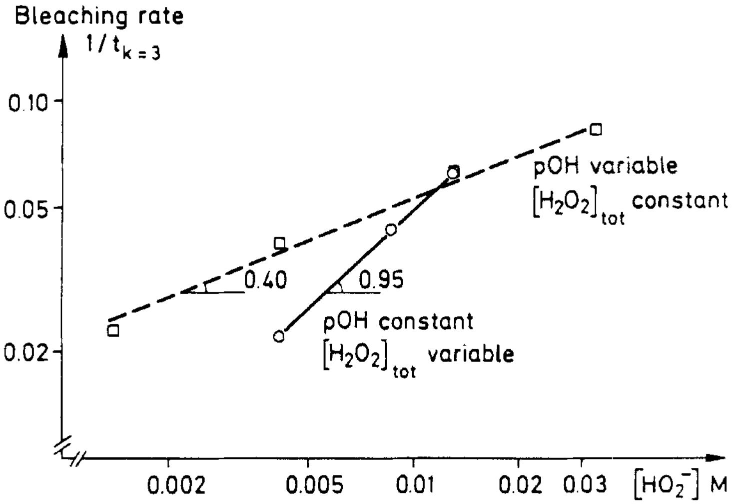

FIGURE 7. The bleaching rate versus peroxide anion concentration. Constant conditions.
____pOH 3 constant, H_2O_2 tot variable
--- pOH variable, H_2O_2 tot = 0.176 mol H_2O_2/l
Constant.
$pK_b = 1.9$

more peroxide, the bleaching rate increase was proportional to the peroxide anion concentration increase.

$$-dC_k/dt \propto [HO_2^-]^1 \quad , \text{ increased } [H_2O_2]_{tot} \qquad [7]$$

When the peroxide anion concentration was increased by adding more alkali, the bleaching rate increase was approximately 0.4 with respect to the peroxide anion concentration increase.

$$-dC_k/dt \propto [HO_2^-]^{0.4} \quad , \text{ increased } [OH^-] \qquad [8]$$

These results differ from those in a study of peroxide bleaching of chromophoric compounds[2]. The reaction rate of chromophoric compounds was proportional to the peroxide anion

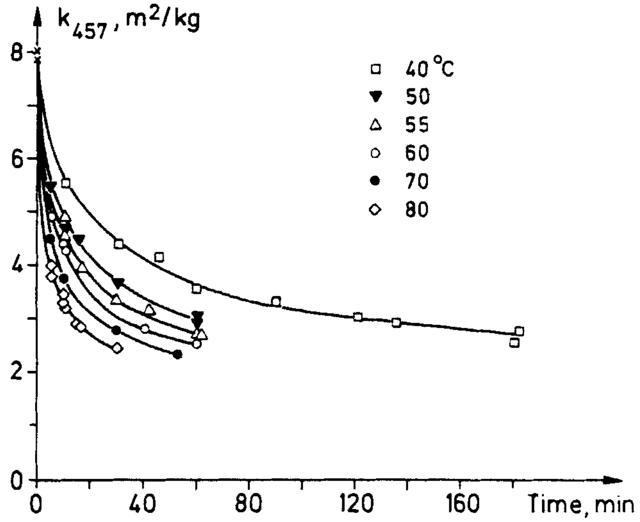

FIGURE 8. The light absorption coefficient versus bleaching time at different temperatures.
pOH 3, 0.176 mol H_2O_2/l. Constant conditions.

TABLE 2

Bleaching Conditions, Differential Method

	pOH_i				
% H_2O_2	3.5	3.3	2.9	2.5	2.1
0.5			X		
1.0		X	X	X	
2.0	X	X	X	X	X
4.0	X	X	X	X	
6.0		X	X		

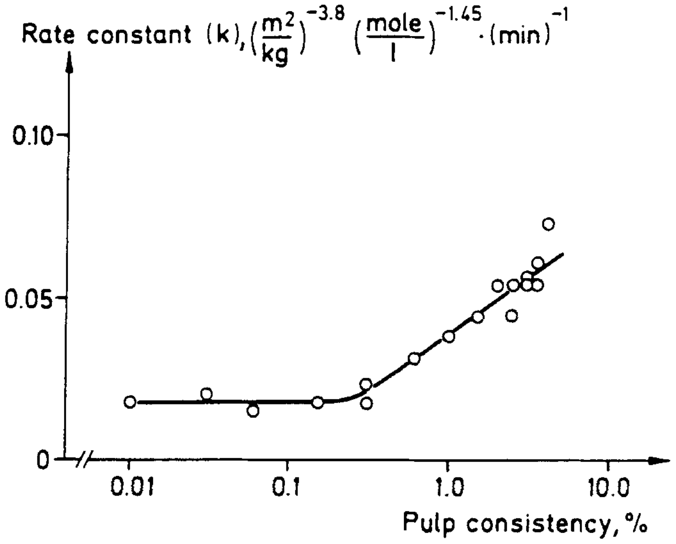

FIGURE 9. Rate constant versus pulp consistency. pOH3, 0.176 mol H_2O_2/l, 60°C. Constant conditions.

and independent of the hydroxide concentration. This is probably due to the fact that in the system with chromophoric compounds there were no compounds which react with alkali to form new chromophores as is the case with pulp.

Effect of temperature

The reaction rate increased with increasing temperature as shown in Figure 8. The activation energy was determined by the Arrhenius correlation to be approximately 45 kJ mol^{-1} in the interval 40-80°C (Table 2).

Effect of pulp consistency

The effect of pulp consistency on the bleaching rate was investigated in the range 0.01 to 4% pulp consistency as shown in Figure 9. A pulp consistency greater than 4% could not be used with this bleaching technique. The rate constant was constant for pulp consistencies below 0.25% but increased at higher pulp consistency. The peroxide and alkali concentrations were the same and constant for the series of bleaches.

The increase in bleaching rate with increasing pulp consistency indicates that there is some short-lived active species that interacts between the pulp particles. An increase in pulp consistency decreases the distance between the pulp particles and hence increases the possibility for some short-lived active species to migrate from one particle to an other. As the distance between the pulp particles, determined by the pulp consistency, is critical, it indicates that the active species has a short "lifetime". Compounds which could act in this way are free radicals. Superoxide and hydroxyl radicals are both present in peroxide bleaching[9].

Differential Method

The results in this part of the investigation are based upon 85 bleachings at 15% pulp consistency with all the bleaching chemicals charged initially. The pulp was a TMP and the peroxide charges and the initial pOH-values are specified in TABLE 3. The initial (pOH_i) is defined as the pOH of the total liquid phase measured at 24°C without pulp and before the bleaching was started.

TABLE 3

Rate Constants and Reaction Orders from Statistical Treatment of the Bleaching Results obtained from the Differential Method. Reaction Orders from Equation 5 are marked □ .

k	a	b	n
0.14	0.67	0.23	2.2
0.33	$\boxed{1.0}$	$\boxed{0.45}$	3.3
0.099	$\boxed{1.0}$	$\boxed{0.22}$	2.8
0.51	0.69	$\boxed{0.45}$	2.6
0.0086	1.0	0.29	$\boxed{4.8}$

Effect of time

The concentrations of peroxide and alkali decreased during the bleac. Due to different bleaching chemical profiles, in comparison with the Constant Conditions Method, the decrease in reaction rate was more pronounced in the Differential Method (Figure 10). But independent of method, the reaction rate is very slow at $k_{457} \sim 2$, as is shown in Figure 11. In this experiment the bleaching time was 94 hours, with a new charge of peroxide and alkali every day. The yield loss was about 1% per day and the lignin-carbohydrate ratio was constant. After 94 hours, the k_{457} value was 0.55 m^2/kg. For comparison, a fully bleached kraft pulp has $k_{457} = 0.2\text{-}0.5$ m^2/kg.

Effect of peroxide and alkali concentration

The separate effects of peroxide and alkali cannot be obtained directly by the differential method. By estimating the reaction rate in a k_{457}-time plot and the peroxide and alkali concentrations at that time, a kinetic equation can be calculated[10]. This is best done by computer. The whole kinetic equation is calculated simultaneously.

$$-dC_k/dt = k \left[H_2O_2\right]_{tot}^{0.67} \cdot \left[OH^-\right]^{0.23} C_k^{2.2} \qquad [9]$$

The reaction orders with respect to both peroxide and alkali are approximately half the values given in Equation 2. This discrepancy is discussed below.

Effect of temperature

The Arrhenius activation energy was found to be 45 kJ mol^{-1} at 60-70°C and 43 kJ mol^{-1} at 30-40°C. Thus, the activation energy is essentially independent of the bleaching technique (see Table 1).

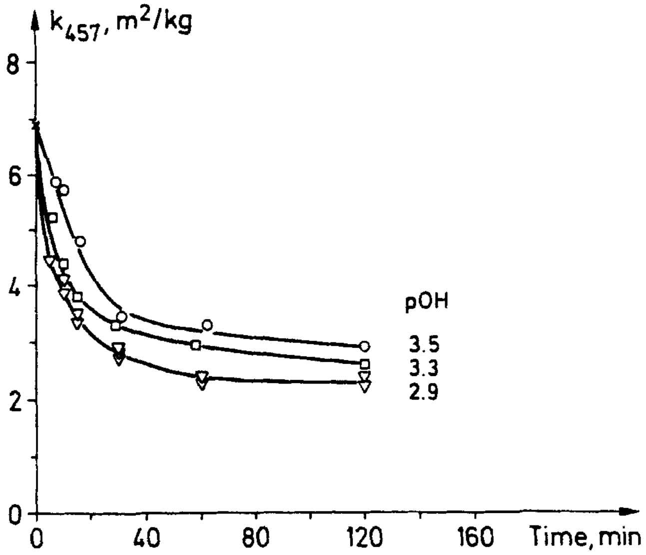

FIGURE 10. The light absorption coefficient versus bleaching time at 40°C and different initial pOH values.

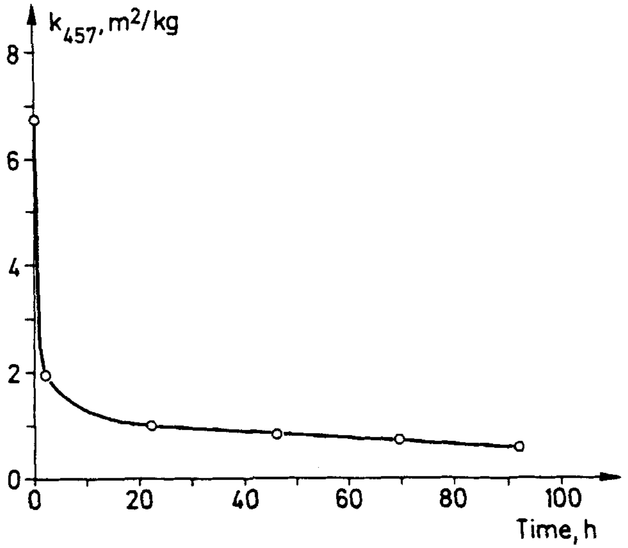

FIGURE 11. Light absorption coefficient versus bleaching time.

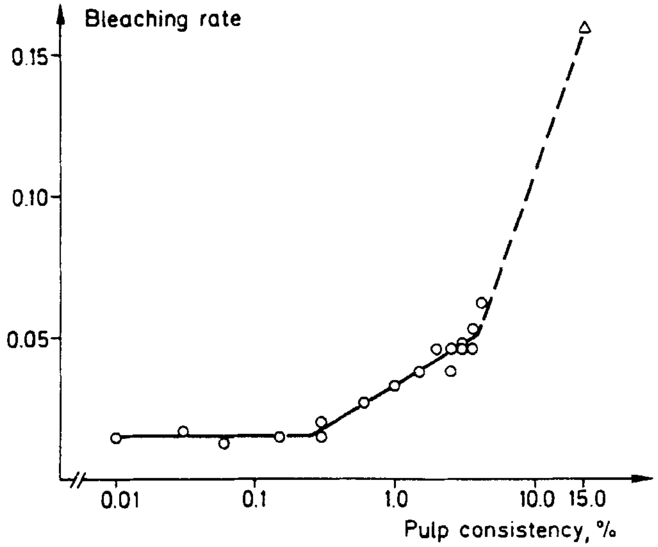

FIGURE 12. Bleaching rate versus pulp consistency. Bleaching rate at pOH 4, 0.07 mol H_2O_2/l, 60°C, $C_k = 4\ m^2/kg$

o Constant conditions

Conventional laboratory bleaching.

Effect of pulp consistency

The effect of pulp consistency was not investigated with this bleaching technique, but the rate of bleaching at 15% pulp consistency according to the Differential Method can be compared with the rate at a lower pulp consistency obtained by the Constant Conditions Method (see Figure 12). The rate constants cannot be compared since the kinetic equations for the two methods differ. Thus, the bleaching rate, $-dC_k/dt$, was calculated for a specified bleaching condition according to Equations 2 and 9. The bleaching rate will vary somewhat, depending on the concentrations at which the comparison is made.

The results shown in Figure 12 supports the results shown in Figure 9 that increased pulp consistency increases the bleaching rate. Note that this is not an effect of increased chemical concentration due to increased pulp consistency at a constant charge, since the concentrations of peroxide and alkali are the same in Figure 12.

Differences between Models

Are the differences between Equations 9 and 2 due to different techniques of evaluating the experimental data or to different bleaching techniques? It was difficult to ascertain how certain the reaction orders are in Equation 9. All four variables, i.e. reaction rate and reaction orders with respect to peroxide, alkali and light absorption coefficient were calculated simultaneously. If one or two reaction orders from Equation 2 were inserted in Equation 9, the remaining two or three variables could be calculated. Thus, the sensitivity of the reaction orders in equation 9 to presetting one or two of the values before the statistic evaluation could be assessed. The results are presented in Table 3. The reaction orders were fairly stable. It was only when n was set at 4.8 that the reaction orders differed substantially.

The evaluation technique cannot be the source of the difference in orders between Equations 9 and 2, as the difference in reaction order is substantial. The difference must be due to the different bleaching procedures. In the Constant C onditions Method, the fiber's environment is constant with respect to peroxide and alkali, but in the Differential Method both the peroxide and alkali concentrations decrease during the bleaching.

If the Constant Conditions Method is used and the peroxide and alkali levels are reduced by steps, the effect of the reaction rate is delayed, Figures 13 and 14. The decrease in bleaching rate is less than expected from the kinetic model according to the Constant Conditions Method. In other words, when the peroxide and alkali concentrations decrease during the bleaching, the effect on the reaction rate is apparently less

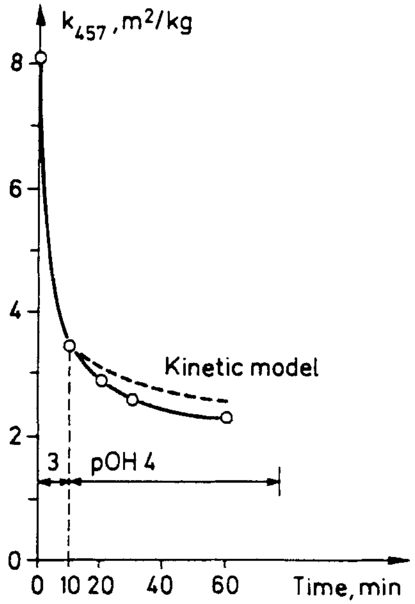

FIGURE 13. Light absorption coefficient versus bleaching time.
Constant conditions:
0-10 minutes; pOH 3, 0.176 mol H_2O_2/l, 60°C.
10-60 minutes; pOH 4, 0.176 mol H_2O_2/l, 60°C.

than that predicted by the Constant Conditions Method, i.e. the reaction orders are lower. The differences between Equations 9 and 2 are therefore in qualitative agreement with results given in Figures 13 and 14.

The delayed effect of a concentration change is probably due to the fact that bleaching of pulp takes place in a heterogenous system with a liquid and a fiber phase that can be considered as a solid or gel phase. When the concentration is changed in the liquid, it will therefore take a few minutes until the fibers have responded to the change.

The different kinetic equations for different bleaching procedures show that pulp bleaching is not a homogeneous reaction system, and that the bleaching rate is not unambiguously related to the chemical concentration outside the fibre, i.e. in the

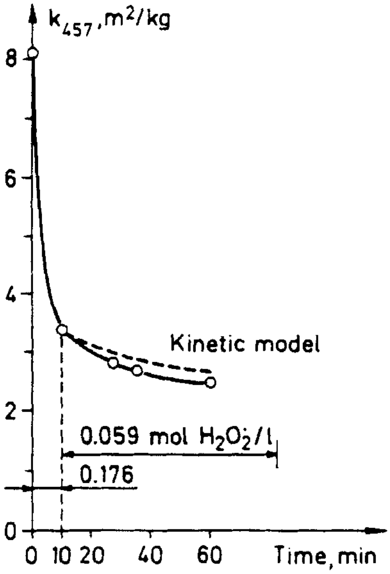

FIGURE 14. Light absorption coefficient versus bleaching time. Constant conditions:
0-10 minutes; pOH 3, 0.176 mol H_2O_2/l, 60°C.
10-60 minutes, pOH 3, 0.059 mol H_2O_2/l

liquid phase. So the pulp bleaching is a heterogeneous reaction system involving two phases, bleaching liquor and pulp, and hence physical factor such as diffusion may be involved in the rate determining step. If both physical and chemical reaction resistances are present, different bleaching conditions may give different kinetic equations.

With the Constant Conditions Method, it is easy to show that the bleaching effect is the result of two counteracting reactions, the peroxide anion bleaching and the alkaline chromophore-creating reaction. Unfortunately this method does not resemble mill conditions. Mill-resembling conditions are obtained with the Differential Method and therefore Equation 9 is the one which ought to be used in practice.

It is important to remember that both equations are empirical ones and are valid only under conditions resembling the conditions used in their determination.

Effect of Electrolyte Strength

The peroxide anion is probably the primary bleaching agent and hence it is interesting to know how the concentration of cations affects the bleaching rate, because of the screening effect of cations towards anions. The only cation of interest is sodium.

The Constant Conditions Method was used and NaCl was added to obtain different sodium ion concentrations. Figure 15 shows that an increase in the sodium ion concentration results in a slight increase in the reaction rate. The peroxide equilibrium constant K_b decreases when $[Na^+]$ increases[8]. According to Equation 6 the reaction rate increases when K_b decreases. The calculated increase in reaction rate due to the increased peroxide anion concentration as a result of increased sodium ion concentration is shown by the broken line in Figure 15.

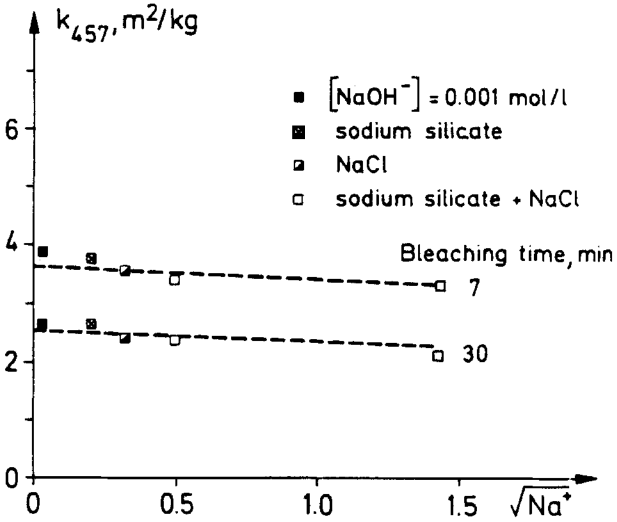

FIGURE 15. Light absorption coefficient versus the square root of the sodium ion concentration.
Constant conditions:
pOH 3, 0.176 mol H_2O_2/l, 60°C.

Thus, the effect of sodium ions upon the bleaching rate can be explained solely by a change in K_b. No additional effect of any ion on the kinetics, as for example from silicate, has to be assumed.

Factors that do not Affect the Kinetics

The effects of some further variables were studies with the Constant Conditions Method.

Mainly flash-dried pulps were used in this study. Flash-drying had no influence on the kinetics of peroxide bleaching.

Extractives consume a minor part of the peroxide during bleaching[11]. Pulps extracted with absolute ethanol and pulps not extracted gave approximately the same light absorption coefficient after bleaching. The rate of bleaching was not affected by the extractives.

The white water in the mills contains organic and inorganic substances, but a change of the water "quality" from a mill white water to deionized water did not affect the bleaching rate. White water causes peroxide decomposition but that is compensated for in the Constant Conditions Method where the peroxide concentration is held constant.

EXPERIMENTAL

Raw Materials

A number of groundwood and thermomechanical pulps were used in this investigation. All pulps except one were flash-dried. Freeness, metal ion content brightness, and light absorption coefficient (k_{457}) are given in Table 4.

Bleaching

The constant condition bleachings were carried out in a thermostated glass vessel at low pulp consistency (0.3%). During each experiment, pOH, concentration of peroxide and temperature were kept constant by successive additions of NaOH and peroxide to the bleach liquor. The bleaching liquor also included 5.2 g/l technical silicate and 0.003 g/l DTPA.

TABLE 4

Characteristics for unbleached Stone Groundwood (SGW) and Thermomechanical (T) Pulps Used in Constant Condition Bleachings.

Pulp	Concentration of metal ions (mg/kg o.d. pulp)						k_{457}	Bright-	Free-
	Fe	Cu	Mn	Al	Ca	Mg	m^2/kg	ness % ISO	ness ml
SGW-1	16	1.5	43	20	2020	165	7.8	63.9	134
SGW-2	34	1.2	9	22	2170	177	7.5	63.7	97
SGW-3	31	0.5	66	29	2870	109	8.0	62.1	156
T-1	6	4.4	92	8	780	107	6.6	63.6	80
T-2	26	2.1	89	16	1390	114	7.8	54.3	114
T-3	25	3.7	91	17	1700	118	7.4	58.1	177

Conventional laboratory bleaching at high consistency (15%) was carried out in plastic bags. Pulp and all bleaching chemicals, including 5% technical silicate (with respect to o.d. pulp) charged at the beginning, were mixed in the bags by kneading them intensively. The pulp was pretreated with 0.1% DTPA at neutral pH (with respect to o.d. pulp) and washed.

Deionized water was used on all occasions including preparation of handsheets. The bleaching was stopped by draining the bleaching liquor through a wire screen. The remaining bleaching liquor was immediately displaced with deionized water. Finally, the pH of the bleached pulp was adjusted to 4-5.

Analytical Methods

The kinetics of peroxide bleaching were investigated by studying the rate of chromophore elimination. The elimination was followed by determination of the light absorption coefficient (k in the Kubelka-Munk equation) measured at 457 nm on a handsheet made according to SCAN-M 5:76. Deionized water was used for the preparation of handsheets.

The concentration of peroxide ($[H_2O_2]_{tot}$) was determined iodimetrically.

CONCLUSIONS

The rate of peroxide bleaching of mechanical pulp can be expressed by a kinetic equation which is the same, within experimental error, for both SGW and TMP. The kinetic expression is dependent on how the bleaching is carried out. The reaction orders determined with the Differential Method are approximately half those determined with the Constant Conditions Method. The bleaching rate is determined not only by the peroxide anion concentration but also by the hydroxide ion concentration. At a given concentration of peroxide anion an increase in hydroxide ion concentration decreases the bleaching rate. The bleaching rate passes through a maximum when the alkali concentration is increased at constant peroxide concentration.

Silicate, electrolyte strength and the quality of the white water have a negligible effect on the reaction rate.

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