

Kinetics of oxygen bleaching mediated by electrochemically generated ferricyanide

Yuan-Shing Perng and Colin W. Oloman

ABSTRACT: *The effects of process variables on the kinetics and selectivity of oxygen bleaching promoted by in situ electrochemically generated ferricyanide are studied to help understand the process mechanism and to show how metal redox species may be used to promote oxygen bleaching with enhanced selectivity. The ferricyanide/oxygen system increases the rate of delignification and cellulose degradation and gives a small increase in selectivity, all at milder operating conditions than in conventional oxygen bleaching. The presence of ferricyanide in the bleaching process shifts the rate determining steps for both the lignin and cellulose oxidation from chemical reaction to ferricyanide diffusion control and makes the reaction rates nearly independent of oxygen pressure above 0.1 MPa. Highest selectivity in the electrochemical process is obtained by in situ generation of ferricyanide with zero oxygen pressure (nitrogen sparge). However the delignification rate under nitrogen is about one-third to half of that under oxygen with the same current. In the presence of oxygen, the selectivity is raised by application of a current together with increasing pH and temperature, but increasing the current decreases the selectivity.*

KEYWORDS: *Bibliographies, bleaching, cyanides, electrochemistry, iron compounds, kinetics, oxygen bleaching, selectivity, stoichiometry.*

Oxygen bleaching is recognized as an environmentally benign pulp bleaching option which can reduce the content of chlorinated organic compounds in bleaching

effluents. However, conventional oxygen bleaching is compromised by the competitive reactions between lignin and cellulose together with the low rate of the delignification pro-

cess (1). Such factors force the conventional processes to operate at high oxygen pressure (above 0.45 MPa), high temperature (above 100°C), and high consistency (above 10%), while only removing 50% of lignin compared to chlorine bleached pulp of equivalent strength (2).

The use of ferricyanide to promote oxygen bleaching of pulp was first explored by Chupka *et al.* (3–5). These workers found that pulp is delignified by electrolyzing an alkaline pulp slurry containing potassium ferro/ferricyanide. This “electrochemical” bleaching was done for 60 min at 2% consistency, 60°C, and atmospheric pressure in 1 M NaOH solution with up to 4.5 mM ferricyanide. Ferricyanide and co-generated oxygen were produced in situ at a nickel anode operating at a current density of 75 A/m². Chupka *et al.* found the extent of delignification and physical properties of pulp bleached by this method to be similar to those of pulp from conventional oxygen or chlorine bleaching processes.

Godsay *et al.* (6–8) extended Chupka’s work by bubbling oxygen into an alkaline bleaching solution containing potassium ferricyanide and recycling this solution through a batch of unbleached chemical pulp with regeneration of the ferricyanide in a separate electrochemical reactor. Ferricyanide loadings of 0.004–0.4 wt% K₃Fe(CN)₆ on oven-dry pulp were used with 3–5% pulp consistency. The 1–2 M NaOH solution was saturated with oxygen

Perng and Oloman are, respectively, post doctoral fellow and professor, Department of Chemical Engineering, University of British Columbia, Vancouver, BC, Canada V6T 1Z4.

Bleaching

at room pressure, the bleaching temperature was 20–65°C and bleaching time from 10 h to 20 h. The researchers claimed that under these mild conditions of temperature and pressure this electrochemical bleaching system could bleach pulp to 80% delignification with a kappa number/viscosity relationship similar to that of conventional oxygen bleaching. These workers also noted a pronounced synergism in the effects of oxygen and ferricyanide on the rate of delignification (3).

Both groups of researchers showed that ferro/ferricyanide electrochemical bleaching can operate at milder conditions than conventional oxygen bleaching, but the process variables, selectivity, and kinetics of the electrochemical bleaching system were not studied extensively.

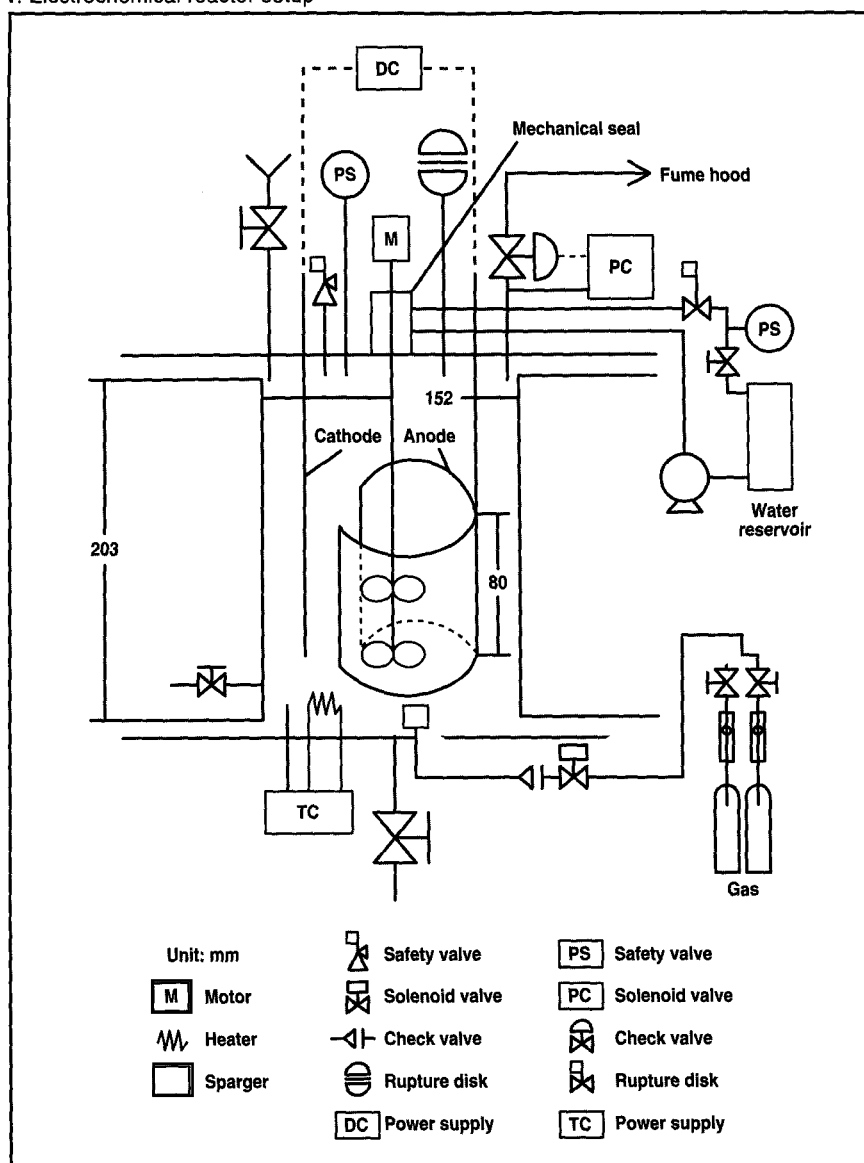
The work reported here is a comprehensive examination of the effects of process variables on the kinetics and selectivity of oxygen bleaching promoted by in situ electrochemically generated ferricyanide (9). The object of this work is to help understand process mechanisms and to show how metal redox species may be used to promote oxygen bleaching with enhanced selectivity.

Apparatus and procedure

Apparatus

Electrochemical bleaching experiments were done in the laboratory apparatus shown in **Fig. 1**. The superatmospheric pressure electrochemical bleaching reactor was constructed from a 203-mm long section of schedule 80, 6-in. nominal diameter 316 stainless steel pipe, coated on the inside with PTFE to reduce metal contamination and sealed with class 300 blind flanges to give an effective reactor volume from 1 L to 3 L. The stirrer, which provided good mixing during the reaction, consisted of a pair of 75-mm diameter 316 stainless steel three-blade propellers on a 12.5-mm shaft driven by a variable speed 93-W motor. The top flange

1. Electrochemical reactor setup



I. Levels of process variables in factorial experiment^a

Symbol	Level	-1	0	+1
<i>O</i>	Oxygen pressure, MPa	0°	0.6	1.1
<i>I</i>	Current, A	0	0.5	1.0
<i>P</i>	pH ^b	11.2	12.5	14.0
<i>T</i>	Temperature, °C	30	53	75

^a Initial ferrocyanide concentration 16 mM.

^b pH measured at 20°C.

^c Purge with nitrogen at 1.1 MPa.

II. Levels of process variables in parametric experiment^a

Process variable	Level			
Oxygen pressure, MPa	0	0.1	0.6	1.1
Current, A	0	0.5	1.0	
pH	11.2	12.5	13.0	14.0
Temperature, °C	30	53	75	84

^a Initial ferrocyanide concentration 16 mM.

III. Oxygen solubility under alkaline conditions

pH	O ₂ , MPa	Oxygen solubility, mM			
		30°C	53°C	75°C	84°C
14.0	0.1	0.8	0.60	0.5	0.5
	0.6	4.5	3.7	3.3	3.1
	1.1	8.3	6.8	5.9	5.7
13.0	1.1			7.9	
12.5	0.6		5.5		
	1.1	12.2	10.0	8.7	
11.2	1.1	12.8		9.2	

was equipped with a feeding funnel and piped to a relief valve, two pressure switches, a rupture disc, and a pressure control valve. Electrodes were introduced through the top flange and connected to a dc power supply capable of delivering up to 2 A at 30 V. The anode was a 20-mesh 316 stainless steel screen with effective area 170 cm², and the cathode was a 6-mm diameter 316 stainless steel rod covered by a polypropylene cloth to suppress cathodic reduction of ferricyanide in the undivided reactor. The bottom flange carried a heating coil and thermocouple for temperature control together with a 19-mm drainage valve and 6-mm gas sparge tube.

During operation of the reactor, a metered gas flow (1700 mL/min STP) was sparged continuously through the pulp slurry and the reactor pressure held by a pressure control loop in the gas outlet line. The operating

range of the reactor was 0.1–1.5 MPa absolute pressure (0–200 psig) and 20–120°C.

Procedure

A series of experiments were carried out to study the stoichiometry and the effects of oxygen pressure, pH, temperature, and current on the rate of delignification and the rate of viscosity loss in electrochemical ferricyanide-promoted oxygen bleaching of an unbleached kraft softwood pulp.

In experiments to study the stoichiometry, 32 mmoles of potassium ferricyanide was added to 2 L of a 0.5% consistency pulp slurry in 1 M NaOH. The pulp kappa number and viscosity plus the ferricyanide concentration in the liquor were measured after 5 min reaction at 30°C, 53°C, and 75°C under nitrogen and under oxygen.

The subsequent experimental design involved an initial 2⁴ factorial experiment to observe the effects and interactions of oxygen pressure, current, pH, and temperature on the bleaching process at times of 5 min, 10 min, 20 min, and 60 min. The levels of process variables used in this factorial study are given in Table I. The factorial experiment was followed by a parametric experiment to explore the effects of each variable separately at the levels shown in Table II, with reaction times of 5 min, 10 min, 20 min, and 60 min.

In each of the bleaching runs, 2 L of aqueous solution was prepared containing 16 mM potassium ferrocyanide. For all runs except those at pH 14, the solution was made up with 20 g/L of sodium tetraborate, then adjusted to the desired pH level (11.2–13) and 1.2 M ionic strength by addition of NaOH and Na₂SO₄. For the pH 14 runs, the ferrocyanide was added to a simple solution of 1 M NaOH without buffer or Na₂SO₄. The reactant concentrations used in these experiments were chosen for academic reasons and represent chemical charges which are too high to be considered for commercial application.

The solution was placed in the electrochemical reactor and heated to reaction temperature then charged with 10 oven-dry grams of pulp (0.5% consistency). The gas sparge was initiated and the mixer speed set at 1000 rpm. When the reactor pressure reached the setpoint (about 10–30 s after pulp addition), the slurry was subjected to dc electrolysis under current control for 5–60 min. The applied current generated ferricyanide from ferrocyanide at the anode in the bleaching solution. Preliminary experiments, performed in the absence of pulp, determined the net current efficiency for anodic generation of ferricyanide in the reactor to be 77% and 72% at 0.5 A and 1 A, respectively.

The unbleached kraft softwood pulp samples had properties of kappa number 29.2, viscosity 34.7 cp ("m_n"

Bleaching

3.4 moles/ton of pulp) and brightness 24.4% ISO. The pulp was not subjected to any pretreatment beyond washing and mixing to obtain consistent samples.

The product pulp was filtered, washed, and tested for kappa number, viscosity, and brightness according to TAPPI Methods T 236 cm-85, T 230 om-89, and T 452 om-87, respectively. The ferricyanide concentration in the filtrate was determined by a thiosulfate titration method (10). The standard deviations of the various measurements (28° of freedom) were 0.4 for kappa number, 0.6 cp for viscosity (0.13 mole/ton of pulp for " m_n "), 0.6% ISO for brightness, and 0.3 mM for ferricyanide concentration.

For the kinetic studies, the cellulose degradation was monitored by the number of moles of "cellulose chains" per ton of pulp (" m_n ") (11). Each time a cellulose bond is broken, one more chain is formed and the number of moles of cellulose chains in the pulp increases. Higher values of m_n represent greater cellulose degradation. Because both the reactants and products are expressed in chemical units, the use of " m_n " is more meaningful than viscosity in the discussion of kinetics. The TAPPI viscosity (V , cp) was converted to the intrinsic viscosity (IV , dm³/kg) and the " m_n " by the following equations (11, 12):

$$IV = 954 \log V - 325 \quad (1)$$

$$\log("m_n") = 4.35 - 1.25 \log IV \quad (2)$$

The oxygen partial pressure was converted to the solubility of oxygen by an in-house computer program based on regression of published data (13-18). The related equilibrium dissolved oxygen data for the experimental conditions are summarized in Table III.

A total of 185 separate bleaching runs, including 27 replicate runs, were carried out in this study.

IV. Ferricyanide stoichiometric ratio experiments^a

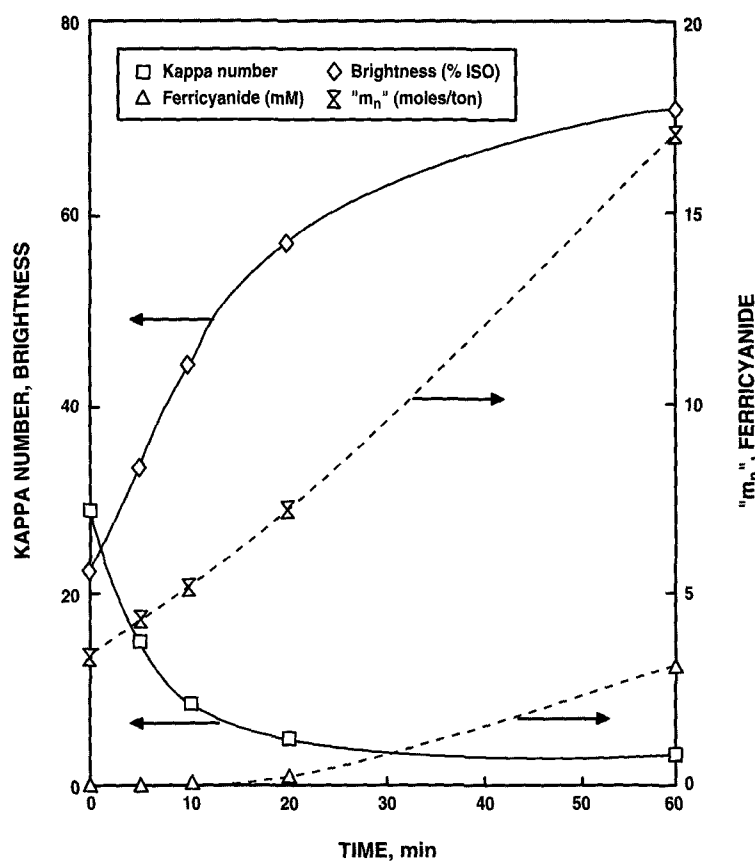
T	O	K	" m_n "	K^b	" m_n " ^b	F	dK/dF	$d"m_n"/dF$	$(dK+d"m_n")/dF$
75	1.1	4.7	13.8	18.0	4.4	11.9	0.7	0.5	1.1
75	0	12.2	5.6	22.6	3.5	13.4	0.6	0.1	0.7
53	1.1	6.7	8.7	23.5	3.7	17.2	1.1	0.3	1.5
30	1.1	12.8	6.6	23.5	3.6	21.1	1.0	0.3	1.3
30	0	19.4	4.0	24.7	3.4	22.0	0.5	0.1	0.6

T , Temp. °C, O oxygen pressure, MPa, K kappa number, F ferricyanide conc., mmole/2 L. Unbleached pulp: K 29.2, " m_n " 3.4 moles/ton of pulp. Initial F 32 mmole/2 L.

^a pH 14, time 5 min, current 0 A, 10 g o.d. pulp.

^b Without ferricyanide addition.

2. Typical kinetics of bleaching runs: pH 14, oxygen 1.1 MPa, current 1 A, temp. 75°C



V. Results of factorial runs at 5 and 60 min reaction time

Variables O I P T	Kappa		"m _n "		[Fe(CN) ₆ ⁻³] ^a	
	5 min	60 min	5 min	60 min	5 min	60 min
-1 -1 -1 -1	28.4	25.5	3.4	3.6	-	-
+1 -1 -1 -1	26.1	24.4	3.5	3.6	-	-
-1 +1 -1 -1	26.5	22.6	3.4	3.9	0.8	10.5
+1 +1 -1 -1	24.4	20.1	3.6	4.1	0.8	10.8
-1 -1 +1 -1	26.7	24.2	3.4	3.5	-	-
+1 -1 +1 -1	23.5	22.2	3.5	3.6	-	-
-1 +1 +1 -1	21.6	15.8	3.6	4.1	0	1.2
+1 +1 +1 -1	18.6	5.2	4.1	8.5	0	10.6
-1 -1 -1 +1	27.3	24.1	3.4	3.5	-	-
+1 -1 -1 +1	24.0	18.6	3.5	3.9	-	-
-1 +1 -1 +1	25.6	19.3	3.4	3.5	0.5	11.0
+1 +1 -1 +1	23.7	12.9	3.5	5.3	0.6	11.8
-1 -1 +1 +1	22.6	21.4	3.5	3.6	-	-
+1 -1 +1 +1	18.0	7.8	4.4	6.1	-	-
-1 +1 +1 +1	21.3	7.1	3.4	5.0	0	1.7
+1 +1 +1 +1	15.0	2.8	4.4	7.0	0	6.1
0 0 0 0	22.7	16.1	3.6	4.8	0.2	5.8

O oxygen pressure, I current, P pH, T temp.
 Unbleached pulp: kappa number 29.2, "m_n" 3.4 moles/ton of pulp.
^a Ferricyanide concentration in bleach liquor, mM.

VI. Factorial analysis of data from Table V

Effect	Kappa		"m _n "	
	5 min	60 min	5 min	60 min
Average	23.3	17.0	3.6	5.2
Center	22.7	16.1	3.6	4.8
O	-3.3	-5.8	0.4	2.7
I	-2.5	-7.8	0.1	2.5
P	-4.8	-7.6	0.3	2.5
T	-2.3	-5.7	0.1	1.6
OI	0.0	-0.2	0.1	1.9
OP	-0.9	-1.9	0.2	2.1
OT	-0.7	-1.7	0.2	1.5
IP	-1.1	-3.4	0.1	2.0
IT	0.9	0.3	-0.1	1.0
PT	-1.1	-1.3	0.1	1.3
OIP	-0.4	0.4	0.1	1.5
OIT	-0.1	2.3	0.0	0.8
OPI	-0.5	0.4	0.2	1.0
IPT	0.5	1.2	-0.1	0.8
OIPT	-0.4	2.2	0.0	0.5

95% Confidence interval
 Kappa number ± 0.4 , "m_n" ± 0.1 mole/ton of pulp

Results and discussion

Stoichiometry

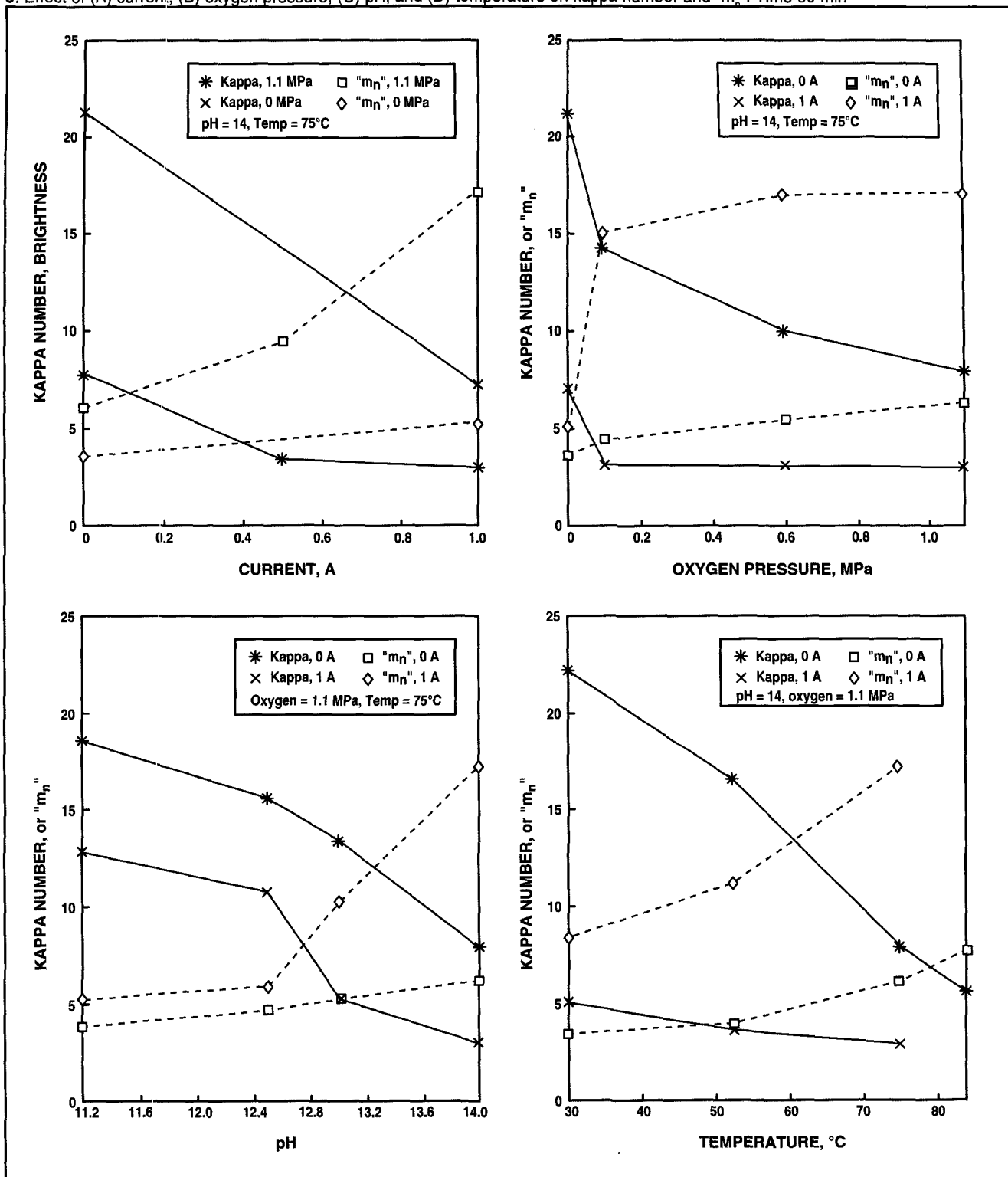
Results of the stoichiometry experiments are presented in Table IV. In order to evaluate the genuine ferricyanide effect on bleaching reactions, stoichiometric calculations were based on the difference between the runs with ferricyanide and the runs without ferricyanide at the same experimental conditions. This calculation removes the effects of alkali and oxygen in the bleaching reactions. The individual ratios of the decrease in kappa (dK) and the increase in cellulose chains ($d\text{"m}_n\text{"}$) to the ferricyanide consumption (dF) are scattered with the oxygen pressure and temperature. However the sum of these ratios $[(dK + d\text{"m}_n\text{")}/dF]$ is constant at about 0.6 per mmole under nitrogen and 1.3 per mmole under oxygen. This result may be useful in subsequent process modeling.

Factorial and parametric experiments

Figure 2 presents kinetic data showing the rates of delignification and cellulose degradation observed in a typical electrochemical bleaching run. In all runs, with or without current, the delignification rate was high in the first 5–10 min, then decreased to low values at 60 min. The rate of cellulose degradation in runs without current was initially high but decreased with time; whereas, in runs with current, this rate was nearly independent of time.

In the runs with current, the ferricyanide concentration remained low (nearly zero in most cases) during the initial fast stage of delignification, then slowly increased to the range 1 mM to 13 mM at the end of each run. Ferricyanide is consumed in the bleaching reactions at a rate equal to the difference between the rate of electrochemical generation (e.g., 0.45 mM/min for 1 A at 72% current efficiency) and the rate of accumulation in the bleaching solution.

3. Effect of (A) current, (B) oxygen pressure, (C) pH, and (D) temperature on kappa number and "m_n": Time 60 min



The factorial experiment with each variable at two levels (plus a "center point") gives an overall perspective of the process and shows interactions among variables which

can be important for mechanistic interpretation and process optimization. The parametric experiment details the effects of each variable at 3 or 4 levels when the level of each of

the other three variables is fixed. Both the factorial and parametric experiments yielded data from the same four dimensional experimental space which were used for kinetic modeling.

Data from the factorial experiment at 5 and 60 minutes bleaching time are summarized in **Table V** and factorial analysis of these data is given in **Table VI**. Confidence intervals for this analysis were established from the deviations of replicated runs at 20 min reaction time with the student's "t" test at the 95% confidence level (9).

The analysis shows that the main effects of all variables *O*, *I*, *P*, and *T* as well as the two factor interactions *OP*, *OT*, *IP*, and *PT* and (at 60 min) the three factor interactions *OIT* and *IPT* are significant with respect to the extent of delignification. A significant interaction *XY* occurs when the effect exceeds the confidence interval and implies that the effect of variable *X* depends upon the level of variable *Y*—for example, the strong *IP* interaction at 60 min reflects the fact that the effect of current on kappa number is greater at high pH than at low pH. The negative sign of the effects indicates that an increase in the level increases the extent of delignification.

For the rate of cellulose degradation (i.e., the increase in " m_n "), only the main effects *O* and *P* are significant at 5 min, but all main effects and interactions become significant at 60-min reaction time. The positive sign of the effects indicates that an increase in level increases the extent of cellulose degradation.

The interaction effects of oxygen and current (*OI*) on both kappa number and viscosity, which were significant under ambient conditions (6, 9), disappear in this factorial study. The lack of significant interaction may well be due to the wide range of variable levels (i.e., oxygen pressure from 0 MPa to 1.1 MPa), which masks the *OI* interaction.

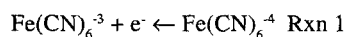
For both kappa number and " m_n ," a comparison of center-point responses with the average of factorial points shows negligible curvature at 5 min and a small curvature at 60-min reaction time. This means close to a linear dependence of kappa number and " m_n " on the

variables over the range of the factorial experiment. Such a result suggests stoichiometric (rather than catalytic) reactions between oxygen/ferricyanide and lignin as well as between oxygen/ferricyanide and cellulose.

The apparent linearity of the system together with the uniformity of the significant main effects of *O*, *I*, *P*, *T*, and the interactions on both kappa number and " m_n " present little scope for choosing conditions from the experimental space to substantially enhance bleaching selectivity.

Selected results of the parametric experiments showing the individual effects of oxygen pressure, pH, temperature, and current on the extent of delignification and cellulose degradation after 60 min reaction time are given in **Fig. 3 (A–D)**. Similar effects were seen in the runs at 5-, 10-, and 20-min reaction time, but data for these times are not presented here. The principal features of the results represented by **Fig. 3** are as follows:

Effect of current (Fig. 3A). Application of current increases the rates of delignification and cellulose degradation at all levels of oxygen pressure, pH, and temperature. These increases of rate are due to reaction of the pulp with ferricyanide, which is generated in situ by anodic oxidation of the ferrocyanide originally added to the bleaching solution.



Effect of oxygen pressure (Fig. 3B). The small amount of delignification and cellulose degradation at zero oxygen pressure (nitrogen purge) without current is due to reaction of the pulp with hydroxide ion. In the absence of current, the rate of delignification increases approximately in proportion to the square root of the oxygen solubility while the rate of cellulose degradation increases with the square of the oxygen solubility in the bleaching solution. However, with the current at 1 A, these reaction rates become

nearly independent of oxygen pressure above 0.1 MPa.

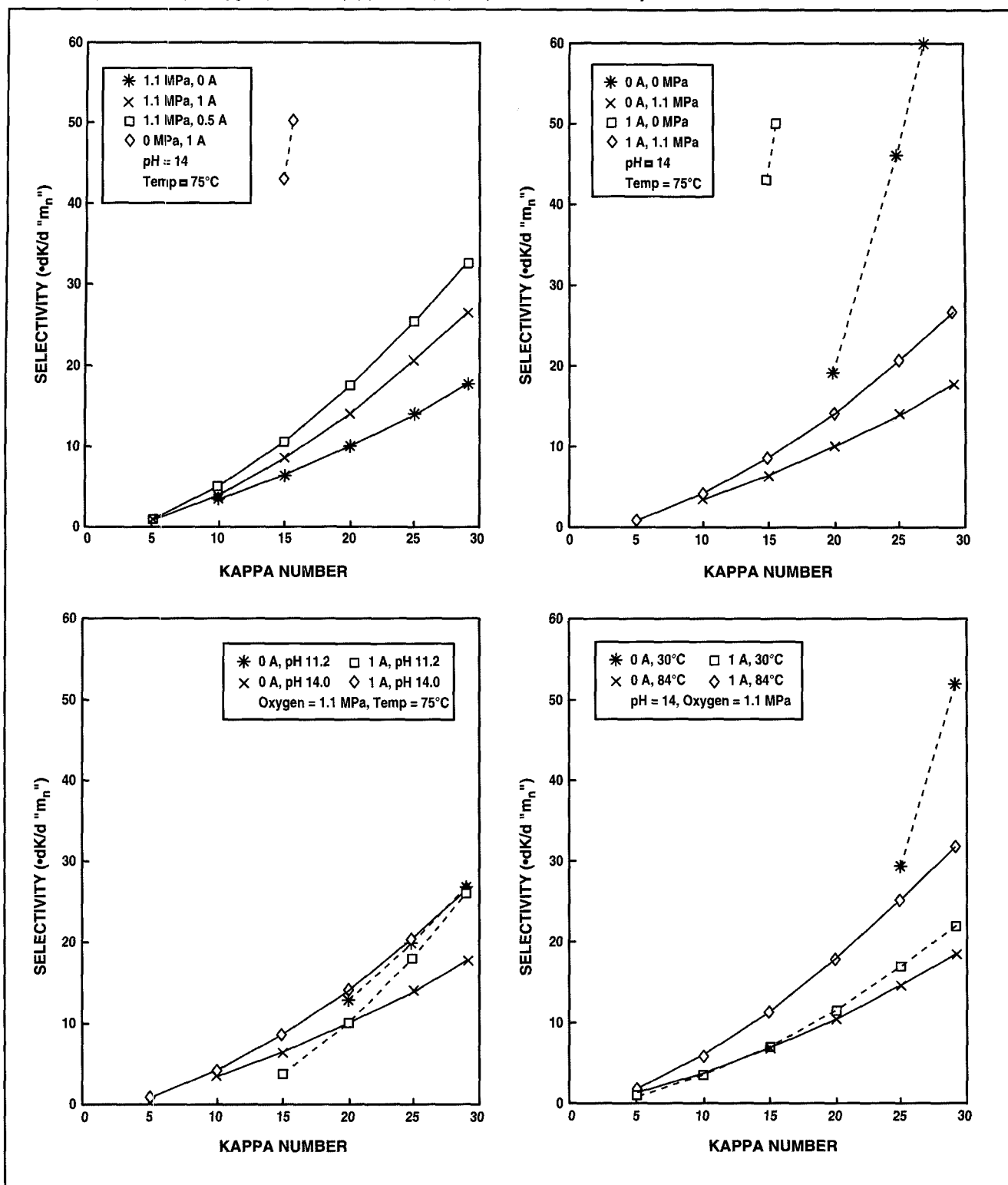
Effect of pH (Fig. 3C). Increasing pH increases both the rate of delignification and the rate of cellulose degradation. The delignification rate is approximately proportional to the cube root of hydroxide ion concentration. Although the delignification rate with current is higher than without current, the reaction order with respect to hydroxide ion is nearly independent of current. The effect of pH on delignification rate supports the hypothesis that phenolic groups are the major active sites in lignin and that reaction of lignin with oxygen or with ferricyanide proceeds through the lignin anion which is produced by reaction of hydroxide ion with phenolic components of lignin.

For cellulose degradation, the reaction order with respect to hydroxide ion is about 0.7 without current but falls to about 0.3 with current. This decrease in reaction order probably reflects a lower proportion of cellulose attack by alkali in competition with ferricyanide.

Effect of temperature (Fig. 3D). The rates of delignification and cellulose degradation increase with temperature, but the effect of temperature on these rates is higher in runs without current than in runs with current. The influence of current is reflected in the activation energies for delignification and cellulose degradation which are respectively 60 and 94 kJ/mole without current but drop to 12 and 15 kJ/mole with a current of 1 A. These levels of activation energy imply that, in the absence of ferricyanide, the reaction of oxygen with pulp is controlled by a chemical process, whereas the presence of ferricyanide raises the process rate and drives the reaction into the regime of diffusion control.

Selectivity. The selectivity of oxygen bleaching is defined as the ratio of the rate of delignification and cellulose degradation at constant kappa number:

4. Effect of (A) current, (B) oxygen pressure, (C) pH, and (D) temperature on selectivity: Time 60 min



$$\text{Selectivity} = \frac{(-dK/dt)}{(d^*m_n''/dt)} \quad K = \text{constant} \quad (3)$$

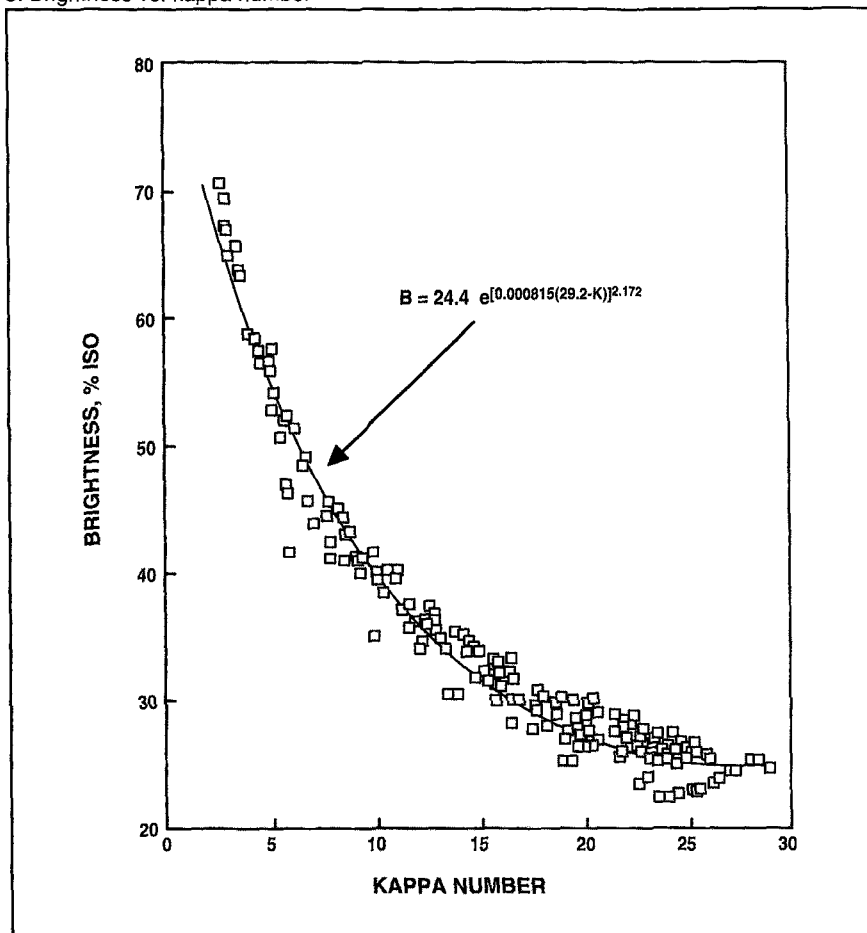
Figure 4 (A-D) contains data showing the effects of process variables on the selectivity in the electrochemical bleaching runs.

Selectivity decreases with decreasing lignin content and appears to be exponentially related to kappa number, so that delignification below kappa 10 under any conditions

VII. Effects of process variables on bleaching selectivity

Variable	Range	Effect	
		Without current	With current
O ₂ pressure	0 → 1.1 MPa	Decrease	Small decrease
pH	11.2 → 14	Small decrease	Small increase
Temperature	30 → 84°C	Decrease	Small increase

5. Brightness vs. kappa number



results in a major loss of selectivity. The effects of the experimental variables on selectivity are summarized in Table VII.

The highest selectivity was obtained with zero oxygen pressure (nitrogen sparge) and current. In runs under oxygen, the selectivity was increased by the application of current. In runs with oxygen and current, the selectivity was increased with increasing pH and temperature but decreased with increasing current. The effects can probably be

rationalized in terms of competitive reactions of ferricyanide and oxygen/radicals with lignin and cellulose.

Brightness vs. kappa number

Figure 5 shows a plot of product pulp brightness versus kappa number obtained in all experiments of this study. Brightness depends on kappa number regardless of bleaching conditions. The relation between brightness and kappa number is represented by Eq. 4.

$$B = B^0 \exp(0.000815)(K^0 - K)^{2.172} \quad (4)$$

$$R^{*2} = 99.7\%$$

Reaction kinetics

Conventional oxygen bleaching is a multiphase process whose kinetics have been investigated by several workers (20-25) and reported in the form of the classical chemical rate expressions in Eqs. 5 and 6. It has been established by Landucci (26) that delignification is catalyzed by trace metal ions (Fe, Mn, Co, Cu), as well as Abrahamsson and Samuelson (27) who have shown substantial effects of transition metal ions on delignification and cellulose degradation in oxygen/alkali pulping and bleaching. However, transition metal catalysis has had little consideration in quantitative studies of oxygen bleaching kinetics.

$$dK/dt = A_1 \exp(-E_1/RT) [\text{OH}^-]^{m_1} [\text{O}_2]^{n_1} K^{p_1} \quad (5)$$

$$dm/dt = A_2 \exp(-E_2/RT) [\text{OH}^-]^{m_2} [\text{O}_2]^{n_2} m^{p_2} \quad (6)$$

The following discussion attempts to interpret the kinetic data in light of these classic rate equations, but it should be observed that such equations may not properly represent the combined phenomena of diffusion and competitive chemical reactions that occur in the real bleaching process.

The kinetic parameters obtained for delignification and cellulose degradation by previous workers are summarized in Tables VIII and IX. Several of these workers considered oxygen delignification as a two-stage process with an initial rapid reaction (I) followed by a slow reaction (F), the two stages being characterized by different kinetic parameters. In the single-stage models, the activation energy for delignification and for cellulose degradation indicate chemical reaction control of the process rates. In the two-stage models, activation energies for delignification and cellulose degradation indicate the first stage is under diffusion and/

Bleaching

or chemical reaction control, whereas the second stage is under chemical reaction control. The controlling mechanism in the first stage probably depends on the process conditions. From their study of oxygen bleaching with vigorous agitation at low consistency (0.4%), Hsu and Hsieh (20) concluded from the Weisz-Prater criterion that the delignification occurred under chemical reaction control.

In the present work, the reaction rate data with oxygen for each of three current levels (0, 0.5, and 1 A) were regressed to fit Eqs. 5 and 6. The bleaching was taken as a single-stage process and the fitted rate equations covered the complete ranges of kappa number and viscosity for each current with the error range from 4% to 24%. The resulting parameters are given in Tables VIII and IX. In these calculations, the measure of oxygen activity was taken as the solubility of oxygen in the liquor rather than the oxygen partial pressure in the gas. The use of oxygen pressure in the kinetic expressions of previous workers [except Myers and Edwards (24)] is problematic because, due to temperature and salt effects, the solubility of oxygen is not only a function of oxygen pressure.

The kinetic parameters of the present work show progressive shifts that indicate changes in the reaction mechanism with current. In the absence of current (i.e., zero ferricyanide), the activation energies for both delignification and cellulose degradation indicate chemical reaction control of these processes. The shift of these processes into diffusion control, as current is applied, is presumably due to the relatively high rate of reaction of ferricyanide with the pulp and/or to a catalytic effect of ferro/ferricyanide on the oxygen-based reactions.

The decrease in reaction orders for oxygen with increased current implies that the rate controlling steps in delignification and cellulose degradation shift from those involv-

VIII. Kinetic parameters for delignification

Literature	Reaction order			E, kJ/mole	A
	m	o	n		
Hartler <i>et al.</i> (22)	b	a	b	69	b
Edwards & Norberg (23)	2.0	b	3.0	49	4000
Teder & Olm (25)	0.6	0.5	3.2	70	b
Evan <i>et al.</i> (21)	I 1.0	1.2	1.0	49	1.0x10 ⁵
	F 0	0	1.0	49	b
Olm & Teder (11)	I 0.1	0.1	1.0	10	b
	F 0.3	0.2	1.0	45	b
Hsu & Hsieh (20)	I 0.8	0.4	3.1	36	2.5
	F 0.7	0.7	3.1	71	143.5
Myers & Edwards (24)	I 0.0	0.4	1.0	32	1.5x10 ⁵
	F 0.9	0.4	1.0	61	1.7x10 ⁷
(0 A)	0.4	0.5	4.8	60	1.8
Present work (0.5 A)	0.3	0.2	2.4	14	0.02
(1 A)	0.4	0.1	1.9	12	0.03

I initial stage, F final stage.
 * Oxygen effect is insignificant.
 b Value not given in source.

IX. Kinetic parameters for cellulose degradation

Literature	Reaction order			E, kJ/mole	A
	m	o	n		
Hartler <i>et al.</i> (22)	b	a	b	86	b
Olm & Teder (11)	I 0.2	0.8	0	40	b
	F 0.6	0.1	0	53	b
(0 A)	0.7	2.1	-5.3	94	4.8x10 ¹²
Present work (0.5 A)	0.3	0.2	0.0	15	2.6
(1 A)	0.3	0.1	0.5	15	1.9

I initial stage, F final stage.
 * Oxygen effect is insignificant.
 b Value not given in source.

ing oxygen to those involving ferricyanide. According to the chain reaction hypothesis of oxygen delignification (19), the initiation step to generate the lignin radical and the superoxide anion radical from the lignin anion and oxygen should depend on oxygen concentration as seen in conventional oxygen bleaching and in the present results. For the runs with current, the ferri/ferricyanide couple may compete with the oxygen/superoxide in the rate-limiting initiation step. This can lessen the influence of oxygen pressure on bleaching rate. The large change in delignification rate

between zero and 0.1 MPa oxygen pressure means the system requires some oxygen to react with lignin radicals in the further propagation step. Similarly, it appears that the presence of ferricyanide with oxygen promotes cellulose degradation, either by direct reaction of ferricyanide with cellulose and/or by catalyzing the generation of hydroxyl radicals from oxygen/peroxide.

The fact that the reaction order for delignification with respect to hydroxide ion is nearly independent of current, implies that hydroxide ion plays a similar role in reactions with both oxygen and ferricyanide.

This role is probably the generation of lignin phenolate anions which are subsequently attacked by the oxidant.

High reaction orders with respect to lignin may be rationalized either as the result of changing lignin chemistry or as the result of the morphology and radial distribution of lignin in the fiber wall (28). The former explanation is supported by the effect of current on the reaction order for lignin because ferricyanide is a more powerful oxidant than oxygen and should diffuse at about the half rate of oxygen through the fiber wall (29).

The rate of cellulose degradation in the absence of current is similar to that reported by Olm and Teder (11), with rapid reaction in the first 10 min followed by a relatively slow increase in " m_n " over the remaining reaction time. Olm and Teder fitted their data with two intersecting zero order reactions where the rate constant for the initial phase was 5 times that of the final phase. For the single-stage process used in the present analysis, the cellulose degradation rate is -5 order with respect to cellulose chains (" m_n ") without current but zero order at 0.5 A and 0.5 order at 1 A. Also, the reaction order with respect to hydroxide ion concentration is 0.7 at zero current but 0.3 at 0.5 and 1 A. This change in reaction order indicates a change in the mechanism of cellulose attack as current is increased.

Cellulose is attacked by the combined reactions of peeling and random chain cleavage. The rate of the peeling reaction depends on the pH and the concentration of reducing end groups of the cellulose chains, whereas the rate of chain cleavage is determined by the concentration of hydroxyl radicals and of cellulose chains (i.e., " m_n ") in the fiber. The peeling reaction leads to a slow indirect increase in " m_n " as the fiber mass decreases, whereas chain cleavage gives a direct increase in " m_n ." The generation of hydroxyl radicals is probably promoted by the current

through the ferro/ferricyanide couple, so the change of reaction order with current may be due to this effect and/or to the parallel effect of current on the rate of delignification.

At zero current, the initial high rate of increase in " m_n " results from cleavage of the accessible cellulose chains, but the rate drops rapidly as this cellulose becomes unavailable (30, 31). As suggested by Olm and Teder (11), the availability of the cellulose may be linked to the rate of delignification. When the current is applied, the activity of oxidants is increased, more cellulose is exposed, random chain cleavage is promoted, and the reaction order with respect to " m_n " increases. The parallel decrease in reaction order with respect to hydroxide ion may reflect the diminished importance of peeling reactions to cellulose degradation in the presence of ferricyanide.

Conclusions

Electrochemically mediated oxygen bleaching of kraft softwood pulp with ferro/ferricyanide increases the rate of delignification and cellulose degradation and gives small increases in selectivity as well as milder operating conditions compared to conventional oxygen bleaching.

A factorial experiment shows strong effects of oxygen pressure, pH, temperature, and current on the extent of delignification and cellulose degradation in electrochemically mediated oxygen bleaching. Kinetic analysis of data from bleaching runs under oxygen shows that the presence of ferricyanide in the electrochemical process shifts the rate determining steps for both the lignin and cellulose oxidation from chemical reaction to diffusion control and makes the reaction rates nearly independent of oxygen pressure above 0.1 MPa.

Highest bleaching selectivity in the electrochemical process was obtained by in situ generation of ferricyanide with zero oxygen pressure (nitrogen sparge) and with current

(1 A) at maximum pH (14) and temperature (75°C). However, the delignification rate under nitrogen was about one-third to half the rate under oxygen with the same current. In the presence of oxygen, the selectivity was raised by application of current. In the runs with oxygen and current, the selectivity was increased with increasing pH and temperature as well as with lower current.

The product pulp brightness from all runs was correlated to kappa number without regard to bleaching conditions. □

Literature cited

1. McDonough, T. J., *TAPPI 1990 Bleach Plant Operations Short Course Notes*, TAPPI PRESS, Atlanta, p. 53.
2. Tench, L. and Harpers, S., *Tappi J.* 70(11): 55(1987).
3. Stromskii, S. V. and Chupka, E. I., *Khimiya Drevesiny (Riga)* (4): 11(1978).
4. Chupka, E. I., Stromskii, S. V., Shulyataikov, O. P., et al., *Bumazh. Prom.* (11): 2021(1978).
5. Chupka, E. I. and Stromskii, S. V., *Bumazh. Prom.* (1): 15(1982).
6. Godsay, M. P., Hull, M. N., and Yasnovsky, V. M., U.S. pat. 4,622,100 (Nov. 11, 1986).
7. Hull, M. N. and Yasnovsky, V. M., U.S. pat. 4,622,101 (Nov. 11, 1986).
8. Godsay, M. P., Hull, M. N., and Yasnovsky, V. M., *TAPPI 1988 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 731.
9. Perng, Y. S., "Electrochemically Mediated Oxygen Bleaching of Pulp", Ph.D. dissertation, UBC, Chem. Eng. (January 1993).
10. Vogel, A. I., *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th edn., Longmans, London, 1978, p. 385.
11. Olm, L. and Teder, A., *Tappi* 62(12): 43(1979).
12. Sihtola, H., Kyrklund, B., Laamanen, L., et al., *Paperi ja Puu* 45(4a): 225(1963).
13. Broden, A. and Simonson, R., *Svensk Papperstid.* 82(16): 487(1979).
14. Rubin, B., IUPAC, "Oxygen and Ozone," *Solubility Data Series*, Pergamon, Oxford, 1981, Vol. 7, p. 2.
15. Linke, W. F., *Solubilities of Inorganic and Metal Organic Compounds: A Compilation of Solubility Data from the Periodical Literature*, American Chemical Society, Washington DC, 1965, 4th edn., Vol. 2, p. 1128.
16. National Research Council, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, McGraw-Hill, New York, 1928, Vol. 3, p. 271.

Bleaching

17. Broden, A. and Simonson, R., *Svensk Papperstid.* 81(17): 541(1978).
18. Meguro, S. and Sakai, K., *Mokuzai Gakkaishi* 30(8): 660(1984).
19. Gierer, J., *Fourth International Symposium on Wood and Pulping Chemistry Notes*, Société Française de Chimie, Paris, 1987, p. 279.
20. Hsu, C. L. and Hsieh, J. S., *AIChE J.* 34(1): 116(1988).
21. Evan, J. E., Venkatesh, V., Gratzl, J. S., et al., *Tappi* 62(6): 37(1979).
22. Hartler, N., Norrstorm, H., and Rydin, S., *Svensk Papperstid.* 73(21): 696(1970).
23. Edwards, L. and Norberg, S. E., *Tappi* 56(11): 108(1973).
24. Myers, M. R. and Edwards, L., *Tappi J.* 72(9): 215(1989).
25. Teder, A. and Olm, L., *Paperi ja Puu* 63(4a): 315(1981).
26. Landucci, L. L., *Chemistry of Delignification with Oxygen, Ozone, and Peroxides Proceedings of First International Symposium*, Raleigh, NC, 1975, Published by UNI Publishers, Tokyo, 1980, p. 189.
27. Abrahamsson, K. and Samuelson, O., *Svensk Papperstid.* 79(9): 281(1976).
28. Jayme, V. G. and von Koppen, A. V., *Papier* 4(23/24): 455(1950).
29. Linde, D.R., Ed., *CRC Handbook of Chemistry and Physics*, CRC, Boca Raton, 1990, 71st edn.
30. Meller, A., *Holzforschung* 14(3): 78(1960).
31. Haas, D. W., Hrutfiord, B. F., and Sarkanen, K. V., *J. Appl. Polymer Sci.* 11(4): 587(1967).

We thank the Natural Sciences and Engineering Research Council of Canada and PAPRICAN for financial support and we acknowledge experimental contributions by R. Kaplan for kappa number and viscosity tests and Y. T. Chen for brightness tests.

Received for Review April 18, 1993.

Accepted Aug. 17, 1993.

Nomenclature

A	= frequency factor
B	= brightness, % ISO
B°	= unbleached brightness, % ISO
E	= Arrhenius activation energy, kJ/mole
F	= ferricyanide concentration, mmole/2 L
I	= current (A)
IV	= intrinsic viscosity, dm ³ /kg
K	= kappa number
K°	= unbleached kappa number
k	= rate constant
k_1, k_2	= rate constants
m_1, m_2	= reaction order with respect to $[OH^-]$
" m_n "	= number of moles of cellulose chains per ton of pulp
n_1, n_2	= reaction order with respect to K or " m_n "
O	= oxygen pressure, MPa
$[OH^-]$	= concentration of hydroxide ion, mmole
$[O_2]$	= oxygen solubility in liquid phase, mM
o_1, o_2	= reaction order with respect to $[O_2]$
P	= pH
R	= universal gas constant, 0.008314 kJ/mole-K
R^*	= correlation coefficient
T	= absolute temperature, K temperature, °C
t	= reaction time, min
V	= TAPPI viscosity, cP