MECHANISM AND KINETICS OF DEMETHYLATION DURING KRAFT PULP CHLORINATION

by

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A Thesis Submitted to the Faculty of Graduate Studies and Research in Partial Fulfillment of the Requirements for the Degree of Master of Engineering

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March, 1989

ABSTRACT

Methanol formation during chlorination of kraft Black Spruce pulp was studied in a continuously stirred batch reactor.

A new chlorination mechanism is proposed for softwood kraft pulp based on experimental evidence that shows there is a close relationship between demethylation and delignification, and that the so-called "floor level" residual lignin consists mainly of polymeric material in which guaiacyl units have been tri-chlorinated. Since lignin consisting of 2,5,6-tri-chloro guaiacyl units cannot be demethylated, these units qualify as "blocking groups" and support the chemical limitation theory to explain incomplete delignification during chlorination. Based on this mechanism and model compound studies in literature, a novel chlorination mechanism is also formulated for hardwood kraft pulp.

Demethylation kinetics are developed based on the new delignification mechanism of kraft pulp chlorination. The kinetic equations show that demethylation and chlorine substitution of unchlorinated lignin monomer units are completed within the first few seconds. The corresponding reactions of mono-chloro lignin monomer units are slower but again one order of magnitude faster than those of the di-chloro lignin units. The demethylation kinetics give realistic prediction of the total organic chlorine content of both chlorinated pulp fibers and chlorination effluent produced in a conventional chlorination stage with low ClO_2 substitution. The present kinetics also give a mechanistic basis

for the recent finding that Cl_2 should be added first at a low chlorine charge factor before addition of ClO_2 to prevent dioxin formation during kraft pulp chlorination.

Finally a new and relatively fast method to determine lignin content in kraft black spruce pulp has been developed, based on conversion of methoxyl groups in lignin to methanol by elemental chlorine. The method is called "Methanol number" and defined as methanol concentration in units of ppm produced during five minutes of chlorination at 25 C, 1% consistency, and an initial chlorine concentration of 3.0 g/l.

RESUME

Nous avons étudié la formation de méthanol pendant la chloration d'une pâte kraft d'épinette noire dans un réacteur discontinu avec agitation continue.

Nous proposons un nouveau mécanisme de chloration pour la pâte kraft de résineux basé sur la preuve expérimentale qui démontre qu'il y a un lien proche entre la déméthylation et la délignification et que la lignine résiduelle aussi dite "niveau de plancher" se compose principalement de matériel polymérique dans lequel les unités guaiacyle ont été trichlorés. Puisque la lignine se composant d'unités 2,5,6-trichloro guaiacyl ne peut être déméthylé, ces unités fonctionnent comme "groupes de blockage", supportant la théorie de la limitation chemique et expliquant la délignification incomplète pendant la chloration. Basé sur ce méchanisme et des études de composés modèles dans la littérature, un nouveau mécanisme de chloration a aussi été formulé pour la pâte de feuillus.

En se basant sur le nouveau mécanisme de délignification de la chloration de pâte kraft, nous avons dévelopé la cinétique de la déméthylation. Les équations cinétiques démontrent que la déméthylation et la substitution de chlore des monomères de lignine non-chloriné sont terminés dans les premières secondes. Les réactions correspondantes pour les monomères le lignine monochloré sont plus lentes mais d'un ordre de grandeur plus rapides que pour les unités de lignine dichloré. La cinétique de déméthylation donne des prédictions réalistes pour la teneur totale de chlore organique pour les fibres de pâte chloriné et l'effluent de chlora-

tion produits dans un stade de chloration conventionel avec une faible substitution de ClO_2. La cinétique donne aussi une base mécanistique pour la récente trouvaille que pour de faibles charges de chlore, le Cl_2 devrait être ajouté en premier avant l'addition du ClO_2 pour prévenir la formation de dioxine pendant la chloration de la pâte kraft.

Finalement, une nouvelle méthode relativement rapide a été développée pour déterminer la teneur de lignine dans la pâte kraft d'épinette noire. La méthode est basée sur la conversion de groupes méthoxyle dans la lignine en méthanol par le chlore élémental. La méthode est nominée "Indice de Méthanol" et est définie comme étant la concentration de méthanol en unités de ppm produite pendant cinq minutes de chloration, à 25 C, 1% de consistance, et une concentration initiale de chlore de 3.0 g/l.

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ACKNOWLEDGEMENTS

It is my great fortune to study under supervision of Dr. A. R. P. van Heiningen and Dr. G. J. Kubes. I would like to give my sincere thanks to them for their guidance, encouragement and financial support.

I also wish to thank Dr. O. M. Fuller and Dr. R. Mortimer for their valuable advice and information.

Special thanks must go to Jian, Xuejun, Omar, John Mackinnon, Paul, Pritham, Aliye, the whole CRISP research group for their friendship and many useful discussions.

The receipt of a Chinese Government scholarship and a Paprican scholarship is gratefully acknowledged.

For the lignin measurement I would like to thank J. Ing and the Chemical Analysis Group in Paprican. For the French abstract translation of the thesis I would like to thank N. Poirier. For typing the French abstract I would like to thank Miss A. McGuinness. My appreciation is also towards Mr. J. Dumont for his very kind help in the selection and ordering of equipment, chemicals and other supplies.

Furthermore, I would like to express my gratitude to my friends and my colleagues for making my days very enjoyable.

Finally, I would like to thank my parents, my brother, and my sister for their love, and those who extended their moral encouragement throughout my time here.

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NOMENCLATURE

$[Cl_2]_i$: Intial chlorine concentration

k_i: Rate constants of reaction i (see Figure 4-7)

M_1: Methoxyl concentration associated with mono-chloro lignin monomer units

M_{10}: Initial methoxyl concentration associated with mono-chloro lignin monomer units

M_2: Methoxyl concentration associated with di-chloro lignin monomer units

M_3: Methoxyl concentration associated with tri-chloro lignin monomer units

S_M: Stoichiometric coefficient of chlorine and methoxyl group

t: Chlorination time

CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

The principal objective of bleaching is to whiten and brighten pulp without severe degradation of carbohydrates. The modern bleach plant usually consists of several steps. Of these stages, chlorination is generally regarded as the most important.

Chlorination of pulp is characterized by initially very fast removal of lignin, followed by much slower further delignification (1,2). No agreement exists concerning the dominant reaction mechanism for delignification during chlorination (3,4). Presently the chlorination stage is intensely studied because of increasing concern about the environmental impact of chlorinated organics produced in this industrial operation (5).

Large fluctuations in lignin content characterize the pulp entering the chlorination stage (6,7). The extremely fast initial reaction, as well as the absence of an on-line measurement of lignin content makes control very difficult The usual control strategy is to supply an excess of chlorine to compensate for the lignin content fluctuations and the changes in pulp flow rate. This control strategy leads to unnecessary chlorine consumption, pulp degradation, and most likely also to increased organic chlorine loadings in the effluent.

Methanol is formed during chlorination from methoxyl groups in the phenyl-propane units of the lignin macro-molecule. Recently (8) it was found for dynamic chlorination of pulp beds that further demethylation does not occur when delignification is complete. This suggests that demethylation and delignification are closely related, and that perhaps the evolution of methanol

can be used as indicator for delignification during pulp chlorination. Another important aspect is that methanol can be determined by gas chromatography in about 1-2 minutes.

In order to evaluate whether the evolution of methanol can be used for control of the chlorination stage, the kinetics as well as mechanism of methanol formation were investigated in this thesis. Also investigated was whether the methanol concentration during chlorination can be used as an indirect fast method to determine the lignin content of pulp.

1.2 OBJECTIVES AND STRATEGY

The general objective is to study the influence of various operating parameters on pulp chlorination kinetics in a batch reactor set-up. More specific objectives are to establish the mechanism of methanol formation as well as to explain the nature of the so-called "floor level" lignin, which is the lignin cannot be removed in a single chlorination stage.

The chlorination experiments were performed in a Continuous Stirred Tank Reactor (CSTR). The following analyses were performed: chlorine concentration, Kappa number of chlorinated and washed (CW) and chlorinated and extracted (CE) pulp, methanol concentration, and organically bound chlorine and methoxyl content of pulp. By measuring the methoxyl content in pulp before and after chlorination, a methoxyl group mass balance can be made. Based on experimental evidence, a mechanism of demethylation and delignification will be formulated. Subsequently, the relevant reaction constants will be determined by minimizing the difference between the theoretical and experimental methanol concentration

using the Hooke and Jeeves (9) search algorithm.

1.3 OUTLINE OF THE THESIS

This thesis is concerned with demethylation kinetics during kraft pulp chlorination.

The experimental set-up and procedures are discussed in chapter 2.

In chapter 3, a new chlorination mechanism is proposed based on evidence of the close relationship between demethylation and delignification during kraft pulp chlorination.

In chapter 4, the demethylation kinetics are developed based on the new delignification mechanism of kraft pulp chlorination described in chapter 3. The kinetic equations are also used to predict the total organic chlorine content of both chlorinated pulp fibers and chlorination effluent.

Finally, a new and fast method of lignin determination of pulp, called "Methanol number" is developed in chapter 5. The method is based on measurement of the methanol concentration by gas chromatography after subjecting a 1% consistency pulp suspension to a high chlorine charge for a relatively short time.

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CHAPTER 2

EXPERIMENTAL

Kraft pulp from Black Spruce wood was prepared at Paprican's chemical pulping pilot plant. Pulp samples were stored in a refrigerator throughout the study.

The experiments were performed in a CSTR The variables were chlorine concentration and temperature. The pulp consistency was kept at 2%, and 10% chlorine dioxide substitution of available chlorine was used to prevent carbohydrate degradation.

The experimental procedures may be grouped into four stages of operation:

1 Reactant Preparations

2 Chlorination Operation

3 Washing and Extraction

4 Analyses

2.1 REACTANT PREPARATION

Chlorine Water

A six-litre carboy was filled with distilled water. Chlorine gas from a gas cylinder was bubbled through the distilled water by means of a glass tube equipped with a fritted glass fitting at the end for good dispersion. When the desired chlorine concentration was reached, the chlorine gas flow was stopped.

Chlorine Dioxide

Chlorine dioxide was prepared by passing chlorine gas diluted with nitrogen through a series of sodium chlorite columns and collecting the evolving chlorine dioxide gas in cold deionized water. It should be pointed out that the N_2 to Cl_2 gas flow rate ratio was larger than 50 so that the colour in the chlorite columns does not become too dark orange, because ClO_2 gas is not

stable at high concentration and could explode.

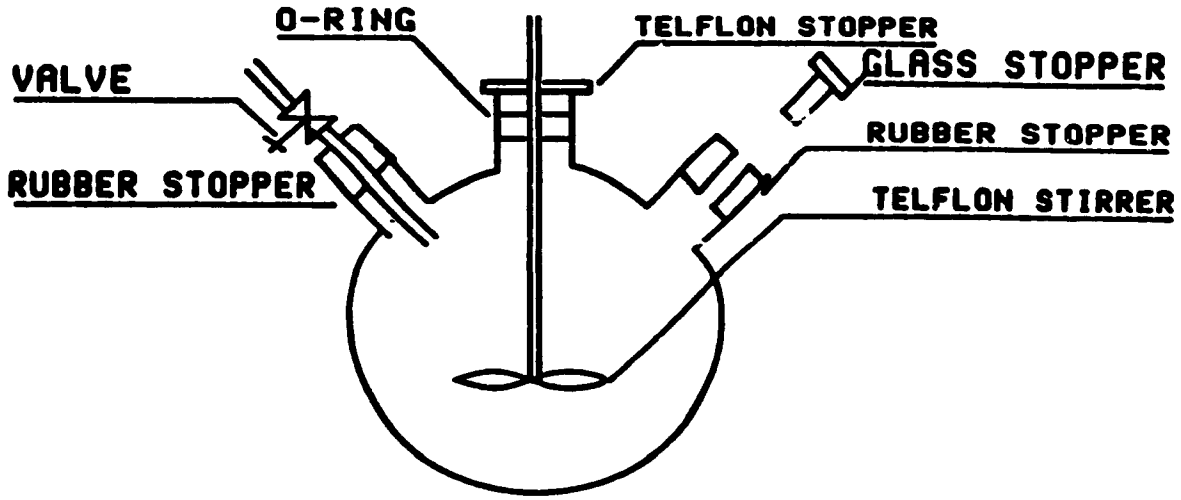
Pulp Sample

7 grams of oven dried sample from air-dried hand-sheet was soaked in excess water for a few hours, after which the pulp was disintegrated in a standard disintegrator. Subsequently, excess water was removed by filtering the pulp suspension on a buchner funnel with a 100-mesh screen. The concentrated pulp sample was filled in a 50-ml syringe, and the pulp sample was ready for chlorination.

2.2 CHLORINATION OPERATION

Chlorination was performed in a CSTR, which is shown in Fig.2-1. The total volume of the reactor is 500 ml. Controlled agitation is achieved by a variable speed electric stirrer. The specified amount of chlorine water was introduced by a pipette into the flask In order to facilitate this procedure, excess gas inside the flask was allowed to escape by opening a glass valve in the third neck of the flask. The flask and the syringe with pulp were submerged in a constant temperature bath for 10-15 minutes to equalize their temperatures. The temperature was measured by a thermocouple. Before the pulp sample was injected into the flask, the chlorine concentration was determined and chlorine water and distilled water were added so that the desired chlorine concentration and consistency of 2% would be obtained. Thereafter, the pulp sample was injected into the flask with the syringe by opening the rubber stopper. The stopper was closed immediately, and stirring was started. It was found that good mixing of chlorine water with pulp could be achieved within two seconds, The

Fig. 2-1 Chlorination apparatus


O-RING
TELFLON STOPPER
VALVE
GLASS STOPPER
RUBBER STOPPER
RUBBER STOPPER
TELFLON STIRRER

reaction was stopped by injection of an excess amount of potassium iodide solution. The liquor separated from the pulp suspension was analyzed for residual chlorine and methanol. The pulp was saved for the next operation.

2.3 PULP WASHING AND EXTRACTION

Pulp separated from chlorination liquor was washed with a large amount of water until no iodide and chloride could be detected with a silver nitrate solution. Then, the pulp sample was divided into two parts. One part was converted into a hand-sheet for further analysis, while the other half was used for standard extraction.

The experimental extraction conditions are listed in Table 2-1. The chlorinated sample was mixed in a 50-ml beaker with the required amount of sodium hydroxide and water to achieve the prescribed caustic dosage and extraction consistency. Mixing was achieved by a glass rod. Then the pulp slurry was transferred into a polyethylene bag, which was placed in a constant temperature bath at 70 C. After one hour, the extracted pulp was thoroughly washed, and air dried handsheets were prepared for further analysis.

2.4 ANALYSES

Measurement of methanol concentration

The methanol concentration in spent liquor is determined by gas chromatography. The analytical conditions are:

Column: Chromosorb 102, mesh size:80/100

Injection temperature (C): 150

Table 2-1

Extraction Conditions

% NaOH based pulp	0.55 * Chlorine charge factor * Initial Kappa No.
Consistency %	10
Temperature C	70
Time hr.	1

Oven temperature (C):	107
Detector temperature (C):	200
Helium flow rate (ml/min):	50
Hydrogen flow rate (ml/min):	22
Air flow rate (ml/min):	250
Sample size (ul):	1.8

A typical chromatogram is shown in Fig.5-2. The retention time for methanol is 1.61 minutes. Complete analysis takes about 2 minutes.

Organically bound chlorine

The sample is analyzed according to the Schöniger combustion method, which is based on the principle that chlorine in organic compounds is completely converted to hydrogen chloride when combusted . Used as wrapping paper is a thin handsheet made from unchlorinated pulp. The produced hydrogen chloride is absorbed in 35 ml deionized water during 30 minutes, and analyzed spectro-photometrically.

Methoxyl group content

The methoxyl group content in the chlorinated samples is measured according to Tappi standard T209. The modification involved in the apparatus is replacement of the ground socket joint by a spherical O-ring joint so that leakage is prevented without use of lubricating oil.

Analyses used

Kappa Number was measured by the CPPA standard method. Klason lignin and UV lignin were analyzed by PAPRICAN's Chemical Analysis Group also according to the CPPA standard methods.

CHAPTER 3

A NEW MECHANISM FOR PULP DELIGNIFICATION DURING CHLORINATION

ABSTRACT

A new chlorination mechanism is proposed for softwood kraft pulp based on experimental evidence that shows there is a close relationship between demethylation and delignification, and that the so-called "floor level" residual lignin consists mainly of polymeric material in which guaiacyl units have been tri-chlorinated.

It is proposed that chlorination involves two competing reactions: demethylation and aromatic substitution of chlorine. Demethylation is followed by cleavage of the adjacent 4-O-ether linkage under the activating influence of the just formed free phenolic group. Aromatic substitution of chlorine at the 6-, 5- and 2- positions deactivates demethylation and thus also delignification. Since lignin consisting of 2,5,6-tri-chloro guaiacyl units cannot be demethylated, these units qualify as "blocking groups" and support the chemical limitation theory to explain incomplete delignification during chlorination. These "blocking groups" are largely destroyed during caustic extraction and render lignin susceptible to delignification in the next chlorination step. Based on this mechanism and model compound studies in literature, a novel chlorination mechanism is also formulated for hardwood kraft pulp. The implications for improving the chlorination efficiency are discussed.

INTRODUCTION

It has been recognized for a long time that pulp cannot fully be delignified in one chlorination stage. Even with an excess of chlorine after several-day contact, some lignin still remains (1). Further delignification can be achieved in a second chlorination stage only after alkaline or hot water extraction. However, chlorination again initially proceeds very rapidly, and stops before complete delignification (1). The concept of a limiting or "floor level" CE Kappa number has been described in a number of references (2,3,5). Mackinnon (6), recently proposed a linear relationship between the CE "floor level" lignin content and the lignin content of unbleached pulp in an attempt to simulate the chlorination and extraction stage of a kraft bleach plant.

Basically, two hypothesis have been proposed which can explain the existence of 'floor level' lignin. The first one, postulated by Karter and Bobalek (4), is based on the idea that a layer of chlorinated lignin is formed starting in the P and S layers of the fibers. The so-called "immobilized chlorolignin" layer gradually becomes impermeable to chlorine and unreacted lignin remains behind the barrier. In a refined version of this model, Pugliese and McDonough (16) recently proposed that the chlorolignin barrier is formed in small lignin-containing grains distributed uniformly throughout the fibers. These two models can be called physical limitation models since diffusion of chlorine is the rate determining step. Berry and Fleming (1) on the other hand, proposed a chemical model whereby alkali-labile "blocking groups" formed during chlorination only allow very slow reaction between

chlorine and residual lignin. As potential candidates for blocking groups they selected chloro-quinones and chlorocarboxylic acids, based on the fact that significant amounts of carbon dioxide and chloride are liberated during hot water extraction of chlorinated pulp. Another physical model was proposed by Rapson and Anderson (14) that chlorine transport external to the fiber is the rate determining step. However, this model cannot explain the existence of a lignin "floor level".

All the above theories have weaknesses. The "immobilized chlorolignin barrier" theory cannot explain the results of Berry and Fleming (1) that residual lignin in chlorinated and extracted (CE) pulp contains about two chlorine atoms per C_9 unit. Another weakness is the requirement of an effective diffusion coefficient for chlorine in the lignin-containing grains of at least 4 orders of magnitude smaller than the binary diffusion coefficient in water when modelling the rate of disappearance of chlorine up to one minute. Even much smaller diffusion coefficients are required when chlorination times of 60 minutes or days are considered. Berry and Fleming (1) selected chloroquinone and chlorocarboxylic acids as "blocking groups". However, quantitative evidence given that these groups are indeed responsible for "floor level" lignin formation was limited. Another problem is that most, if not all of the residual lignin should be in the form of "blocking groups" in order to prevent further reaction with chlorine. Considering the non-aromatic character of chlorocarboxylic acids, these groups are less probable candidates as "blocking groups" because most of the lignin in chlorinated and water washed (CW) pulp is aromatic.

The present work was started after Ali (22) found in dynamic

chlorination experiments that methanol could be used as an indicator for delignification. By examining the changes in methoxyl group, chlorine and lignin contents of kraft pulp as it is chlorinated, we concluded that demethylation and delignification are closely connected. We also present evidence for a new type of "blocking group" and formulate a new chlorination mechanism based on the chemistry of these groups.

EXPERIMENTAL

The chlorination experiments were performed in a 500 ml thermostated Continuous Stirred Tank Reactor (CSTR). The reactor initially contained an aqueous chlorine solution with 10% chlorine dioxide substitution to minimize cellulose degradation. At the start of an experiment, a medium consistency pulp suspension was injected with a large syringe. After a predetermined time interval of 1/6, 1/2. 1.5, 5, 15, 45 or 90 minutes, the reaction was stopped by injection of an excess amount of KI solution. Iodometric titration provided the chlorine concentration at the time when the reaction was stopped. The methanol concentration in the liquid phase was measured by GC. Other analyses performed were the lignin content, Kappa number, chlorine content of the CW and CE pulps, and the methoxyl content of the CW pulp. The methoxyl group content was determined according to Tappi standard T209, and the chlorine content in pulp was determined after combustion of the pulp according to the Schöniger method. Chlorine charge factors of 0.16, 0.22 and 0.33, temperatures of 25, 35, 45 C and a consistency of 2% were used. The charge factor is defined as the chlorine charge in percentage divided by the Kappa number of the

unchlorinated pulp. Kraft black spruce pulps of various Kappa numbers were used. The standard extraction procedure was: NaOH charge of 0.55 times the Cl_2 charge, 70 C, 10% consistency, and 60 minutes reaction time.

RESULTS

Fig.3-1 shows the methanol concentration in the chlorination liquor for different times of chlorination. Also shown are the Kappa numbers of the chlorinated and washed (CW) pulps as well as the values obtained after caustic extraction. As expected, the initial rapid delignification is followed by a slower period during which a "floor level" is approached asymptotically for both the CW and CE Kappa numbers. Another interesting observation is that the variation in methanol concentration is a mirror image of the CW Kappa number development, and to a lesser extent of the CE Kappa number.

The methanol concentration in the chlorination liquor and the methoxyl group content of the CW pulp for typical industrial conditions are listed in Table 3-1. A mass balance for methoxyl group was attempted by assuming that all methoxyl groups removed from the pulp are converted into methanol, and that further reaction of methanol in chlorine water can be neglected.The last column in Table 3-1 shows that the $-OCH_3$ mass balance is satisfied with less than 5% error. This shows that all removed methoxyl groups are accounted for as methanol, and proves that all dissolved lignin fragments are demethylated. Therefore, the methoxyl group content of any chlorinated pulp can be calculated from the initial methoxyl group content and methanol concentration

Fig.3-1 Methanol concentration, CW and CE Kappa number development during chlorination

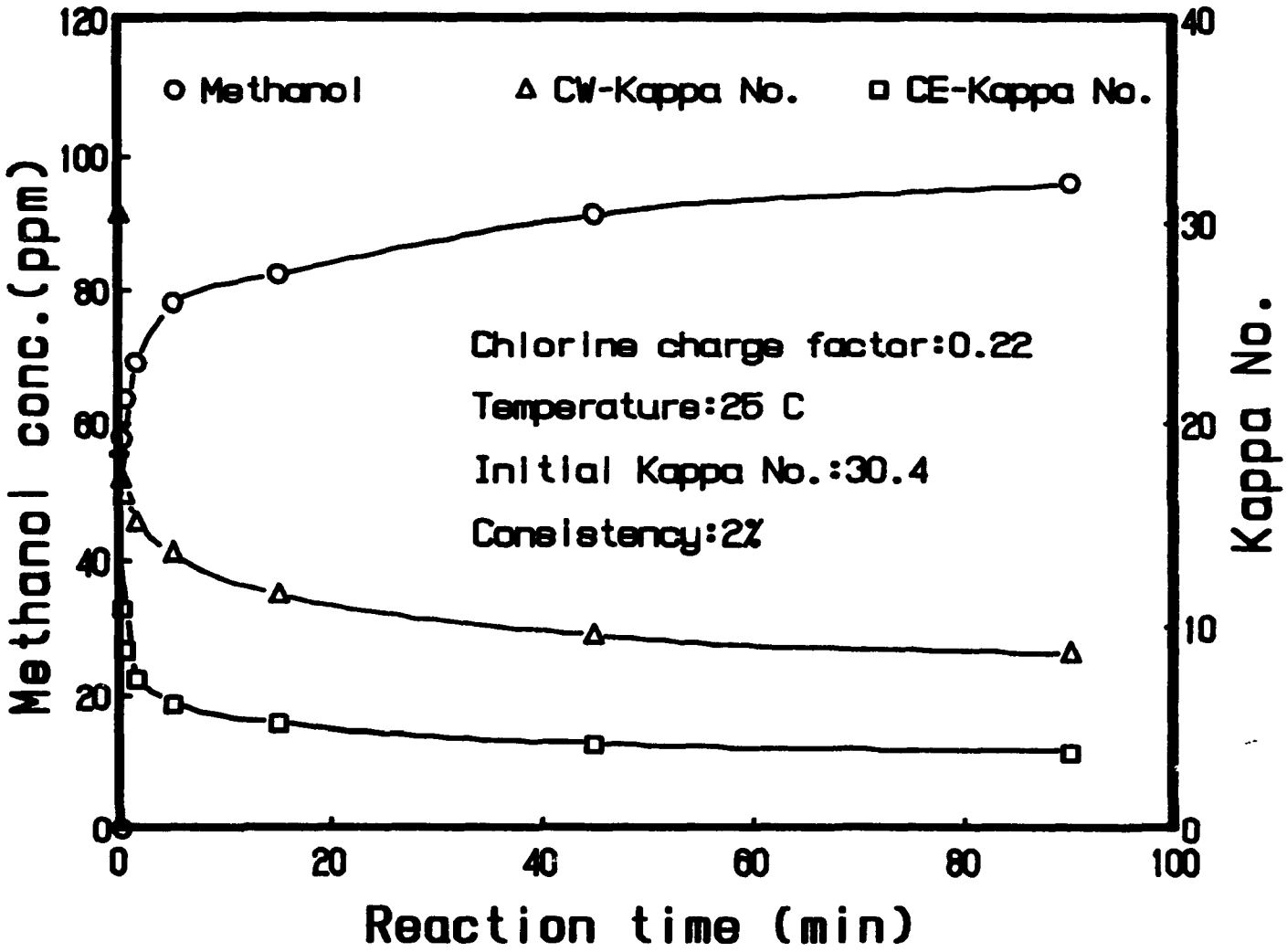

o Methanol
Δ CW-Kappa No.
□ CE-Kappa No.
Chlorine charge factor:0.22
Temperature:25 C
Initial Kappa No.:30.4
Consistency:2%
Methanol conc.(ppm)
Kappa No.
Reaction time (min)
0
20
40
60
80
100
120
10
30

Table 3-1

Methoxyl group mass balance during chlorination

Reaction time (min.)	Chlorine conc. (g/l)	Methanol conc. (ppm)	OCH3 content % on pulp	CW-Kappa No.	CE-Kappa No.	OCH3 balance (%)
0.0	1.34	0	0.59	30.4	18.9	100.0
0.167	0.73	63.7	0.31	16.1	9.5	104.8
0.5	0.69	67.7	0.25	15.5	7.7	98.3
1.5	0.60	74.1	0.21	14.0	6.6	96.6
5.0	0.46	84.4	0.20	12.2	5.4	103.2
15	0.38	92.7	0.16	9.7	4.4	103.2
45	0.18	94.9	0.13	7.5	3.5	99.9

Chlorine charge factor o.22, 35 C, Consistency 2%,
Chlorine dioxide 9.89%, Initial Kappa number 30.4

found in solution.

During pulp chlorination, chlorine is introduced in lignin by aromatic substitution. The chlorine content of CW pulp as a function of chlorination time in column 2 of Table 3-2 displays a weak maximum at a reaction time of one and half minutes. This can be attributed to the opposing effects of increasing chlorine substitution and dissolution of chlorinated lignin. Also shown in Table 3-2 is the Klason lignin content of CW pulp (column 3) and chlorine content of the Klason lignin samples (column 5). The chlorine free (UV +Klason) lignin content of CW pulp is listed in column 6 of Table 3-2. It was calculated by assuming that the chlorine content of UV lignin was the same as for the corresponding Klason lignin. [With an assumption of chlorine-free UV lignin, the total chlorine-free lignin content increases in the worst case by only 8%, because of the relative small weight percentage of chlorine in Klason lignin.]

The chlorine content of the Klason lignin of CW pulp is approximately 12.3%, independent of chlorination time. This corresponds to a chlorine-lignin monomer (Cl/C9) molar ratio of about 0.8, obtained after multiplication by 196/35.5, the ratio of molecular weights of lignin monomer and chlorine. The Cl/C9 molar ratio compares reasonably well with a ratio of 1.0 for chlorinated ball-milled kraft pulp (9). A molecular weight of 196 is used for the lignin C9 monomer based on the empirical formula determined by Kempf and Dence (9) for kraft milled-wood lignin.

The methoxyl content of CW pulp (column 7) is plotted against the chlorine-free total lignin content in Figure 3-2. The straight line fitted to the data, including the initial pulp, almost passes

Table 3-2

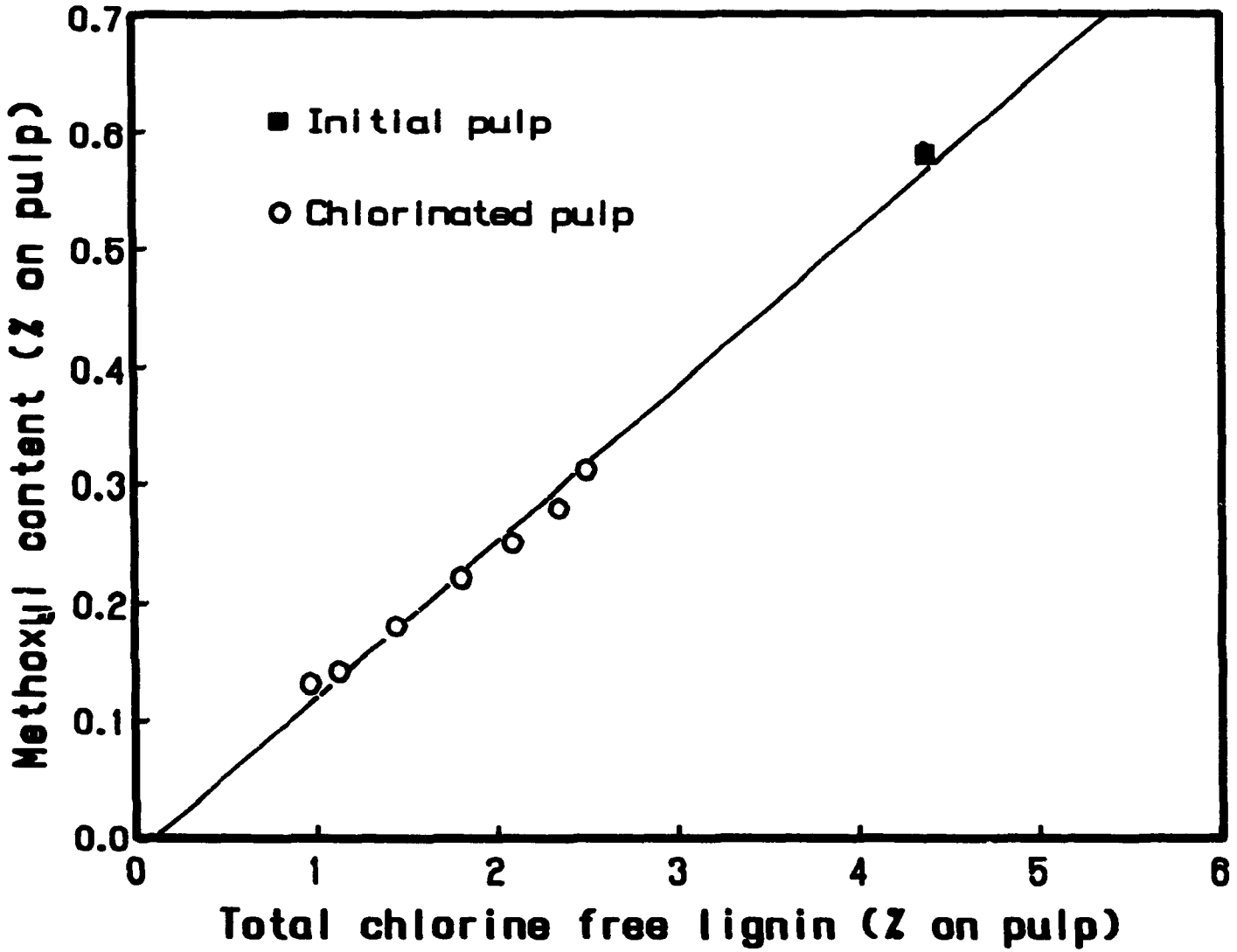
Development of chlorine, lignin and methoxyl contents of CW pulp

Time (min)	Chlorine (mg/g)*	Klason Lignin (%)*	UV Lig (%)*	Cl in Klason (%)	Lignin Cl-free (%)*	OCH3 (%)*	OCH3/C9 molar ratio	Cl/C9 molar ratio	CW Kappa
0	0	4.15	0.36	0	4.51	0.59	0.83	0	30.4
0.167	5.56	2.17	0.65	11.6	2.49	0.31	0.79	1.2	17.3
0.5	6.09	1.93	0.73	11.9	2.34	0.28	0.76	1.4	16.5
1.5	6.12	1.64	0.72	11.9	2.08	0.25	0.76	1.6	15.1
5	5.93	1.33	0.72	12.1	1.80	0.22	0.77	1.8	13.6
15	5.76	0.98	0.66	11.8	1.44	0.18	0.79	2.2	11.7
45	5.73	0.61	0.66	12.8	1.12	0.14	0.79	2.8	9.6
90	5.62	0.52	0.58	13.0	0.96	0.13	0.86	3.2	8.7

* based on CW pulp

Initial Kappa No.:30.4,Chlorine charge factor:0.22,25 C,2% consistency

Fig. 3-2 Relationship between demethylation and delignification


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Methoxyl content (% on pulp)
■ Initial pulp
○ Chlorinated pulp
0
1
2
3
4
5
6
Total chlorine free lignin (% on pulp)

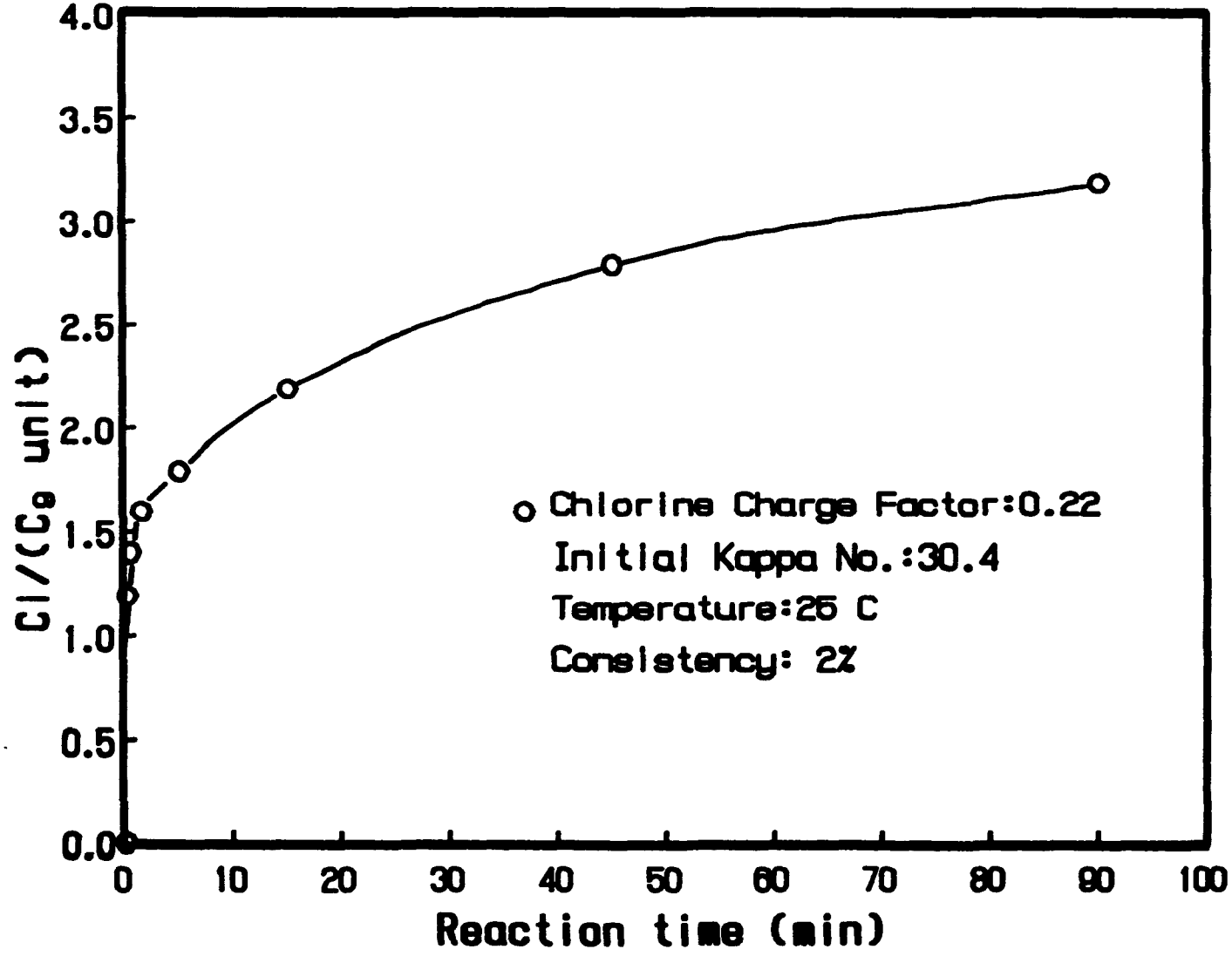
through the origin. Thus, the methoxyl group removal is proportional to lignin removal at any time during chlorination, suggesting that demethylation and delignification are closely related. The OCH_3/C_9 molar ratio (column 8) of the residual lignin remains constant at about 0.8 when a molecular weight of 196 for the C_9 lignin unit is used. Even after a long chlorination, the value of the OCH_3/C_9 molar ratio is not significantly different from that of the initial pulp. The implication is that the lignin which has not dissolved is the one which has not been demethylated.

The one before last column of Table 3-2 shows the Cl/C_9 molar ratio obtained by dividing column 2 by column 6 and multiplying by 196/35.5. In the above calculation we have assumed that chlorine which is physically adsorbed on pulp or bound to carbohydrates can be neglected.

The development of the Cl/C_9 molar ratio during chlorination is more clearly seen in Figure 3-3. From a molar ratio slightly above one after 10 seconds, the ratio increases to about three after 90 minutes. This could be interpreted as substitution of three chlorine atoms at all available sites in the aromatic ring of the C_9 unit. The results are in agreement with those of Kempf and Dence (9) who also found that the chlorine content in CW pulp increases with increasing chlorine charge until a maximum is approached asymptotically.

Considering the asymptotic behavior of the Cl/C_9 molar ratio it is of interest to examine the molar ratios for "floor level" chlorinated pulps prepared from unchlorinated samples of different initial Kappa numbers. The "floor level" is arbitrarily defined as

Fig.3-3 The development of the Cl/C9 molar ratio during chlorination


4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Cl/(Ca unit)
0
10
20
30
40
50
60
70
80
90
100
Reaction time (min)
Chlorine Charge Factor:0.22
Initial Kappa No.:30.4
Temperature:25 C
Consistency: 2%

pulp after 90 minutes chlorination at a charge factor of 0.33 and 45 C. Table 3-3 shows analyses of these "floor level" CW pulps.

The total chlorine free lignin (column 7) content of CW pulp decreases with lignin content (column 2) of the initial pulp. This relationship is approximately linear, as can be seen in Fig.3-4. The CW Kappa number also decreases linearly with the lignin content of the unchlorinated pulp. This result supports the idea that formation of "floor level" lignin is chemically limited rather than diffusion limited. In the latter case, one would expect a lower relative delignification of the larger lignin "grains" at higher initial lignin content, because the diffusion depth of chlorine is almost independent of the "grain" size.

The Cl/C9 molar ratio (column 10) of the CW "floor level" pulp is 3.6-3.9 over the wide range of CW lignin content of 2.90 to 0.58%. This range is slightly above the maximum ratio of 3.2 (Fig.3-2) obtained under more standard chlorination conditions. A molar ratio higher than 3.0 suggests that substitution also takes place in the aliphatic side chain, besides the three available positions (2,5,6) in the aromatic ring of the phenylpropane unit.

The OCH_3/C9 molar ratio of about 0.8 for all CW "floor level" pulp samples is the same as obtained after different chlorination times (Table 3-2). The above results show that the chemical structure of "floor level" lignin in CW pulp is similar regardless of the initial Kappa number of the unchlorinated pulp. Even though the yield of "floor level" lignin varies by a factor of five, the OCH_3/C9 and Cl/C9 molar ratios are remarkably constant. This fact, as well as the linear relationship between the initial and "floor level" lignin contents, supports the model that "floor level"

Table 3-3

Analysis of "floor level" CW pulp

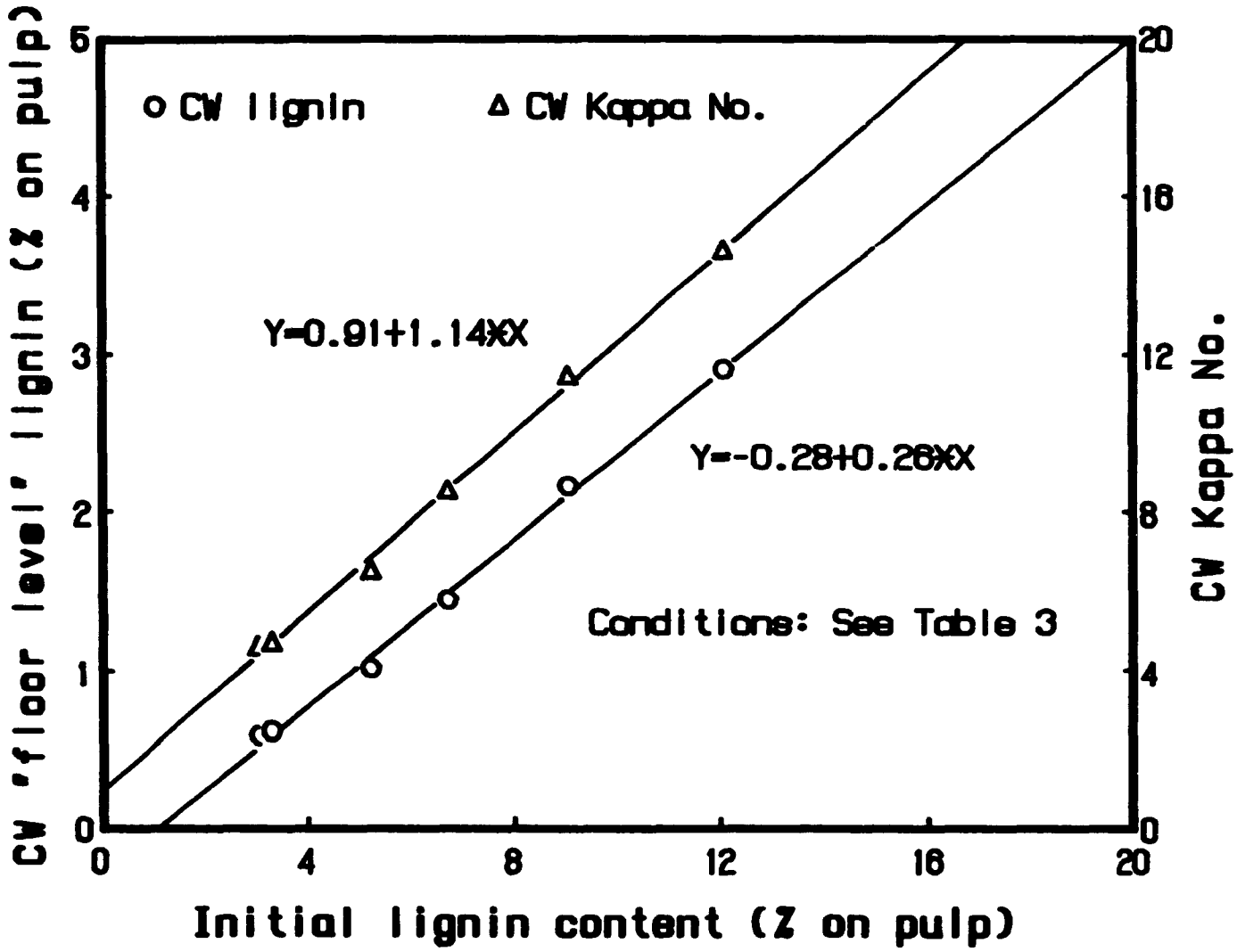
Initial Kappa	Total Lignin (%)**	Chlorine (mg/g)*	Klason lignin (%)*	UV lignin (%)*	Cl in Klason (%)	Lignin Cl-free (%)*	OCH3 (%)*	OCH3/C9 molar ratio	Cl/C9 molar ratio
78.4	11.63	19.55	2.62	0.68	12.3	2.90	0.35	0.76	3.7
60.0	8.81	14.02	1.81	0.66	12.5	2.16	0.25	0.73	3.6
44.7	6.70	9.58	1.07	0.59	11.9	1.45	0.17	0.74	3.6
36.0	5.23	6.59	0.61	0.56	13.0	1.02	0.12	0.74	3.6
30.4	4.71	5.60	0.40	0.56	/	0.84	0.11	0.83	3.7
22.0	3.31	4.31	0.18	0.52	/	0.61	0.08	0.83	3.9
20.5	3.05	4.16	0.14	0.53	/	0.58	0.08	0.87	3.9

* based on CW pulps

** unchlorinated samples

Conditions:Chlorine charge factor:0.33,45 C, 90 min., 2% consistency

Fig.3-4 Relationship between initial lignin and "floor level" lignin


o CW lignin
Δ CW Kappa No.
Y=0.91+1.14XX
Y=-0.28+0.26XX
Conditions: See Table 3
CW "floor level" lignin (% on pulp)
CW Kappa No.
Initial lignin content (% on pulp)
0
1
2
3
4
5
0
4
8
12
16
20

lignin formation is determined by the chlorination chemistry.

Finally it should be noticed that the Cl/C9 molar ratio of the 'floor level' CW pulp (column 10) is considerably larger than that of CW Klason lignin (about 0.8 calculated from column 7). This indicates that a large amount of chlorine is lost during treatment of CW pulp with 72% H_2SO_4 for the Klason lignin determination as well as during ball milling as was done by Kempf and Dence (9).

The CW pulp loses most of its chlorine when treated with sodium hydroxide during extraction. Column 6 and 7 in Table 3-4 show that during extraction the "floor level" CW pulp retains only 6 to 20% of its chlorine and 16-53% of its chlorine-free lignin, with the less removal corresponding to a sample with a lower initial Kappa number. Similar chlorine removal was reported by Kempf and Dence (9). The chlorine-free total lignin content is calculated using the measured average chlorine content of the CW Klason lignin of 12.3% (Table 3-2). Again it was assumed that the chlorine content of CE UV lignin is the same as the CE Klason lignin. The constant Cl/C9 molar ratio of 1.5±0.1 in Table 3-4 suggests that the chemical composition of CE "floor level" lignin obtained from different initial Kappa number pulps are similar.

It is well known that demethylation accompanies delignification. Fig.3-5 summarizes the presented results for the weight ratio of methoxyl group to lignin content after chlorination. Also included in the figure are this ratio obtained after pulping and for black spruce milled-wood lignin, reported by Björkman and Person (19). It can be seen that the weight ratio of methoxyl group to lignin after kraft pulping and chlorination is not much different from that in original wood.

Table 3-4

Analysis of "floor level" CE pulp

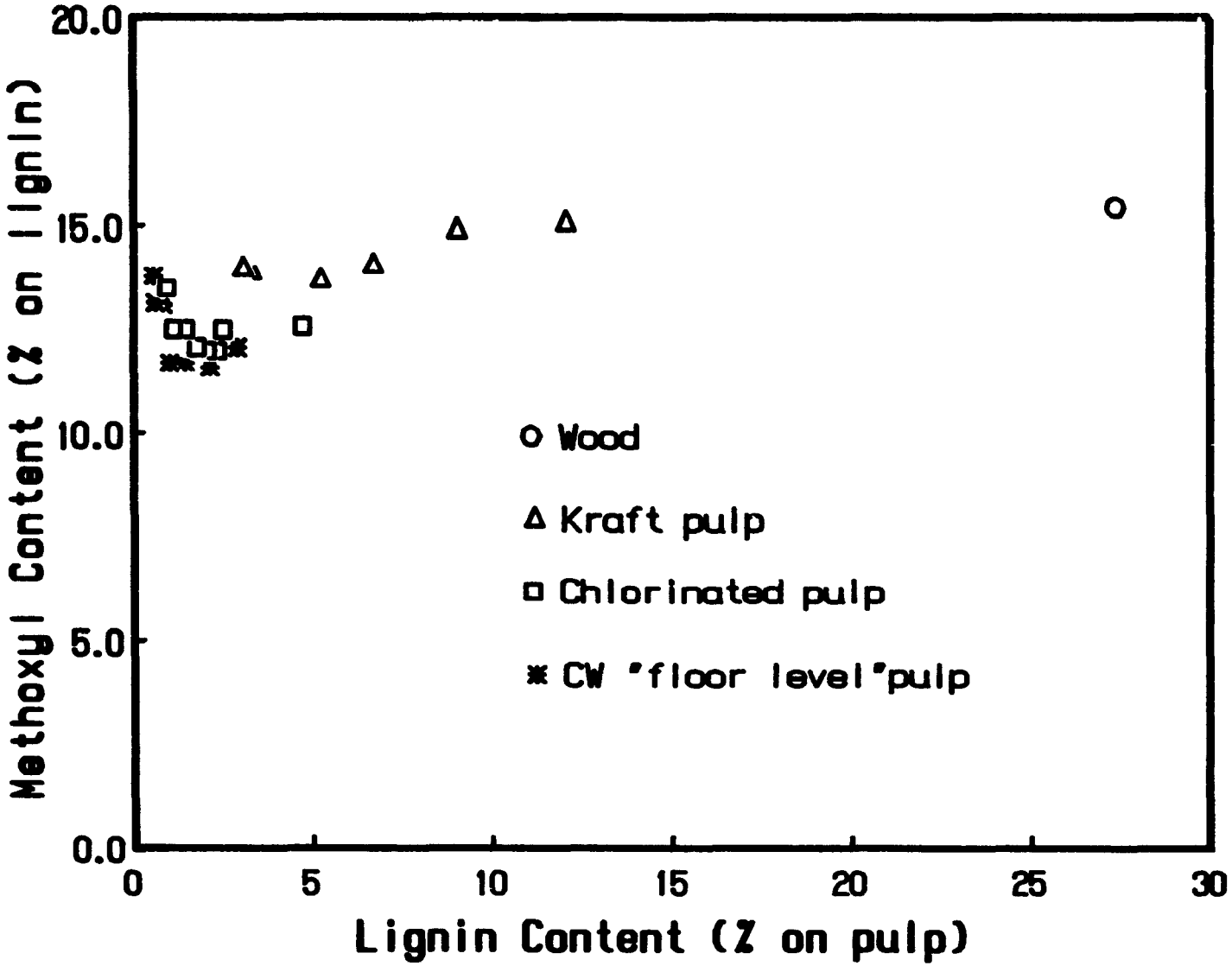
Initial Kappa	Chlorine (mg/g)*	Klason lignin (%)*	UV lignin (%)*	Lignin Cl-free (%)*	Chlorine remaining (%)**	Lignin remaining (%)**	Cl/C9 molar ratio
78.4	1.16	0.35	0.16	0.45	5.9	15.9	1.4
60.0	1.15	0.31	0.14	0.40	8.2	19.9	1.6
44.7	0.92	0.26	0.14	0.35	9.6	26.2	1.5
36.0	0.89	0.27	0.09	0.32	13.5	34.3	1.5
30.4	0.88	0.28	0.11	0.34	16.7	40.9	1.4
22.0	0.84	0.28	0.09	0.33	19.5	52.5	1.4
20.5	0.81	0.24	0.09	0.29	19.5	53.4	1.5

* based on CE pulp

** Compared to chlorine or lignin content in corresponding CW pulp

Conditions: Chlorine charge factor:0.33,45 C,90min,2% consistency

Fig.3-5 Methoxyl group to lignin content ratio after pulping and chlorination


20.0
15.0
10.0
5.0
0.0
0
5
10
15
20
25
30
Methoxyl Content (% on Lignin)
Lignin Content (% on pulp)
Wood
Kraft pulp
Chlorinated pulp
CW "floor level" pulp

DISCUSSION

1. Chlorination Mechanism

Two delignification mechanisms have been proposed for chlorination. Hibbert et al.(12) claimed that chlorine is first substituted in the aromatic ring at either the 6- or 5- position depending on respectively whether the para-hydroxyl group is free or not. They also claimed that the presence of substituted chlorine in the aromatic ring promotes cleavage of the bond with the methoxyl group. At the same time, an oxidative degradation of lignin occurs through cleavage of 4-O ether linkage. Dence and Sarkanen (7) postulated that chlorine substitution takes place both at the 6- and 5- positions. This is followed by cleavage of the bond between the benzene nucleus and the aliphatic side chain, independent of whether the 4-position is etherified or not. They did not consider the cleavage of the phenolic ether linkage at the 4-position to be important for lignin degradation during chlorination.

The two proposed mechanisms agree on the initial rapid substitution of chlorine in the aromatic ring, and that demethylation accompanies lignin degradation. The main difference is that Hibbert proposed an oxidative degradation of the lignin polymer whereby the 4-O ether linkage was cleaved and a carboxyl group formed, whereas Dence and Sarkanen indicated that degradation occurs by replacement of the side chain by chlorine. Moreover, Hibbert claimed that oxidation is involved in demethylation while Dence and Sarkanen, on the other hand, stated that demethyiation is a hydrolysis reaction.

Various opinions have been expressed concerning the nature of

the demethylation reaction in aromatic methyl ethers. It has been suggested (12) that chlorine substitution in the phenol structure may make the methoxyl group more susceptible to oxidative degradation. Ivancic and Rydholm (13) proposed that demethylation may be due to an acid-catalyzed hydrolysis of the methoxyl group. Sarkanen and Strauss (10) considered two other mechanisms, based on studies with lignin model compounds, and the knowledge that molecular chlorine is strongly electrophilic and can act similar as a proton in acid-catalyzed hydrolysis. In the first, a polarized chlorine molecule attacks at the position para to the methoxyl group, while in the second mechanism chlorine attacks the ether oxygen of the methoxyl group, In a later publication (15), they claimed that the former mechanism seems less probable because no major effect was found on the demethylation rate whether the substituent para to methoxyl was chlorine or an aldehyde group.

The experimental results presented in the previous section can be summarized as follows:

— all methoxyl groups removed from pulp during chlorination are accounted for as methanol

— the molar ratio $-OCH_3/C_9$ of chlorinated pulp remains approximately constant during chlorination

— the Cl/C_9 molar ratio in chlorinated lignin increases from 1 within the first few seconds and asymptotically approaches 3 during a normal chlorination

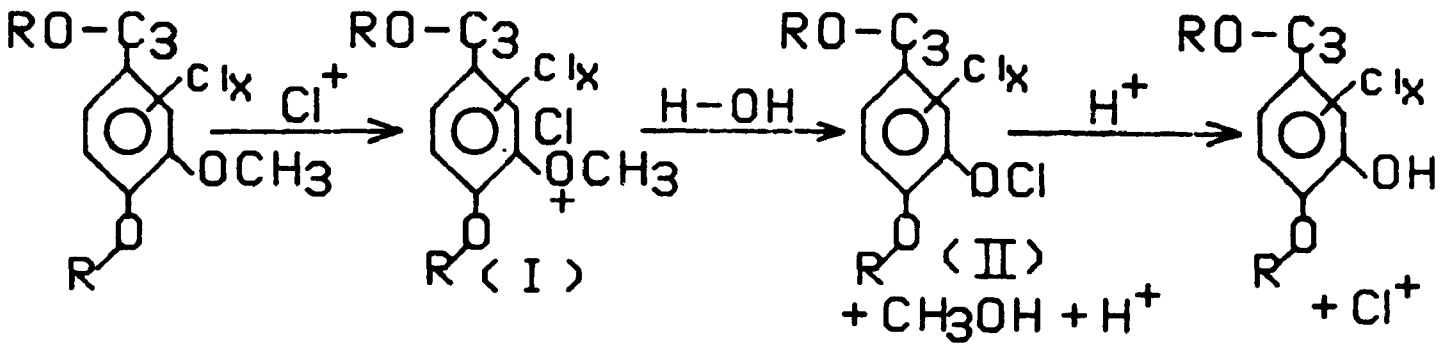
— the OCH_3/C_9 and Cl/C_9 molar ratios of CW "floor level" lignin are respectively about 0.8 and between 3 and 4, independent of the initial lignin content

In view of this evidence, we propose the chlorination mechanism

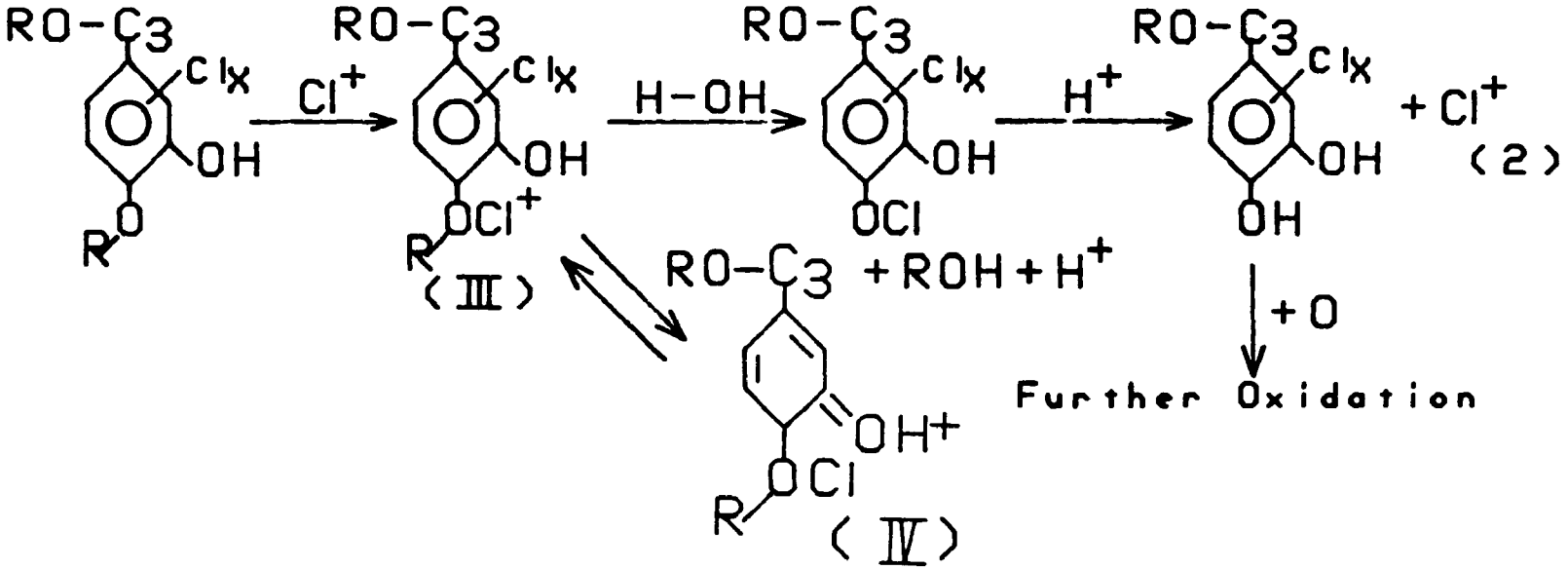
in Fig.3-6 showing demethylation reaction (1), delignification reaction (2) and oxidation reaction (3). In reaction (1), the methoxyl group of the guaiacyl unit is first removed to form a hydroxyl group and methanol. Then, via the same mechanism the adjacent phenol ether bond is broken whereby a 3,4-dihydroxylphenylpropane structure is formed. This compound can subsequently further be oxidized. The attacking demethylation reagent is the chloronium ion, Cl^+, generated from elemental chlorine or hypochlorous acid through the polarizing effect of the aromatic π electrons. Cleavage of the methyl ether linkage is stimulated by the formation of the conjugated ether (I) .Because of the low reactivity of the bond between oxygen and the aromatic ring, the methyl ether undergoes cleavage at the methyl-oxygen bond. Methanol and intermediate (II) are then formed under the polarizing influence of water.The oxygen-chlorine bond of the intermediate (II) is unstable, and a hydroxyl group is produced following attack by H^+. The regenerated chloronium ion (Cl^+) might react with ClO^- to form atomic oxygen (reaction 3) or be used in a similar bond cleavage mechanism at the 4-position of the guaiacyl unit (reaction 2). In the former reaction path, molecular chlorine is consumed with the formation of chloride and atomic oxygen, which is responsible for oxidation during chlorination.

The formation of the phenolic hydroxyl group ortho to the 4-O ether linkage in the lignin monomer is responsible for the close relationship between demethylation and delignification. The hydroxyl group in reaction (2) stabilizes the carbonium ion (III) by resonance with compound (IV). Therefore, the delignification

Fig.3-6 Chlorination mechanism



(1)



(2)

$$Cl^+ + ClO^- + H_2O \longrightarrow 2Cl^- + 2H^+ + 2O \qquad (3)$$

X=0,1,2

R:Lignin

(reaction 2) is facilitated after demethylation (reaction 1).

Two reasons can be given why chloronium ion first attacks the methoxyl group in preference to the 4-O ether linkage: firstly, the methoxyl group is more reactive than the 4-O ether linkage (20); secondly, the 4-O ether bond is more difficult to attack because of steric hindrance effects.

During demethylation and delignification, chlorine substitution is proceeding simultaneously. The order of preference of aromatic substitution is 6>5>2. This can be explained by the activating effect of the $-OCH_3$ and -OR groups at the ortho and para positions. Since the activating effect of $-OCH_3$ is stronger than that of -OR, substitution at the 6 position is favored over the 5 position. However,the 2 position activated by the $-OCH_3$ group is not favored over the 5 position due to steric hindrance by the lignin chain and methoxyl group.

It is likely that displacement of the propane group by chlorine only takes place after the β-O-4 ether linkage is broken, because the newly formed hydroxyl group at β position weakens the bond between the α carbon and benzene ring. This is confirmed (7,8) by the formation of tetrachloro-guaiacol compounds during chlorination of lignin model compounds.

Oxidation by chlorine does not contribute to delignification because, according to the present mechanism, oxidation only occurs after cleavage of the 4-O-ether bond. Thus the chlorine consumed in reaction (3) of Figure 3-6 is wasteful in terms of lignin solubilization. However, based on toxicity considerations, oxidation by chlorine is useful because of the destruction of the aromatic character of soluble chloro organics.

2. Blocking Group

In the presented chlorination mechanism, it is proposed that the 4-O ether linkage is broken as a result of the activating influence of the hydroxyl group at the 3 position after the methoxyl group has been removed. Similarly, it is proposed that if demethylation does not take place, cleavage of the 4-O ether bond will be inhibited, thus limiting further delignification.

Electrophilic aromatic substitution of chlorine in lignin also takes place concurrently with the three reactions in Fig.6. The rate of substitution decreases as the degree of substitution increases because of the deactivating effect of the electron withdrawing chlorine. This effect can be seen in Fig.3-3 where substitution of the first chlorine atom into lignin monomer unit is essentially instantaneous, while further substitution take progressively more time. Similarly, chlorine substitution deactivates electrophilic attack of the chloronium ion on the methoxyl group (reaction 1). Moreover it is likely that demethylation is limited by steric hindrance of chlorine at the 2 position. Since the present results show that methanol formation closely follows delignification, it is proposed that demethylation and thus delignification is totally inhibited when the three available 6, 5 and 2 positions are occupied by chlorine. Based on the present chemical characterization of the CW "floor level" lignin, it is proposed that fully chlorine substituted lignin monomer units with the methoxyl group still attached can not further be demethylated. In effect, this means that these units are the so called "blocking groups" in the chemical model proposed by Berry and Fleming (1) to explain the formation of a lignin

"floor level" during chlorination.

The identification of "blocking groups" as fully aromatic chlorine substituted guaiacyl units is supported by lignin model compound studies of Sarkanen and Strauss (10). They found that 3,4,5,6-tetra-chloroguaiacol and 2,4,6-trichloroanisole, show little tendency to demethylate in the presence of chlorine. Analogous effects of ortho-substituents on demethylation of anisole derivatives by nitric acid were observed (11); p-chloroanisole was found to yield substantial amount of 2,6-dinitro-4-chlorophenol, while o,o'-disubstituted 2,6-dichloroanisole was completely resistant towards demethylation by nitric acid. The proposed mechanism is also supported by the evidence that the dominant chloro phenolics in C-stage effluent are chlorocatechols, while chloro guaiacols are the major species in E-stage effluent (21).

A reasonable explanation for the "floor level" Cl/C9 molar ratio somewhat higher than 3 found under extreme chlorination conditions (Table 3-4), is that chlorine is also substituted in the aliphatic side chain of the lignin macromolecule by attack of chlorine free radicals (8,18).

Finally a remark should be made about the molecular weight distribution of chlorinated organics in C stage effluents. According to the present mechanism, only chlorinated propyl catechol and their oxidized derivatives should be present in chlorination liquor. It has indeed been found (17) that a major fraction of the total organic chlorine (TOCl) in C stage liquor has a molecular weight less than 1000, while in E stage effluent the major fraction has a molecular weight above 25000. A possible

explanation for the presence in C stage effluent of TOCl with a molecular weight above 1000 is that the originally dissolved (chlorinated and oxidized) propyl catechols react with each other in the presence of chlorine to form larger molecular weight compounds. Future work with a displacement type reactor rather than a CSTR is planned to verify this explanation.

From the proposed mechanism, it follows that aromatic chlorine substitution is undesirable, not only because chlorine is consumed without lignin solubilization, but also because demethylation and thus lignin degradation is inhibited. Eventually, complete substitution leads to the formation of the lignin which is totally blocked and cannot be removed by further chlorination.

3. Chlorination of Hardwood Kraft Pulp

Based on the present mechanism for softwood kraft pulp and studies with syringyl model compounds by Dence et.al. (23), an attempt is made to formulate the chlorination mechanism of hardwood kraft pulp. Dence et. al. (23) showed that deisopropylation of the syringyl model compound 2-isopropoxy-3 methoxyanisole is much slower than that of guaiacyl model compound 2-isopropoxyanisol. In terms of pulp chlorination this means that cleavage of the 4-O-ether linkage in hardwood lignin is much slower than that in softwood lignin. It is also shown (23) that guaiacyl compounds are tri- (i.e. fully) chlorine substituted with about the same ease as syringyl compounds are dichlorinated. This is in agreement with the higher reactivity of the syringyl nucleus toward electrophilic agents such as chlorine. Consequently it is expected that syringyl units in hardwood kraft lignin are rapidly fully substituted with aromatic chlorine, without considerable

progress of the parallel reaction which leads to cleavage of the 4-O-ether linkage. In other words, it is expected that the equivalent of the softwood kraft lignin "blocking group" is rapidly formed during chlorination of hardwood kraft lignin without considerable progress of the parallel delignification reaction.

Dence et.al. (23) and Sarkanen and Strauss (10) found that the ether bonds of guaiacyl model compounds with chlorine substituted at positions ortho to the alkoxyl groups, were completely stable in aqueous chlorine. In contrast, however, isopropyl ether of 2,6-dimethoxy-3,4,5-trichlorophenol, a syringyl model compound with chlorine ortho to the two methoxyl groups, is slowly deisopropylated (23). Apparently the combined inductive effect of the two methoxyl groups is sufficient to make the isopropyl ether bond susceptible to cleavage by chlorine. Similarly, it can be expected that the syringyl units of hardwood kraft lignin, fully (i.e. di-) substituted with aromatic chlorine, can still be hydrolyzed. Therefore, contrary to the behavior of guaiacyl units in softwood kraft lignin, no "blocking groups" are formed during chlorination of syringyl units of hardwood kraft lignin. Since hardwood lignin contains approximately equal amount of syringyl units and guaiacyl units it is expected that the ratio ("floor level" lignin of CW pulp)/(lignin content of unchlorinated pulp) is lower for hardwood than softwood kraft pulp. Implicit is the assumption that the chlorination conditions are such that cleavage of 4-O-ether bond fully chlorinated syringyl units is complete. Additionally, it follows from the above results and mechanism that the initial delignification during chlorination is significantly

faster for softwood than hardwood kraft pulp. However, after some chlorination time, the delignification rate of hardwood kraft pulp will be larger than softwood kraft pulp because of continuing cleavage of 4-O-ether bonds of the syringyl units.

Further confirmation of the above chlorination mechanism for hardwood kraft pulp is the result (23) that the deisopropylation rate of 2-isopropoxy-3-methoxyanisole is comparable to that of the same compound fully (i.e. tri-) substituted with aromatic chlorine. This result confirms that the rate determining step for delignification of hardwood kraft pulp is cleavage of the 4-O-ether bond of syringyl units fully substituted with aromatic chlorine. Thus, the unchlorinated units are rapidly converted in fully chlorinated units without considerable dealkoxylation. These units then determine the further chemical behavior of hardwood kraft lignin. The present mechanism also predicts that two chlorine molecules per syringyl units are initially consumed without significant delignification.

The close relationship between delignification and demethylation still appears to be valid for chlorination of hardwood kraft pulp. Dence et.al. (23) showed that demethylation and deisopropylation of isopropyl ether of 2,6-dimethoxy-3,4,5-trichlorophenol occurred to nearly the same extent. This is also valid for the unchlorinated 2-isopropoxy-3-methoxy anisole when the extent of demethylation is corrected for the small amount of methanol formed at a molar chlorine/substrate ratio of 3. At this ratio it is expected that the formation of the trichlorinated model compound is mostly completed. These model compound studies are again in agreement with the general chlorination mechanism,

that the newly formed phenolic group after dealkoxylation activates rapid cleavage of the adjacent methoxyl groups.

In summary, the following chlorination mechanism is proposed for the syringyl units of lignin in hardwood kraft pulp. First, 2 moles of chlorine are very rapidly substituted in the syringyl nucleus, accompanied by only a small percentage (about 10%) demethylation and no significant delignification. Subsequently the 4-O-ether linkage is slowly hydrolyzed following a mechanism analogous to reaction (1) in Figure 3-6. The main differences between the chlorination mechanism of hardwood and softwood kraft lignin are:

(1) softwood (guaiacyl) kraft lignin is first demethylated before being delignified, while the opposite order is followed for hardwood (syringyl) kraft lignin;

(2) "blocking groups" are formed during chlorination of softwood (guaiacyl) kraft lignin, while no such stable compounds are formed in hardwood (syringyl) kraft lignin;

(3) the rate of aromatic substitution for chlorine is comparable to the rate of demethylation of ((chloro) guaiacyl) softwood kraft lignin, while substitution is much faster than demethylation for ((chloro) syringyl) hardwood kraft lignin.

4. Function of Extraction

With the proposed formation of "blocking groups" during chlorination, the purpose of extraction with sodium hydroxide can now be redefined as:

(1) destroy the "blocking groups" so that demethylation and delignification can again take place during a subsequent

bleaching stage.

(2) solubilize chlorinated lignin fragments.

From organic chemistry reactivity studies it is known that nucleophilic substitution of aromatic chlorine by hydroxide does not take place easily (20). However, Dence and his students (9) found that aromatically chlorine in model compounds and chlorinated kraft pulp can be displaced under conditions similar to standard caustic extraction. Presumably the presence of electron-withdrawing chlorines in the aromatic ring facilitates the displacement of chlorine by hydroxide. The present data would suggest that about two of the three chlorine molecules are displaced from the trichloro-guaiacyl "blocking group" during extraction. On subsequent chlorination, the hydroxyl groups activate the electrophilic attack of the chloronium ion leading to further demethylation and delignification. However, new blocking groups are formed so that again some residual lignin remains after chlorination. This is confirmed by Berry and Fleming (1) who showed that a new but much lower "floor level" is formed again when chlorination and extraction are repeated.

5. Improving Bleaching Efficiency

Based on the proposed chlorination mechanism for softwood kraft pulp, two alternative routes can be formulated which would allow complete delignification in one bleaching step:

(1) replace chlorine by another electrophilic reagent which attacks the ether bonds, but is either not substituted in the aromatic ring or favors demethylation when substituted (for example $-NO_2$ group).

(2) modify the chlorination stage by adding another reagent or

changing the operating conditions so that aromatic chlorine is removed again during chlorination. The latter route in essence proposes to combine the effect of chlorination and alkaline extraction in one step. The problem of course is to find a reagent or operating conditions whereby chlorine in the "blocking group" is hydrolyzed in an acidic aqueous solution.

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CHAPTER 4

DEMETHYLATION KINETICS OF KRAFT PULP CHLORINATION

ABSTRACT

Demethylation kinetics are developed based on a new delignification mechanism of kraft pulp chlorination. The kinetic equations show that demethylation and aromatic substitution of chlorine in lignin monomer units take place simultaneously at comparable rates. Demethylation and chlorine substitution of unchlorinated lignin monomer units are completed within the first few seconds. The corresponding reactions of mono-chloro lignin monomer units are slower but again one order of magnitude faster than those of the di-chloro lignin units. Tri-chloro lignin monomer units are stable towards further chlorination or demethylation and form the so-called "floor level" lignin.

The demethylation kinetics give realistic prediction of the total organic chlorine content of both chlorinated pulp fibers and chlorination effluent produced in a conventional chlorination stage with low ClO_2 substitution.

The present kinetics also give a mechanistic basis for the recent finding that Cl_2 should be added first at a low chlorine charge factor before addition of ClO_2 to prevent dioxin formation during kraft pulp chlorination.

INTRODUCTION

The most recent attempt to model chlorination kinetics of softwood kraft pulp was made by Mackinnon (1). By order of magnitude analysis he showed that if chlorine is uniformly dispersed in small bubbles over a pulp suspension, the rate of disappearance of chlorine is determined by chemical reaction. The resistance associated with physical transport processes such as intra- and inter fiber diffusion can only not be neglected during the first few seconds of reaction. The mechanism presented in the previous chapter strongly supports that pulp chlorination is chemical reaction limited, by identifying the so-called "blocking groups" first proposed by Berry and Fleming (2). As a consequence, the heterogeneous reaction between chlorine and lignin can be represented by homogeneous reaction kinetics. This treatment differs fundamentally from the heterogeneous model recently proposed by Pugliese and McDonough (3). They claimed that chlorination is limited by diffusion of chlorine through a chlorolignin barrier formed in the outer shell of lignin "grains" distributed uniformly in the fiber wall.

Homogeneous reaction kinetics of chlorination of softwood kraft pulp have been presented by a number of authors. Ackert (12) concluded that chlorination kinetics are best modelled by two parallel reactions, identified as fast substitution and slow oxidation. He also assumed that only active lignin, i.e., total lignin minus so-called "floor level" lignin, participates in the reactions. In his experiments, Ackert applied a large excess of chlorine so that the decrease in chlorine concentration during

reaction can be neglected. Mackinnon (1) recently showed that Ackert's model resulted in unrealistic predictions of the chlorine concentration and lignin content for practical conditions whereby most of the applied chlorine is consumed. Using the chlorination experiments of Liebergott et al (4) which covered practical operating conditions, Mackinnon adapted Ackert's model so that it could be used for mill simulation and control. However, a weakness of both studies is that the kinetic equations were selected based on their ability to represent the data rather than on fundamental understanding of the chlorination mechanism. The main selection criteria was that two parallel reactions, one fast and one slow, and the presence of unreactive lignin, could represent the characteristics of fast initial delignification followed by slow asymptotic approach of the lignin "floor level".

With the new chlorination mechanism proposed in the previous chapter it is now possible to formulate kinetic equations based on the actual reactions between lignin and chlorine. In this chapter, the development of kinetic equations for demethylation during chlorination as well as predictions of pulp and effluent properties will be presented.

EXPERIMENTAL

The chlorination kinetics of a 2% consistency suspension of black spruce kraft pulp of 30.4 Kappa number were measured in a Continuous Stirred Tank Reactor (CSTR). The chlorine and methanol concentration in solution, and the methoxyl group content and the C and CE Kappa number at reaction times varying from 10 seconds to 45 minutes were measured. Experiments at a full factorial of

three temperatures (25, 35 and 45 C) and three chlorine charge factors (0.16, 0.22 and 0.33) were performed. For a complete description of experimental procedures and set-up, see Chapter 2.

RESULTS

Demethylation accompanies delignification during chlorination of kraft pulp. Removal of methoxyl groups from lignin leads to the formation of methanol in the effluent, as can be seen in Fig.4-1. Included in Figure 4-1 are also the C and CE Kappa numbers.

Shown in Fig.4-2 is the decrease in methoxyl group content in pulp versus methoxyl group content calculated from the methanol concentration for all chlorination experimental conditions and various times. Since the data are around the forty-five degree straight line through the origin, it can be concluded that all reacted methoxyl groups are accounted for as methanol, and that further reaction of methanol in chlorine water can be neglected. This was also found by Sarkanen and Strauss (5) for chlorination of lignin model compounds. Another conclusion which can be drawn is that all dissolved lignin is demethylated. Consequently, the methoxyl content of other chlorinated pulp samples was calculated from the methanol concentration and the methoxyl group content of the unchlorinated pulp.

The effect of chlorine charge factor on development of demethylation and chlorine concentration at 35 C is shown respectively in Figure 4-3 and 4-4. Figure 4-4 shows that at a charge factor of 0.16, the residual chlorine concentration approaches zero at relatively short chlorination times. As a result, not sufficient chlorine is available for maximum

Fig.4-1 Typical chlorination behavior

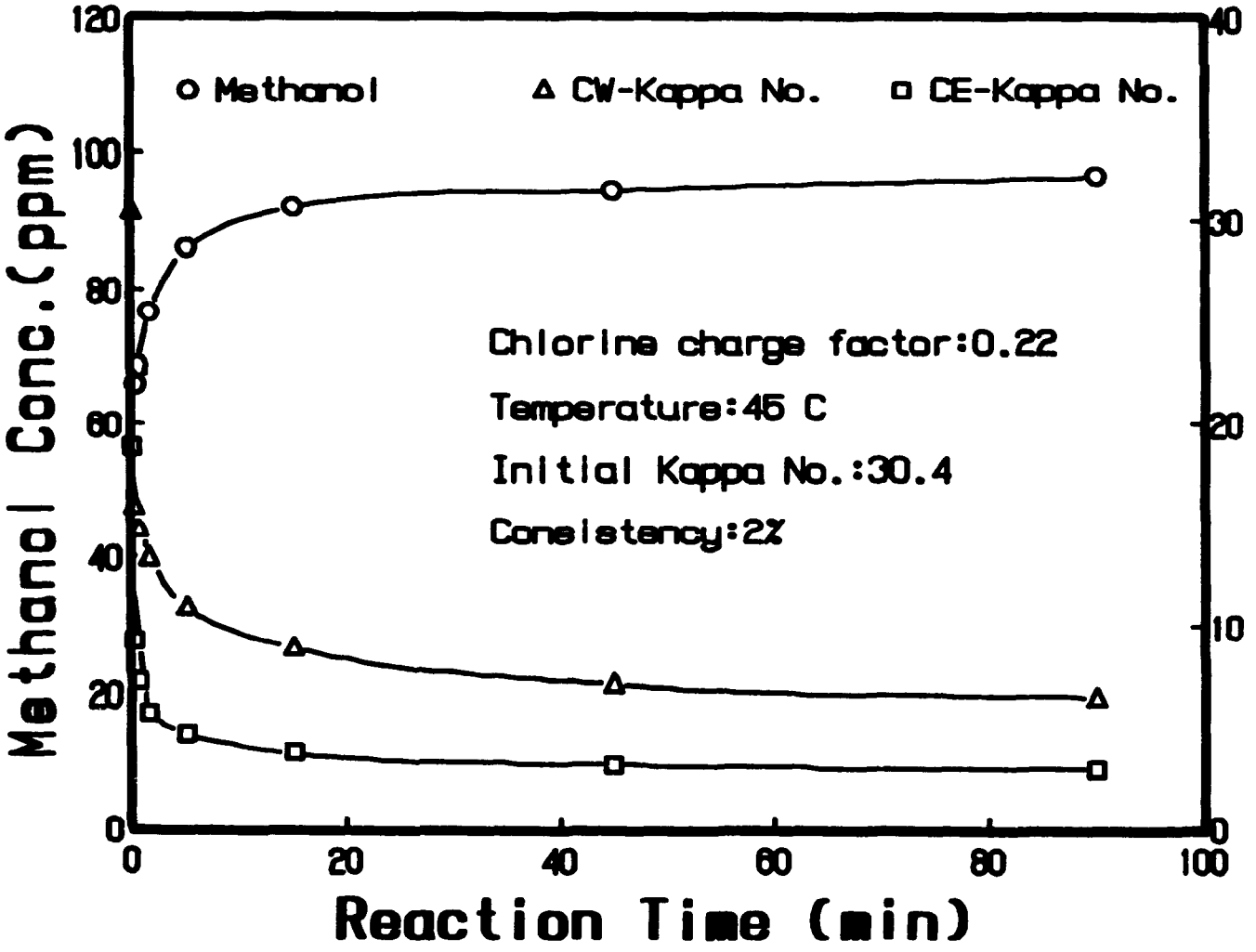

o Methanol
Δ CW-Kappa No.
□ CE-Kappa No.
Chlorine charge factor:0.22
Temperature:45 C
Initial Kappa No.:30.4
Consistency:2%
Methanol Conc.(ppm)
Reaction Time (min)
0
20
40
60
80
100
120
10
30

Fig. 4-2 Methoxyl group mass balance

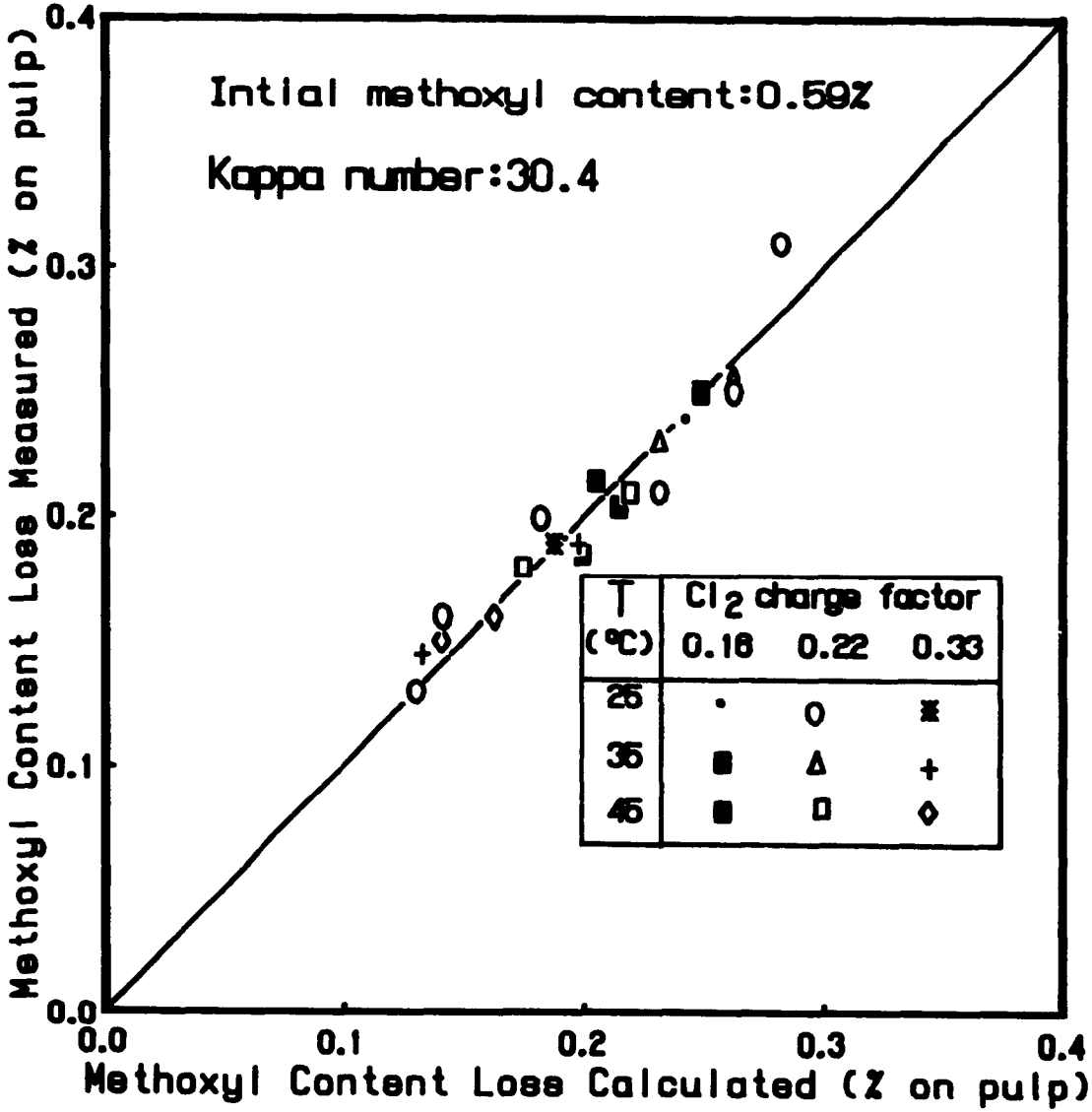

Intial methoxyl content:0.59%
Kappa number:30.4
Methoxyl Content Loss Measured (% on pulp)
Methoxyl Content Loss Calculated (% on pulp)
0.0
0.1
0.2
0.3
0.4
T (°C)
Cl2 charge factor
0.16
0.22
0.33
25
35
45

Fig. 4-3 Effect of Cl2 charge factor on demethylation

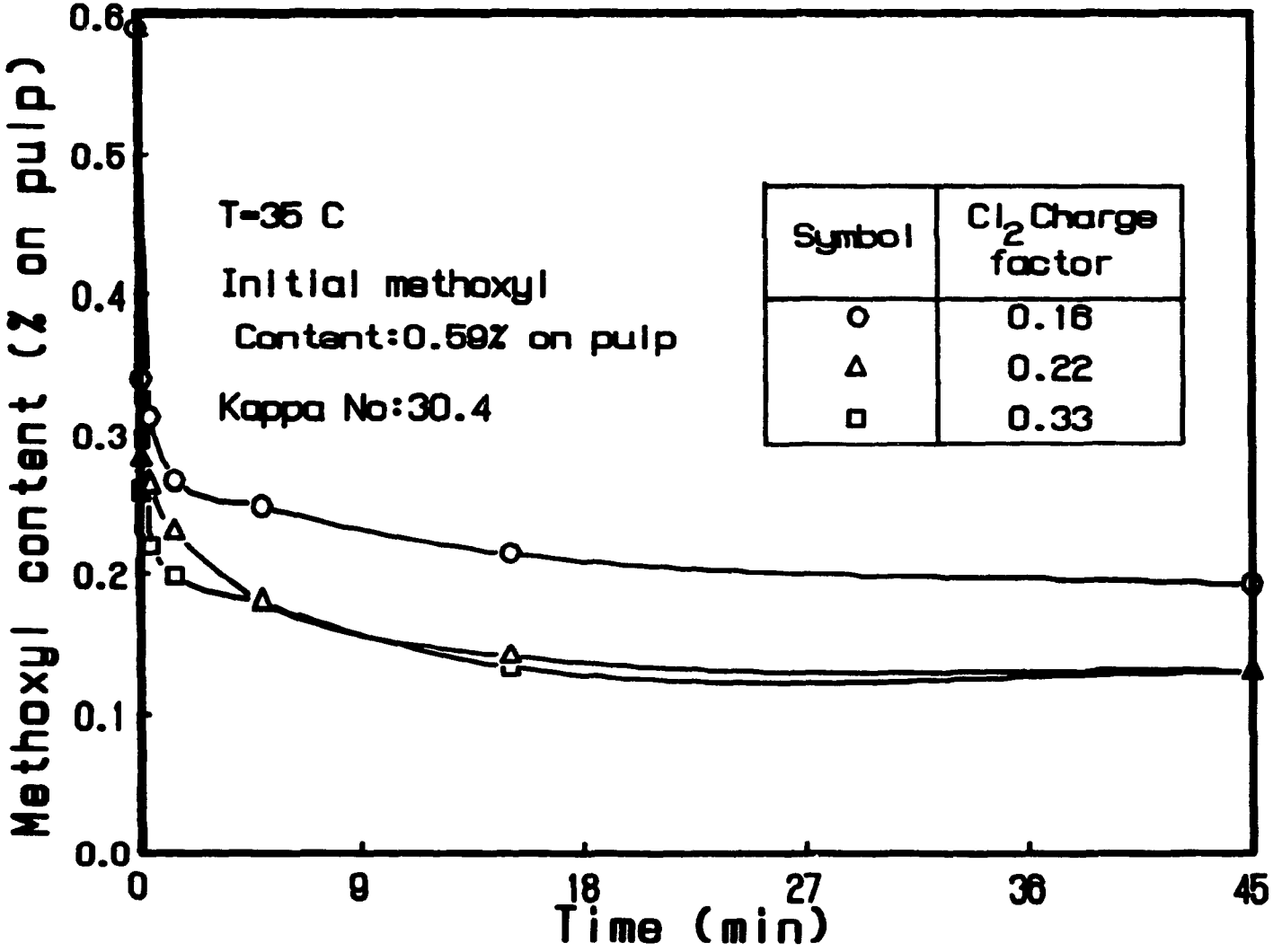
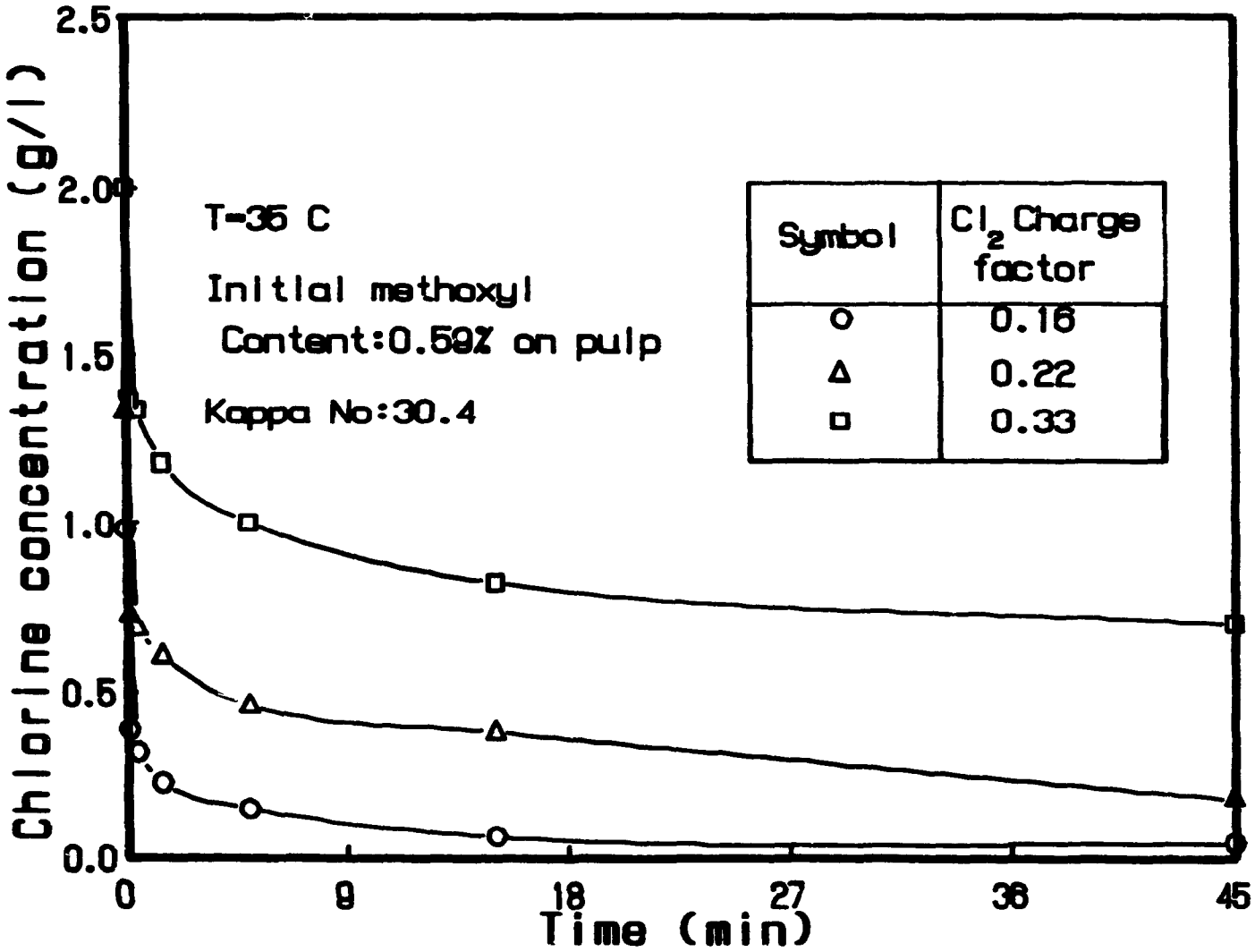

Methoxyl content (% on pulp)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
9
18
27
36
45
Time (min)
T=35 C
Initial methoxyl
Content:0.59% on pulp
Kappa No:30.4
Symbol
Cl2 Charge factor
0.16
0.22
0.33

Fig. 4-4 Effect of Cl_2 charge factor on chlorine consumption


Chlorine concentration (g/l)
2.5
2.0
1.5
1.0
0.5
0.0
0
9
18
27
36
45
Time (min)
T=35 C
Initial methoxyl
Content:0.59% on pulp
Kappa No:30.4
Symbol
Cl2 Charge factor
0.16
0.22
0.33

demethylation so that the methoxyl group content remains relatively high compared to charge factors of 0.22 and 0.33 (Figure 4-3). For the latter two charge factors the development of the methoxyl group content is very similar and a "floor level" methoxyl content is approached asymptotically. Only the initial demethylation rate is faster at a chlorine charge factor of 0.33.

The effect of temperature on demethylation and chlorine concentration at a charge factor of 0.22 is shown respectively in Figure 4-5 and 4-6. Comparison of the two figures shows that the initial demethylation rate is as fast as the initial chlorine consumption rate. However, at longer chlorination times, the demethylation rate approaches zero, especially at the higher temperature, while a small but distinct chlorine consumption rate is measured. It should be noted that the differences in methoxyl group content at 35 C and 45 C are insignificant. The explanation for these observations is that methoxyl group content is determined only by reaction between chlorine and undissolved lignin, while residual chlorine is affected by reactions between chlorine and dissolved and undissolved lignin, as well as between chlorine and carbohydrates.

DEVELOPMENT OF KINETIC MODEL

As described in chapter 3, demethylation and aromatic substitution of chlorine occur simultaneously during pulp chlorination. Substitution decreases the demethylation rate until no further demethylation takes place when the guaiacyl lignin monomer units contain three aromatic chlorine atoms. Also the deactivating effect of aromatic chlorine decreases the rate of

Fig.4-5 Effect of temperature on demethylation

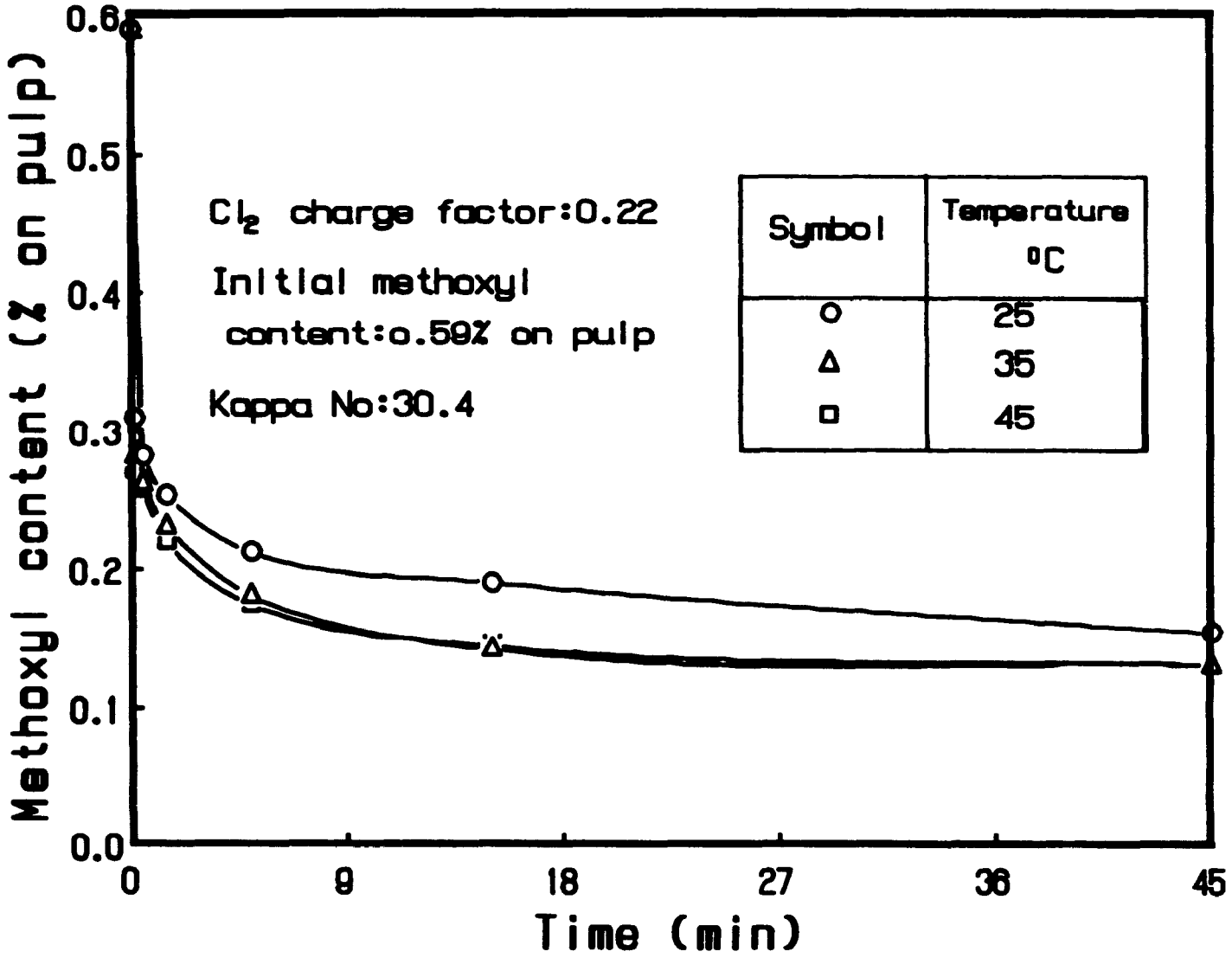
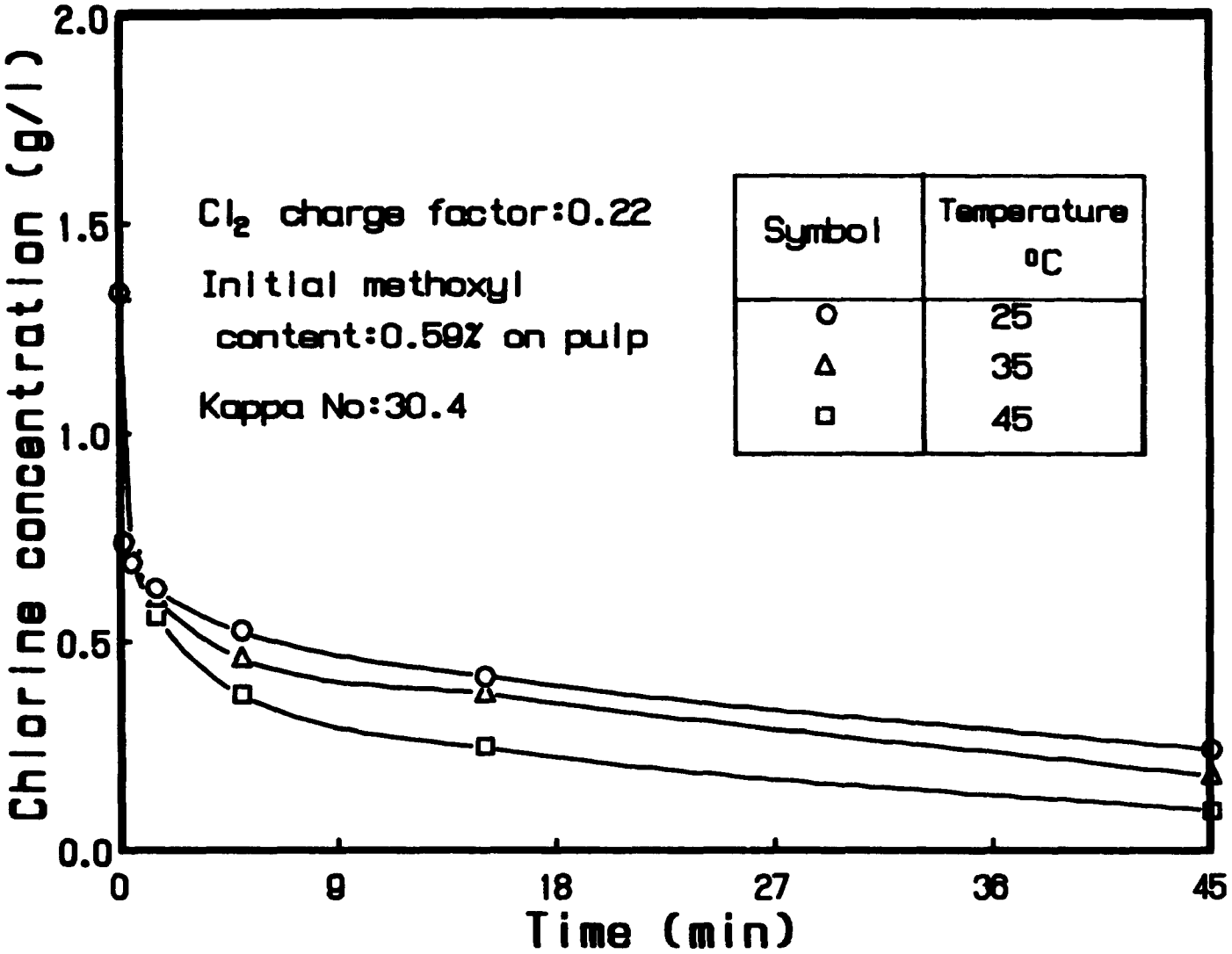

Methoxyl content (% on pulp)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
9
18
27
36
45
Time (min)
Cl_2 charge factor:0.22
Initial methoxyl content:0.59% on pulp
Kappa No:30.4
Symbol
Temperature °C
○ 25
△ 35
□ 45

Fig. 4-6 Effect of temperature on chlorine consumption


Chlorine concentration (g/l)
2.0
1.5
1.0
0.5
0.0
0
9
18
27
36
45
Time (min)
Cl_2 charge factor:0.22
Initial methoxyl content:0.59% on pulp
Kappa No:30.4
Symbol
Temperature °C
○ 25
△ 35
□ 45

further substitution of chlorine in the aromatic ring of the lignin monomers. Demethylation is the rate determining step for delignification since the formation of the free phenolic group during demethylation activates cleavage of the adjacent 4-O ether linkage. Finally, it is likely that the lignin catechol structures formed after cleavage of the 4-O ether linkage are further oxidized by chlorine.

All these reactions are in principle represented in the reaction scheme shown in Figure 4-7. Reactions (1), (5) and (9) represent demethylation of respectively unchlorinated, mono- and di-chloro substituted guaiacyl units of the lignin macromolecules (i.e. respectively L-OR-OCH_3, L-ORCl-OCH_3 and L-$ORCl_2$-OCH_3). Reactions (2), (6) and (10) correspond to delignification of the demethylated products, respectively L-OR-OH, L-ORCl-OH, and L-$ORCl_2$-OH. It should be noted that no chlorine is consumed in the demethylation and delignification reactions, since the detailed reaction mechanism (Chapter 3) stipulates that the reactive chloronium is reformed, i.e. acts as a catalyst. Reactions (3), (7) and (11) represent oxidation of the corresponding catechols, while reactions (4), (8) and (12) describe aromatic substitution of chlorine in respectively unchlorinated, mono and di chloro substituted guaiacyl units of lignin. The so called "blocking group" is formed in reaction (12) and is represented by L-$ORCl_3$-OCH_3. The oxidation and substitution reactions are responsible for the consumption of chlorine and production of HCl.

It is apparent from Fig.3-4 in the previous chapter that on average aromatic substitution of the first chlorine atom in the lignin monomer units is completed within 10 seconds of reaction.

$$\text{L-OR-OCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{Cl}_2} \text{L-OR-OH} + \text{CH}_3\text{OH} \quad (1)$$

$$\text{L-OR-OH} + \text{H}_2\text{O} \xrightarrow{\text{Cl}_2} \text{L-OH} + \text{HO-R-OH} \quad (2)$$

$$\text{HO-R-OH} + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + \text{Oxidized HO-R-OH} \quad (3)$$

$$\text{L-OR-OCH}_3 + \text{Cl}_2 \longrightarrow \text{L-ORCl-OCH}_3 + \text{HCl} \quad (4)$$

$$\text{L-ORCl-OCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{Cl}_2} \text{L-ORCl-OH} + \text{CH}_3\text{OH} \quad (5)$$

$$\text{L-ORCl-OH} + \text{H}_2\text{O} \xrightarrow{\text{Cl}_2} \text{L-OH} + \text{HO-RCl-OH} \quad (6)$$

$$\text{HO-RCl-OH} + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + \text{Oxidized HO-RCl-OH} \quad (7)$$

$$\text{L-ORCl-OCH}_3 + \text{Cl}_2 \longrightarrow \text{L-ORCl}_2\text{-OCH}_3 + \text{HCl} \quad (8)$$

$$\text{L-ORCl}_2\text{-OH} + \text{H}_2\text{O} \xrightarrow{\text{Cl}_2} \text{L-ORCl}_2\text{-OH} + \text{CH}_3\text{OH} \quad (9)$$

$$\text{L-ORCl}_2\text{-OH} + \text{H}_2\text{O} \xrightarrow{\text{Cl}_2} \text{L-OH} + \text{HO-RCl}_2\text{-OH} \quad (10)$$

$$\text{HO-RCl}_2\text{-OH} + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + \text{Oxidized HO-RCl}_2\text{-OH} \quad (11)$$

$$\text{L-ORCl}_2\text{-OCH}_3 + \text{Cl}_2 \longrightarrow \text{HCl} + \text{L-ORCL}_3\text{-OCH}_3 \quad (12)$$

Fig. 4-7 Lignin-chlorine Reaction Scheme

Figure 4-1 further shows that simultaneously the C Kappa Number decreases by about 50% and the methanol concentration increases to approximately two-third of the methanol concentration at the end of chlorination. Based on these results, it was assumed that the corresponding reactions (1), (2) and (4) are instantaneous for all practical purposes.

Assuming that the demethylation reactions are first order in chlorine and corresponding lignin monomer unit concentrations, the rate of decrease of methoxyl group concentration after completion of these three instantaneous reactions can be written as:

$$[M] = [M_1] + [M_2] + [M_3] \qquad (13)$$

$$-\frac{d[M_1]}{dt} = (k_5 + k_8) * [M_1] * [Cl_2] \qquad (14)$$

$$-\frac{d[M_2]}{dt} = (k_9 + k_{12}) * [M_2] * [Cl_2] - k_8 * [M_1] * [Cl_2] \qquad (15)$$

$$-\frac{d[M_3]}{dt} = -k_{12} * [M_2] * [Cl_2] \qquad (16)$$

where [M] is the methoxyl group content in CW pulp (mole/ g pulp) and $[M_1]$, $[M_2]$ and $[M_3]$ are respectively the contents of mono-, di- and tri- chloro guaiacyl units in pulp (mole/ g pulp). The constants k_5, k_8, k_9 and k_{12} are reaction rate constants (l/mol*min) of the corresponding reactions in Figure 4-7.

In order to solve equations (13) to (16), the initial value of $[M_1]$, immediately after completion of the instantaneous reactions must be known. In the initial stage of chlorination, $[M_2]$ and $[M_3]$ are much smaller than $[M_1]$ so that as a first approximation, equations (13) and (14) can be combined as:

$$\frac{d[M]}{dt} = (k_5+k_8) * [M] * [Cl_2] \qquad (17)$$

The above equation can be solved when the chlorine concentration

[Cl2], is known during the course of reaction. For reaction times less than 5 minutes, the amount of chlorine consumed was linearly related to the remaining methoxyl content for the three chlorine charge factors as shown in Fig.4-8 through 4-10. It can be seen that the slope of the linear correlation at each charge factor is not a function of temperature. Since the remaining methoxyl content is directly proportional to the CW lignin content (Chapter 3) , this result is in agreement with Histed et. al (8) who reported that the CW Kappa number was only a function of chlorine consumed and not of temperature.

The three straight line fits can be written as:

$$[Cl_2] = [Cl_2]_i - S_M * (A - [M]) * C_P$$

where $[Cl_2]_i$ is the initial chlorine concentration (mole/ l), S_M is the stoichiometric ratio of chlorine consumed per methoxyl group removed (mol/mol), C_P is the pulp/liquor ratio of the pulp suspension (g/l) and A is the extrapolated initial methoxyl group content (mol/ g pulp). Listed in Table 4-1 are S_M and A obtained respectively from the slopes and the intersections with the Y-axis of the straight line fits in Figure 4-8 to 4-10 as function of chlorine charge factor.

It is apparent that S_M increases or that the lignin removal efficiency by chlorine decreases with increasing chlorine charge factor or chlorine concentration. A similar trend in chlorine to lignin stoichiometric ratio was found by Russel (6) and Berry and Fleming (7). At the lowest chlorine charge factor of 0.16, the extrapolated initial methoxyl group content, A, is almost the same as the actual initial methoxyl group content, $[M]_i$, of 0.59%. However, as the chlorine charge increases, the difference

Fig. 4-8 OCH_3-Cl_2 stoichiometric ratio at

Cl_2 charge factor of 0.16

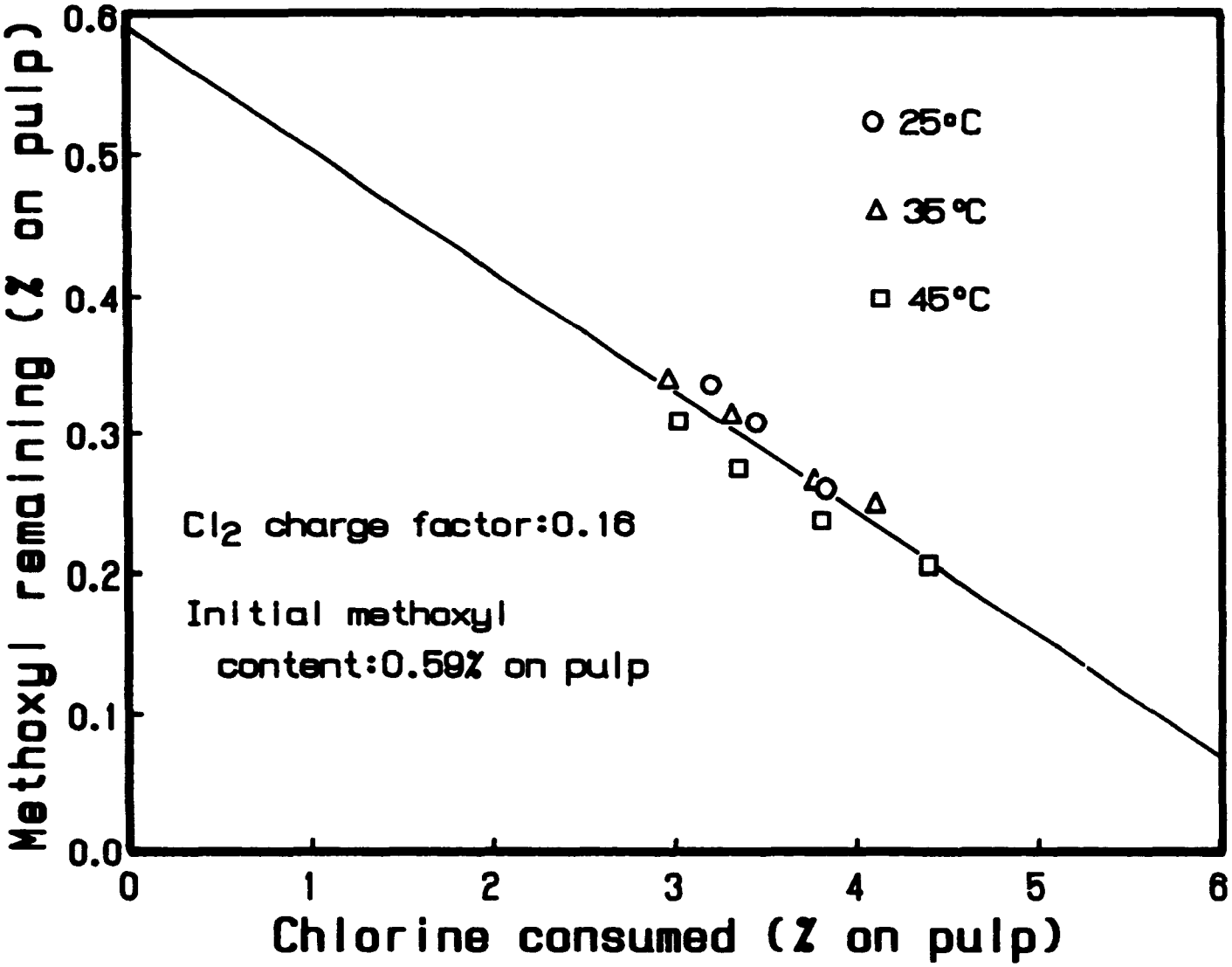

Methoxyl remaining (% on pulp)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
1
2
3
4
5
6
Chlorine consumed (% on pulp)
○ 25°C
△ 35°C
□ 45°C
Cl2 charge factor:0.16
Initial methoxyl
content:0.59% on pulp

Fig.4-9 OCH_3-Cl_2 stoichiometric ratio at

Cl_2 charge factor of 0.22

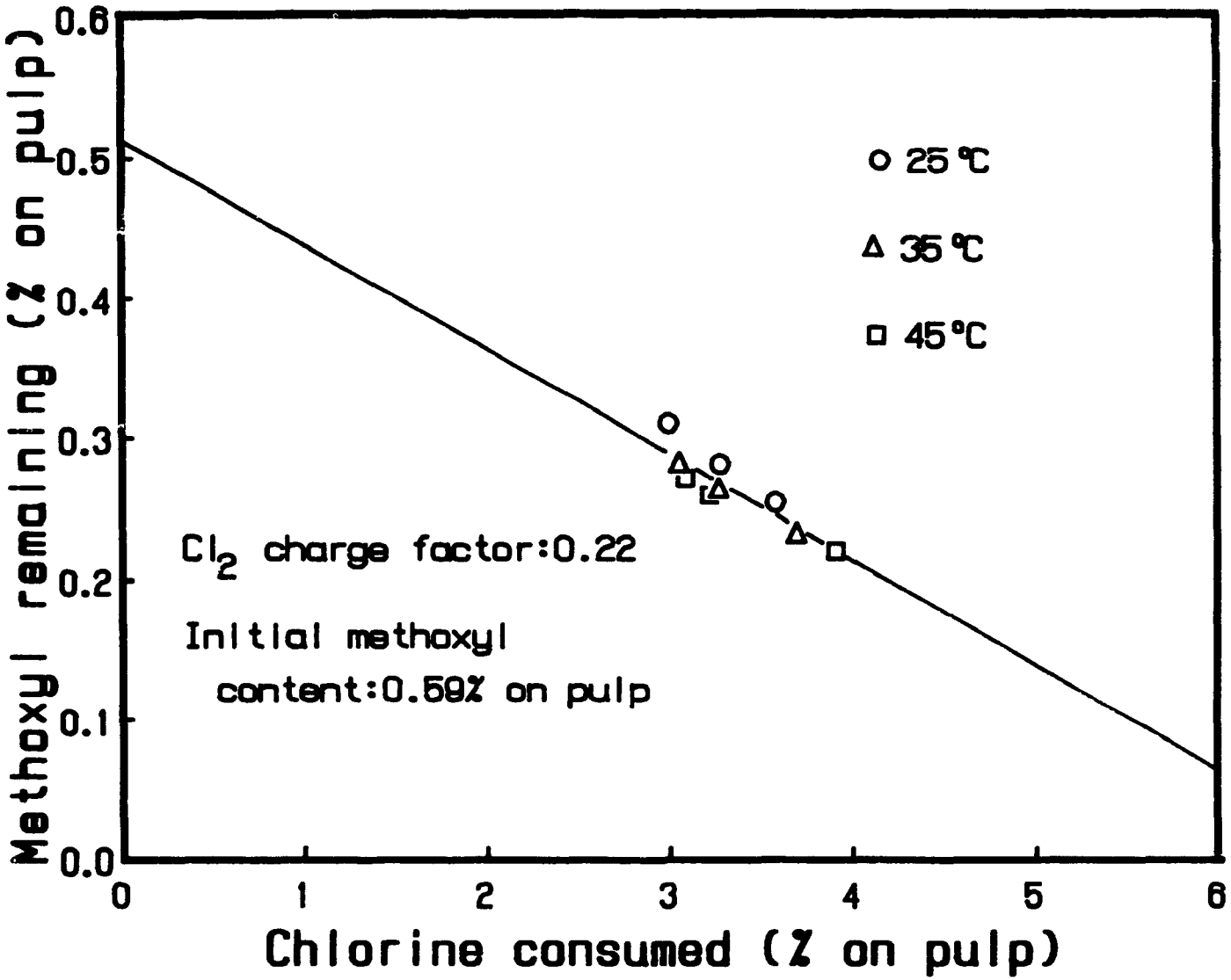

Methoxyl remaining (% on pulp)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6
Chlorine consumed (% on pulp)
○ 25℃
△ 35℃
□ 45℃
Cl2 charge factor:0.22
Initial methoxyl
content:0.59% on pulp

Fig. 4-10 OCH_3-Cl_2 stoichiometric ratio at

Cl_2 charge factor of 0.33

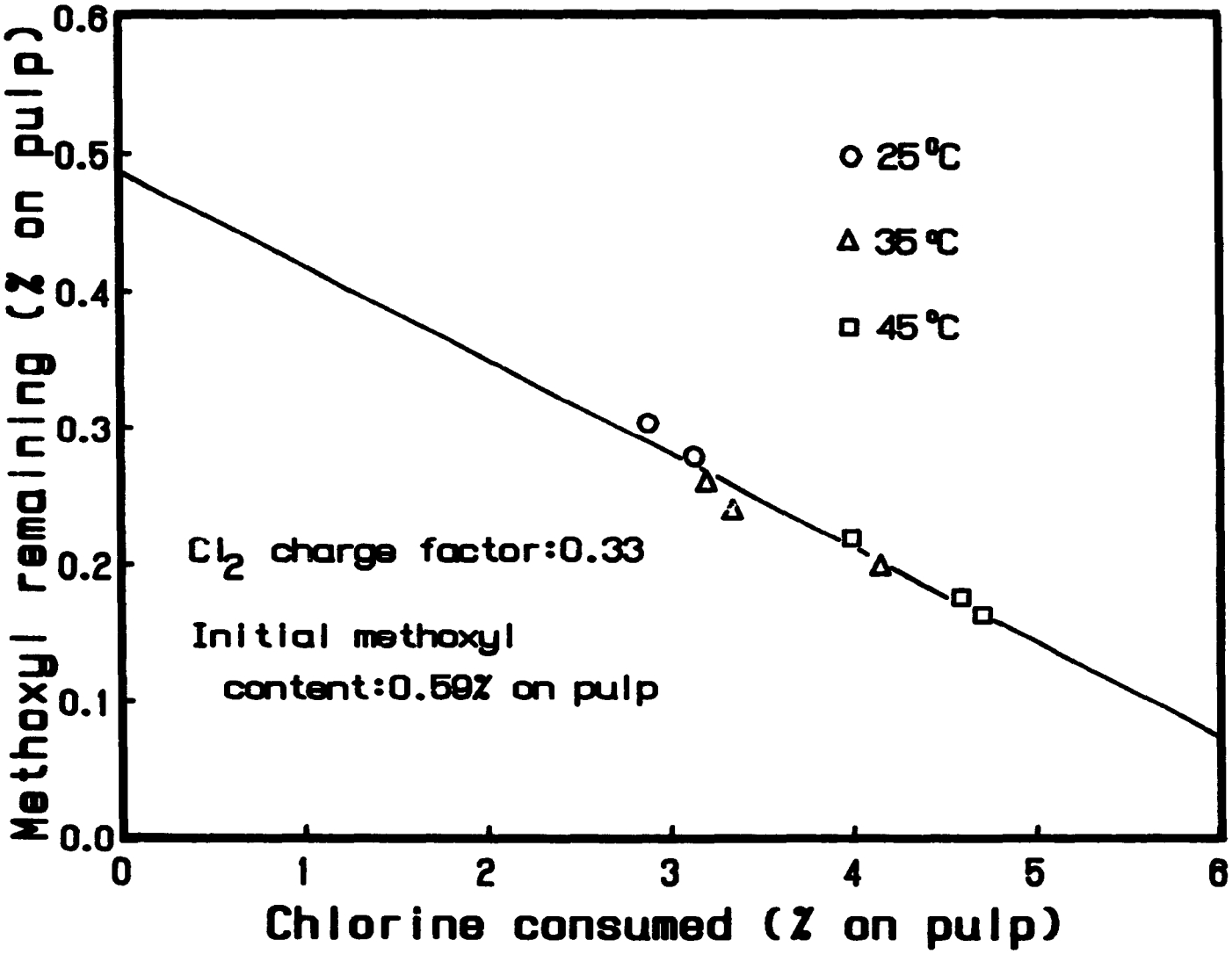

Methoxyl remaining (% on pulp)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
1
2
3
4
5
6
Chlorine consumed (% on pulp)
○ 25℃
△ 35℃
□ 45℃
Cl2 charge factor:0.33
Initial methoxyl
content:0.59% on pulp

Table 4-1. Cl_2 to OCH_3 stoichiometric ratio, S_M

as function of Cl_2 charge factor

Cl_2 charge factor	S_M (mol/mol)	A (m mol/g)
0.16	5.02	0.1905
0.22	5.82	0.1659
0.33	6.34	0.1572

between A and $[M]_1$ increases, reflecting that demethylation by chlorine becomes less efficient later in the chlorination stage. A possible explanation for this behavior is that the relative contribution of oxidation to chlorine consumption increases with increasing chlorine charge. The extrapolated initial methoxyl group content will not be used in subsequent solution of the kinetic equation.

Insertion of equation (18) in (17) and integration gives:

$$\frac{1}{a} * \{ \ln \frac{S_M * C_P * [M] + a}{[M]} - \ln \frac{S_M * C_P * [M]_o + a}{[M]_o} \} = (k_5 + k_8) * t \qquad (19)$$

where $a = [Cl_2]_1 - S_M * C_P * A$

and $[M]_o$ is the methoxyl group content (mol/l) immediately after the instantaneous reaction

When $\frac{1}{a} * \ln \frac{S_M * C_P * [M] + a}{[M]}$ is plotted versus time, approximate straight line relationships were obtained for the first three data points at all temperatures and charge factors, as shown in Fig. 4-11 to Fig. 4-13. The straight lines confirm the assumption of reaction kinetics of the form given by equation (17). From the intersection with the y-axis, $[M]_o$ can be calculated. The values of $[M]_o$ are listed in Table 4-2 for the different experimental conditions. With $[M]_1 \cong [M_1]_1$, the initial condition for equation (14) is now known.

The methoxyl group content after the instantaneous reaction, $[M]_o$, listed in Table 4-2, decreases somewhat with increasing chlorine charge factor and temperature. However, kinetic theory requires that $[M]_o$ is not a function of chlorine charge factor, but can be a function of temperature. The decrease in $[M]_o$ with charge factor especially at higher temperature might be due to

Fig. 4-11 Correlation to obtain $[M_1]_o$ at a chlorine charge factor of 0.16

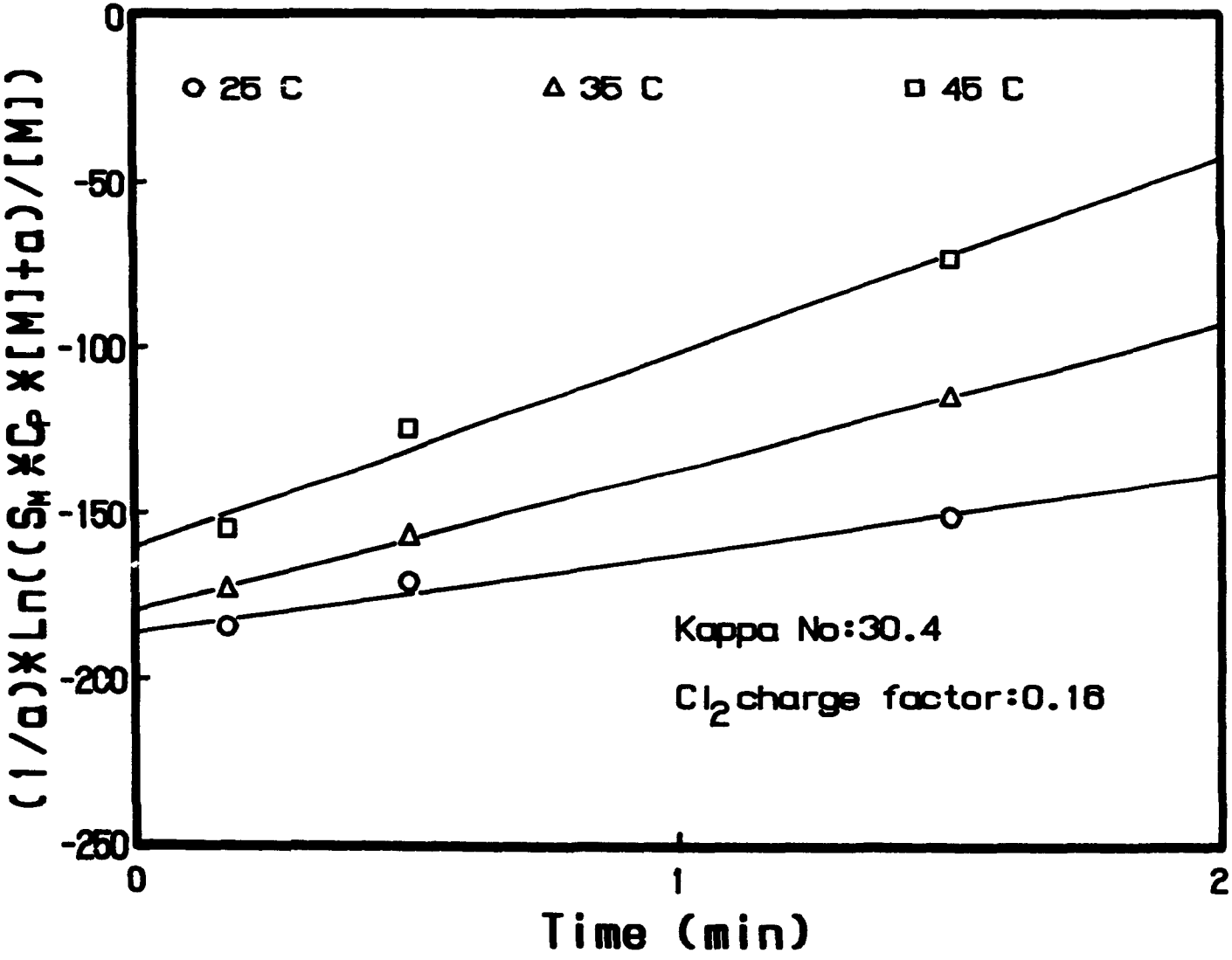

0
-50
-100
-150
-200
-250
(1/α)*Ln((S_M*C_P*[M]+α)/[M])
○ 25 C
△ 35 C
□ 45 C
Kappa No:30.4
Cl2 charge factor:0.16
0
1
2
Time (min)

Fig. 4-12 Correlation to obtain $[M_1]_o$ at a chlorine charge factor of 0.22

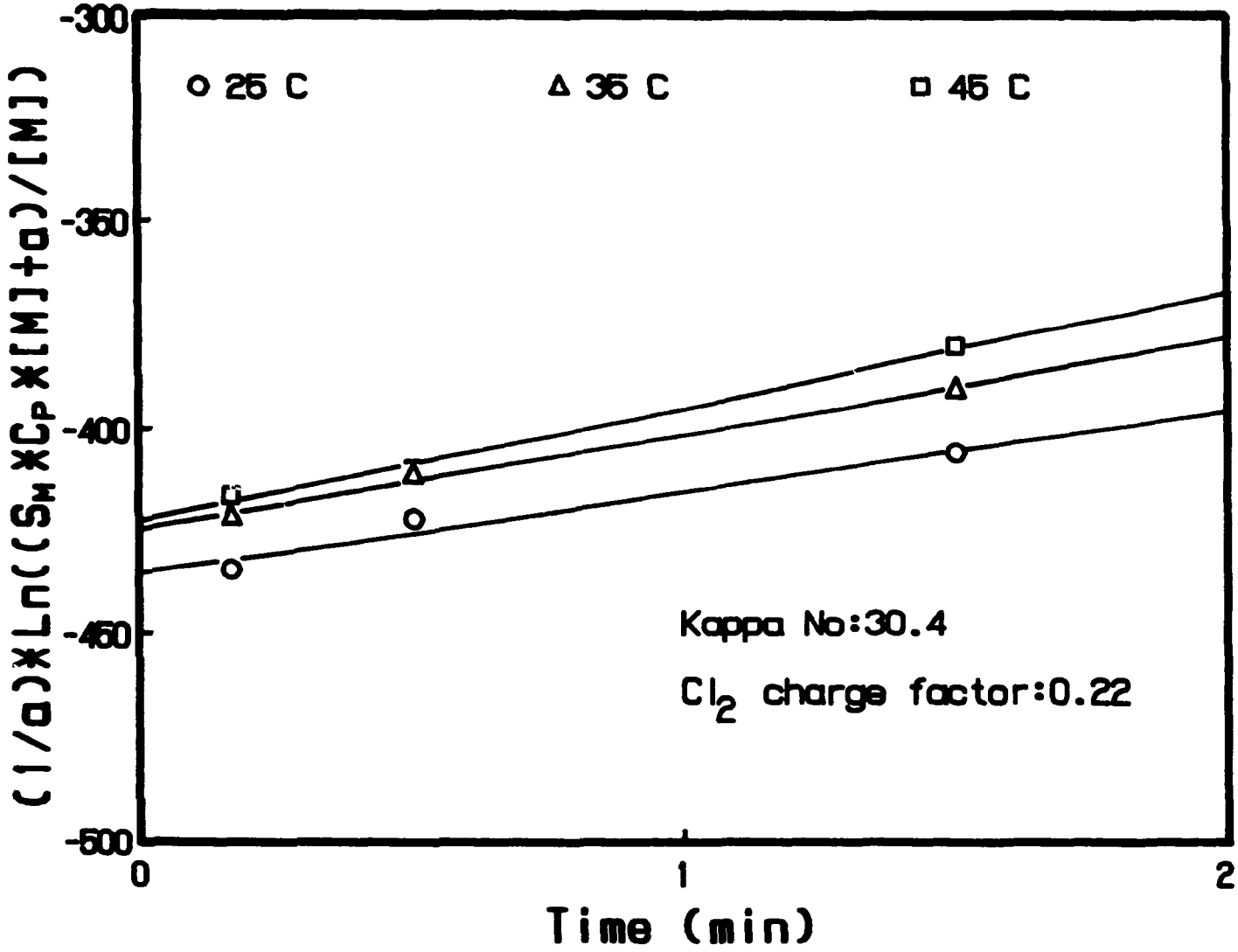

-300
-350
-400
-450
-500
0
1
2
Time (min)
(1/α)*Ln((S_M*C_P*[M]+α)/[M])
○ 25 C
△ 35 C
□ 45 C
Kappa No:30.4
Cl2 charge factor:0.22

Fig. 4-13 Correlation to obtain $[M_1]_0$ at a chlorine charge factor of 0.33

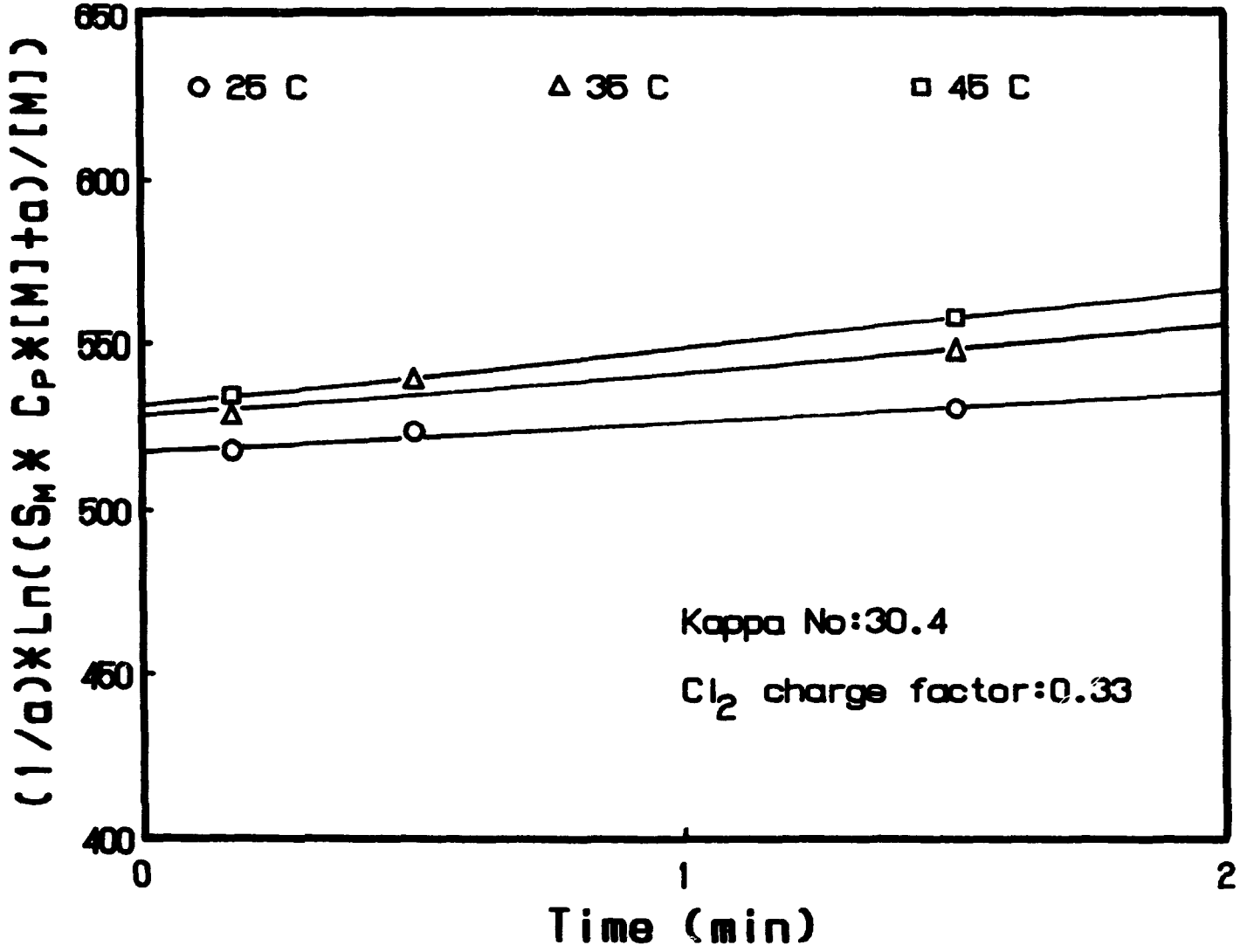

650
600
550
500
450
400
0
1
2
(1/a)*Ln((S_M* C_P*[M]+a)/[M])
Time (min)
○ 25 C
△ 35 C
□ 45 C
Kappa No:30.4
Cl2 charge factor:0.33

Table 4-2 Parameters obtained from Figure 4-11 to 4-13

Experimental Conditions		$[M]_o$ (m mol/g pulp)	$\frac{k_1}{k_4}$
	T=25 C	0.0988	0.93
CF=0.33	T=35 C	0.0824	1.31
	T=45 C	0.0718	1.64
	T=25 C	0.1007	0.89
CF=0.22	T=35 C	0.0928	1.05
	T=45 C	0.0911	1.09
	T=25 C	0.1118	0.70
CF=0.16	T=35 C	0.1134	0.68
	T=45 C	0.1024	0.86

CF: Charge Factor

breakdown of the assumptionof [M_2] << [M_1].

Also included in Table 4-2 is the ratio of reaction constants of the instantaneous demethylation and chlorine substitution reactions, k_1/k_4, calculated from the ratio of methoxyl group removed to methoxyl group remaining after the instantaneous reactions. Corresponding to the changes in $[M]_0$, k_1/k_4 increases with increasing chlorine charge factor and temperature.

FINAL MODEL

With the determination of $[M_1]_0$ and the measurements of [M] and $[Cl_2]$ during the course of chlorination, it is possible to determine the rate constants of equations (14) to (16) by an optimization technique. The Hooke and Jeeves (9) search algorithm was used to find the rate constants by minimizing the sum of squares of the differences between experimental values of [M] and model predictions. The procedure was considered converged when for each data set at a fixed charge factor and temperature the sum of squares changed by less than 0.1% between iterations.

The four reaction constants obtained after computer optimization are listed in Table 4-3. The activation energy for each reaction was obtained from Arrhenius plots, shown in Fig. 4-14, 4-15, 4-16 and 4-17. The values of the pre-exponential factors, k_{10}, and apparent activation energies (E_1) in $k_1=k_{10}*\exp(-E_1/RT)$ are summarized in Table 4-4.

The predicted methoxyl group content at a chlorine charge factor of 0.22 are compared with the experimental values in Fig. 4-18 to Fig. 4-20 for respectively 25, 35 and 45 °C. It is apparent that the proposed kinetic equations very well predict

Fig.4-14 Arrhenius plot of ks

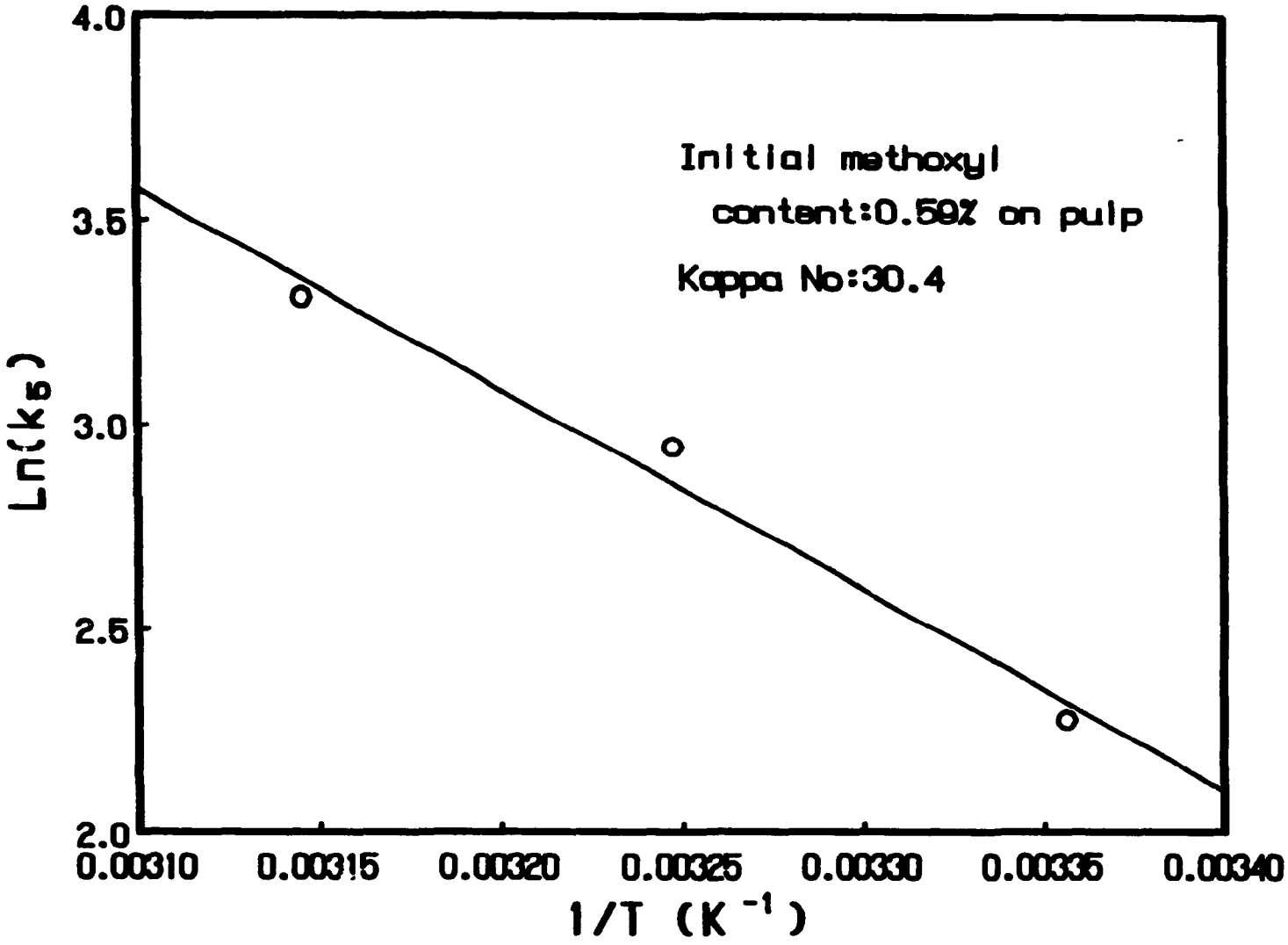

Initial methoxyl
content:0.59% on pulp
Kappa No:30.4
Ln(k5)
4.0
3.5
3.0
2.5
2.0
0.00310
0.00315
0.00320
0.00325
0.00330
0.00335
0.00340
1/T (K-1)

Fig. 4-15 Arrhenius plot of k_8

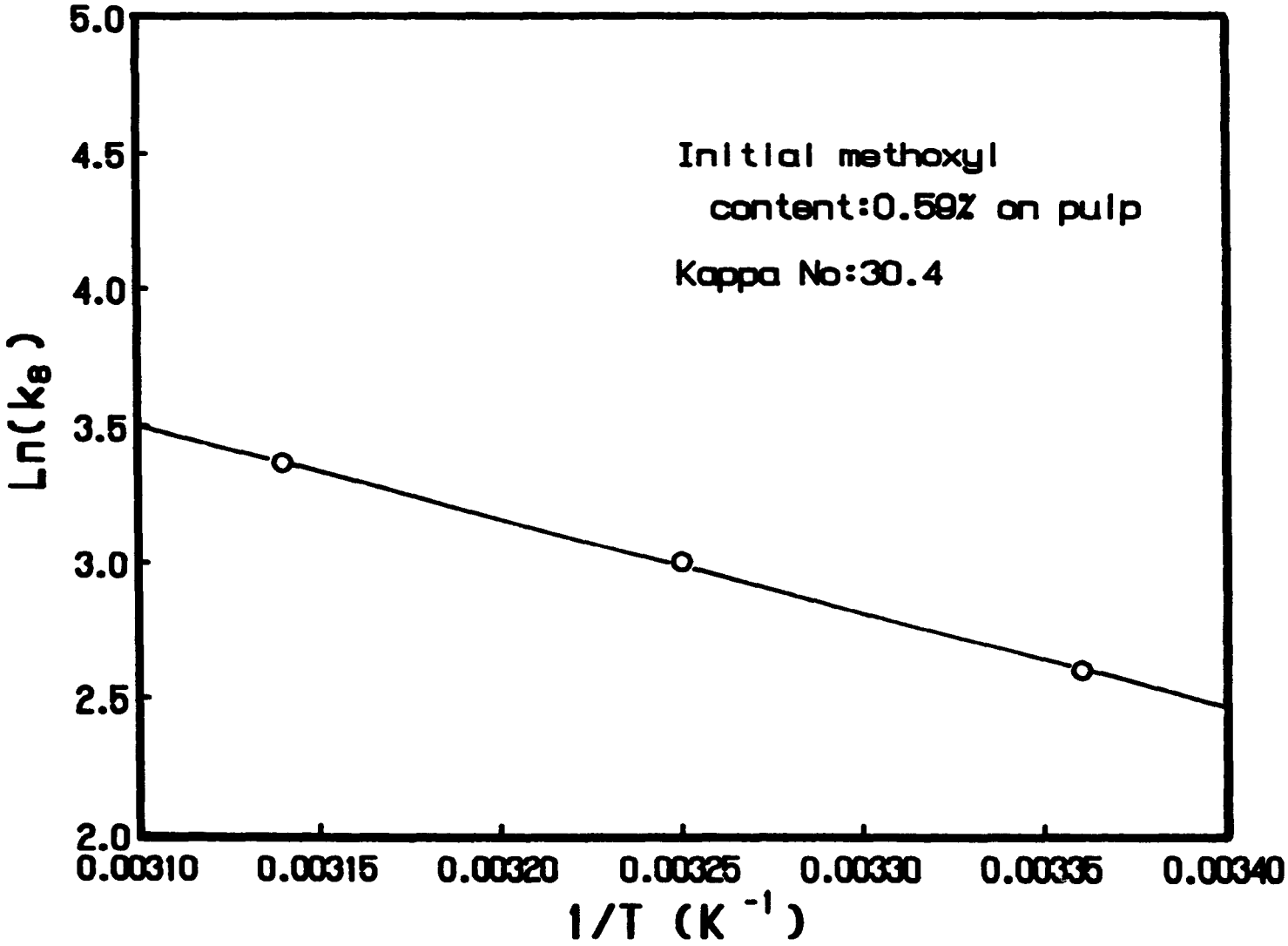

5.0
4.5
4.0
3.5
3.0
2.5
2.0
Ln(k8)
Initial methoxyl
content:0.59% on pulp
Kappa No:30.4
0.00310
0.00315
0.00320
0.00325
0.00330
0.00335
0.00340
1/T (K-1)

Fig. 4-16 Arrhenius plot of k_9

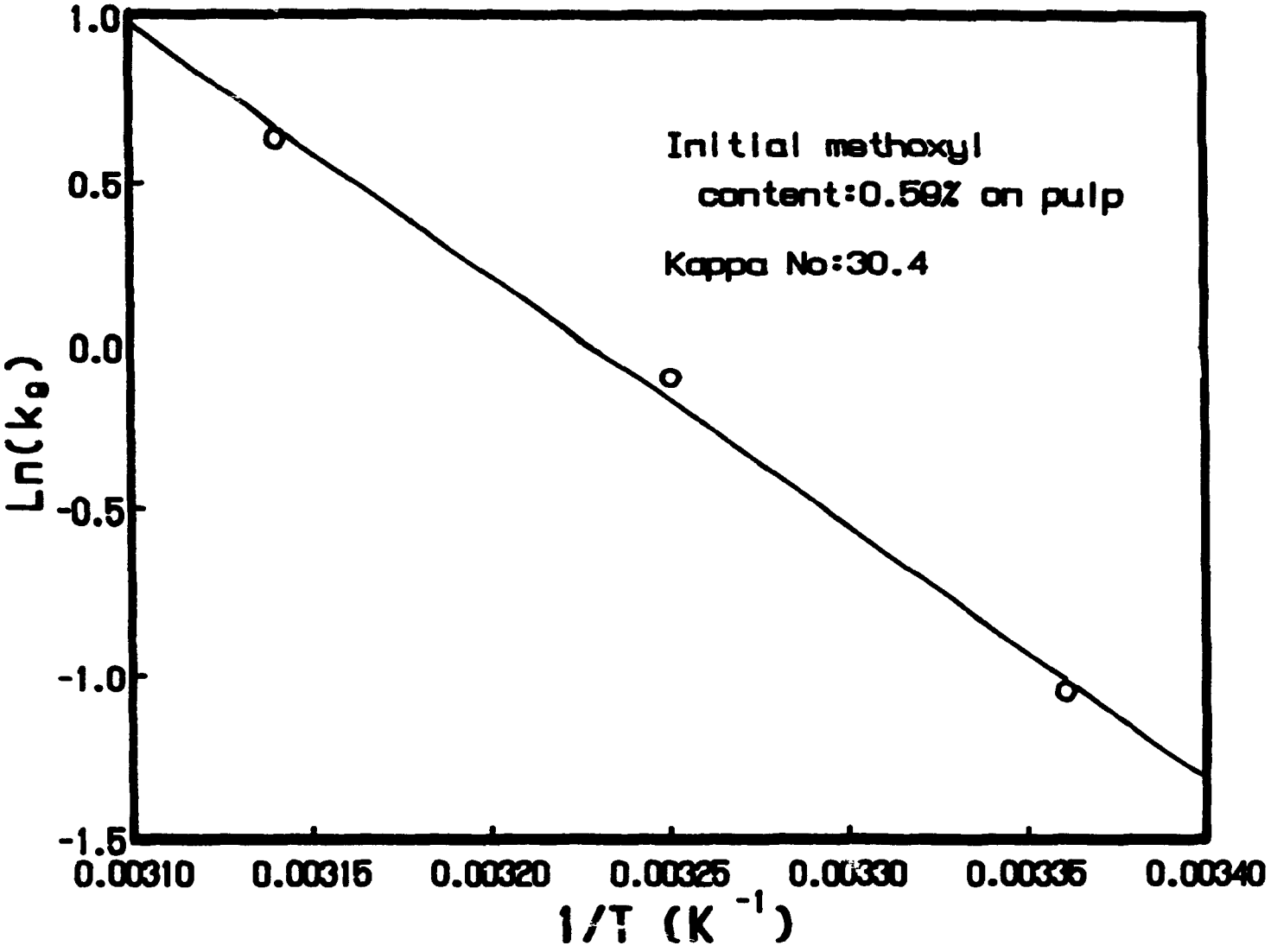

Initial methoxyl
content:0.59% on pulp
Kappa No:30.4
Ln(k_a)
1.0
0.5
0.0
-0.5
-1.0
-1.5
0.00310
0.00315
0.00320
0.00325
0.00330
0.00335
0.00340
1/T (K^-1)

Fig.4-17 Arrhenius plot of k_{12}

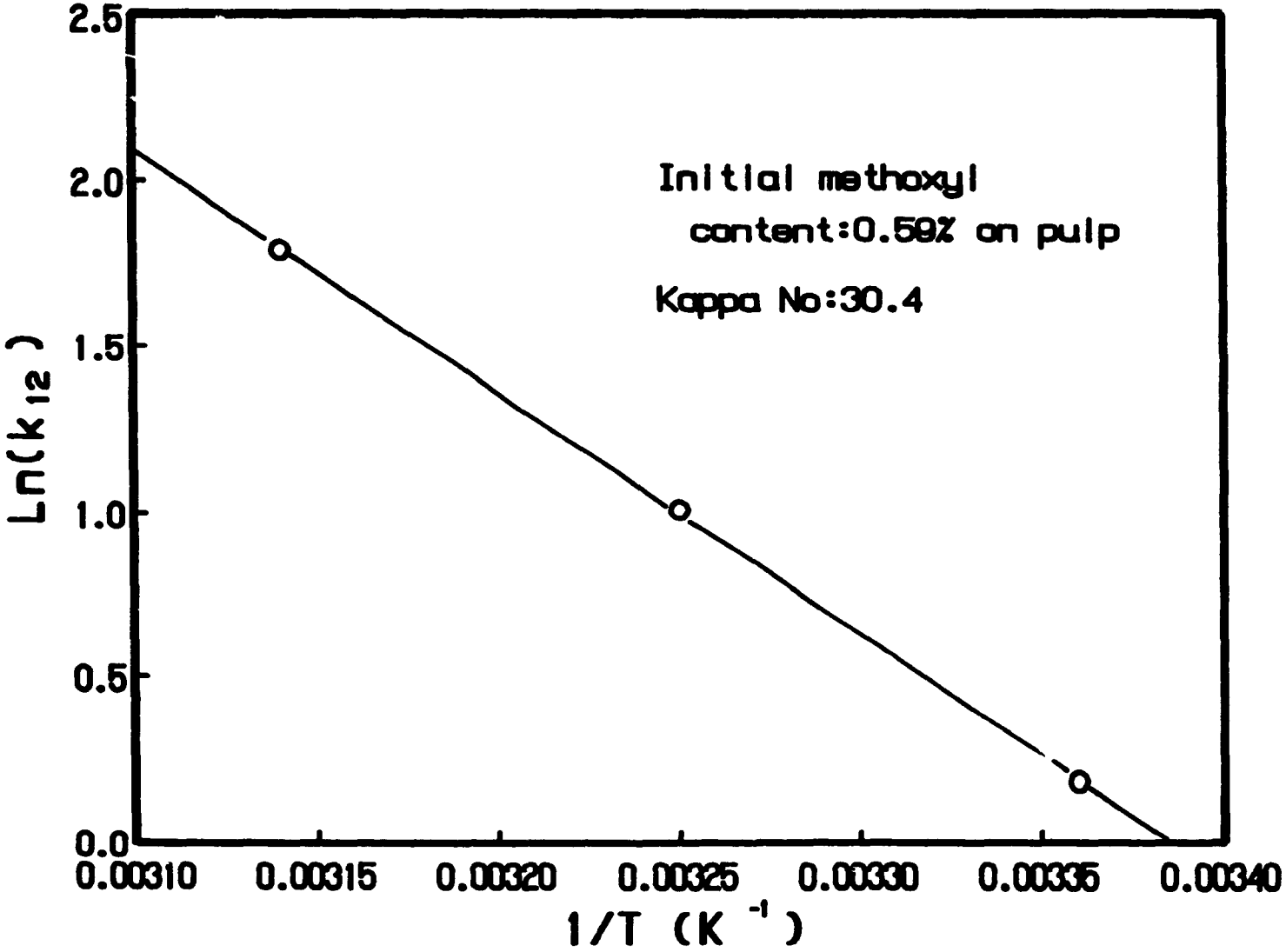

2.5
2.0
1.5
1.0
0.5
0.0
Ln(k12)
Initial methoxyl
content:0.59% on pulp
Kappa No:30.4
0.00310
0.00315
0.00320
0.00325
0.00330
0.00335
0.00340
1/T (K-1)

Table 4-3 Rate constants at different temperatures

Rate constants (l/mol*min)	T=25 C	T=35 C	T=45 C
k_5	9.77	18.95	25.30
k_8	13.46	19.80	23.53
k_9	0.349	0.903	1.89
k_{12}	1.20	2.75	6.00

Table 4-4 Activation energies and pre-exponential constants

Reaction No.	E (kJ/mol)	ko (l/mol*min)
5	39.8	$1.38*10^{8}$
8	28.1	$1.49*10^{6}$
9	62.5	$5.86*10^{10}$
12	59.5	$5.75*10^{10}$

Fig. 4-18 Comparison of model prediction and experimental results of demethylation at 25 °C and a Cl_2 charge factor of 0.22

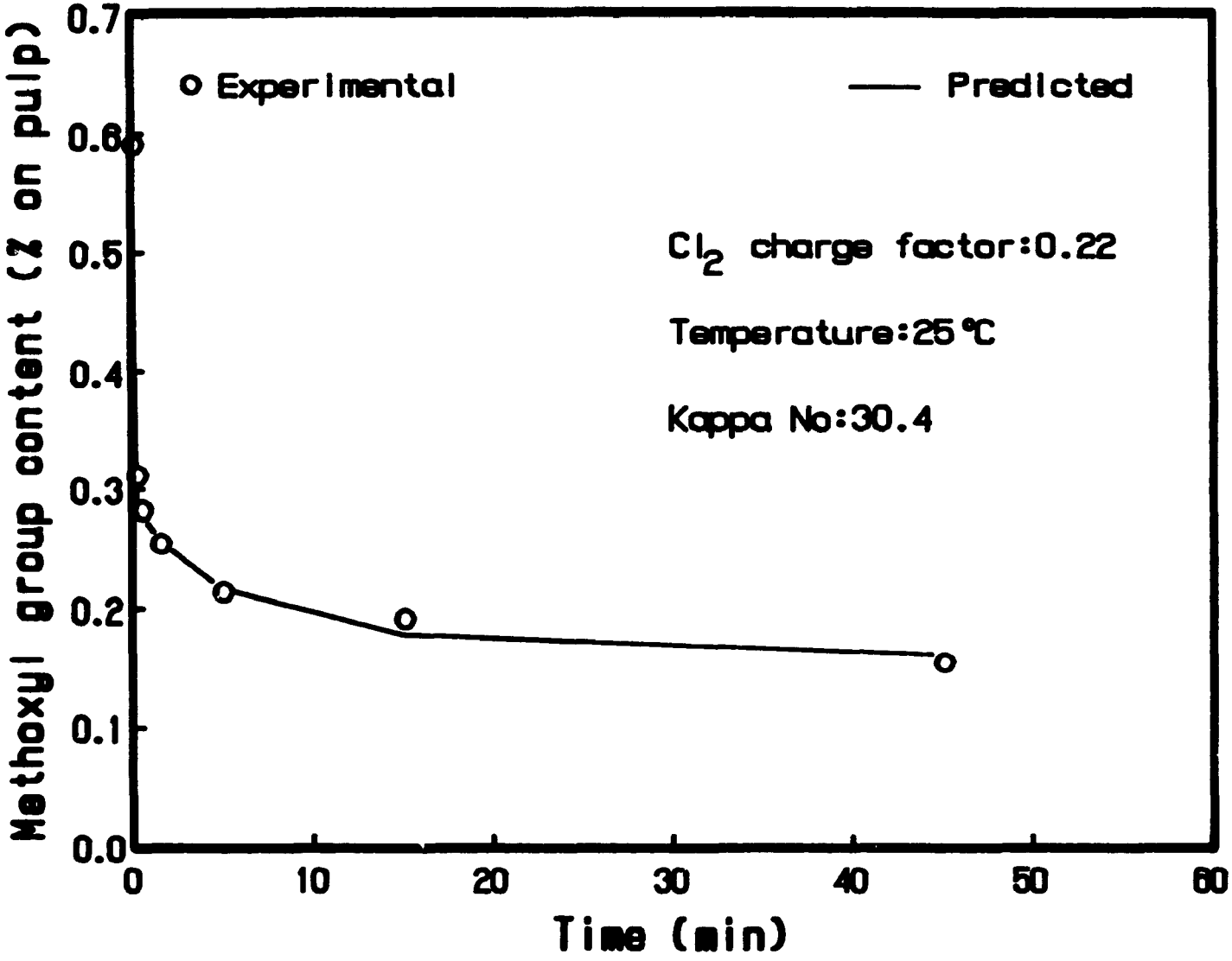

o Experimental
—— Predicted
Cl_2 charge factor:0.22
Temperature:25℃
Kappa No:30.4
Methoxyl group content (% on pulp)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
10
20
30
40
50
60
Time (min)

Fig. 4-19 Comparison of model prediction and experimental results of demethylation at 35 °C and a Cl_2 charge factor of 0.22

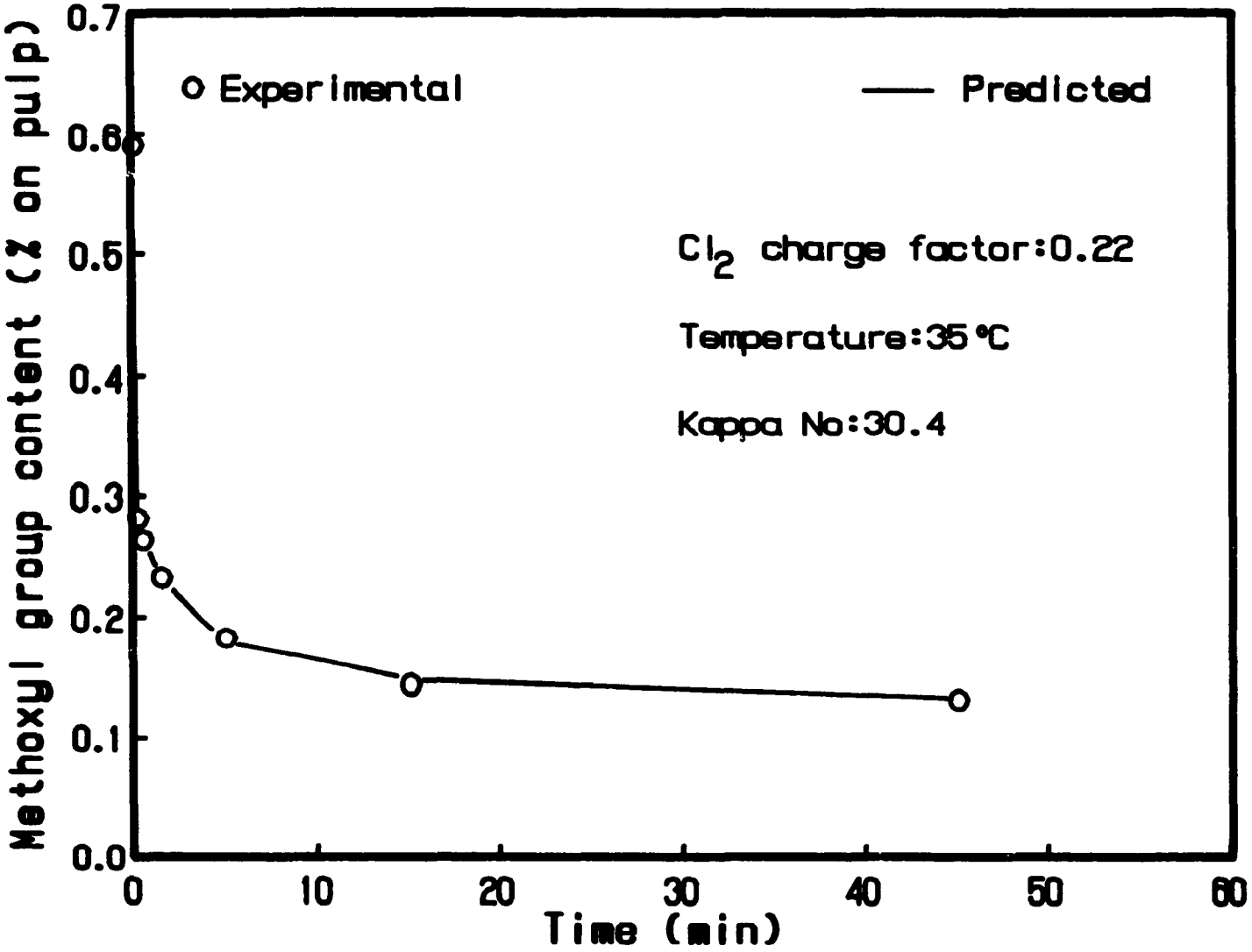
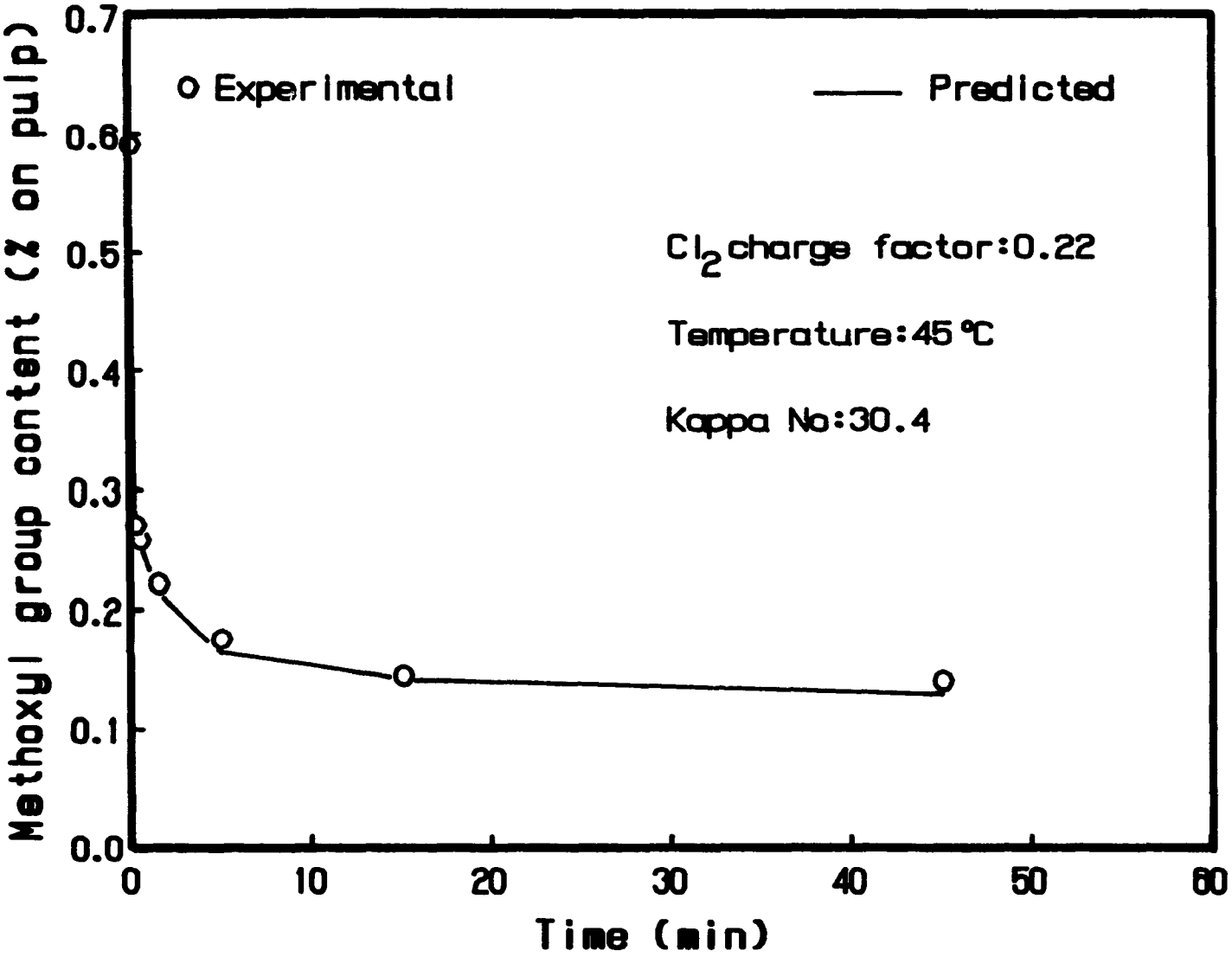

o Experimental
—— Predicted
Cl_2 charge factor:0.22
Temperature:35 °C
Kappa No:30.4
Methoxyl group content (% on pulp)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
10
20
30
40
50
60
Time (min)

Fig.4-20 Comparison of model prediction and experimental results of demethylation at 45 °C and a Cl_2 charge factor of 0.22


o Experimental
—— Predicted
Cl_2 charge factor:0.22
Temperature:45 ℃
Kappa No:30.4
Methoxyl group content (% on pulp)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
10
20
30
40
50
60
Time (min)

the development of lignin demethylation during chlorination of kraft pulp.

MODEL EVALUATION

According to the present model, the lignin macromolecule in CW pulp contains mono-, di-,and tri-aromatic chlorine substituted guaiacyl units after completion of the instantaneous reactions. The prediction of the development of [M_1],[M_2] and [M_3] during chlorination for three different conditions is shown in Figure 4-21 to 4-23. The experimental conditions in Figures 4-21 to Fig.4-23 cover the range from weak chlorination (Fig.4-21) to very strong chlorination (Fig.4-23). It illustrates that the mono-chloro lignin units are still prominent after 45 minutes at 25 °C and a chlorine charge factor of 0.16 (Figure 4-21), while they are completely eliminated after about 5 minutes at a high chlorine charge and temperature (Figure 4-23). Similarly, the di-chloro units are dominant at the end of chlorination in Figure 4-21 but essentially absent at the end of chlorination in Figure 4-23. At a chlorine charge factor of 0.33 and temperature of 45 °C, the tri-chloro units or the so called "blocking groups" are dominant after 45 minutes, indicating that further delignification cannot be achieved.

Since the present kinetic model predicts the content of mono-, di-, and tri-chloro lignin monomer units, it is possible to calculate the organically bound chlorine in CW pulp. This value is multiplied by 1/0.79 = 1.27, to account for the finding of chapter 3 that the average OCH_3/C_9 molar ratio during chlorination is 0.79. Implicit in this calculation is the assumption that the

Fig.4-21 Prediction of development of [M_1], [M_2] and [M_3] at 25 °C and a Cl_2 charge factor of 0.16

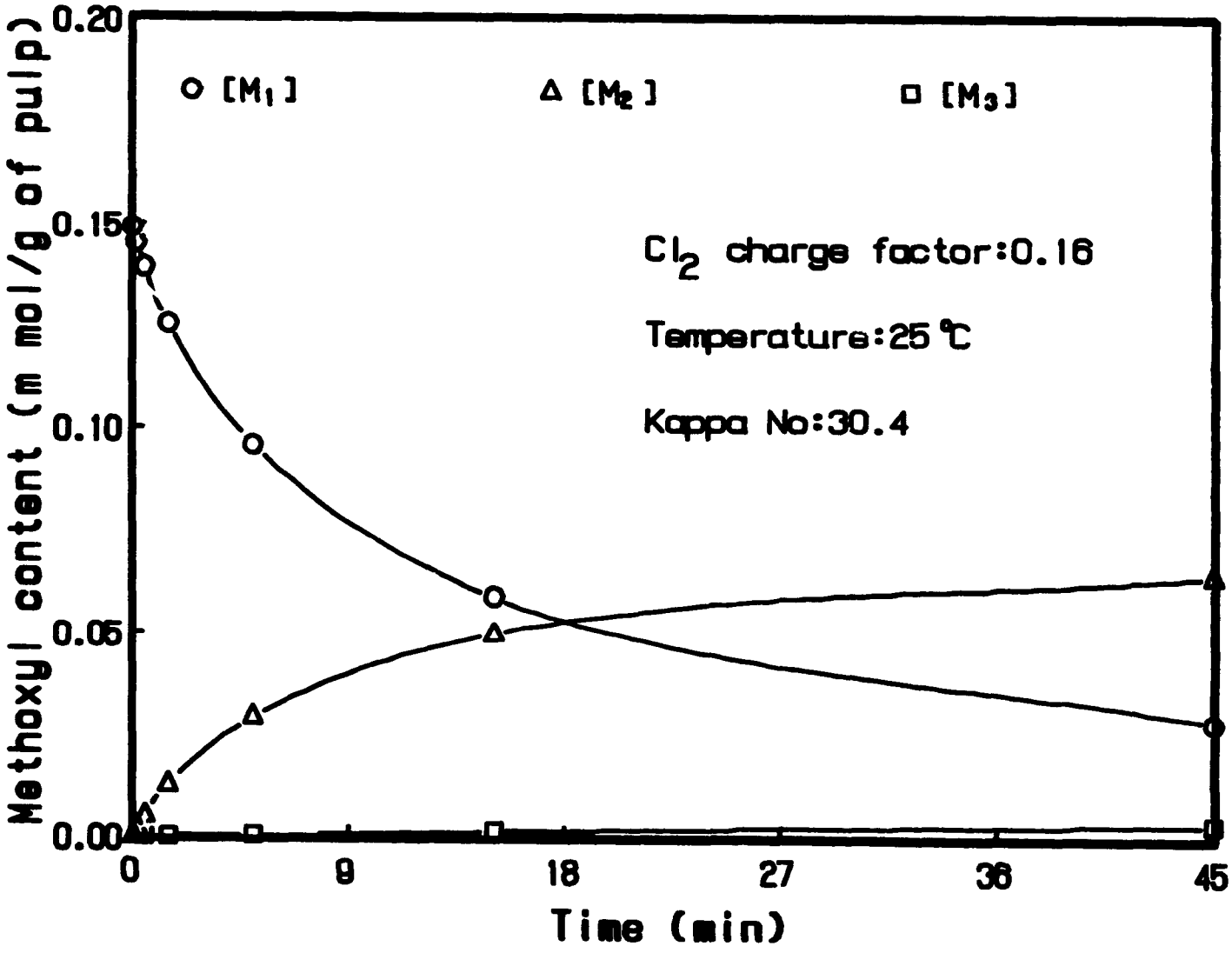

0.20
0.15
0.10
0.05
0.00
Methoxyl content (m mol/g of pulp)
○ [M1]
△ [M2]
□ [M3]
Cl2 charge factor:0.16
Temperature:25 ℃
Kappa No:30.4
0
9
18
27
36
45
Time (min)

Fig. 4-22 Prediction of development of [M_1], [M_2] and [M_3] at 35 °C and a Cl_2 charge factor of 0.22

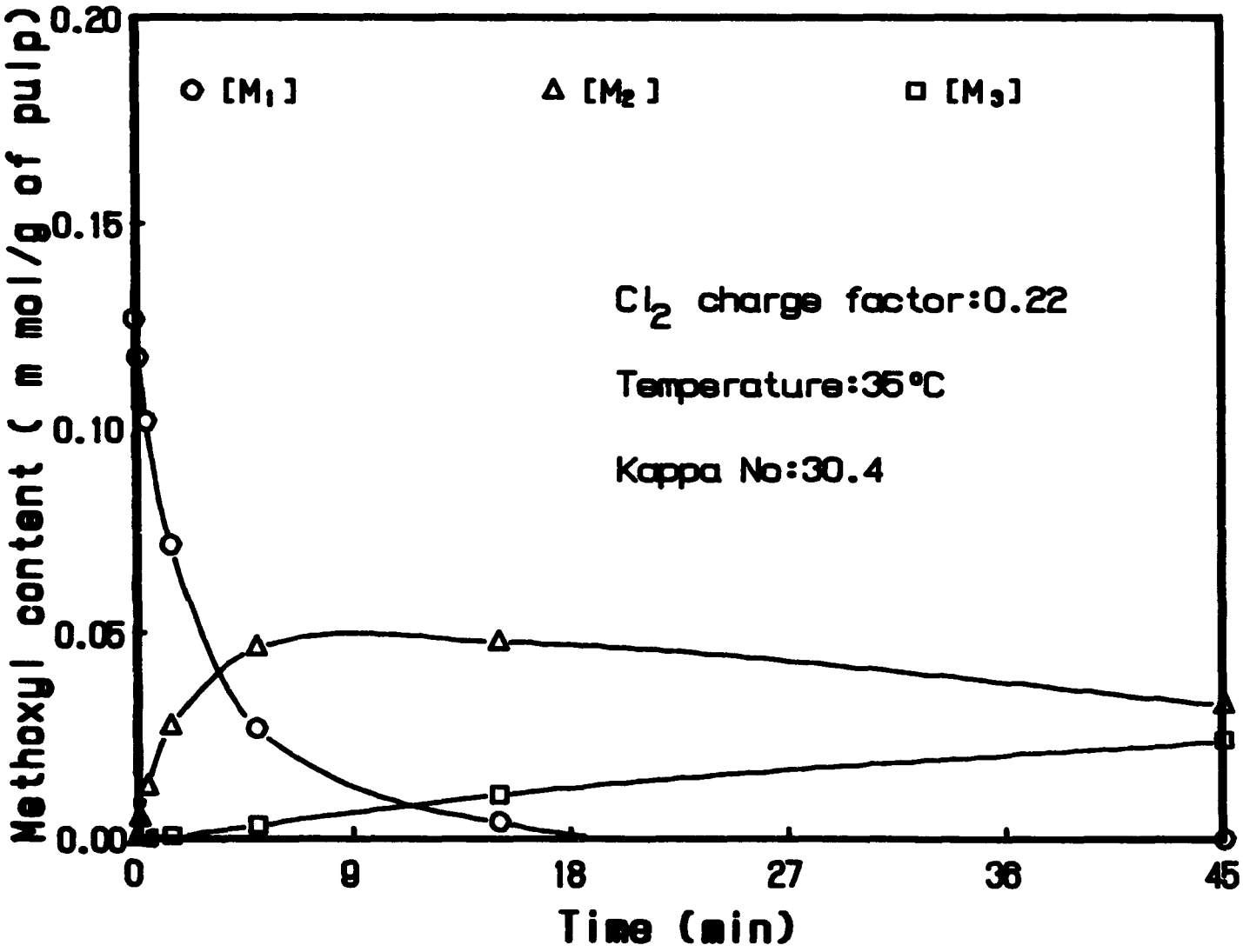
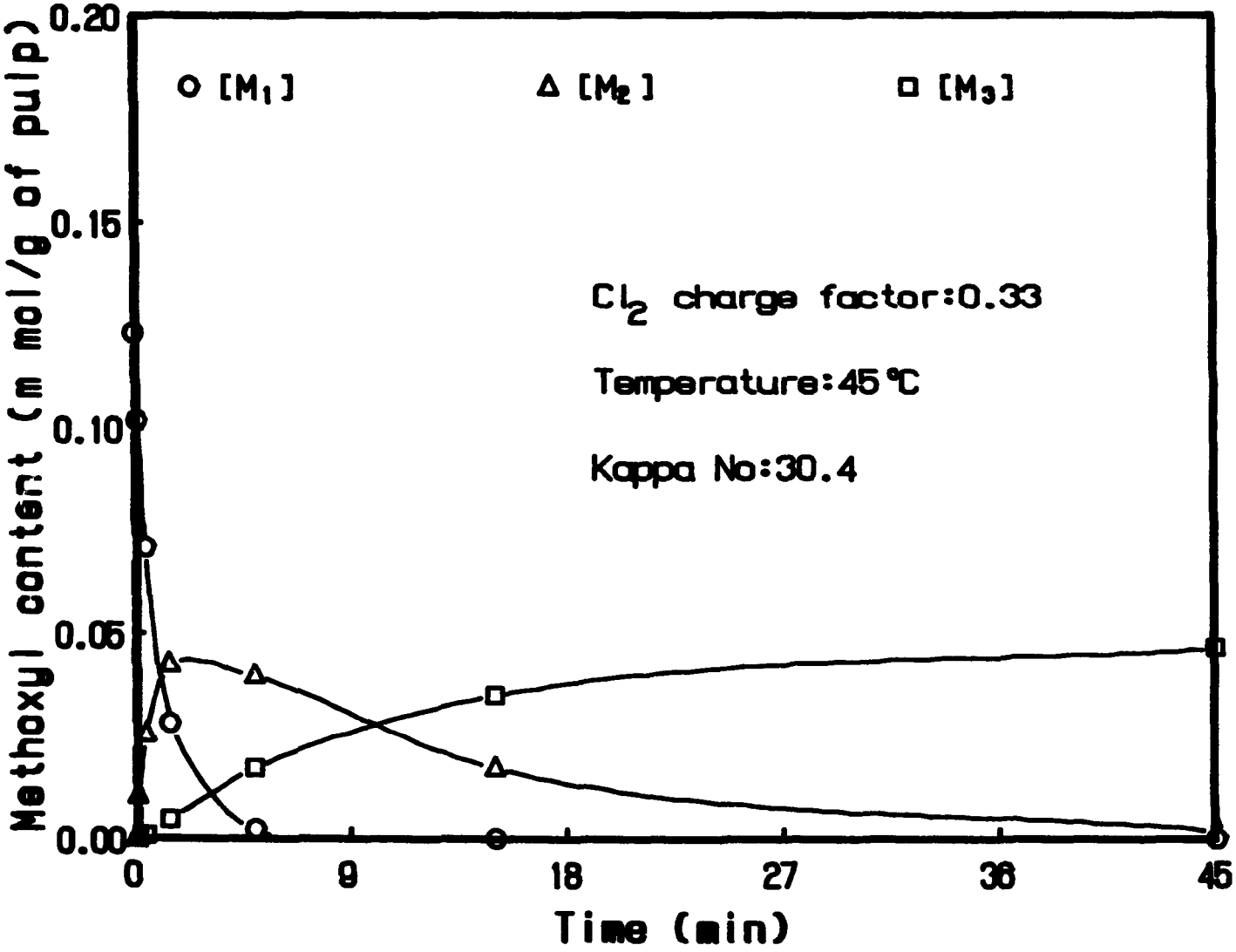

○ [M1]
△ [M2]
□ [M3]
Cl2 charge factor:0.22
Temperature:35°C
Kappa No:30.4
Methoxyl content (m mol/g of pulp)
0.20
0.15
0.10
0.05
0.00
0
9
18
27
36
45
Time (min)

Fig. 4-23 Prediction of development of [M_1], [M_2] and [M_3] at 45 °C and a Cl_2 charge factor of 0.33


O [M1]
Δ [M2]
□ [M3]
Cl2 charge factor:0.33
Temperature:45℃
Kappa No:30.4
Methoxyl content (m mol/g of pulp)
0.20
0.15
0.10
0.05
0.00
0
9
18
27
36
45
Time (min)

average Cl/C9 ratio is the same for lignin monomer units with or without a methoxyl group. The results in terms of Cl/C9 ratio are shown in Figure 4-24. It is apparent that the model predictions follow the trend of the experimental data, but are always slightly lower than the measurements. This could be explained by two effects. Firstly it is likely that the Cl/C9 ratio of the monomer units without OCH_3 group is slightly higher because one more ring position is available for aromatic substitution. Secondly, the molecular weight of the monomer units without OCH_3 group is lower than that of the OCH_3 containing units, so that the actual OCH_3/C9 molar ratio is slightly lower than 0.79. (From a mass balance it can be shown that the actual OCH_3/C9 molar ratio is 0.76). The total organic chlorine (TOCl) content of CW pulp was also predicted for a chlorine charge factor 0.22 and 35 °C. As can be seen in Table 4-5, the predicted results agree reasonably well with the experimental values.

The kinetic model can also predict the TOCl in the chlorination effluent. The assumptions made for the prediction are:

(1) TOCl originating from lignin monomer units with an OCH_3 group is only formed by rapid and complete conversion of reactions (6) and (10), following the respective rate controlling demethylation reactions (5) and (9)

(2) the TOCl formation rate per lignin monomer unit is the same for units with or without a methoxyl group.

(3) no further chlorine substitution into dissolved lignin

(4) no dechlorination of dissolved lignin

With these assumptions, the TOCl in solution at time t is:

Fig.4-24 Comparison of predicted and measured Cl/C9 ratio in CW pulp at 25 C and a Cl2 charge factor of 0.22

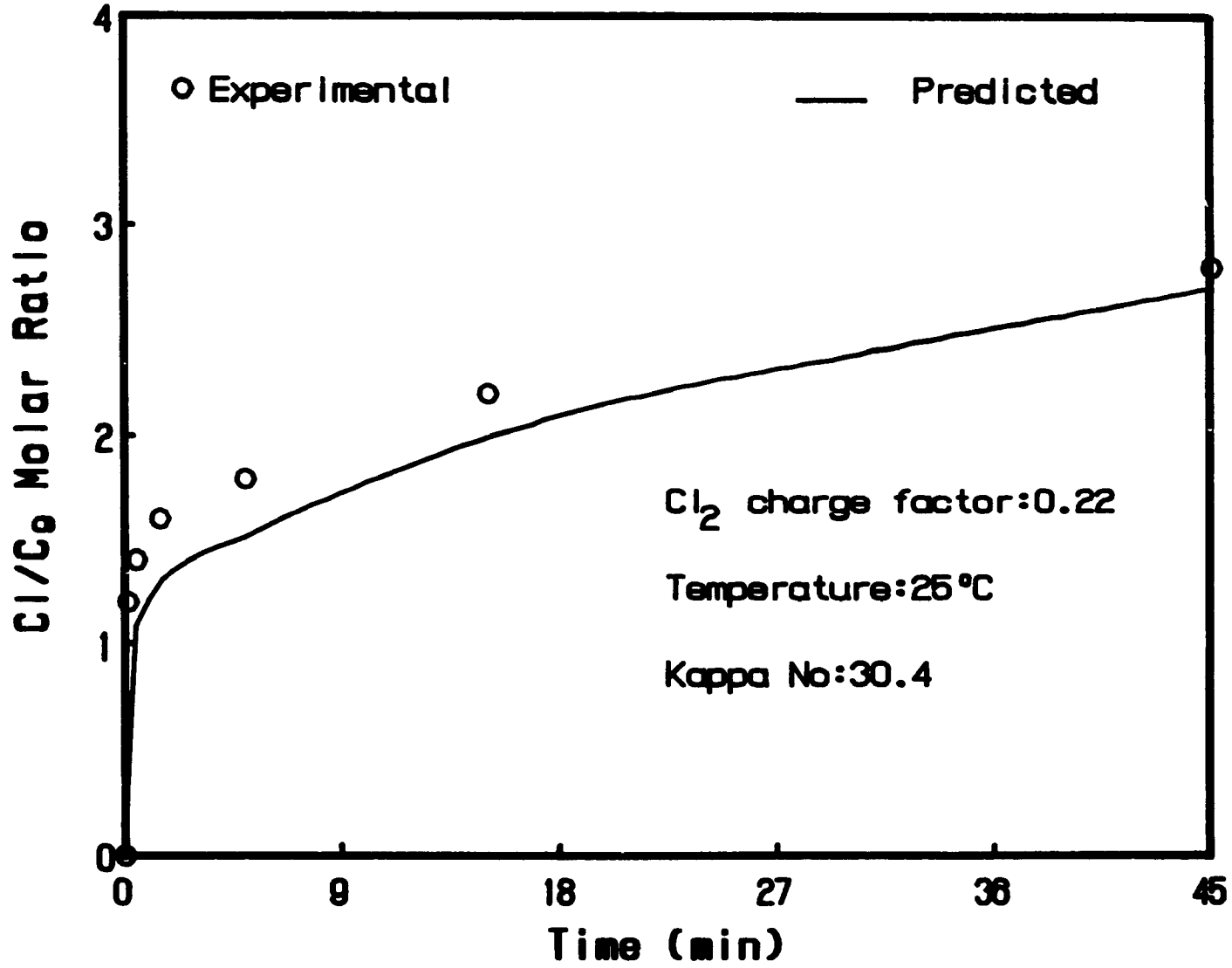

o Experimental
Predicted
Cl/Co Molar Ratio
Time (min)
Cl2 charge factor:0.22
Temperature:25°C
Kappa No:30.4
0
1
2
3
4
0
9
18
27
36
45

Table 4-5 Comparison of predicted and measured total organic chlorine (TOCl) in CW pulp at a Cl_2 charge factor of 0.22 and 35 °C

Time (min)	Measured TOCl (mg/g of pulp)	Predicted TOCl (mg/g of pulp)
0.167	4.97	4.51
0.5	5.24	4.53
1.5	5.18	4.55
5	5.08	4.61
15	4.84	4.72
45	4.36	4.87

Cl_2 charge factor: 0.22, 35°C, 2% consistency

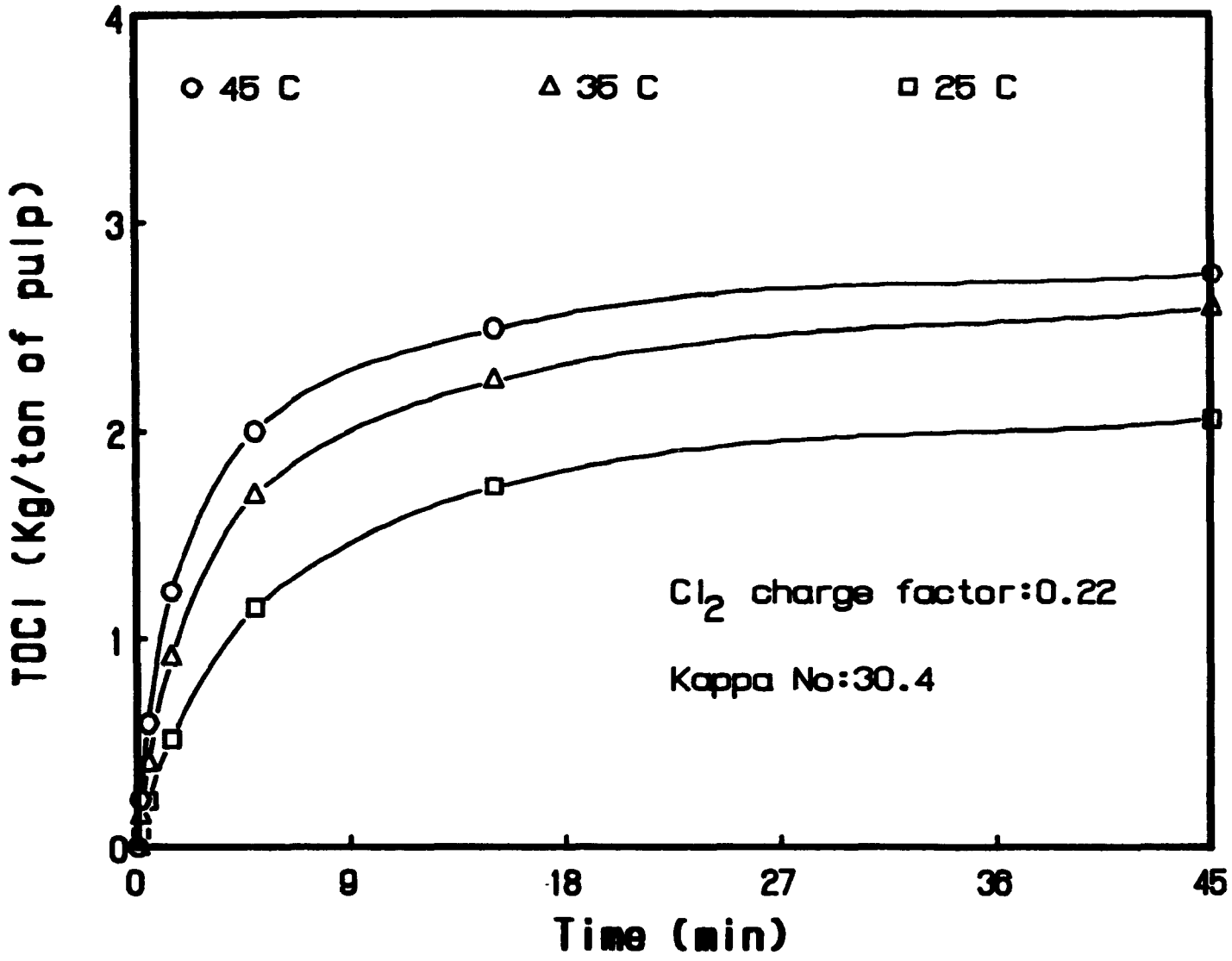
$$TOCl = \frac{35.5}{(OCH_3/C_9)} \int_0^t (k_5 [Cl_2] [M_1] + 2 k_9 [Cl_2] [M_2])\, dt \qquad (20)$$

where OCH_3/C_9 is the molar content of methoxyl groups per lignin monomer unit, which was constant at 0.79 throughout the chlorination process (see chapter 3). With equations (14) and (15), and boundary conditions $[M_1]_{t=0}=[M_1]_0$ and $[M_2]_{t=0}=0$, equation (20) can be integrated to:

$$TOCl = \frac{35.5}{(OCH_3/C_9)} \left[\frac{k_5}{k_5+k_9} ([M_1]_0 - [M_1]_t) + \frac{2k_9}{k_9+k_{12}} \left\{ \frac{k_8}{k_5+k_8} ([M_1]_0 - [M_1]_t) - [M_2]_t \right\}\right] \qquad (21)$$

The prediction of TOCl with equation (21) at a chlorine charge factor of 0.22 is shown in Fig.4-25. A rapid increase in TOCl with time is seen. The higher TOCl levels at higher temperature are the result of increased progress of reactions (5) and (8). The predicted TOCl production at 45 minutes and 45 C of about 2.75 kg per metric ton of pulp compares well with a value of approximately 3 kg TOCl/ton for the effluent of the chlorination stage of a softwood kraft bleach plant (10). Finally, the Cl/C9 molar ratio in the effluent at a chlorine charge factor of o.22, 45 C and 45 minutes can be predicted with the present kinetics. The predicted value of 1.2 (mol Cl/mol C9) is comparable to the Cl/C9 ratio in the chlorination stage effluent of 1.0-1.5, recently reported by Annergren (15).

Fig. 4-25 Prediction of TOCl in chlorination effluent at a Cl_2 charge factor of 0.22


o 45 C
Δ 35 C
□ 25 C
TOCl (Kg/ton of pulp)
Time (min)
Cl2 charge factor:0.22
Kappa No:30.4
0
1
2
3
4
0
9
18
27
36
45

This good agreement gives further support to the reaction scheme in Figure 4-7 and the assumptions underlying equation (21). An explanation for the validity of assumption (3) might be that the soluble lignin fragments formed in delignification reactions (2), (6) and (10) undergo oxidation rather than further chlorination. Aromatic ring opening during oxidation reaction (3), (7) and (11) is expected to considerably reduce further chlorine substitution. This might also explain the relative small fraction of aromatics in TOCl in chlorination effluent (14).

GENERAL DISCUSSION

The rate constants in Table 4-3 show that the demethylation and substitution rates of the mono- chloro guaiacyl monomer units are comparable and about one order of magnitude larger than the respective rates of the di-chloro guaiacyl units. Table 4-4 shows that the activation energy of demethylation is larger than substitution for M_1, and somewhat larger for M_2. Similarly, Table 4-2 shows that k_1/k_4, the ratio of the reaction constants of demethylation and substitution of unchlorinated lignin monomer units, increases with increasing temperature. The increased demethylation compared to substitution for M_1, M_2 and unchlorinated units leads to a smaller content of "blocking group" units (M_3) at complete pulp chlorination. Since the final M_3 content is proportional to the "floor level" lignin content (chapter 3), the lower "floor level" lignin content with increasing chlorination temperature can be explained in terms of increased demethylation compared to substitution.

Table 4-2 shows that the amount of methoxyl groups removed

during the instantaneous reactions for a chlorine charge factor of 0.16 increases from 0.0785 to 0.088 m mol/g pulp when the temperature is increased from 25 C to 45 C. This corresponds to a fractional OCH_3 removal of respectively 41 to 46%. With a stoichiometric ratio S_M of 5.02 mol Cl_2/mol OCH_3, it can be calculated that the instantaneous reactions consume chlorine equivalent to a chlorine charge factor of respectively 0.09 and 0.10. According to the present reaction scheme, this leads to the interesting conclusion that if chlorine is supplied at a chlorine charge factor of only about 0.10, significant (41-46%) delignification will occur but the dissolved lignin will be free of organic chlorine. The TOCl of the chlorination stage effluent can be kept low when further chlorination is done with ClO_2. It should be noted , however, that a large fraction of organic chlorine in pulp in the form of M_1 will end up in the extraction effluent. Still, and most importantly, the above analysis gives a more mechanistic basis for the recent explanation given by Berry et.al.(11) that Cl_2 should be added first at a relative low chlorine charge factor (less than 0.14) before addition of ClO_2 to prevent dioxin formation in the pulp chlorination stage.

It is generally believed that the low molecular weight material of the chlorination stage is mainly responsible for toxicity of the effluent. Also the bioaccumulative properties of chloro- organics increase with increasing chlorine content. Since sequential addition of first Cl_2 at a chlorine charge factor of about 0.10, and then ClO_2, will lead to a combined chlorination and extraction effluent with mainly high molecular weight material of relative low Cl/C9 molar ratio, it is expected that the

effluent of such a bleach plant operation will be less toxic.

The size of the activation energies in Table 4-4 are expected for a chemically controlled process. They are generally larger than previously reported in literature (1,3,12,13) for delignification during pulp chlorination. It is expected that with a major fraction of lignin removed in the first few seconds and the existence of a "floor level" lignin content, representation of the reactions in Figure 4-7 by a single reaction will lead to a much smaller overall activation energy than those of the individual reactions. Therefore, the explanation for the low activation energies reported in literature is that the previously proposed reaction schemes were too simplified.

The rate determining step for delignification is demethylation of M_2 units via reaction (9). Thus, the influence of temperature on the time to achieve complete delignification is governed by the activation energy of 62.5 kJ/mol for reaction (9). In other words, by increasing the temperature from 25 °C to 45 °C, the time to achieve complete delignification is reduced by a factor of about 5. This implies that the residence time in chlorination towers with low ClO_2 substitution can be reduced by a factor 5 per 20 C temperature increase.

Finally, from the demethylation kinetics given by equation (13) to (16) and the reaction constants defined by Table 4-4, the methanol concentration in the chlorination liquor can be obtained when the development of the chlorine concentration is known. Alternatively, it is possible to calculate the methoxyl group content and thus lignin content of pulp when the methanol and chlorine concentrations and OCH_3 - Cl_2 stoichiometric ratio are

known. This forms the subject of a future paper on control of the chlorination stage, which is not part of the thesis.

CONCLUSION

Demethylation kinetics are developed based on a new delignification mechanism of kraft pulp chlorination proposed in the previous chapter. The kinetic equations show that demethylation and aromatic substitution of chlorine in lignin monomer units take place simultaneously at comparable rates. Demethylation and chlorine substitution of unchlorinated lignin monomer units are completed within the first few seconds. The corresponding reactions of mono-chloro lignin monomer units are slower but again one magnitude faster than those of the di-chloro lignin units. Tri-chloro lignin monomer units are stable towards further chlorination or demethylation and form the so-called "floor level" lignin.

The demethylation model gives realistic prediction of the total organic chlorine content of both chlorinated pulp fibers and chlorination effluent produced in a conventional chlorination stage with low ClO_2 substitution. Further evaluation of the kinetic equations suggests that:

(a) the lower "floor level" lignin content with increasing temperature is caused by increased demethylation compared to aromatic chlorine substitution

(b) the combined chlorination and extraction effluent is less toxic when Cl_2 is added first in the chlorination stage before ClO_2

(C) the residence time in chlorination towers with low ClO_2

substitution can be reduced by a factor of 5 per 20 C temperature increase.

Finally, the present kinetics also give a more mechanistic basis for the explanation given recently by Berry et.al. (11) that Cl_2 should be added first at a low chlorine charge factor before addition of ClO_2 to prevent dioxin formation during kraft pulp chlorination.

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CHAPTER 5

METHANOL NUMBER: A FAST METHOD TO DETERMINE LIGNIN CONTENT OF PULP

ABSTRACT

A new and relatively fast method to determine lignin content in kraft black spruce pulp has been developed, based on conversion of methoxyl groups in lignin to methanol by elemental chlorine. The method is called "Methanol number" and defined as methanol concentration in units of ppm produced during five minutes of chlorination at 25 C, 1% consistency, and an initial chlorine concentration of 3.0 g/l.

With analysis of the methanol concentration by gas chromatography, the total analysis time is approximately 7 minutes.

The Methanol number and lignin content of kraft black spruce are linearly related over a range of total lignin of 3.05% to 11.63% as

$$\text{Lignin (\%)} = 0.07 + 0.0822 * \text{Methanol No.}$$

Temperature deviations can be accounted for by the expression:

$$\text{Methanol No.} = \text{Methanol conc.(ppm)} + (25-T) * 0.45$$

where T is the temperature in degree Celsius

The Methanol number is relatively insensitive to deviations from the specified initial chlorine concentration of 3.0 g/l.

INTRODUCTION

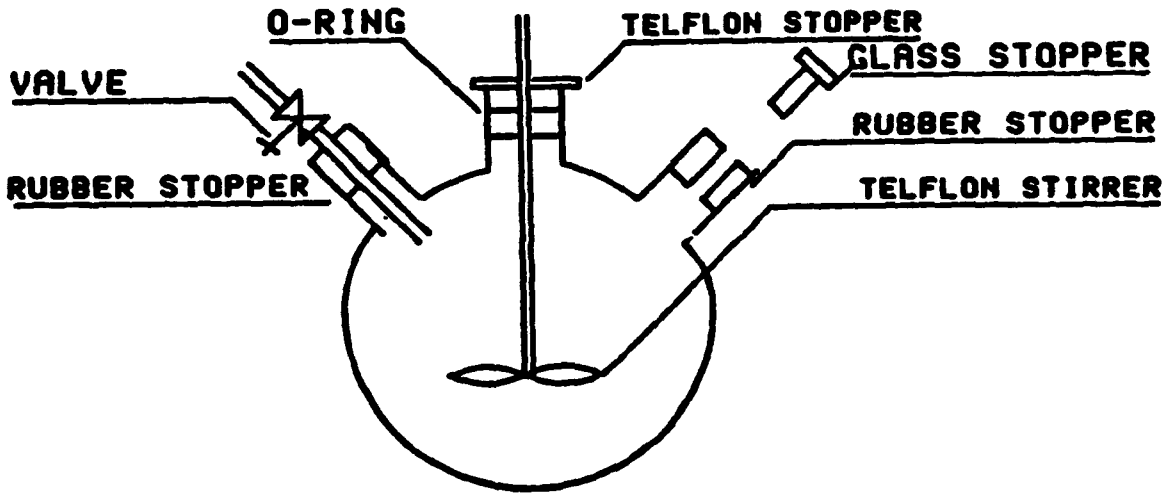
In the newly developed chlorination mechanism described in Chapter 3, it was shown that demethylation and delignification are closely related, and that all methoxyl groups removed during chlorination are converted to methanol. It was also shown that demethylation is the rate determining step for delignification of softwood kraft pulp. It is interesting to note that the similar behaviour of demethylation and delignification rates during chlorination was found as early as 1941 for soda and sulphate pulps(1). Furthermore, Ali (2) recently established that methanol formation stops when "dynamic" chlorination of a packed bed of softwood kraft fibers is complete.

It is known that the lignin content of wood and pulp can be quantified indirectly by determination of the methoxyl group content (3,4). A prerequisite is that the relation between methoxyl content and lignin content must be known (5). Since the methoxyl content can be determined from methanol during chlorination (chapter 4), and the analysis of methanol by gas chromatography is fast and simple, it was investigated whether pulp lignin content can be determined rapidly by measuring the amount of methanol produced during chlorination. The detailed experimental procedure and the influence of operating parameters on this so called "Methanol number" test, are presented in this chapter.

EXPERIMENTAL

The apparatus consisting of a three neck flask and a variable speed stirrer is shown in Fig.5-1. Chlorine water is introduced

Fig. 5-1 Chlorination Apparatus


O-RING
TELFLON STOPPER
VALVE
GLASS STOPPER
RUBBER STOPPER
RUBBER STOPPER
TELFLON STIRRER

into the flask using a pipette inserted through a small hole in the rubber stopper. Air displaced by chlorine water is removed via a valve in the other neck of the flask. A weighed amount of pulp of about 3.5 g from an air-dried handsheet is dispersed in water. Subsequently, excess water is removed by filtering the pulp suspension on a buchner funnel. The concentrated pulp mass was transferred quantitatively into a 50 cc syringe, weighed and thermostated in a constant temperature bath. After analysis of the chlorine concentration in the flask, additional water and chlorine water were added so that after quantitative introduction of the pulp mass, the required chlorine concentration and a consistency of 1% would be obtained. The pulp sample was then injected into the flask, followed immediately by starting a stopwatch and agitation at about 10 rps. After exactly 5 minutes, the chlorination was stopped by rapid injection of an excess amount of potassium iodide solution. The pulp was separated from the suspension by filtration in a buchner funnel with a 100 mesh screen. 10 ml spent liquor was saved for gas chromatographic analysis.(see chapter 2) A typical methanol gas chromatogram is shown in Figure 5-2.

Five methanol standards were prepared in the concentration range of 29.35 to 125 ppm by mixing known volumes of methanol with know volumes of water. The standards were stored in a refrigerator. A calibration curve was determined each time when samples were analyzed. A typical linear calibration curve is shown in Fig.5-3.

The Methanol number is defined as methanol concentration in units of ppm produced during five minutes of chlorination at 25 C,

Fig.5-2 Typical methanol gas chromatogram

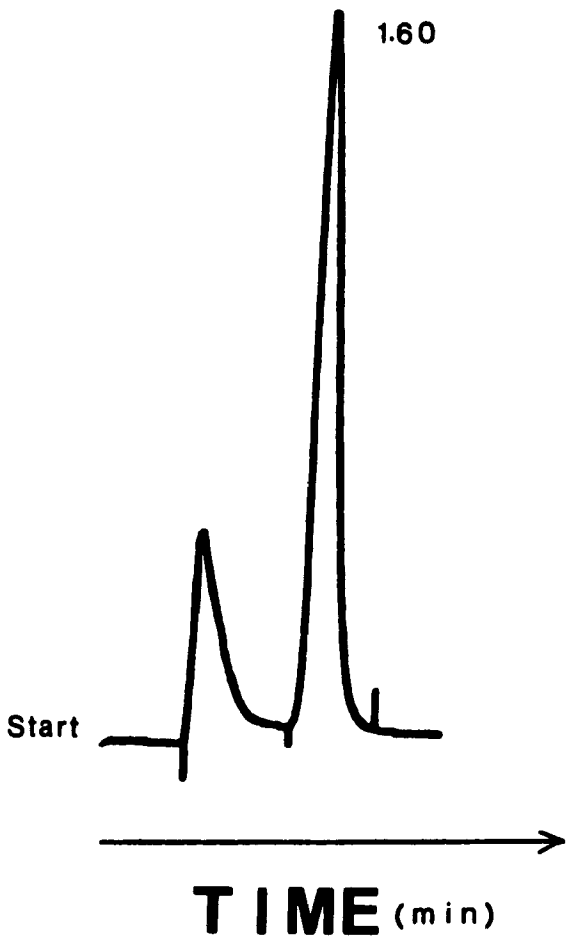
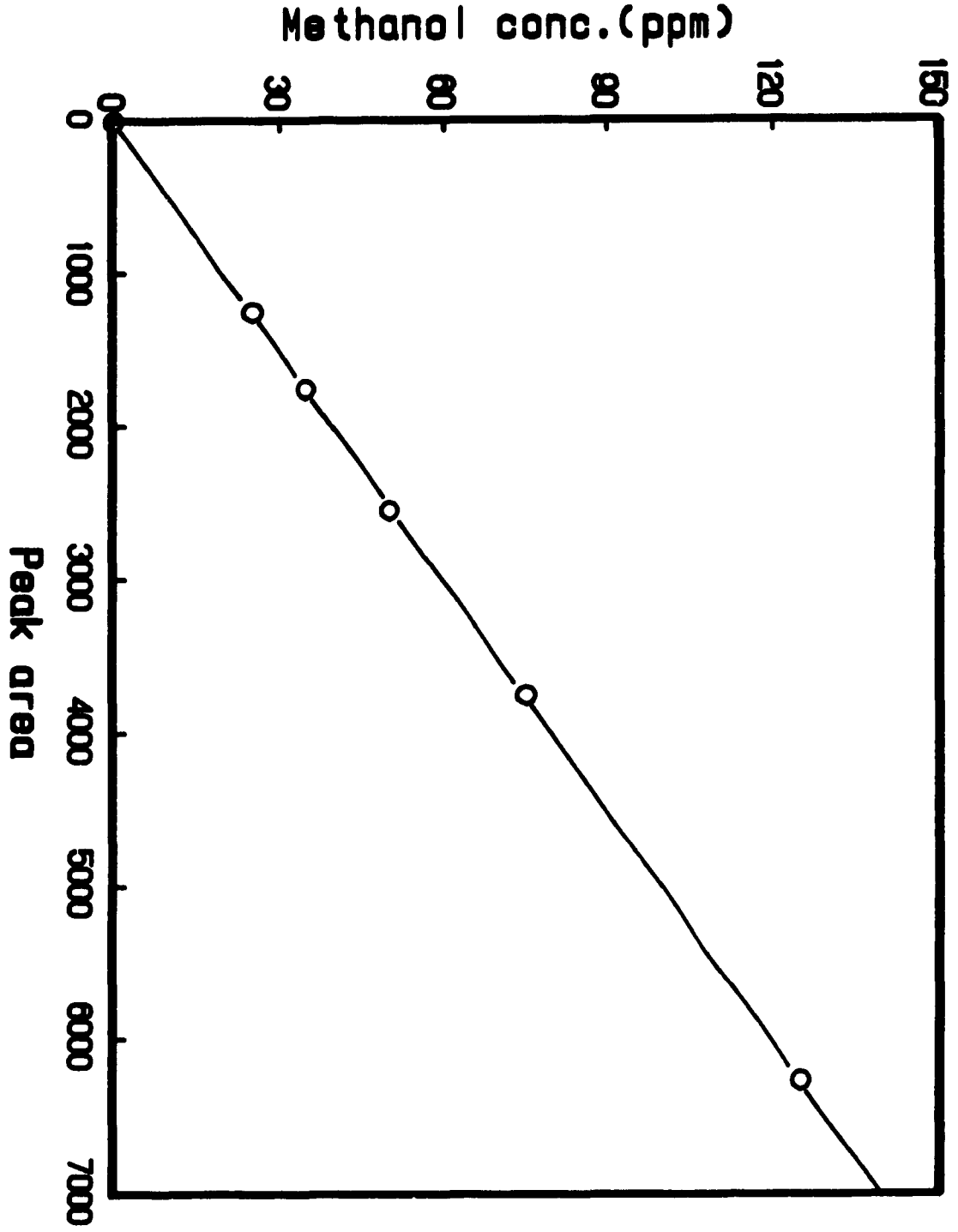

1.60
Start
TIME (min)

Fig.5-3 Typical calibration curve


Methanol conc.(ppm)
0
30
60
90
120
150
Peak area
0
1000
2000
3000
4000
5000
6000
7000

1% consistency, and an initial chlorine concentration of 3.0 g/l.

RESULTS AND DISCUSSION

Chlorine concentration

The amount of methanol produced during 5 minutes chlorination increases with increasing chlorine concentration, as can be seen in Fig.5-4. However, the increase in methanol concentration for chlorine concentration above 2.0 g/l,or a charge factor of 0.255, is small. Since the results in Fig.5-4 were obtained with pulp containing the highest lignin content used in this study of 11.63%, these results correspond to the lowest chlorine charge factor at a fixed chlorine concentration. For the samples with less lignin, the same charge factor will be reached at lower chlorine concentration, so that the corresponding curve will level off at lower chlorine concentration. To assure that the procedure is not sensitive to the chlorine concentration, a chlorine concentration of 3.0 g/l was selected for the Methanol number. This corresponds to a chlorine charge factor of at least 0.383 in the present study. With such a high chlorine application, it is expected that the so called lignin "floor level" is reached rapidly.

Reaction time

The methanol concentration versus reaction time is shown in Fig.5-5 for a pulp with initial lignin content of 4.12%. It demonstrates that after an initial fast reaction, demethylation takes place continuously at a slow rate. From 2 to 10 minutes, the demethylation rate slows down gradually so that the reaction time

Fig.5-4 The influence of Cl_2 concentration on methanol production

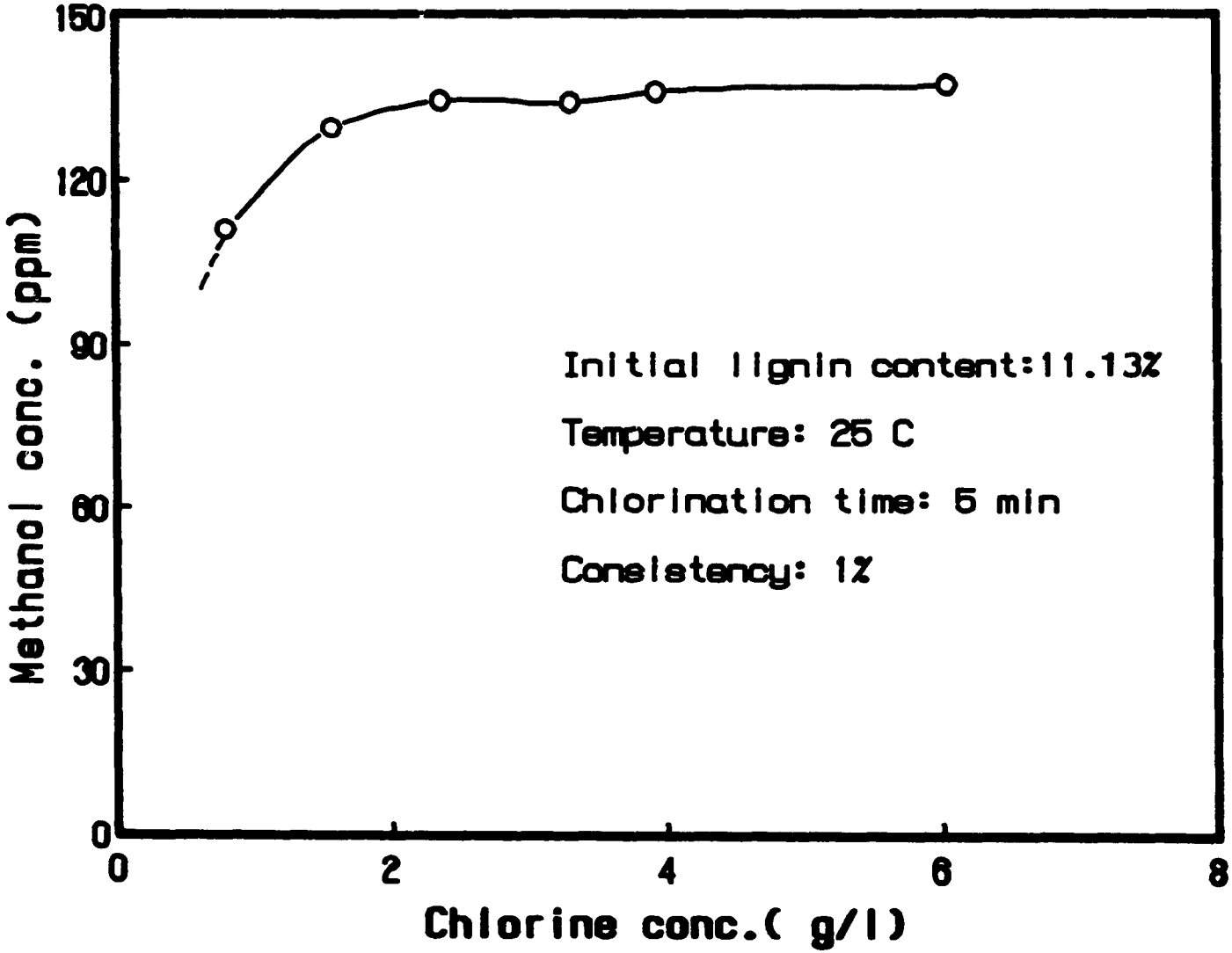
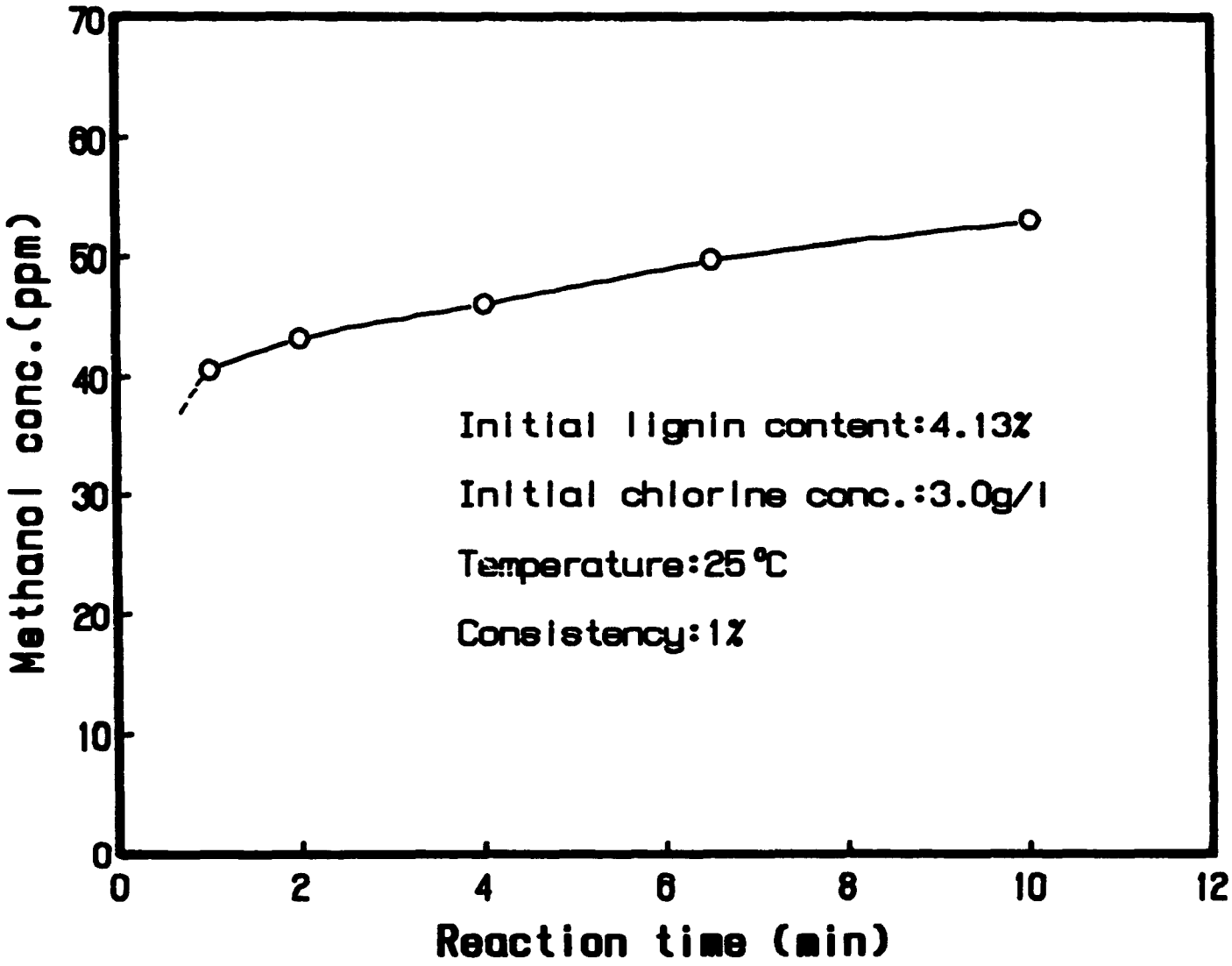

150
120
90
60
30
0
Methanol conc. (ppm)
0
2
4
6
8
Chlorine conc.(g/l)
Initial lignin content:11.13%
Temperature: 25 C
Chlorination time: 5 min
Consistency: 1%

Fig.5-5 The influence of time on methanol production


Methanol conc.(ppm)
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
Reaction time (min)
Initial lignin content:4.13%
Initial chlorine conc.:3.0g/l
Temperature:25℃
Consistency:1%

was arbitrarily set at 5 minutes. This compares to reaction times for the Hypo number and Roe number of respectively 10 and 15 minutes. It should be noted that the present reaction time could be further reduced to about 2 minutes without incurring a large error since the mixing times associated with the start and end of the test procedure was only about 2 seconds. The mixing time was qualitatively determined by using coloured pulp dispersed in the pulp suspension. On the other hand, Berzins and Tasman (6) noted for the Kappa number determination that at 5 minutes reaction time, significant differences can be obtained by small errors in timing and differences in initial mixing rate. The reason for the lesser sensitivity to reaction time in the present test is probably related to the difference in reaction mechanism between permanganate oxidation and demethylation by chlorine.

Effect of reaction temperature

The effect of reaction temperature on methanol concentration is shown in Fig.5-6. The slope of the straight line fit of the data allows for correction of the Methanol number when temperature control at 25 °C is not available as:

$$\text{Methanol number} = \text{Methanol conc.} + (25-t)*0.45$$

where t is the test temperature in degree Celsius.

Relationship between Methanol number and lignin content

Shown in Fig.5-7 is the relationship between Methanol number and total lignin for kraft black spruce pulp, The initial total lignin content in pulp ranges from 3.05 to 11.63%. The data are very well correlated by the linear relationship:

Fig.5-6 The influence of temperature on methanol concentration

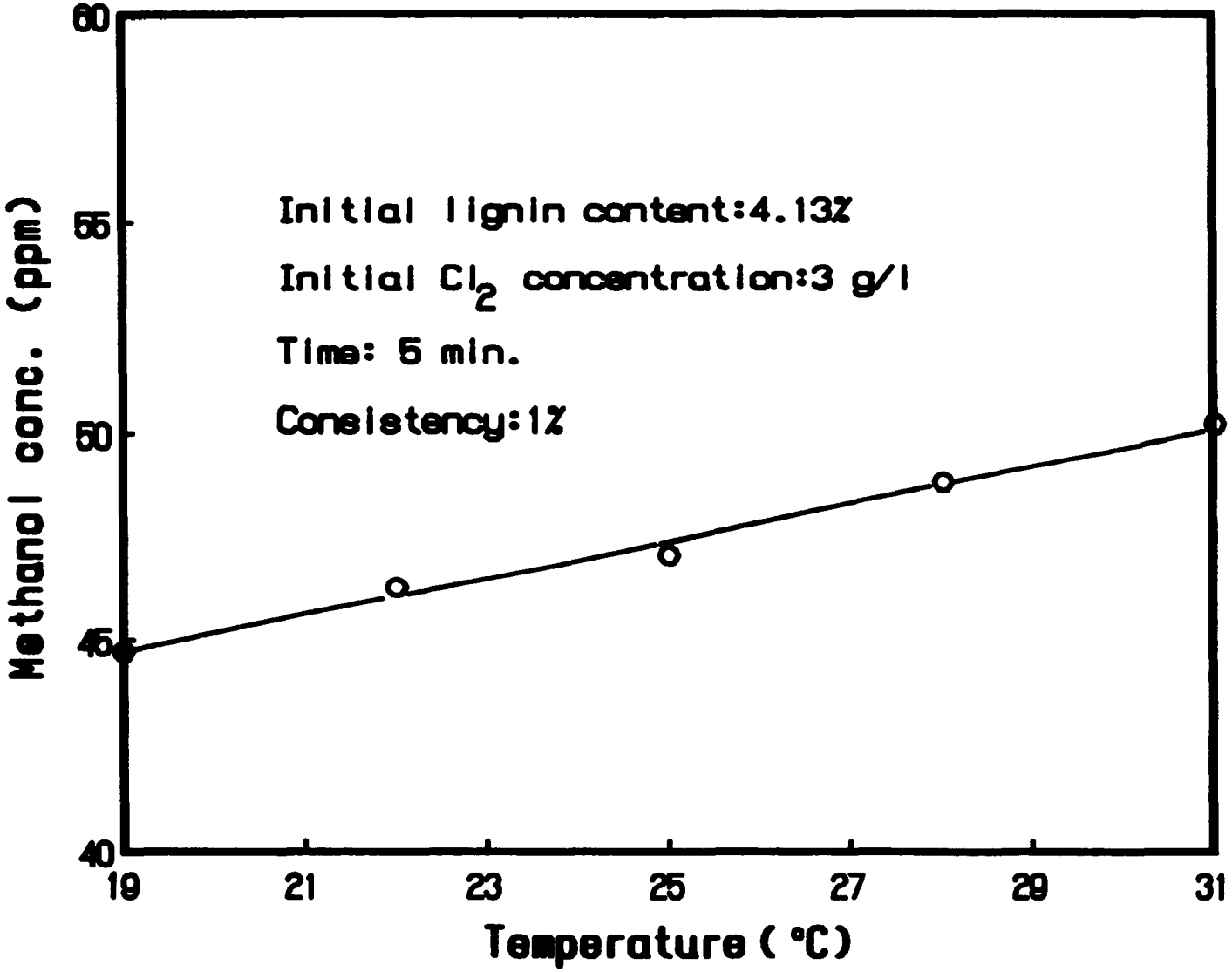
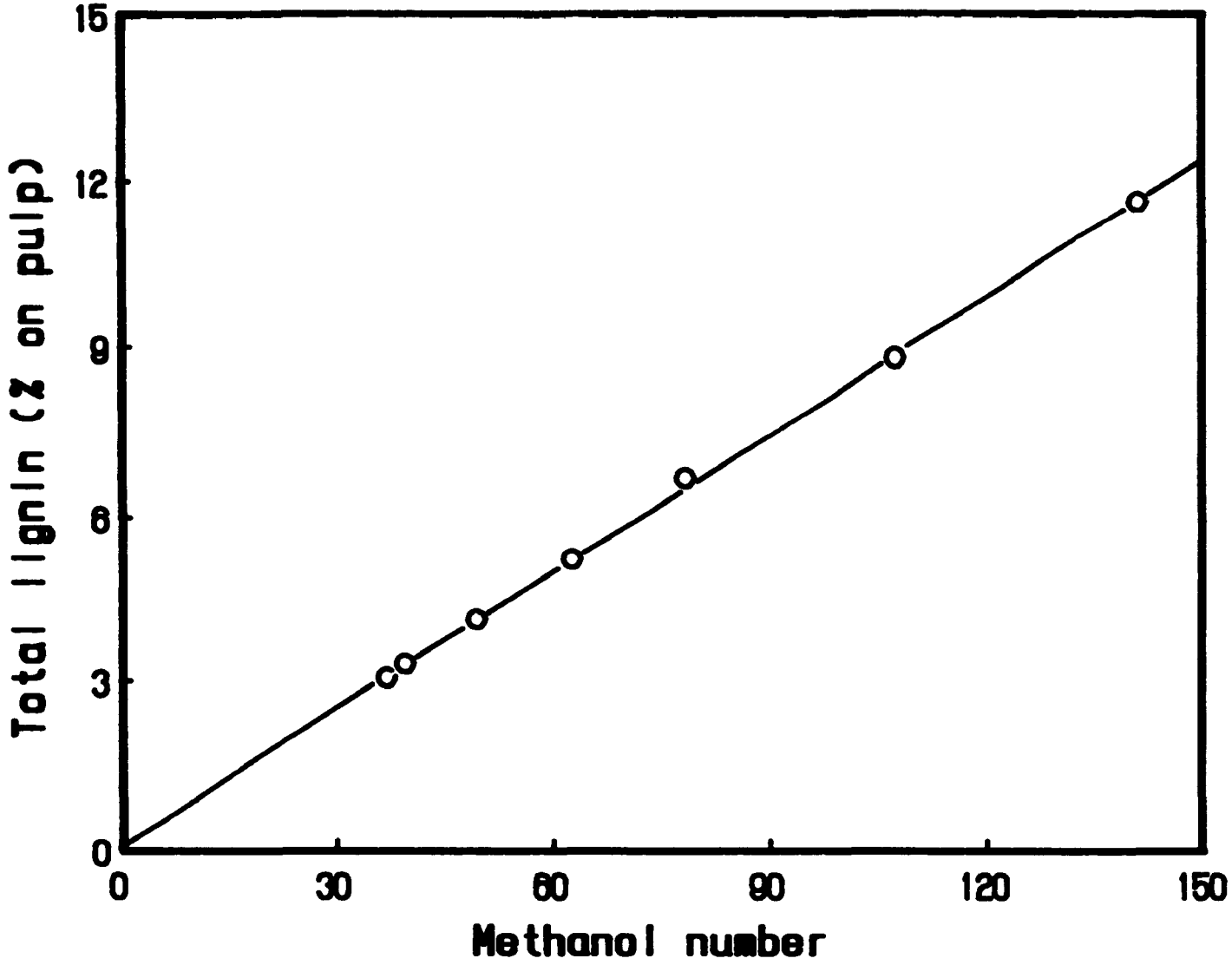

Initial lignin content:4.13%
Initial Cl_2 concentration:3 g/l
Time: 5 min.
Consistency:1%
Methanol conc. (ppm)
60
55
50
45
40
19
21
23
25
27
29
31
Temperature (°C)

Fig.5-7 Relationship between Methanol number and total lignin content


15
12
9
6
3
0
Total lignin (% on pulp)
0
30
60
90
120
150
Methanol number

$$\text{Lignin (\%)} = 0.07 + 0.0822 * \text{Methanol No.} \qquad (1)$$

It should be noted that within experimental error, this equation goes through the origin.

Fig.5-8 shows a comparison between the data of Figure 5-7 and the methanol concentration obtained with the same samples at a fixed chlorine charge factor of 0.68 but otherwise the same experimental conditions. It can be seen that the latter results closely agree with the data of Figure 5-7 obtained at chlorine charge factors varying from 0.383 to 1.47. This shows again that with sufficient large excess of chlorine, the Methanol number is independent of chlorine charge factor or chlorine concentration. Importantly, it removes the requirement for the Methanol number of using of chlorine water of very accurately known chlorine concentration. In order to test the Methanol number as method for determination of total lignin content, four new kraft black spruce samples were tested. Listed in Table 5-1 are the measured total lignin content and the lignin content calculated from the Methanol number by equation (1). The small differences of less than about 2% confirms the accuracy of the Methanol number test.

GENERAL DISCUSSION

The methoxyl group content of unchlorinated kraft pulp varies proportional to its total lignin content over a wide range of lignin content, as shown in Table 5-2. The last column shows that the weight ratio of methoxyl group to total lignin remains approximately constant at 0.143. This ratio corresponds to an OCH_3/C_9 molar ratio of 0.904 when a molecular weight of 196 is used for the lignin monomer units.

Fig.5-8 Sensitivity of Methanol number to chlorine charge factor and chlorine concentration

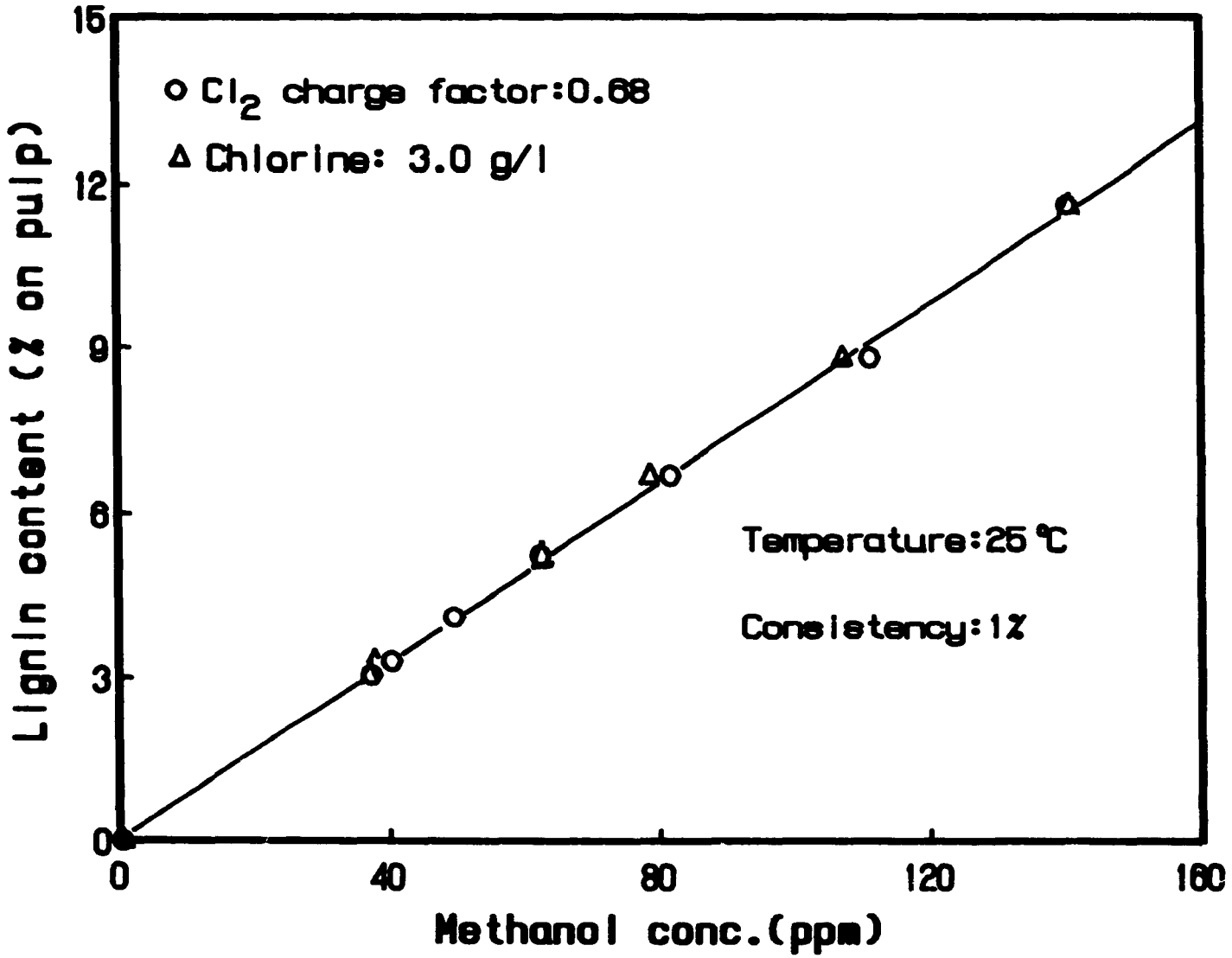

○ Cl_2 charge factor:0.68
△ Chlorine: 3.0 g/l
Temperature:25 ℃
Consistency:1%
Lignin content (% on pulp)
Methanol conc.(ppm)
0
3
6
9
12
15
0
40
80
120
160

Table 5-1 Accuracy of the Methanol number test

Methanol No. (ppm)	Total lignin content (%)		Difference (%)
	Calculated	Measured	
136.6	11.30	11.18	+1.06
98.1	8.13	8.11	+0.25
65.5	5.45	5.58	-2.38
37.8	3.18	3.16	+0.63

Table 5-2 Relationship between methoxyl group content and total lignin content of kraft pulp

Methoxyl (mg/g pulp)	Klason lignin (% on pulp)	UV lignin (% on pulp)	$\frac{OCH_3}{\text{total lignin}}$
1.82	11.74	0.29	0.151
1.34	8.70	0.32	0.149
0.93	6.38	0.32	0.140
0.71	4.91	0.32	0.137
0.45	2.97	0.34	0.139
0.42	2.70	0.34	0.140

In chapter 4, it was shown (Figure 4-2) that all methoxyl groups removed during kraft pulp chlorination are converted into methanol. It was also shown in Figure 3-2 that the methoxyl group content of "floor level" chlorinated kraft pulp is linearly related to its chlorine-free lignin content. Since the Methanol number test gives a linear relationship between total lignin content in unchlorinated pulp and methanol produced, all these results suggest that the "floor level" lignin content is approached in the Methanol number test.

The influence of temperature on the Methanol number can be explained by the results of chapter 4 that with increasing temperature, demethylation is favored over substitution and a lower lignin "floor level" is obtained.

The results given here were obtained with black spruce kraft pulp. In order to make the Methanol number more suitable as a method for total lignin analysis and perhaps develop it into an alternative test for the Kappa number, further work needs to be done, such as:

(1) to establish the total lignin - Methanol number relationship, for both softwood and hardwood pulps, and for pulp types prepared by different pulping process. It is anticipated that the relationship between Methanol number and lignin content will be very different for hardwood and softwood pulps because of the larger methoxyl content of lignin in hardwood.

(2) to shorten the reaction time to 2-3 minutes so that the method truely can be characterized as a fast test.

(3) to use hypochlorite for chlorine generation instead of using chlorine water,

(4) to use standard glassware to simplify the execution of the test.

CONCLUSION

A relatively simple method has been developed for determination of total lignin content of kraft black spruce pulp. This method, called Methanol number, relies on determination by gas chromatography of methanol formed during chlorination of pulp for a short time at a relatively high chlorine charge factor.

The method is based on a linear relationship between chlorine free lignin and methoxyl content for both kraft pulp and chlorinated pulp, and on quantitative conversion into methanol of methoxyl groups removed during chlorination of kraft pulp.

With further development, the Methanol number also has potential as an alternative Kappa number test. The advantages compared to the Kappa number test are (a) elimination of titration (b) potential reduction of analysis time by a factor of 2 to 3 (c)accurately standardized solutions are not needed.

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CHAPTER 6

CONCLUSIONS

6.1 GENERAL SUMMARY

This thesis is dealing with the mechanism and kinetics of softwood kraft pulp chlorination.

A new chlorination mechanism is proposed for softwood kraft pulp based on experimental evidence that shows there is a close relationship between demethylation and delignification, and that the so-called "floor level" residual lignin consists mainly of polymeric material in which guaiacyl units have been tri-chlorinated.

It is proposed that chlorination involves two competing reactions: demethylation and aromatic substitution of chlorine. Demethylation is followed by cleavage of the adjacent 4-O-ether linkage under the activating influence of the just formed free phenolic group. Aromatic substitution of chlorine at the 6-, 5- and 2- positions deactivates demethylation and thus also delignification. Since lignin consisting of 2,5,6-tri-chloro guaiacyl units cannot be demethylated, these units qualify as "blocking groups" and support the chemical limitation theory to explain incomplete delignification during chlorination. These "blocking groups" are largely destroyed during caustic extraction and render lignin susceptible to delignification in the next chlorination step. Based on this mechanism and model compound studies in literature, a novel chlorination mechanism is also formulated for hardwood kraft pulp.

Two alternative routes can now be formulated which would allow complete delignification in one bleaching step:

(1) replace chlorine by another electrophilic reagent which

attacks the ether bonds, but is either not substituted in the aromatic ring or favors demethylation when substituted (for example -NO_2 group).

(2) modify the chlorination stage so that aromatic chlorine is removed again during chlorination. The latter route in essence proposes to combine the effect of chlorination and alkaline extraction in one step. The problem of course is to find a reagent or operating conditions whereby chlorine in the "blocking group" is hydrolyzed in an acidic aqueous solution.

Demethylation kinetics are developed based on the new delignification mechanism of kraft pulp chlorination. The kinetic equations show that demethylation and aromatic substitution of chlorine in lignin monomer units take place simultaneously at comparable rates. Demethylation and chlorine substitution of unchlorinated lignin monomer units are completed within the first few seconds. The corresponding reactions of mono-chloro lignin monomer units are slower but again one order of magnitude faster than those of the di-chloro lignin units. Tri-chloro lignin monomer units are stable towards further chlorination or demethylation and form the so-called "floor level" lignin.

The demethylation kinetics give realistic prediction of the total organic chlorine content of both chlorinated pulp fibers and chlorination effluent produced in a conventional chlorination stage with low ClO_2 substitution. Further evaluation of the kinetic equations suggests that:

(a) the lower "floor level" lignin content with increasing temperature is caused by increased demethylation compared to aromatic chlorine substitution

(b) the combined chlorination and extraction effluent is less toxic when Cl_2 is added first in the chlorination stage before ClO_2

(C) the residence time in chlorination towers with low ClO_2 substitution can be reduced by a factor of 5 per 20 C temperature increase.

The present kinetics also give a mechanistic basis for the recent finding that Cl_2 should be added first at a low chlorine charge factor before addition of ClO_2 to prevent dioxin formation during kraft pulp chlorination.

Finally a new and relatively fast method to determine lignin content in kraft black spruce pulp has been developed, based on conversion of methoxyl groups in lignin to methanol by elemental chlorine. The method is called "Methanol number" and defined as methanol concentration in units of ppm produced during five minutes of chlorination at 25 C, 1% consistency, and an initial chlorine concentration of 3.0 g/l.

With analysis of the methanol concentration by gas chromatography, the total analysis time is approximately 7 minutes.

The Methanol number and lignin content of kraft black spruce are linearly related over a range of total lignin of 3.05% to 11.63% as

$$\text{Lignin (\%)} = 0.07 + 0.0822 * \text{Methanol No.}$$

Temperature deviations can be accounted for by the expression:

$$\text{Methanol No.} = \text{Methanol conc.(ppm)} + (25-T) * 0.45$$

where T is the temperature in degree Celsius

The Methanol number is relatively insensitive to deviations from

the specified initial chlorine concentration of 3.0 g/l.

6.2 CONTRIBUTIONS TO KNOWLEDGE

1. Demethylation and delignification are closely related during pulp chlorination. Removal of a methoxyl group from the lignin structure precedes dissolution of lignin fragments. Demethylation is the rate determining step for the delignification process.

2. Substitution of chlorine into the lignin structure competes with demethylation and thus delignification during chlorination of softwood pulp. Substitution is mainly taking place in the aromatic ring instead of the aliphatic propane unit of lignin and does not contribute to dissolution of lignin. The "floor level" lignin content is associated with the so-called "blocking groups" which are identified as 2,5,6-tri chloro guaiacyl monomer units. The identification of the "blocking groups" strongly supports that chlorination of pulp is chemical reaction limited rather than diffusion controlled.

3. One of the functions of caustic extraction is to remove the substituted chlorine in the "blocking groups". This renders the CE pulp susceptible to further delignification during a subsequent bleaching stage.

4. A new chlorination mechanism is formulated for hardwood kraft pulp.

5. Demethylation kinetics have been developed for chlorination of kraft Black Spruce pulp.

6. A method to predict TOCl in chlorinated pulp fibers and chlorination effluent has been developed and tested.

7. A mechanistic basis has been provided for the recent finding that Cl_2 should be added first at a low chlorine charge before addition of ClO_2 to prevent dioxin formation during kraft pulp chlorination.

8. The residence time in chlorination towers with low ClO_2 substitution can be reduced by a factor of 5 per 20 °C temperature increase.

9. A fast determination method of pulp lignin content was developed based on formation of methanol from methoxyl groups in the lignin structure during chlorination.

6.3 RECOMMENDATIONS AND SUGGESTIONS FOR FURTHER WORK

1. to test the proposed chlorination mechanism for hardwood kraft pulp.

2. to establish the molecular weight distribution of dissolved lignin during chlorination of pulp in a batch and displacement reactor.

3. to replace chlorine by another electrophilic reagent which attacks the ether bonds, but is either not substituted in the aromatic ring or favors demethylation when substituted (for example -NO_2 group)

4. to modify the chlorination stage by adding another reagent or changing the operating conditions so that aromatic chlorine is removed again during chlorination.

5. to study the delignification mechanism and kinetics of pulp bleaching with ClO_2 or ClO_2/Cl_2 mixtures.

6. to study the TOCl formation rate and mechanism during pulp bleaching with ClO_2 and ClO_2/Cl_2 mixtures in a batch and displacement reactor.

7. to develop kinetic equations of methanol formation which can be used for control of industrial pulp chlorination.

8. to generalize and simplify the Methanol number test by:
   a. establishing the relationship between total lignin content and methanol number for different coniferous and deciduous wood species, and for pulp types prepared by different pulping processes.
   b. studying the effect of consistency on the methanol number.
   c. shortening the reaction time to 2-3 minutes.
   d. reducing the total volume of the 1% consistency pulp suspension to 100 ml so that the pulp sample weight can be

reduced to 1 gram.

e. using hypochlorite to produce elemental chlorine.

f. making the methanol number procedure more practical by:

- employing an erlemeyer flask instead of a 3 neck flask
- first dispersing 1 gram of air dried pulp in a erlemeyer
- using hypochlorite rather than chlorine water
- reducing the reaction time to 2 to 3 minutes

APPENDIX

LITERATURE REVIEW

1. INTRODUCTION

Bleaching is an important process step in the production of bleached pulp and it can also be qualified as an extension of the pulping stage in which the remaining lignin in pulp is selectively removed. The pulp brightness is a function of the amount of lignin remaining in pulp. A typical softwood species contains about 29% lignin, of which 24% is removed in the pulping process and the remainder is removed in the bleaching process.

The bleaching process consists of two steps, delignification and oxidation (or brightening). At present, the most common commercially used delignification agent is chlorine, mainly because of its relatively low cost and high selectivity for lignin.

2. CHLORINATION

When chlorine is dissolved in water, the following equilibrium is established:

$$Cl_2 + H_2O \rightleftharpoons HClO + HCl$$

The composition of the solution depends upon the pH. When the pH is low, the equilibrium moves to the left side, and molecular chlorine is the dominant species. On the other hand, if the pH is relatively high, hypochlorous and hydrochloric acids are the dominant components of the solution. Because molecular chlorine is preferred in the chlorination stage, the pH of the system is kept low, usually at about 2.

Lignin is a random cross-linked three dimensional polymer. The common repeating units in softwood and hardwood are the guaiacyl

unit and syringyl unit respectively. The main difference of the two lignin units is that the syringyl structure contains an extra methoxyl group in the 5- position of the aromatic ring. The exact chemical structure of lignin is not exactly known, and small differences are expected among different softwood species. Another complicating factor is that lignin remaining in the fibers after pulping is greatly modified.

Among the numerous reactions between chlorine and lignin, substitution and oxidation predominate. The chlorinated pulp also obtains a characteristic yellow colour due to formation of quinones (1,2). Model compound studies have helped considerably to understand the chlorination process.

Chlorine substitution includes the following two types of reactions:

(1) substitution on the aromatic ring at sites 2, 5, and 6, with preference of substitution site 6>5>2.

(2) electrophilic displacement of the propyl side chain resulting in substitution of chlorine at site 1

Electrophilic displacement may be restricted to such cases where excess chlorine remains after complete substitution of the reactive aromatic sites (3).

It is believed that the organically bound chlorine present in pulp is mainly due to aromatic substitution of chlorine(4,5). The average ratio of substituted chlorine to lignin monomer unit was reported as 0.75 to 1.5 (6). Berry and Fleming found 1.5 to 2.0 Cl/C9 for alkali extracted chlorinated pulp (7).

The main oxidation reactions are:

(1) rupture of interunitary ether linkage, resulting in the

formation of o-benzoquinones (8)

(2) hydrolysis, and cleavage of methoxyl groups, forming methanol (9,10)

(3) oxidation and degradation of unstable o-benzoquinoid structure through a complex series of reactions (11)

(4) oxidation of the propyl side chain liberated by electrophilic displacement

In summary, oxidation is most likely to be the reaction that solubilizes the lignin. Other authors (5,12) claimed that solubilization is due to substitution (5,12). Oxidation reactions degrade lignin and chlorolignin to varying degrees of solubility by providing products of lower molecular weight (1).

3 DEMETHYLATION DURING CHLORINATION

Various opinions have been expressed concerning the nature of the demethylation reaction in aromatic methyl ethers. It has been suggested (13) that chlorine substitution in the aromatic ring may make the methoxyl group more susceptible to oxidative degradation. Another explanation (14) by Ivancic and Rydholm is that the demethylation may be due to an acid-catalyzed hydrolysis of the methoxyl group. Sarkanen and Dence (15) concluded that demethylation by chlorine water is essentially a hydrolytic cleavage of the ether bond, catalyzed by molecular chlorine. They proposed two mechanisms for the demethylation reaction. Firstly, molecular chlorine, by virtue of its strongly electrophilic character, may play a role similar to a proton in an acid-catalyzed hydrolysis. Secondly, attack of a chlorine molecule at the position para to the methoxyl group, resulting in the

formation of the quinone-like intermediate. A free phenolic group is then formed at the original methoxyl position, with simultaneous generation of methanol and regeneration of molecular chlorine. However, in a later paper (9), Sarkanen and Strauss concluded that the attack of the polarized chlorine molecule at the position para to the methoxyl group seems less probable because there is no major effect on the demethylation rate whether the group para to the methoxyl group is chlorine or an aldehyde group.

Sarkanen and Dence (16) also noted that the demethylation reaction appears to be rapid only in aqueous or partially aqueous media, and that no oxidative mechanism is involved in the demethylation. On the other hand, van Buren and Dence (17) concluded that a substantial fraction of demethylation is the result of oxidation (oxidative demethylation).

Sarkanen and Strauss (5) found that the lignin model compounds, 4,5-dichloroveratrole and 6-chloroveratraldehyde can be demethylated for 80 to 85% in a few minutes, while 3,4,5,6-tetrachloroguaiacol and 3,4,5-trichloroveratrole are only 55 to 60% demethylated. However, 2,4,6-trichloroanisole and 3,4,5,6-tetrachloroveratrole do not undergo any demethylation. For spruce wood meal, lignosulfonic acid and softwood kraft lignin, they found that the major fraction of methanol is liberated during the first few minutes. Although chlorination of spruce wood meal takes place in a two phase system, demethylation is still very rapid, indicating that accessibility is not a major factor. Even though kraft lignin is considered to be highly condensed, methanol formation is still very quick. This is presumably because kraft

lignin contains more phenolic groups, and their presence will facilitate demethylation.

Satσ and co-workers (18) published data on the amounts of methanol liberated during the chlorination of spruce and beech, lignosulfonic acid, hydrochloric acid lignin. Their results are in general agreement with levels of demethylation observed by Sarkanen and Strauss.

The degree of demethylation is dependent on the chlorine dosage. van Buren and Dence (6), using pine kraft pulp (Kappa number 32.8, Klason lignin content 4.7%), performed chlorination at 3% consistency and 24 C for an hour in a sealed glass reactor to investigate the methanol formation using varying amounts of chlorine applied. The results showed that the amount of chlorine causes almost a proportional increase in methanol production. Approximately 70% of the methoxyl groups are removed when 5% of chlorine based on pulp is applied, i.e. at a level approaching that of conventional pulp chlorination. They also used lignin model compounds such as veratryl ethyl carbinol and guaiacyl ethyl carbinol to investigate their behavior during chlorination. It was found that with 1 mole of chlorine addition per mole of guaiacyl ethyl carbinol, 30% of the methoxyl content is recovered as methanol. On the other hand, with application of 1 mole of chlorine per mole of veratryl ethyl carbinol, only 10-15% of the methoxyl groups is recovered. The reason is likely that guaiacyl ethyl carbinol has a free phenolic hydroxyl group, while veratryl ethyl carbinol does not.

In summary, when lignin or lignin model compounds are subjected to chlorine, a substantial amount of methanol is formed.

From the references in literature, it appears that the demethylation reaction is initially very fast, followed by a much slower production of methanol in the later stage of the reaction. Given sufficient time for reaction, the total amount of methanol produced increases almost linearly with chlorine addition. However, complete demethylation is not necessarily achieved when an excess of chlorine is added. The extend of demethylation increases with increasing content of free phenolic groups on lignin or lignin model compounds.

4 LIGNIN "FLOOR LEVEL"

It has been recognized for a long time that pulp cannot fully be delignified in one chlorination stage. Even with an excess of chlorine after several days of contact, some lignin still remains (7). Further delignification can be achieved in a second chlorination stage only after alkaline or hot water extraction. However, chlorination again initially proceeds very rapidly, and stops before complete delignification (7). The concept of a limiting or "floor level" CE Kappa number has been described in a number of references (19,20,21). Mackinnon (22), recently proposed a linear relationship between the CE "floor level" lignin content and the lignin content of unbleached pulp in an attempt to simulate the chlorination and extraction stage of a kraft bleach plant.

Basically, two hypothesis have been proposed which can explain the existence of 'floor level' lignin. The first one, postulated by Karter and Bobalek (23), is based on the idea that a layer of chlorinated lignin is formed starting in the P and S layers of the

fibers. The so-called "immobilized chlorolignin" layer gradually becomes impermeable to chlorine and unreacted lignin remains behind the barrier. In a refined version of this model, Pugliese and McDonough (24) recently proposed that the chlorolignin barrier is formed in small lignin-containing grains distributed uniformly throughout the fibers. These two models can be called physical limitation models since diffusion of chlorine is the rate determining step. Berry and Fleming (7) on the other hand, proposed a chemical model whereby alkali-labile "blocking groups" formed during chlorination only allow very slow reaction between chlorine and residual lignin. As potential candidates for blocking groups they selected chloro-quinones and chlorocarboxylic acids, based on the fact that significant amounts of carbon dioxide and chloride are liberated during hot water extraction of chlorinated pulp. Another physical model was proposed by Rapson and Anderson (25) that chlorine transport external to the fiber is the rate determining step. However, this model cannot explain the existence of a lignin "floor level". Hibbert and his students (13) in 1941 concluded that chemical factors control the chlorination rate because they found that the kinetics of insoluble lignin residue in cellulosic pulp and soluble lignosulphonic acids are the same.

5. KINETIC STUDIES

Chlorination kinetics has been the subject of numerous studies.

Chapnerkar (19) performed experiments with kraft pulps containing initial lignin contents of 5.65% and 11.5%. He considered a model incorporating instant removal of a fraction of

lignin, followed by two consecutive reactions, both first order in lignin.

Russell (26) studied the chlorination of kraft pulp meal in a tubular reactor, at reaction times of less than one minute. His results were described by the following rate expression:

$$-dL/dt = k' L^a$$

$$k' = k f"[C]$$

where k' is the pseudo rate constant and reaction orders "a" varied between 1.6 to 2.0. The pseudo rate constant was found to depend strongly on chlorine concentration over the first 25% of delignification.

Karter (23) studied the chlorination kinetics during the first 2.5 minutes. He considered a heterogeneous model and found that the unreacted core model using non-Fickian diffusion: $D_{eff}=D_o(\frac{r}{R})^n$ could describe his experimental chlorination rate during the first minute.

Ackert (27) tested four homogeneous and three heterogeneous models against his experimental data for varying chlorine charges and temperatures. The heterogeneous models included two shrinking core models: one reaction controlled, another diffusion controlled. The third model considered external mass transfer, diffusion of chlorine in the fiber, and chemical kinetics. All three models gave poor fits, and were rejected. In the four homogeneous models, he assumed that only active lignin, or total lignin minus "floor level" lignin, participated in the reactions. He found that two models which incorporated series or parallel reactions best fitted his data. Because of its simplicity and the similarity with the long standing view of chlorination as a rapid

substitution and slow oxidation, the two parallel reaction model was preferred by Ackert. The final form was:

$$-dL_1/dt = fk_1 L_1 C$$

$$-dL_2/dt = fk_2 L_2 C$$

$$dL_1/dt + dL_2/dt = dL/dt$$

$$L_1 + L_2 = L - L_f$$

The most recent chlorination kinetics study was performed by Mackinnon (22). He represented the chlorination kinetics by two parallel non-linear reactions. Mackinnon suggested different stoichiometries for the "fast" and "slow" reactions:

$$-dL_1/dt = k_1 L_1^e C^f$$

$$-dL_2/dt = k_2 L_2^g C^h$$

$$dL_1/dt + dL_2/dt = dL/dt$$

$$L_1 + L_2 + L_f = L$$

The most serious weakness of the reference studies is that the kinetic equation were selected based on their ability to represent the data rather than on fundamental understanding of the chlorination mechanism.

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