A KINETIC STUDY OF THE CHLORINATION OF UNBLEACHED KRAFT PULP

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INTRODUCTION

The main object of bleaching pulp is to remove the incrusting substances which cause discoloration and thus obtain a white pulp. The sources of Kraft color are tannins and phlobaphenes, sulfur dyes, lignin and its reaction products, the carbohydrate degradation products and the condensation product of tannins and alkali-labile carbohydrates. The color is mainly due to the oxidation or condensation products of phlobatannin and lignin and its derivatives. It has been shown that the brightness of the pulp increases with decrease in lignin content of the pulp, and the amount of bleach required by the pulp to attain a fixed brightness is also a function of lignin content of the pulp (1). In case of sulfite pulp, the colored impurities appear to consist entirely of lignin compounds (2).

The bleaching process is really a continuation of the pulping process in which it is a matter of converting the lignin products into water soluble form. This process must be carried out as gently as possible so that the carbohydrate is not attacked; if it were, the strength would be decreased in the case of paper pulp, while the rayon pulp would show irregular decreases in viscosity and in \( \alpha \)-cellulose content (3). If an attempt is made to remove most of the lignin in the pulping process, it has been
noticed that more and more holo-celluloses are hydrolyzed and hence lower yields are obtained (4) and also the D. P. (Degree of Polymerization) number is decreased. Hence, recent trends in the development of the bleaching techniques have therefore been to adapt the bleaching conditions in such a way that the attack on cellulose constituents is minimized, or to introduce new bleaching agents with such properties that only the lignin compounds, and, if necessary, the other discoloring matters, are attacked while the cellulosic material is left intact.

Chemical constituents of sulfate pulp indicate that it is a pure form of wood cellulose (5) and capable of high yields of white fibrous and resistant materials. Most of the action of cooking is to reduce bleach consumption and not to dissolve and degrade the cellulose. Modifications in bleaching methods give promise of greater results than modifying cooking methods. Modifications in which the bleaching operation is two or three stages, with washing between stages, can cut the bleach requirements considerably. Pulps of better quality, both from physical and chemical considerations, can be obtained by cooking the wood as little as possible in isolating the fibers and by accomplishing as much of the burden of purification in the bleaching and washing operations. The degree of purification is however limited by economic considerations.
Chlorine had been found to be quite selective in its action on lignin, and does not attack the cellulosic matter in the pulp to any appreciable extent. But, the main obstacle in the use of chlorination as a step in the bleaching process was the difficulty, until recently, of the handling of liquid chlorine. Moist chlorine is very corrosive and hence ordinary materials of construction could not be utilized to fabricate the chlorination equipment. But, now with the help of the development of certain alloys and various corrosion resistant coatings, it is possible to handle moist chlorine quite effectively. It was only in 1909 that liquid chlorine in steel cylinders appeared on the market. Hence, nowadays more and more Kraft pulp is being bleached. Earlier, the main use of Kraft pulp was to make unbleached paper or paperboard, as it was found to be very difficult to bleach with hypochlorite without severe degradation of the fiber.

Since chlorine was first used by A. Payen in 1839 (6) to delignify plant tissue, an enormous amount of experimental work has been carried out in an attempt to understand better the mechanism of the reactions involved. Because of the lack of knowledge of the chemical structure of lignin and its relationship to the carbohydrates in the fiber, as well as the inherent complexity of aqueous solutions of chlorine, progress has been slow.
In industry, chlorination of pulp is accomplished at about 3 to 3 1/2 per cent consistency, with the addition of chlorine amounting to 60 to 65 per cent of the test bleachability. The chlorine is either added as a gas or as solution in water. The time of reaction is usually one hour and the temperature is usually the prevailing seasonal temperature of the mill water. Chlorination is either carried out batchwise or continuously. Continuous chlorination is carried out in a retention tower of sufficient capacity to allow about one hour of retention time. The chlorinated pulp is washed with water in order to remove the chlorinated products which have been rendered water soluble. The washing is followed by hot alkaline extraction. Alkaline extraction is carried out at 10 to 12 per cent consistency for about one hour at about 60°C. The amount of sodium hydroxide added is about 1 to 2 per cent of the weight of the pulp. The alkaline extracted pulp is later washed with water and is further treated with either chlorine, hypochlorite or chlorine dioxide, depending on the end use of the pulp.

The purpose of this investigation is to study the mechanism of the removal of lignin in the chlorination of unbleached Kraft pulp. Although there are many variables which could be considered, attention is mainly concentrated on chlorine concentration, time and temperatures. An attempt is also made to determine the effect of higher pulp
consistency on lignin removal and the degradation of the cellulose, as well as the effect of amounts of chlorine consumed by substitution and oxidation on lignin removal and the degradation of the cellulose.
CHAPTER I

LITERATURE REVIEW

A far reaching change in the character of the bleaching industry commenced in the year 1787. In that year chlorine, discovered by Scheele in 1773, was used in the works of Macgregor, of Glasgow, where its application had been suggested by James Watt. Watt had gained his information about oxygenated muriatic acid, as chlorine was then called, from Berthellot, who was the first to record the effect of the gas in bleaching the natural color of linen. In a paper read before the Academy of Sciences in Paris in 1875, Berthellot mentioned that he had found the gas to be perfect in the bleaching of cloth. At this period, the bleacher made his own chlorine and exposed the fabric in chambers to the action of the gas, or steeped them in the aqueous solution. The process was inconvenient, disagreeable, and, worst of all, detrimental to the health of the workers, so it was not surprising that in spite of the rapid bleaching action the method did not gain great favor.

Chlorination as a step for the bleaching of wood pulp had been first suggested by Watt and Burgess (7), who obtained a United States patent in 1854, for a process in which wood pulp produced by the soda process was first
chlorinated and subsequently bleached with hypochlorite. But the chemistry of chlorination of the cellulosic materials was apparently investigated first by Cross and Bevan (8) during the latter part of the nineteenth century.

There are no further references to the commercial application of chlorination of pulp in the literature until 1913, when a patent was granted to DeVains (9). This was mainly due to the difficulty of handling chlorine. It was only in 1909 that chlorine was available on the market in steel cylinders. DeVains' patent was for bleaching Kraft pulp in two stages in which chlorination was the first stage. Cataldi (10) obtained a patent in 1916 for the bleaching of straws and grasses, the first stage of which was chlorination. Drewson (11) obtained a patent in 1918 for the bleaching of pulp for nitration in which the first step was chlorination.

E. Oppermann (12) had made laboratory study of the method of DeVains and Peterson in which the pulp was first bleached with chlorine gas, washed with alkali, and then bleached with bleaching powder. The cost varied, as compared with the use of bleaching powder alone, but it averaged 60 to 70 per cent of the older method. The author was of the opinion that the older method might be improved if the process were carried out in steps and the products washed with alkali as an intermediate step.
During the period from 1921 many attempts were made to chlorinate the pulp continuously and at higher consistencies. Hayward (13) bleached pulp at 20 per cent consistency and showed that the pulp used 25 per cent less bleach at 20 per cent consistency than that at 5 to 6 per cent consistency. The failure of the commercial application of this process was attributed to the fact that the chlorination reaction is very rapid. This rapidity of the reaction presents the difficulty of proper control of overheating caused by the heat of the reaction, and the action of hydrochloric acid formed on the cellulose. Hence, the cellulose thus obtained would be degraded.

C. E. Curran and P. K. Baird (14) gave results of their experiments which showed that the rate of bleach consumption appeared as a linear function of the logarithm of the time during the main course of the reaction and probably within temperature limits of zero to 50°C. Hibbert and Taylor (15) found that between wide limits, the rate of bleaching was independent of the concentration of the hypochlorite. They also described the chemistry of the reactions involved in the chlorination of pulp. Hisey and Koon (16) studied the bleaching action in solutions buffered at pH of the solutions from 0.9 to 12.5 and found that the reaction velocity was greatest in the strongly acid solutions, and decreased steadily as the pH of the solutions was raised. Carmody and Mears (17) bleached samples of pulp with
chlorine solution under conditions of constant hydrogen ion concentration. Combining their data with that of Hisey and Koon, they made an analysis of the mechanism of the reactions involved. Two separate and distinguishable reactions were noted, (a) a very fast reaction, the rate of which was proportional to the first power of the "active lignin" concentration, and (b) a much slower reaction of the second order involving "inactive lignin." In alkaline solution both of these reactions were entirely oxidation, while in acid solution they appeared to be mixtures of oxidation and chlorination. Study of the amounts of the "active lignin" for runs at several hydrogen ion concentrations indicated that sixteen units or molecules of chlorine unite with one unit or empirical molecular weight of lignin.

Arnold, Simmonds and Curran (18) determined that chlorination of sulfate pulp was exothermic. Direct exposure to sunlight or oven drying caused decomposition of cellulose, but when air dried at room temperature out of direct sunlight, no decomposition was noticed. They also indicated the presence of carboxyl group in chlorinated lignin and that part of the chlorine was lost upon treatment with an alkaline solution.

Larson (19) in 1941, showed that chlorination of pulps splits methoxyl groups from lignin; the greater the degree of chlorination, the greater the loss of methoxyl group. Caustic extraction of the residues from chlorination waste
liquors apparently had no effect on the methoxyl content, but when chlorinated pulps were extracted, the lignin with the lowest methoxyl content was removed.

About the same time, Hibbert, McCarthy and others (5) concluded from kinetic measurements that the rate of chlorination is similar with both soluble lignosulfonic acid and insoluble lignin resided in the pulp, thus indicating that diffusion of the halogenating reagent plays a minor part in the actual chlorination and subsequent reactions. However, the physical phenomena of diffusion and dissolution are of considerable importance in the removal of potentially soluble lignin from cellulose fibers. As evidence for this, it was apparent that the amount of residual lignin depended very markedly upon the temperature and time of alkaline washing.

Hedborg (20) studied the chlorination of sulfate pulp and the succeeding treatment with alkali. The course of different processes was followed by the determination of permanganate consumption and the viscosity of the pulp. He studied the effect of chlorine concentration and temperature on the rate of lignin removal. Several other investigators (21, 22) also studied the effect of temperature of chlorination on the extent of pulp degradation.

The reaction kinetics of chlorine cleavage from chlorinated lignin in water and sodium carbonate solution
was studied by Jan Pokin (23). He found that the chlorine is bound to aliphatic groups and its degree of reactivity depends on the carbon to which it is bound and on the functional side groups.

Grangaard (24) indicated that upon the addition of an excess of chlorine to an unbleached pulp, the consumption by the oxidation reaction amounted to 40 to 70 per cent of the total chlorine consumption. In fact, for the pulps of low permanganate numbers, the consumption of chlorine might be entirely by oxidation reaction. On chlorinating pulps in 0.1 normal sulfuric acid, in contrast to a pulp where the acidity was solely the result of the action of chlorine water, a slight decrease in the consumption of chlorine by oxidation, together with a slight increase in the consumption by substitution, occurred. Lowering the temperature also decreased the consumption of chlorine by oxidation without appreciable change in the consumption by substitution. It was shown that the lignin solubilization which occurs as a result of chlorination might be the result of the consumption of chlorine by oxidation rather than by substitution. It was indicated that, during the chlorination reaction, it was not so much the question of getting the chlorine to the lignin as it was of getting the chlorinated products out of the pulp.

Kress and Davis (25) studied different chlorination,
alkali extraction and hypochlorite bleaching stages with different variations. They concluded that the resulting pulp hydrates too rapidly and hence makes tinny sheets; alkali extraction in between stages raises strength, and use of alkali in chlorination stage was not beneficial. Several investigators have studied the merits of combinations of different bleaching stages.

Sprout and Toovey (26) working with sulfate and sulfite pulps observed that these pulps were most effectively and economically bleached when chlorinated to an optimum degree which was characteristic of the pulp. They showed the necessity of alkaline extraction between two chlorination stages. It was also indicated that a three-stage chlorination procedure employing recycled chlorination liquors for sulfate pulp bleaching had afforded reduction in operating time as well as in cost of bleaching chemicals over a single stage chlorination bleach and, to a lesser extent, over a two-stage chlorination bleach when producing pulps of comparable brightness and physical properties. Rapson and Anderson (27) proposed three stage bleachings. The first stage was chlorination with addition of little chlorine dioxide, the second stage was sodium hydroxide extraction with addition of a little of chlorine and the third stage was the treatment with chlorine dioxide.

Due to the recent development of methods to regulate automatically the addition of chlorine to the pulp with
the help of oxidation-reduction potential cell, uniform chlorination is accomplished (35). The automatic control compensates for the variations in brown stock entering the chlorination tower because of poor cooking, inefficient mixing, poor blending, tower channeling, temperature, etc., (36).
CHAPTER II

THEORETICAL CONSIDERATIONS

Although a large amount of experimental work has been done on the chlorination of pulp, in acid or alkaline medium, no exact analysis of the chemical reactions involved has been made. The problem is very complex, as there are many variables involved. The important variables in chlorination are:

1. The initial lignin content of the pulp.
2. Concentration of molecular chlorine in the bleaching solution.
3. Hydrogen ion concentration.
4. Concentrations of Hypochlorous acid, hypochlorite and chlorite ions. These are dependent on 2 and 3.
5. Time of chlorination.
6. Temperature of chlorination.
7. Consistency of the reaction mixture.
8. The origin of the pulp.

There is also the possibility of numerous reactions taking place simultaneously since each of chlorine, hypochlorous acid and hypochlorite ion may react in more than one way. The analysis of such a complex system of reactions would demand the acquisition of exact data from a series of experiments over a broad range in which each factor is
regulated or calculable from known relationships.

In commercial application, 5 to 8 are usually constant. Three and 4 are not controlled specifically, but are dependent on the concentration of chlorine and the equilibrium between chlorine and water.

In order to understand the mechanism involved in the reaction of chlorine in aqueous solution with pulp, consideration must be given to what happens when chlorine gas is dissolved in water. When chlorine gas is dissolved in water, the following reversible hydrolysis occurs:

\[ \text{Cl}_2 + \text{H}_2\text{O} = \text{HCl} + \text{HOCl} \]  

On the right hand side, there exists both hydrochloric acid and hypochlorous acid, one of which, namely, hydrochloric acid is strongly dissociated in dilute aqueous solution, while hypochlorous acid is comparatively little dissociated. Equation (I) may therefore be written as follows:

\[ \text{Cl}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{Cl}^- + \text{HOCl} \]  

The hydrolysis constant of this equilibrium was shown by Jakowkin (28) to be represented as follows at 25°C:

\[ K = \frac{[\text{H}^+][\text{Cl}^-][\text{HOCl}]}{[\text{Cl}_2]} = (4.84)(10^{-4}) \]  

From this value it is possible to calculate the amounts of the several constituents and the acidity of the
solution when increasing amounts of chlorine are dissolved in water. It can be seen from equation (II) that, as dilution is increased, the equilibrium shifts more and more to the right, and at very high dilution there can exist substantially no elemental chlorine in solution.

Hypochlorous acid also can ionize as follows:

$$\text{HOCl} = \text{H}^+ + \text{OCl}^-$$  \hspace{1cm} (IV)

and numerous evaluations of this ionization constant have been made. For example, Davidson (29) has found the following value at 18° C:

$$K = \frac{(\text{H}^+)(\text{OCl}^-)}{\text{HOCl}} = (3.7)\times10^{-8}$$  \hspace{1cm} (V)

It is apparent that the relative amounts of molecular chlorine, hypochlorous acid and hypochlorite ions existing in a given solution are markedly dependent upon the acidity of the solution. The composition at various values of hydrogen ion concentration of a solution is shown in Figure 1 (30). Below pH of the solution of 4.5, the hypochlorite ion disappears and the available chlorine is present in the form of molecular chlorine and hypochlorous acid. In this range of pH of the solution between 4.5 and 9, the activity of hypochlorite solutions of the same concentration
Figure 1.— The Distribution of Chlorine among Elementary Chlorine, Hypochlorous Acid, and Hypochlorite Ion in a Solution of Chlorine in Water at Various pHs.
of available chlorine are definitely dependent on the hydrogen ion concentration. The higher the hydrogen ion concentration of the liquor, the greater the activity, viz., concentration of molecular chlorine.

With this knowledge of the equilibrium of chlorine and water, the reactions between chlorine and organic compounds will be considered. It is known that chlorine reacts in absence of water with saturated organic compounds by direct substitution as follows:

\[ \text{RH} + \text{Cl}_2 = \text{RCl} + \text{HCl} \]  \hspace{1cm} (VI)

In this equation, R represents organic groups attached to the hydrogen atom, which is replaced by chlorine atom with simultaneous formation of one molecule of hydrochloric acid. With unsaturated compounds, two atoms of chlorine may enter the molecule at the location of the double bond, thus forming a saturated chlorine derivative according to the following equation:

\[ \text{Cl}_2 + \text{R}_2\text{C:C} = \text{R}_2\text{C} = \text{CClR}_2 \]  \hspace{1cm} (VII)

It has been found in the chlorination of pulp that the amount of chlorine used by addition should be neglected as there is no evidence of double bonds in the lignin molecule (31) which could be easily chlorinated.

Though equations (VI) and (VII) have been represented as applying in the absence of water, this is not
necessarily true (32). The hydrogen atoms located in readily replaceable positions in the molecule can be substituted by chlorine in the presence of water and, in many cases, chlorine will add to the double bond in the presence of water. In the presence of water, chlorine may also act as an oxidizing agent according to the following reactions:

\[ \text{RH} + \text{Cl}_2 + \text{H}_2\text{O} = \text{ROH} + 2\text{HCl} \quad (\text{VIII}) \]
\[ \text{RCH}_3 + 3\text{Cl}_2 + 2\text{H}_2\text{O} = \text{RCOOH} + 6\text{HCl} \quad (\text{IX}) \]
\[ \text{RCHO} + \text{Cl}_2 + \text{H}_2\text{O} = \text{RCOOH} + 2\text{HCl} \quad (\text{X}) \]

In the chlorination of pulp, it had been found earlier that 60 to 80 per cent of the chlorine reacts by substitution and the remainder by oxidation (30).

Possible Mechanisms and their Rate Equations:

Chlorination of pulp with chlorine water is an heterogeneous reaction. The system can be considered as consisting of fibers suspended in chlorine water, which is maintained at constant temperature. When the pulp is added to the chlorine water, the lignin and the other coloring bodies at the surface of the fiber react with the constituents of the chlorine water. At the same time, chlorine water diffuses and penetrates the inner layers and reacts with lignin in the inner layers.

From the standpoint of kinetics, a reaction occurring on a surface usually is regarded as involving the
following steps:

1. The transfer of the reactants and the products to and from the surface of the solid and main body of the fluid.

2. The diffusional and flow transfer of the reactants and the products in and out of the pore structure of the solid when reaction takes place at interior interfaces.

3. The activated adsorption of the reactants and the activated desorption at the solid-liquid interface.

4. The surface reaction of the adsorbed reactants to form chemically adsorbed products.

The rates of these four types of operations are dependent on widely different factors in addition to concentrations or concentration gradients (33). The rate of the overall reaction is dependent on the slowest step.

When temperature and all other conditions are maintained constant, the rate equation can be supposed to assume the following form:

\[- \frac{dL}{dt} = r = k ( L_o - L )^a ( C )^b \]  

(XI)

Where

\[ r = \text{instantaneous rate of lignin removal expressed lignin still remaining after a time, } t, \text{ per unit time,} \]

\[ L_o = \text{Original lignin content of the pulp,} \]

\[ L = \text{Lignin remaining after time, } t. \]

\[ C = \text{Concentration of elemental chlorine in chlorine water,} \]

\[ k = \text{Reaction velocity constant,} \]

\[ a \text{ and } b \text{ are also constants.} \]
If C were held constant throughout an experiment, equation (XI) can be written as:

\[ r = k \left( L_0 - L \right)^a \]  

(XII)

Taking logarithms of both sides of the equation (XII), we get:

\[ \log r = \log k + a \log (L_0 - L) \]  

(XIII)

According to equation (XIII), if r is plotted against \( (L_0 - L) \), on log-log paper, then a straight line should be obtained with slope equal to 'a' and intercept on the x-axis equal to \( \log k \). It has to be assumed that 'a' is constant and hence independent of the concentration of the chlorine water. If it is not so, then this approach cannot be applied.

From equations (XI) and (XII), it can be seen that

\[ k = k' (C)^b \]  

(XIV)

Taking logarithm of equation (XIV), we get

\[ \log k = \log k' + b \log C \]  

(XV)

Equation (XV), indicates that if k is obtained for each corresponding value of C, then with the use of this equation values of \( k' \) and \( b \) can be evaluated. If k is plotted against C on log-log paper, a straight line is obtained with slope equal to 'b' and intercept on the X-axis equal to \( \log k' \).
The exponent \( b \) can also be evaluated with the use of initial rates.

Another possible mechanism may be one in which the final reaction rate may be a combination of two or more simultaneous reaction rates. It is possible that two or more different reaction rates exist due either to physical or chemical factors, or to a combination of physical and chemical phenomena. The concept of two delignification reactions or steps has been applied to Sulfate (4) and Sulfite (34) cooking.

The most widely used correlation between the temperature and the reaction velocity constant is the empirical Arrhenius equation, which is mathematically expressed as:

\[
k = D e^{-\frac{\Delta E}{RT}}
\]

(XVI)

where

\( \Delta E = \) energy of activation, calories per gram mole,
\( D = \) proportionality factor, characteristic of the system and termed frequency factor, Min.\(^{-1}\),
\( R = \) gas constant, calories per gram mole, degree K.
\( k = \) reaction velocity constant, Min.\(^{-1}\),
\( T = \) absolute temperature, degree K.

As the temperature increases, the reaction rate usually increases in accordance with the above equation.
CHAPTER III

CHLORINATION EQUIPMENT

This investigation is divided into two parts:

Part A: Chlorination of the unbleached pulp was carried out with falling chlorine concentration.

Part B: Chlorination of the unbleached pulp was carried out under constant chlorine concentration.

Requirements and Description of Equipment:

Part A: Chlorination with falling chlorine concentration:

In this part of the investigation, the concentration of the chlorine was not maintained constant. It was allowed to fall with the consumption of chlorine by the unbleached pulp. The chief object of this part of the investigation was to determine the amount of chlorine being used as substituting agent or as oxidizing agent. As discussed earlier, chlorine in water can react as either a substituting agent or as an oxidizing agent.

Chlorination of the pulp was carried out in glass bottles with airtight screw caps. The size of the bottles used was dependent on the size of the pulp sample used. This was because of the fact that air space in the bottle has to be kept at a minimum. Otherwise, the chlorine losses in the
air space would be large, vapor pressure of chlorine being quite high.

A water bath was provided in order to carry out the experiments at constant temperature. The bath was equipped with either heating or cooling coils, depending on the room temperature with respect to the temperature specified for the experiment. The cooling coil was used when the specified temperature was lower than the prevailing water temperature and vice versa. The bath was also equipped with thermostat accompanied by Fischer Unitized Bath Electronic control unit and a stirrer.

Addition of the predetermined amount of chlorine water was accomplished with the help of the apparatus shown in Figure 2. The primary purpose of such a setup was to eliminate the loss of chlorine from chlorine water by flashing while the chlorine water was being added to the pulp. The chlorine water from the polyethylene bottle was transferred to the graduated measuring cylinder with stopcocks A, B and D open and stopcocks C, M and L closed. After the graduated cylinder was filled with a sufficient amount of chlorine water, stopcocks A, B and D were closed. Then, with stopcocks C, D and L open, the predetermined amount of chlorine water from the graduated cylinder was added to the pulp in the glass bottle, after which stopcocks L, C and D were closed. The tube passing through the opening N was
Figure 2.— Apparatus for Addition of Chlorine Water.
removed from the glass bottle and the opening closed with a rubber stopper. The rubber tube connecting to stopcock L and the conical flask, serving to trap any trace of escaping chlorine gas, were also removed. Finally, the glass bottle was placed in the water bath after thorough shaking.

The screw cap of the reaction glass bottle had to have openings for adding chlorine water and also removing samples of the liquor for analysis from the bottle. The screw cap is shown in Figure 3. It was made of stainless steel and had two stainless steel tubes and an opening N with a rubber stopper. The lower end of the tube with stopcock M was covered with glass wool in order to filter out the pulp when sampling the liquor.

As the vapor pressure of chlorine is very high, the cap of the bottle could not be removed in order to remove the sample, otherwise, there would be an appreciable loss of chlorine gas. Hence, a sample of the liquor was forced out of the bottle with the help of a slight nitrogen pressure. This was accomplished by connecting the tube equipped with stopcock L (Figure 3) on the cap of the glass bottle to the nitrogen cylinder. The tube with stopcock M was then connected to the special pipets. These pipets, to measure out the liquor samples, were specially designed to suit the purpose. The stopcocks L, M, I, J and K were opened so that the pipets E and F were filled with the
Figure 3.— Assembly for the Analysis of Liquor Samples.
liquor samples after a slight nitrogen pressure was applied. Both the pipets E and F were calibrated. After the pipets were filled, stopcocks I and J were reversed so that the liquor samples from the pipets E and F emptied into the flasks G and H. The samples were then analyzed for residual chlorine and total chloride ion.

Part B: Chlorination with constant chlorine concentration:

The principle variables to be considered in this study are chlorine concentration, temperature and the time of chlorination. Hence, the chlorination equipment had to be designed in such a way that proper control of chlorine concentration and temperature of chlorination could be obtained.

The chlorination of the pulp was carried out in a chlorination tank. It consisted of a cylindrical pyrex glass jar 11.25 inches in diameter and 23.4 inches high, having a total capacity of 37.2 liters. On its front wall was marked a vertical scale indicating the contents in liters corresponding to the height. It had near its base an outlet which was fitted with an outlet of a 5/8 inch rubber tube for sampling. The complete assembly is shown in Figure 4.

Over the tank there was mounted a stirrer driven by a 1/12 H. P. variable speed motor. The stirrer had short stainless steel paddles with straight blades, four in number, each 7 inches long, 5/8 inch wide and spaced 4 1/2 inches apart. The lowest blade was 3 inches from the bottom of the
Figure 4.-- Chlorination Tank.
tank. The stirring paddles were set at right angles to each other. Four stainless steel baffles were hung at the sides of the tank to effect efficient mixing of the stock. Because of the severe corrosive action of moist chlorine, all the stainless steel parts were coated with a corrosion resistant film. Bitumastic super service black paint made by Koppers was found to be very satisfactory. Because of the high vapor pressure of chlorine, the tank was covered with a wooden top in order to eliminate the loss of chlorine from the chlorine water. An appropriate opening with stoppers was provided in the cover so as to facilitate removal of liquor samples from the tank for analysis. The cover was sealed to the top of the tank with Permatex.

As the temperatures used in this investigation were usually less than the room temperature, the stock in the tank must be cooled. This was accomplished with the help of a glass cooling coil provided in the tank. In order to maintain the temperature constant, a Fischer Unitized Bath Electronic Control unit accompanied with a Vapor Pressure Thermoregulator was used. With the help of this setup, the pump circulating the cold water through the cooling coil was automatically operated so that a predetermined temperature was constantly maintained. The sensitivity of this control was 0.1°C.

As the chlorination reaction proceeds, more and more chlorine from the chlorine water in the tank was being consumed and the concentration of the chlorine had decreased. In
order to maintain the chlorine concentration constant, chlorine from a gas cylinder was added at the rate at which it was consumed. The addition of the chlorine to the tank was accomplished with a glass tube provided in the tank. This glass tube had a fritted glass fitting attached to the end which was immersed in the stock. The fritted glass fitting dispersed the gas into small bubbles and hence facilitated its uniform distribution throughout the stock. A Fischer and Porter flowrator and a needle valve were provided in the gas supply line in order to regulate exactly the flow of the chlorine gas.
CHAPTER IV

METHOD OF PROCEDURE

1. Preparation of Samples for Chlorination:

The high lignin Kraft pulp used in this investigation was prepared in the Pulp and Paper Laboratory at the University of Florida. The slash pine mill chips were fed to the Rotopulper set at a 15/16 inch opening. This shredding of chips splits the chip along the grain, retaining the same length of the shredded chip as the original chip. The shredded chips were then screened by a gyratory screen, and the fraction through 3 mesh on 8 mesh was used for cooking. The shredded chips were cooked in a digester with cooking liquor having 23.8 per cent sulfidity and 49.7 grams per liter alkali as Na₂O. The liquor to wood ratio was 3.4 to 1.0. The cooking pressure was 115 psi gage and cooking time was 90 minutes to bring to pressure and then 15 minutes at the full pressure. The cooked wood was washed with hot water and then screened through an 0.010 inch cut screen. Most of the water from the screened pulp was squeezed out with the help of an hydraulic press and then broken up in laboratory shredder and air dried. The air-dried pulp was stored in airtight cans, protecting it from sunlight, dust and moisture. The air-dried pulp was 91.8 per cent dry. This pulp analyzed
11.50 per cent lignin and had a permangante number of 37.9.

The ground wood sample used in this investigation was prepared by passing air-dried, shredded pine chips through a Wiley mill provided with a 20 mesh screen. The ground wood sample was screened and the fraction -20 + 35 was then extracted with alcohol and benzene in order to remove resins, gums, turpentine, etc., and later washed with hot water and air dried. The cold soda pulp used for the experiment was prepared by soaking air-dried, shredded pine chips in sodium hydroxide liquor (63.9 grams Na₂O per liter) and raising the temperature of the mixture to 190°F. in a steam-jacketed vessel. The steam was then cut off and the mixture was allowed to stand over-night. Chips thus soaked were refined in the Rotopulper set at an 0.16 inch opening. The refined pulp was washed with hot water, screened through an 0.018 inch cut screen, squeezed and air dried.

For each experiment, a predetermined quantity of air-dried pulp was taken from the storeroom. The quantity of the pulp was based on oven dryness and hence the moisture content of the pulp in the storeroom was periodically determined. The weighed quantity of pulp was then soaked in water at about 80°C for about 30 minutes. The purpose of this treatment was twofold: first, it inactivated any catalyse in the pulp; second, it returned the pulp to a uniformly wet condition and thus facilitated subsequent
disintegration in the laboratory disintegrator (Appendix A, TAPPI Standard No. T-205). The weighed quantity was mixed in the laboratory disintegrator for 300 revolutions of the agitator per gram of dry sample. It was found that 300 revolutions per gram of pulp gave reproducible results. Depending on the consistency specified for the experiment, a definite quantity of water is filtered from the pulp on a Buchner funnel.

2. Preparation of Chlorine Water:

A two-gallon polyethylene bottle was filled with distilled water at about 35° to 40°F. The bottle had a screw cap at the top and an outlet with a valve at the bottom. Chlorine gas from a gas cylinder was bubbled through the distilled water in the bottle with the help of a glass tube having a fritted glass fitting for good dispersion. The solubility of the chlorine gas in water depends on the temperature. The relation between the solubility of chlorine gas and water is shown in Figure 5. When the chlorine water reached the desired concentration, the flow of chlorine gas was cut off. The concentration was determined by volumetric analysis of a sample. The chlorine water thus prepared was placed in a water bath maintained at about 35°F until it was ready to be used.

3. Chlorination Procedure:

Part A: Chlorination with falling chlorine concentration:
Figure 5.—Solubility of Chlorine in Water
The specified amount of disintegrated pulp was placed in the proper glass bottle. A sufficient amount of distilled water was added to the pulp so that after the addition of the calculated amount of chlorine water, the specified consistency was attained. The cap of the bottle was then placed in position and the bottle made airtight. The chlorine water from the polyethylene bottle was transformed to the measuring cylinder. After a 25-milliliter sample of the chlorine water in the measuring cylinder had been analyzed, the calculated amount of chlorine water was added to the pulp. The amount of chlorine gas displaced when the chlorine water was added to the pulp was trapped in the flask which was provided with potassium iodide and acetic acid. The amount of chlorine added to the pulp in the glass bottle was later corrected for this loss. The temperature of the mixture had been adjusted to the specified value with the addition of hot or cold distilled water. The opening N (Figure 3) for addition of chlorine water was closed with a rubber stopper and the bottle was shaken vigorously and placed in the water bath. This shaking was repeated at regular intervals of two minutes.

Just before the end of the specified time of chlorination treatment, the tube with stoplock L on the cap of the glass bottle was connected to the nitrogen cylinder. The tube with stopcock M was connected to the special pipet. The three-way stopcock K was opened in such a way that some of
the liquor could be drained out in the beaker P. This insures a better sampling of the liquor for analysis. The stopcock K was then opened in the direction permitting the liquor to flow into the pipets. Then stopcocks I and J were opened in such a way that under a slight pressure from the nitrogen cylinder, the pipets E and F were filled with liquor. Then stopcocks I and J were set so that the liquor from the pipets dropped into the flasks G and H. G was filled with potassium iodide and acetic acid and H was filled with sodium pyrosulfite and sulfuric acid. The samples in flasks G and H were then analyzed for residual chlorine and total chloride ion, respectively.

Immediately after the liquor samples were removed, the cap of the glass bottle was opened and the pulp poured into a large beaker which had been filled with hot distilled water. This terminated the chlorination reaction. The pulp was filtered on a Buchner funnel and washed twice, each time re-pulping in warm distilled water at a consistency of about 2 per cent and filtering. One quarter of the filtered chlorinated pulp sample was air dried in a constant humidity room and another quarter was treated with chlorine dioxide. The other half of the pulp was immediately extracted with alkali. The air-dried samples were later analyzed for lignin content and viscosity.

When the time of chlorination was 15 minutes or less, the analysis of the liquor and the subsequent treatment
of the chlorinated pulp could not be done on the same unbleached pulp sample. Hence, two separate but identical experiments were performed: one in which the attention was given to the analysis of the liquor; the other in which the attention was given to the subsequent treatment and analysis of the chlorinated pulp.

Part B: Chlorination with Constant Chlorine Concentration:

The glass jar was filled with distilled water at the temperature specified for the experiment. The strong chlorine water in the polyethylene bottle was analyzed and the exact amount of chlorine water needed was determined. Then the calculated amount of chlorine water from the polyethylene bottle was added to the water in the glass jar. The total amount of water in the glass jar was adjusted so that after the addition of the pulp suspension, the volume of the stock was 33.0 liters. The chlorine water in the glass jar was analyzed before addition of the pulp suspension and adjustments in the chlorine concentration were made, if necessary, with the addition of more chlorine water from the bottle. The reason for analyzing each batch prior to chlorination instead of the apparently much simpler method of using a calculated amount of chlorine water of known strength is because the analysis of chlorine water of high concentrations is subject to inaccuracy. Either loss of vapor or the slightest inconsistency in draining the sample pipet could result in an appreciable error. The temperature of the
solution was adjusted and maintained with the help of the temperature regulating system. The solution was agitated with the stirrer in the tank.

After the chlorine water in the chlorination tank had been adjusted to the required chlorine concentration and temperature, the pulp suspension at approximately the same temperature was poured in the tank, and the cover immediately closed and the stop clock started. As an alternative procedure, the calculated amount of chlorine might be added to the tank containing the pulp suspended in solution which had been adjusted to the specified temperature. However, this alternative procedure was found to yield inconsistent results and abnormal chlorine consumption, presumably due to the effect of localized high concentration before mixing is complete.

As the reaction between chlorine and the unbleached pulp proceeds, the chlorine concentration decreases. If the exact rate of this concentration decrease is known, the amount of addition of chlorine to maintain the chlorine concentration can be determined. It would seem that potentiometric measurement of the chlorine concentration would provide a means of indicating and thus controlling the chlorine concentration. However, it was soon found that this method was not accurate enough as the electromotive force measured by the potentiometer is a logarithmic function of the chlorine concentration. Hence trial runs were made under
identical conditions but without an attempt to maintain the chloride concentration constant in order to determine chlorine consumption.

A trial batch, which was identical in composition to the regular batch, was prepared and chlorination was carried out under the same conditions as the regular run, except that the chloride concentration was not controlled. By analyzing the samples of chloride water at definite intervals, the time rate of consumption of chlorine was calculated. From these data a schedule of make-up additions of chlorine as chlorine gas during the regular run was set up.

Pulp samples were withdrawn at fixed time intervals through the outlet provided near the bottom of the tank. When it was time for the sample to be withdrawn, the stopcock at the bottom was opened and a predetermined amount of pulp suspension was allowed to flow into a laboratory centrifuge. Some water for washing the sample was also added in the centrifuge. This insured the instantaneous termination of the reaction. The centrifuged pulp was further washed twice with hot water and filtered on a Buchner funnel in order to remove the water soluble products. The chloride water in the tank was also analyzed at fixed intervals by siphoning out a 25-milliliter sample with the help of a pipet. The inlet of the pipet was covered with glass wool to keep pulp out of the liquor sample. If these analyses showed that chlorine concentration was not constant, then that
particular run was rejected. The chlorinated sample was further treated in the same manner as explained in Part A.

4. Alkaline Extraction Procedure:

In this investigation, emphasis had been on the chlorination reaction and hence a standard alkaline extraction procedure was determined and used for all the experiments. For determining this procedure, a sample of the unbleached pulp was chlorinated under the conditions of the highest concentration used in this investigation. This chlorinated sample was later alkali extracted at consistency of 10 per cent. The temperature of extraction was about $130^\circ F$. The amount of alkali (sodium hydroxide) to be added was determined with the help of $p_H$ determinations. The amount which extracted most of the alkali soluble constituents of the chlorinated sample was found to be 3 per cent sodium hydroxide by weight of oven-dry pulp. The $p_H$ of the mixture at the end of one hour was about 9.0.

The sample of chlorinated pulp to be extracted was mixed in a 400-milliliter beaker with the predetermined amount of alkali and sufficient water to result in a final consistency of 10 per cent. Mixing was accomplished with the help of a polyethylene spoon. The beaker was covered with a watch glass and placed in a hastelloy pot in a water bath at 160-165$^\circ F$. The mixture was mixed periodically with the help of the spoon to insure uniform temperature and concentration.
of alkali. At the end of extraction, the pulp was washed in the same manner as after chlorination. Half of the extracted pulp was later air dried and analyzed for lignin content and viscosity. The other half was treated with chlorine dioxide and analyzed for viscosity.

5. Chlorine Dioxide Treatment:

In order to evaluate the extent of degradation in chlorination and alkali extraction, the chlorinated and alkali extracted samples of pulps were completely delignified by chlorine dioxide treatment. The wet sample was mixed in an airtight, small glass bottle with 50 per cent by weight of sodium chlorite, 10 per cent by weight of glacial acetic acid and sufficient water to result in a consistency of 5.0 per cent. All percentages were based on the dry weight of pulp. The mixture was well stirred and heated in a water bath at 150-160°F. for 30 minutes. The pulp was washed as before, air dried and then analyzed for viscosity.

6. Analytical Procedure:

(a) Available chlorine in chlorine water.—TAPPI standard T-611 was used. Accordingly, a 25-milliliter sample of the chlorine water was pipetted into a 250-milliliter flask containing approximately 25 milliliters of distilled water, 10 milliliters of 20 per cent acetic acid and 10 milliliters of 20 per cent potassium iodide. The contents of the flask were mixed by swirling and then titrated with 0.1 normal sodium
thiosulfate solution until the iodine color was almost discharged. Then a starch indicator was added and titration continued to the disappearance of blue color. A duplicate sample was then analyzed using the same procedure. The analysis was reported as grams of chlorine per liter.

(b) Permanganate number.—The permanganate number of the pulp was determined according to TAPPI Standard T-214 m-42. The permanganate number of the pulp was reported as milliliter of 0.1 N KMnO₄ consumed per gram of moisture free pulp.

(c) Lignin content.—TAPPI Standard Testing Procedure No. T-222 m-43 was used to analyze for lignin content of the samples. As this is a standard procedure used in every laboratory, it will not be elaborated on here other than mentioning that the lignin referred to here is the fraction which is not soluble in 72 per cent sulfuric acid at 20°C after two hours of treatment. The weight of lignin was reported as percentage by weight of the moisture free sample.

(d) Degree of polymerization.—TAPPI Standard No. T-230 using 0.5 molal cupriethylene diamine [Cu(En)₂] was used. Cu(En)₂ solution was purchased from Ecusta Paper Company and adjusted to a molarity of 0.500 ± 0.0025. Fenske-Ostwald viscosity pipets were used. Stirring of pulp and Cu(En)₂ solution was carried out with a copper stirrer under an atmosphere of nitrogen in order to avoid oxidation and consequent degradation of the cellulose. Degree of
polymerization (D. P. number) of the pulp was evaluated from the viscosity measurements by means of Hercules Conversion Chart for Cellulose Viscosities, Form 803, ZM 11-48, Hercules Powder Company, Wilmington, Delaware.

(e) Residual chlorine.--Residual chlorine was determined according to TAPPI Standard Testing Procedure No. T-611. The liberated iodine was titrated against standard sodium thiosulfate.

(f) Total chloride.--A measured quantity of liquor sample was pipetted into a 250-milliliter flask which contained 25 milliliters of 3 per cent sodium pyrosulfite and 10 milliliters of 10 per cent sulfuric acid. Pyrosulfite was used to convert the residual chlorine to chloride according to the following equation:

\[ \text{Cl}_2 + 2 \text{Na}_2\text{S}_2\text{O}_5 = 2 \text{NaCl} + \text{Na}_2\text{SO}_4 + \text{SO}_2 \]  

(XVI)

The mixture was boiled for about one minute to remove the excess sulfur dioxide, then cooled and the chloride determined. The determination of chloride by volumetric methods, by titrating with silver nitrate using internal indicators, was found to be quite difficult as the determination of the end point was not distinct. Hence, potentiometric titration was employed. The chloride was determined by titrating against standard silver nitrate solution using silver and silver/silver chloride electrodes in association with Beckman pH
Meter, Model G. The change in electromotive force across the two electrodes with the addition of standard silver nitrate was measured. When there was a sudden increase in the e.m.f., the quantity of silver nitrate added was noted. This value was then converted to give the total chloride ion content of the liquor sample.
CHAPTER V

DISCUSSION OF THE DATA AND RESULTS

Part A: Chlorination with Falling Chlorine Concentration:

The main purpose of this investigation was to determine the effects of pulp consistency and of initial chlorine concentration on the rates of lignin removal and the degradation of the cellulose, and also to determine the amounts of chlorine being used up in substitution and oxidation. To achieve this, samples of high lignin Kraft pulp were chlorinated at consistencies of 1, 2 and 3 per cent using identical amounts of chlorine per gram of dry pulp. All of the experiments were carried out at a constant temperature of 77°F and varying chlorination time. The amount of chlorine applied was determined from the chlorine number of the pulp. The chlorine number represents the grams of chlorine absorbed by 100 grams of moisture-free pulp at 20°C in 15 minutes. In this investigation the chlorine number was calculated from the permanganate number of the pulp and a relation between the permanganate number and the chlorine number (TAPPI Standard T-214 m-42).

Data from these experiments are recorded in Tables 1, 2 and 3 as amounts of chlorine used for substitution and
for oxidation, and percentage residual chlorine. The data tabulated in Tables 5, 6 and 7 are the amounts of lignin removed by chlorination and also by chlorination and alkali extraction, and the degree of polymerization of the cellulose.

As indicated earlier, chlorination of the pulp occurs by two processes: one by substitution; the other by oxidation, neglecting any possible addition process. From equation (VI), it can be seen that in a substitution reaction, for every mole of chlorine reacting, there is one mole of hydrochloric acid formed. On the other hand, equations (VIII), (IX) and (X) show that, for every mole of chlorine reacting by oxidation, there are formed two moles of hydrochloric acid. Thus, if one knows the amount of total hydrochloric acid formed, the amounts of chlorine used for substitution and for oxidation can be evaluated.

Suppose \( X \) = weight of total chlorine used, grams,

\[
Y = \text{weight of chlorine in the hydrochloric acid formed, grams,}
\]

\[
C = \text{weight of chlorine used in substitution, grams,}
\]

\[
D = \text{weight of chlorine used in oxidation, grams,}
\]

then \( X = C + D \).

As half of the chlorine used in substitution and all of the chlorine used in oxidation appears as hydrochloric acid in the liquor,

\[
Y = \frac{1}{2} C + D
\]
Solving the above equations for X and Y, one obtains:

\[ C = 2(X-Y) \]

and

\[ D = Y - (X-Y) = 2Y - X. \]

For each experiment the exact amount of chlorine added to the pulp was known and the residual chlorine and the total chloride ions in the liquor were determined analytically. If it could be experimentally proved that there was no hydrochloric acid adsorbed on the surface of the pulp, then all the hydrochloric acid formed must be in the liquor. Under such circumstances, the analysis of the liquor would give the correct indication of the amount of hydrochloric acid formed.

In order to prove this absence of adsorption, a sample of pulp was chlorinated at 3 per cent consistency for 15 minutes with the application of 10 per cent chlorine on the basis of the pulp. Previous experiments had shown that under these conditions all of the applied chlorine was consumed. The complete reacted mixture containing both pulp and liquor was analyzed for hydrochloric acid. In a duplicate experiment, instead of analyzing the complete mixture, a sample of the liquor was filtered from the pulp and analyzed for hydrochloric acid. The hydrochloric acid in the complete reaction mixture determined by both methods was found to be the same. This indicates that all of the hydrochloric acid formed was uniformly distributed in the liquor and that there was no adsorption of hydrochloric acid.
acid on the surface of the pulp.

Through the use of the above relations for determining C and D, the actual weights of chlorine used in substitution and oxidation of the pulp were calculated and these values have been listed in Tables 1 to 4. The results in Tables 1, 2 and 3 were later calculated on the basis of 100 grams of pulp and plotted in Figure 7, and the percentages of residual chlorine were plotted in Figure 6. The residual chlorine concentrations in the liquor in grams per liter at different times are shown in Table 11.

Figure 6 indicates that increased chlorine consumption occurs as the consistency of the reaction mixture is increased. At first glance, it might be assumed that the use of higher consistencies could reduce the reaction time since the reaction rates would be increased. Actually, the increased consumption of chlorine may be due either to the increase in chlorine concentration or to the increase in the pulp surface caused by the increase in pulp consistency. It should be pointed out that pulp consistency, chlorine concentration and the weight of chlorine applied per gram of pulp are three interdependent variables. By fixing the value of any two of them, the value of the third becomes automatically fixed.

From Figure 7, it can be seen that the higher the consistency the larger is the amount of chlorine used by substitution and the lower the amount of chlorine used by
oxidation. As discussed earlier, substitution is the desired reaction. Increase in the pulp consistency would increase the amount of chlorine used in substitution and decrease the amount of chlorine used for oxidation. Reduction in the amount of chlorine used by oxidation should tend to decrease the degradation of the cellulose. However, it has been found by earlier investigators (3) that some slight degree of oxidation of the Kraft lignin is required, because in sulfate cooking the lignin undergoes condensation to such an extent that a large part of it cannot be dissolved by alkaline treatment after chlorination.

Some authorities (3) have implied that upon the addition of chlorine to the pulp, 40 to 20 per cent of the chlorine is consumed by oxidation reaction, while 60 to 80 per cent of the chlorine is consumed by substitution reaction. In Figure 8, the percentage of chlorine consumption by substitution is plotted against time at various pulp consistencies. It can be observed that the percentage of chlorine consumption by substitution reaction ranges from 37 to 58 per cent, a range smaller than observed earlier. The discrepancies in these observations can be attributed to the inefficiency in analyzing the liquor samples since any chlorine losses during the analysis show up as chlorine consumption by substitution. In this investigation, much care was taken in order to keep such chlorine losses to a minimum and all the experiments had been duplicated.
Since the principle object of chlorination of the pulp is to remove lignin without degradation of the cellulose, the pulps were analyzed for the degree of polymerization of the cellulose, as well as for lignin content. These data, recorded in Tables 5, 6 and 7, have been plotted in Figures 9, 10, 11 and 12. The Figures 9 and 10 show the percentages of the original lignin removed by the chlorination treatment and by chlorination and alkali extraction, respectively, as a function of time. Figures 11 and 12 show the degree of polymerization of the chlorinated, and chlorinated and alkali extracted samples.

The lignin has not been removed completely from the pulp in any of the experiments. Neither residual lignin nor residual chlorinated lignin compounds are soluble in cupriethylenediamine, which is used as a solvent for the determination of the degree of polymerization of the cellulose. The presence of these residues tends to give erroneous results with the viscometer and hence should be removed before viscosity determinations. This was done through the chlorine dioxide treatment of the pulp. It has been found that chlorine dioxide does not degrade the cellulose to any appreciable extent, but removes all of the residual lignin and thus makes it possible to find the true viscosity of the pulp. Quantitative determination on the chlorine dioxide treatment showed that the loss in weight of the
chlorine-dioxide treated pulp corresponded exactly to the amount of lignin removed. The amount of lignin remaining after the treatment was practically zero.

From the results in Tables 1, 2, 3, 5, 6 and 7, the consumption of chlorine per gram of lignin removed was determined, basing the calculations on 100 grams of dry pulp. These calculated values have been listed in Table 9. It can be seen that the amount of chlorine consumed per gram of lignin removed is approximately constant, indicating that about 1.30 grams of chlorine should be used to remove each gram of lignin. This quantity seems to be independent of the pulp consistency or initial chlorine concentration. Hence knowing the lignin content of the pulp, one can determine the amount of chlorine actually needed for removing the lignin from the pulp. A previous reference (17) has noted that one unit of lignin reacts with 16 units of chlorine. Taking the often reported value of the molecular weight of lignin to be 840, the amount of chlorine reacting per gram of lignin is \( \frac{16 \times 71}{840} = 1.35 \) grams as compared to 1.30 found in this investigation.

The amount of maximum chlorine which can be added in a single chlorination stage is a function of the consistency of the pulp and solubility of chlorine in water. Basis: 100 grams of mixture of pulp and liquor.

Let \( X = \) percentage of pulp consistency \( = \) grams of pulp,
then $$(100-X) = \text{milliliter of water.}$$

Maximum weight of chlorine in $(100-X)$ milliliter of water

$$= \frac{S_T (100-X)}{1000}$$

where $S_T = \text{solubility of chlorine in water at temperature of $T^\circ\text{C}$ and 760 mm mercury pressure, in grams per liter.}$

Hence, maximum chlorine applied per 100 grams of the pulp

$$= C = \frac{(S_T)(100-X)}{(10)(X)} \quad (XVII)$$

This equation has been plotted in Figure 13 with $C$ and $X$ as the ordinates and $T$ as the parameter.

The low solubility of chlorine in water limits the amount of lignin that can be removed for any particular consistency. Therefore, the maximum amount of lignin which could be removed for any consistency was determined in the following manner:

The chlorine needed by the pulp $= \frac{(X)(L)}{100} \times (1.30) \text{ grams,}$

where $L = \text{maximum lignin removed as percentage of the pulp.}$

$(1.30) = \text{grams of chlorine required to remove each gram of lignin.}$

The maximum chlorine available in chlorine water

$$= \frac{S_T (100-X)}{1000}$$

Equating the chlorine needed by the pulp to the maximum chlorine available in the chlorine water, one obtains:
\[ L = \frac{(S_T)(100-X)}{(13.0)(X)} \]  

This equation has been plotted in Figure 14 with \( L \) and \( X \) as the ordinates and \( T \) as the parameter. The figure gives an approximation of the upper limits of consistency for pulp with varying percentages of lignin removed. The curves do not apply if higher vapor pressures of chlorine are used as the above calculations have been based on a vapor pressure of 760 mm mercury.

It has been discussed earlier that some portion of the chlorinated lignin is soluble in the chlorine solution itself and in wash water. About 55 to 60 per cent of the total lignin is removed in the spent solution and subsequent washings. The amount of this acid-soluble lignin is definitely dependent on the temperature of the wash water used. Hence in all washings of chlorinated pulps, distilled water at 50 to 60° C. was used.

The portion of the chlorinated lignin insoluble in the chlorine water is reacted and solubilized by alkaline extraction. It is felt that this is not mere solubilization of chlorinated compounds in alkali, since there is actual consumption of alkali during alkaline treatment. It would appear that sodium-salts are formed which are, themselves, soluble in alkali.
The total amount of lignin removed increases with increase in the pulp consistency and initial chlorine concentration. But, it has been found that at initial chlorine concentrations of 3.30 and 5.00 grams per liter there is no appreciable difference in the lignin removal. This may be attributed to the fact that most of the accessible lignin has been removed and hence further increase in the chlorine concentration without any decrease in the chlorination time would not be beneficial. It appears that as lignin concentration decreases, concentration of chlorine is not the controlling factor.

From Figure 12, it can be seen that increase in the initial chlorine concentration has practically no effect on the degree of polymerization of the cellulose for short chlorination times. But, as the time of chlorination is increased the degree of polymerization of the cellulose drops considerably. This implies that use of higher initial chlorine concentrations would not degrade the cellulose to any appreciable extent provided the chlorination time is less than 5 minutes.

Experiments were also carried out to determine the effect of initial chlorine concentration on chlorine consumption at 3 per cent pulp consistency. The data are listed in Tables 4 and 8. The data in Table 4 show the amounts of chlorine consumed for substitution and also for oxidation.
In Table 8 is recorded the percentage of the original lignin removed by the chlorination treatment and the chlorination and alkali extraction for various initial chlorine concentrations. The data in Table 4 indicate that the amount of chlorine used for substitution is fairly constant for chlorine concentrations from 5.00 to 3.85 grams per liter but it tends to drop below a chlorine concentration of 3.85 grams per liter. This implies that higher chlorine concentrations should be used in order to have more substitution and less oxidation reaction. Tables 4 and 8 indicate that at 3 per cent consistency and varying chlorine concentrations approximately 1.30 grams of chlorine are also required to remove one gram of lignin from the pulp.

Two Chlorination Stages:

In order to determine the effect of two chlorination stages, as opposed to one chlorination stage, a pulp sample was chlorinated for 5 minutes at 3 per cent consistency with an initial chlorine concentration of 5.00 grams per liter and subsequently alkali extracted (reference Table 7). This pulp was given a second chlorination for 5 minutes at a consistency of 3 per cent with a chlorine concentration of 1.21 grams per liter. This chlorine concentration was deliberately made equal to the concentration of chlorine in the liquor at the end of the first chlorination (reference Table 11). It was found that after the two
chlorinations and alkali extractions, 98 per cent of the original lignin was removed. However, from Figure 10 it can be seen that after a total of 10 minutes continuous chlorination time, the percentage of the original lignin removed would be only 88. This shows that two chlorinations of short time duration are more effective in lignin removal than a single stage chlorination at a time duration equal to the sum of the time intervals used for the two chlorination stages. This indicates that the chlorinated products might have formed incrustations on the fiber walls which hinder further reaction between pulp and chlorine.

The filtered spent liquor was found to contain 65.3 per cent of the original chlorine as unconsumed. This liquor was found also to contain two moles of hydrochloric acid for every mole of chlorine. This constitutes further proof that all chlorine applied appears in the liquor as residual chlorine and as chlorine in hydrochloric acid. It would seem obvious that no hydrochloric acid is adsorbed on the surface of the pulp and hence unaccounted for by liquor analysis.

**Heat of Reaction:**

The chlorination of pulp is an exothermic reaction and hence in the industry the generation of heat in the chlorination stage should be taken into consideration. Although the reaction rates would be higher at higher chlorination temperatures, the rate of degradation of the cellulose
increases likewise (21) due to the additional heat resulting from the reaction itself. The amount of temperature rise depends on the heat of reaction, the heat capacity of the system and radiation properties of the equipment. Hence, in this investigation an attempt was made to determine the heat of chlorination reaction.

In order to determine the heat of the chlorination reaction, the calorimetric method was used. The calorimeter used was a Dewar flask which was provided with a top made of 3/4 inch thick asbestos pad, a stirrer and a thermometer which could be read exactly to the second decimal place.

The standard reaction used to determine the water equivalent of this calorimetric system was the neutralization of an acid with an alkali, viz:

\[
\text{NaOH (Solution) + HCl (Solution) = NaCl (Solution) + H}_2\text{O} \quad \text{(XIX)}
\]

This is an exothermic reaction with the heat of reaction equal to 2,490 BTU per pound mole. The water equivalent of the calorimetric system was determined to be 4.07 pounds.

A 20 gram sample of the pulp was chlorinated in the Dewar flask at 1.25 per cent consistency with the application of 16.2 per cent chlorine, based on the pulp. The initial temperature of both the pulp suspension and the
chlorine water was 77.90°F. The maximum rise in temperature of the reaction mixture was found to be 2.09°F. Using this value of temperature rise and the water equivalent of the calorimetric system, the heat of reaction of chlorination of the Kraft pulp was found to be 360 BTU per pound of pulp treated. For the same pulp and with the same chlorine concentration, the heat of reaction of sodium hypochlorite and pulp was found to be 375 BTU per pound of pulp treated.

The heat of reaction of 360 BTU per pound of pulp treated would give respective temperature rises for chlorinations carried out at various consistencies. At a pulp consistency of 3 per cent the temperature rise would be 5.10°F and at a consistency of 9 per cent the temperature rise would be 16.40°F. These magnitudes of temperature rises would not cause serious pulp degradation in industrial operations.

Part B: Chlorination with Constant Chlorine Concentration.

In studying the effects of Cl₂ concentration, chlorination time and temperature on the delignification of the Kraft pulp, a pulp containing 11.50 per cent lignin was used. It had been found in preliminary work with pulp containing 5.65 per cent lignin that the reaction rates for chlorination of the pulp were quite high. If this pulp of low lignin content were used, practically all the lignin would be removed in the first few minutes, making it impractical to study the effect of chlorination time on the lignin removal.
With the present available equipment in the laboratory it took about one minute to withdraw the sample for analysis. When attempts were made to study reaction times of less than 5 minutes, the results could not be duplicated. This was because the reaction rates were quite high in the early stages, but after 5 minutes the reaction rates had decreased to such an extent that the results could be duplicated with reasonable accuracy.

Chlorination experiments were conducted with Kraft pulp under conditions of constant Cl\textsubscript{2} concentration, constant temperature and varying time. The experimental conditions used were: Cl\textsubscript{2} concentration from 0.36 to 1.63 grams per liter; chlorination temperatures of 66°F, 77°F and 87°F; chlorination times from 5 to 60 minutes. The data obtained from these experiments are listed in Tables 12-17. The lignin removal data from these tables are plotted versus time in Figures 15-17. The data on D. P. number of the cellulose are plotted versus time in Figures 18-21.

It has been discussed in Chapter II that if the rates of delignification were to follow equation (XI), the slopes, which are the instantaneous rates of delignification (\(-dL\)) when plotted versus percent of lignin remaining \(\frac{dL}{dt}\) (L), should give straight lines on log-log paper. Such straight lines obtained for various constant Cl\textsubscript{2} concentrations should be parallel to each other.

The curves of percent lignin removed versus time in
Figure 15 were graphically differentiated to determine
the value of slope (-dL). The graphical differentiation
\( \frac{\text{d}L}{\text{d}t} \)
was carried out with the help of a mirror. Figure 25 shows
the log-log plot of (-dL) versus L. This plot gives ac-
ceptable straight lines, but the lines are not parallel.
This means that the slopes of these lines vary with chlo-
rine concentration. Hence, as discussed in Chapter II,
equation (XI) could not be applied to the data.

An examination of the curves in Figure 15 indicates
that the curves approach straight lines at both ends. Thus,
there is a possibility that more than one reaction is taking
place. This would be quite plausible because of the complex
nature of the system. This complexity prohibits any attempt
at defining the exact mechanism of the reactions between
pulp and chlorine water. Therefore, an attempt was made to
find an empirical relation between rate of lignin removal,
chlorine concentration, chlorination time and temperature.

Under conditions of constant Cl\(_2\) concentration and
temperature, for a first order reaction, the quantity of a
component reacting in a definite time is proportional to
the quantity of unreacted component in the solid at that
time.

In the case of lignin removal,

\[
-\frac{\text{d}L}{\text{d}t} = k(L)
\]  

(XX)
which becomes, on integration

\[
L = L_0 e^{-kt}
\]  \hspace{1cm} (XXa)

taking logarithm

\[
\log L = -kt + \log L_0
\]  \hspace{1cm} (XXb)

where

- \(L_0\) = percent of the original lignin in the pulp at the start of the reaction,
- \(L\) = percent of the original lignin remaining after time, \(t\),
- \(k\) = reaction velocity constant.

Therefore, from equation (XXb), a first order reaction should give a straight line when \(L\) is plotted versus time on semi-logarithmic coordinates.

The percentages of the original lignin remaining after chlorination were plotted versus time on semi-logarithmic paper as shown in Figures 26-28. All the lines were curves. The shapes of these curves very early in the reaction indicate, in all cases, that there is a certain percentage of lignin removed extremely rapidly. In fact, it is this highly reactive lignin which prevented accurate evaluation of reaction rate in the first 5 minutes. If it can be assumed for estimating purposes that this highly reactive lignin is removed instantaneously, it might be possible to fit the remainder of the data into the scheme involving two straight line relationships.

The curve in Figure 26 where \(\text{Cl}_2\) concentration was 0.36 grams per liter was fitted with two straight lines
designated as A and B. First, line B was drawn so that it was asymptotic with the data curve at longer chlorination times. The equation of this line is

\[ L'' = Be^{-k_2t} \]  

(XXc)

taking logarithm

\[ \log L'' = -k_2t + \log B \]  

(XXd)

where

\[ L'' = \text{percent of the original lignin remaining from reaction B at time, } t, \]

\[ B = \text{intercept on the Y-axis } = L''_o = 42 \]

\[ k_2 = \text{apparent reaction velocity constant } = 0.00146. \]

The subscript 'o' indicates the value at the start of the reaction.

For each value of time, the value of \( L'' \) was obtained and then subtracted from the experimental value of \( L \) at that time. These differences when plotted on the same figure gave a straight line, designated A. The equation of this line is as follows:

\[ L' = Ae^{-k_1t} \]  

(XXe)

where

\[ L' = \text{per cent of the original lignin remaining from reaction A, at time, } t, \]

\[ A = \text{intercept of the Y-axis } = L'_o = 36, \]

\[ k_1 = \text{apparent reaction velocity constant, } = 0.0369. \]
The combination of equations (XXc) and (XXe) gives the relationship between \( L \) for the chlorinated pulp and time. The combined equation is as follows:

\[
L = L' + L'' = Ae^{-k_1t} + Be^{-k_2t}
\]  

(XXI)

Substituting the values of constants, the equation becomes

\[
L = 36e^{-0.0369t} + 42e^{-0.00146t}
\]  

(XXIa)

At time zero, equation (XXIa) indicates that \( L = 36 + 42 = 78 \). However at the start of the reaction, the value of \( L_0 = 100 \). This \( L_0 \) must be the sum of \( L'_0, L''_0 \) and the percent of lignin removed instantaneously. Therefore percent of original lignin removed instantaneously

\[
= L_0 - L'_0 - L''_0
= 100 - 36 - 42
= 22
\]  
i.e., \( L_0 = 22 + L'_0 + L''_0 \)
or \( L_0 = 22 + Ae^{-k_1t} + Be^{-k_2t} \)

This 22 per cent instantaneous removal is possibly due to the fact that in the early part of chlorination, chlorine reacts with the solid wall of lignin on the surface of the fiber. It might also be that this 22 per cent is not removed instantly, but is removed in the first 1-2 minutes. This point can be clarified when equipment becomes available so that chlorinations can be carried out accurately at very
short time intervals. As this 22 per cent of the original lignin is removed instantaneously, it does not enter into further consideration. It has similarly been found by Findley (34) that in neutral sulfite pulping about 12.5 per cent of the wood is removed very rapidly and hence does not affect the kinetics.

Equation (XXI) indicates that there are two apparent simultaneous or subsequent first order reactions in chlorination in addition to the instantaneous reaction. These two apparent reactions have different reaction rates which can be seen from the difference in the apparent reaction velocity constants \( k_1 \) and \( k_2 \).

The apparent reaction velocity constants \( k_1 \) and \( k_2 \) were similarly determined from Figures 27 and 28 for chlorination experiments carried out at chlorine concentration of 0.57, 0.90 and 1.63 grams per liter. The values of \( k_1 \) and \( k_2 \) are as follows:

\[
A = \text{intercept for line } A = 36 \\
B = \text{intercept for line } B = 42
\]

<table>
<thead>
<tr>
<th>( \text{Cl}_2 \text{ Conc. g/l.} )</th>
<th>( k_1, \text{min}^{-1} )</th>
<th>( k_2, \text{min}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.36</td>
<td>0.0369</td>
<td>0.00146</td>
</tr>
<tr>
<td>0.57</td>
<td>0.0791</td>
<td>0.00234</td>
</tr>
<tr>
<td>0.90</td>
<td>0.1316</td>
<td>0.00403</td>
</tr>
<tr>
<td>1.63</td>
<td>0.1316</td>
<td>0.00403</td>
</tr>
</tbody>
</table>
It can be seen from the above tabulation that $k_1$ and $k_2$ are functions of chlorine concentration. Hence, an attempt was made to find a mathematical relationship between the $Cl_2$ concentration and the apparent reaction velocity constant. This attempt was not successful because the values of $k_1$ and $k_2$ became constant at concentration of 0.90 grams per liter or higher.

Some authorities have indicated that such a phenomenon may be due to the fact that when chlorine concentration is low, the lignin molecules are not surrounded by a sufficiently large number of $Cl_2$ molecules. Therefore, reaction rate increases rapidly with increase in concentration. But, when the solution surrounding lignin has attained saturation with respect to the chlorine demand of lignin, then beyond this saturation further increase will have no effect.

In the light of this particular system, the above reasoning does not seem to apply. It seems more probable that concentration of lignin remaining, rather than the concentration of chlorine, might be the controlling factor for pulp containing about 10 per cent lignin. Under such circumstances, when lignin content of the pulp has decreased to a certain extent, then further increases in concentration would not affect the rate of reaction.

The same mathematical analysis, using equation (XXI), was applied to pulps which had been alkali extracted
after chlorination. The data listed in Tables 12-15, were plotted in Figure 29 as logarithm of L versus time. Each curve in Figure 29 for different Cl<sub>2</sub> concentration was fitted with two respective straight lines as shown in Figure 30.

The percent of original lignin instantly removed was found to be 55. The values of constants determined from Figure 30 are as follows:

\[
A = \text{intercept of line } A = 29 \\
B = \text{intercept of line } B = 16
\]

<table>
<thead>
<tr>
<th>Cl&lt;sub&gt;2&lt;/sub&gt; Conc. g/l</th>
<th>(k_1), min&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>(k_2), min&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.36</td>
<td>0.0825</td>
<td>0.0135</td>
</tr>
<tr>
<td>0.57</td>
<td>0.1142</td>
<td>0.0153</td>
</tr>
<tr>
<td>0.90</td>
<td>0.1684</td>
<td>0.0181</td>
</tr>
<tr>
<td>1.63</td>
<td>(\infty)</td>
<td>0.0181</td>
</tr>
</tbody>
</table>

In this case, when the pulps had been alkali extracted after chlorination, the constancy of reaction constant \(k_2\) occurs at high values of concentration just as with chlorination. But, in the case of \(k_1\), however, Figure 30 shows that line A for Cl<sub>2</sub> concentration of 1.63 grams per liter, is a vertical straight line coinciding with the Y-axis. This means that the value of \(k_1\) increases without limits and that the time interval is equal to zero. Therefore, according to equation (XXe),
\[ L = Ae^{-kt} = Ae^{-(\infty)(0)} = A = 29 \]

This indicates that at concentration of 1.63 grams per liter, this 29 per cent is removed so rapidly as to be considered as instantaneously removed. Therefore, this 29 per cent of the lignin falls in the same category as the 55 per cent which had already been assumed to be removed instantaneously. This means that 84 per cent of the lignin is removed instantaneously.

When the chlorinations and alkali extractions were carried out under falling concentrations, it can be seen from Figure 10, by extrapolation, that 83.0 per cent of the lignin was removed instantaneously when the initial concentration was 1.63 grams per liter. For an initial concentration of 3.33, this value was 84.2 per cent and for an initial concentration of 5.00, this value was 85.5 per cent. These values of instantaneous removal of lignin agree very well with that of 85 per cent, as found above.

**Effect of Chlorine Concentration and Temperature on the Degradation of the Cellulose:**

Degree of polymerization numbers of cellulose after chlorination treatment and chlorination followed by alkali extraction are plotted in Figures 18-21 for various chlorine concentrations and temperatures. These figures appear to indicate that degradation of cellulose increases with increase in chlorine concentration and chlorination temperature.
From Figures 16 and 19 it can be seen that for 85.6 per cent of original lignin removal at a Cl₂ concentration of 1.63 grams per liter, the degree of polymerization number falls to 1454. For the same quantity of lignin removed at 0.57 grams per liter, time of chlorination is 21.7 minutes and the degree of polymerization number is 1540. Extrapolation of the curves on Figure 16 can show that a chlorination time of 2 minutes at 1.63 grams per liter, the degree of polymerization number is about 1520. But, for the same chlorination time at 0.57 grams per liter, the degree of polymerization number is about 1555. Therefore, it is quite possible that, at very short reaction times, chlorinations may be carried out at relatively high chlorine concentrations without extensive cellulose degradation.

Effect of Chlorination Temperature on the Delignification of Kraft Pulp:

This set of experiments was conducted with the Kraft pulp. The chlorine concentration of the liquor used in each case was 0.57 grams per liter. The temperature was varied from 66°F to 87°F. The data are shown in Tables 16, 17 and plotted in Figure 17.

The data for chlorination at various temperatures were plotted on semi-logarithmic paper in Figures 31 and 32, with L and time as the coordinates. The curves obtained were similarly fitted with two straight line relationships. Then the values of constants \( k_1 \) and \( k_2 \) were determined.

If the Arrhenius equation, which has been
mathematically explained as,

\[ k = \text{De}^{-\Delta\varepsilon/RT} \]  

(XVI)
taking logarithm,

\[ \log k = \log D - (\Delta\varepsilon)(1/R) \frac{1}{T} \]  

(XVIa)

were to hold true for \( k_1 \) and \( k_2 \), straight lines should be obtained when logarithms of \( k_1 \) and \( k_2 \) are plotted versus the reciprocal of absolute temperature.

The values of \( k_1 \) and \( k_2 \) for chlorination at various temperatures are as follows:

<table>
<thead>
<tr>
<th>T°F</th>
<th>T°R</th>
<th>((10^4)(1/T))</th>
<th>(k_1,\text{min.}^{-1})</th>
<th>(k_2,\text{min.}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>526</td>
<td>1.90</td>
<td>0.0585</td>
<td>0.00061</td>
</tr>
<tr>
<td>77</td>
<td>537</td>
<td>1.86</td>
<td>0.0791</td>
<td>0.00234</td>
</tr>
<tr>
<td>87</td>
<td>547</td>
<td>1.83</td>
<td>0.0980</td>
<td>0.00464</td>
</tr>
</tbody>
</table>

These values of \( k_1 \) and \( k_2 \) were plotted versus \( 1/T°R \) on semi-logarithmic graph paper as shown in Figure 33. It was found that acceptable straight lines were obtained, indicating applicability of the Arrhenius equation.

Similarly data for chlorination at various temperatures followed by alkali extraction were plotted on semi-logarithm coordinates as shown in Figures 34 and 35. The curves obtained were fitted with two straight line relationships. Then the values of constants \( k_1 \) and \( k_2 \) were determined. These values are as follows:
These values of \( k_1 \) and \( k_2 \) for chlorination followed by alkali extraction were plotted versus \((1/T^0)\) on semi-logarithm coordinates as shown in Figure 36. It was found that acceptable straight lines were obtained.

The energies of activation for chlorination and for chlorination followed by alkali extraction obtained from the slopes of the straight lines in Figures 33 and 36 are as follows:

<table>
<thead>
<tr>
<th>Chlorination</th>
<th>Chlorination followed by Alkali Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy of Activation for Reaction A ((\text{cal/mole}))</td>
<td>14,000</td>
</tr>
<tr>
<td>Energy of Activation for Reaction B ((\text{cal/mole}))</td>
<td>7,850</td>
</tr>
<tr>
<td>Energy of Activation for Reaction B ((\text{cal/mole}))</td>
<td>40,800</td>
</tr>
<tr>
<td>Energy of Activation for Reaction B ((\text{cal/mole}))</td>
<td>22,600</td>
</tr>
</tbody>
</table>

The values for constants \( D_1 \) and \( D_2 \) for chlorination are 1.12 x \( 10^{12} \) and 1.72 x \( 10^{32} \), respectively. For chlorination followed by alkali extraction \( D_1 \) and \( D_2 \) are 1.70 x \( 10^{40} \) and 1.18 x \( 10^{55} \), respectively.

The values of energy of activation indicate that reaction A needs less energy for its activation and hence is more rapid than reaction B.
In order to obtain relationship between \( L \), temperature and time, equations (XVI) and XXI) were combined. The combined equation is as follows:

\[
L = Ae^{-\frac{\Delta E_1}{RT}t} - Be^{-\frac{\Delta E_2}{RT}t} \tag{XXII}
\]

substituting the values of constants for chlorination carried out at 0.57 grams per liter, equation (XXII) becomes

\[
L = 36e^{-1.12 \times 10^{12} e^{-14,000/RT}t} - (3.32 \times 10^{10} e^{-40,800/RT}t) \tag{XXIIa}
\]

Study of Rates of Delignification of Wood:

It has just been pointed out that there was no increase of rate of delignification as chlorine concentration increased above 0.90 grams per liter. This was attributed to the decrease in lignin content to such an extent that it controlled the delignification rates.

If a pulp of sufficiently high lignin content could be used, the true effect of chlorine concentration might be evaluated. It was felt that if ground wood, instead of a pulp, were used, then a material containing 29.05 per cent lignin could be obtained for experimentation. The Kraft pulp which was used contained 11.50 per cent lignin.

In order to provide an extremely large surface, air-dried wood was ground, screened and extracted as described
in Chapter III. This extracted wood fraction passing through 28 mesh and retained by 35 mesh was used for chlorination. The chlorination was carried out at constant concentration of 0.80 grams per liter and 77°F. The results have been listed in Table 18 and plotted in Figure 22 as percent lignin removed versus time.

From this figure it can be seen that after one hour of chlorination followed by alkali extraction, the percent of original lignin removed was 41.7. But, under the same experimental conditions, the percent of original lignin removed from Kraft pulp was 93.6 (reference Table 16). This indicates that the reaction rate for chlorination of the Kraft pulp was much higher than for chlorination of wood. This is possible because of the nature of the surface exposed for reaction.

The Kraft pulp is made of individual whole fibers coated with lignin and hence presents a large lignin surface. But, ground wood does not consist of individual whole fibers. When the wood is ground in Wiley mill, most of the fibers are cut in sections. As a fiber is made up of cell walls with hollow lumens at the center, this cross-cutting of fibers exposes the hollow lumens. And, as most of the lignin is present in the outer cell wall, the actual exposed lignin surface would be at the outer edge of the cut.

The pine wood whole fibers are 2-3 mm long and
0.04 to 0.07 mm in diameter. Whereas, the ground wood fraction used in this work consisted of spheres, cubes or any other shapes between 0.4 and 0.6 mm in cross-section. This seems to indicate that a cubical piece of ground wood might consist of 30 to 150 sections of individual fibers. These 30 to 150 fiber sections in a particle of ground wood are cemented together by lignin. Thus, this lignin surface between these fiber sections would not be available for the reaction at the particle surface. Hence, for ground wood the actual lignin surface exposed for reaction at the surface would be quite small.

Effect of Change in Chlorine Concentration on the Rates of Delignification of Cold Soda Pulp:

From this preliminary work on ground wood, it was felt that material which would have a surface comparable to that of Kraft pulp and having high lignin content should be used. Such a type of material might be cold soda pulp.

In this cold soda process, wood chips are steeped in alkali at temperatures below 100°C. This steeping in alkali softens the wood chips without removing any of the lignin. This softened wood is passed through an attrition mill. The rubbing in the attrition mill separates the wood into fibers or fiber bundles without extensive cutting of the fibers. But, when the wood is ground in a Wiley mill, the fibers, instead of being separated by rubbing, are cut into sections of fiber bundles.
The cold soda pulp, prepared as described in Chapter IV, was chlorinated at constant chlorine concentrations of 0.80, 1.14 and 1.50 grams per liter and 77°F. Half of the chlorinated sample for all experiments was alkali extracted. The data for chlorination and for chlorination followed by alkali extraction are recorded in Tables 19-21 and plotted in Figures 23 and 24.

The same method of attack was used as that described for delignification of Kraft pulp. The data for chlorination were plotted on semi-logarithmic coordinates as shown in Figures 37-39. The data for chlorination followed by alkali extraction were plotted on semi-logarithmic coordinates in Figure 40.

The curves obtained in Figures 37-40 are similar to those obtained for Kraft pulp. Hence, the curves in Figures 37-40 were fitted with two straight line relationships as shown in Figures 38-40 and 42.

It was found that the percent of original lignin removed instantaneously was 22 for both chlorination and chlorination followed by alkali extraction. The values of constants A and B, and the apparent reaction velocity constants $k_1$ and $k_2$ determined from Figures 37-39 and 41, are as follows:
Chlorination:

\[ A = 26 \] \[ B = 51 \]

<table>
<thead>
<tr>
<th>Cl(_2) Conc. g/l</th>
<th>(k_1, \text{min}^{-1})</th>
<th>(k_2, \text{min}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.0785</td>
<td>0.0032</td>
</tr>
<tr>
<td>1.14</td>
<td>0.1121</td>
<td>0.0038</td>
</tr>
<tr>
<td>1.50</td>
<td>0.1566</td>
<td>0.0043</td>
</tr>
</tbody>
</table>

Chlorination and Alkali Extraction:

\[ A = 51 \] \[ B = 26 \]

<table>
<thead>
<tr>
<th>Cl(_2) Conc. g/l</th>
<th>(k_1, \text{min}^{-1})</th>
<th>(k_2, \text{min}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.0635</td>
<td>0.0006</td>
</tr>
<tr>
<td>1.14</td>
<td>0.1247</td>
<td>0.0031</td>
</tr>
<tr>
<td>1.50</td>
<td>0.2504</td>
<td>0.0097</td>
</tr>
</tbody>
</table>

It can be seen from the above tabulation that both \(k_1\) and \(k_2\) are functions of chlorine concentration. This constitutes further proof that in the case of the Kraft pulp, constancy of reaction rates at higher Cl\(_2\) concentrations was not because of saturation of chlorine. Rather, it was low lignin concentration which caused the constancy of reaction rates.

An analysis was made of the variation of \(k_1\) and \(k_2\) with chlorine concentration. It was found that a log-log plot of \(k_1\) and \(k_2\) versus chlorine concentration, C, resulted in acceptable straight lines for both chlorination and chlorination followed by alkali extraction. The plots are shown in Figures 42-43. This indicates the following relationships:
\[ k_1 = \beta_1 c^{\alpha_1} \]  
(XXIII)

\[ k_2 = \beta_2 c^{\alpha_2} \]  
(XXIIIa)

From Figures 42 and 43, the values of constants \( \alpha \) and \( \beta \) were determined. These values are as follows:

<table>
<thead>
<tr>
<th></th>
<th>( \alpha_1 )</th>
<th>( \beta_1 )</th>
<th>( \alpha_2 )</th>
<th>( \beta_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorination</td>
<td>1.07</td>
<td>0.108</td>
<td>0.474</td>
<td>0.0037</td>
</tr>
<tr>
<td>Chlorination and Alkali Extraction</td>
<td>2.18</td>
<td>0.103</td>
<td>3.09</td>
<td>0.0030</td>
</tr>
</tbody>
</table>

In order to find a mathematical relationship between \( L \), chlorine concentration and time, equations (XXIII) and (XXIIIa) were combined with equation (XXI). The resulting combined equation is as follows:

\[ L = A e^{-(\beta_1 c^{\alpha_1})t} + B e^{-(\beta_2 c^{\alpha_2})t} \]  
(XXIV)

Substituting the values of constants for chlorination reaction in equation (XXIV), one obtains:

\[ L = 26e^{-(0.108 c^{0.07})t} + 51e^{-(0.0037 c^{0.474})t} \]  
(XXIVa)

Through the use of equation (XXIV), one can determine the values of \( L \), if the values of \( C \) are known at a time, \( t \).

Application of Equation (XXIV) to the Data in Part A:

When chlorination experiments on Kraft pulp were carried out at a pulp consistency of 3 per cent and under falling
concentrations, chlorine concentration was a function of time. The values of concentration at different times are listed in Table 11.

Equation (XXIVa) was applied to the chlorination data at 3 per cent consistency. The calculated values of L for chlorination are shown in the following tabulation along with the observed value. Similarly equation (XXIV) with appropriate values of constants was used to calculate the values of L for chlorination followed by alkali extraction. These calculated values of L, along with the observed values, are also shown in the following tabulation:

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Cl₂ Conc. (g/l.)</th>
<th>L Calculated from Eq. (XXIV)</th>
<th>L Observed from Table 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorination</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.192</td>
<td>64.4</td>
<td>51.6</td>
</tr>
<tr>
<td>20</td>
<td>0.815</td>
<td>53.1</td>
<td>47.3</td>
</tr>
<tr>
<td>40</td>
<td>0.550</td>
<td>49.0</td>
<td>43.1</td>
</tr>
<tr>
<td>60</td>
<td>0.457</td>
<td>45.9</td>
<td>40.2</td>
</tr>
<tr>
<td>Chlorination and Alkali Extraction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.192</td>
<td>50.9</td>
<td>13.0</td>
</tr>
<tr>
<td>20</td>
<td>0.815</td>
<td>41.9</td>
<td>10.0</td>
</tr>
<tr>
<td>40</td>
<td>0.550</td>
<td>39.0</td>
<td>6.5</td>
</tr>
<tr>
<td>60</td>
<td>0.457</td>
<td>38.6</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The above tabulation indicates that the residual lignins, calculated by the equation, are much higher than those
actually observed. This indicates that the constants and exponents derived for the cold soda pulp do not apply to the Kraft pulp. The most logical explanation of this fact would be that the ratio of surface to weight for the cold soda pulp is much less than that for the Kraft pulp.

A comparison of Figure 16, the lignin removal curves for Kraft pulp, and Figure 23, a similar plot for cold soda pulp, show a similar discrepancy for rates of lignin removal for the two materials. For example, Figure 16 shows that for 20 minutes chlorination time, 84.5 per cent of the total lignin is removed at a concentration of 0.90 grams per liter. But, Figure 23 shows that chlorination of cold soda pulp at considerably higher Cl₂ concentration of 1.63 grams per liter removed only 45.8 per cent of the total lignin after 20 minutes. If cold soda pulp and Kraft pulp were exactly the same material, the lignin removed under the same conditions should be higher for cold soda pulp than for Kraft pulp.

The lignin in the cold soda pulp is uniformly distributed on the surface of the fibers. In the Kraft pulp 60 per cent of the lignin has been removed in cooking, and distribution of the lignin on the fibers is not known. But, at any rate, the lignin surface exposed cannot be greater than that of the cold soda pulp. Under such circumstances, the rate of delignification for the cold soda pulp should be as high or higher than for Kraft pulp. However, the data
prove that this is not true. Therefore, there must be some explanation for this fact that the rate of delignification of cold soda pulp is slow.

Two possible explanations become immediately apparent. On the one hand, it is possible that the alkali used to soften the lignin may have brought about a chemical change, making it less reactive to chlorination. On the other hand, lignin may have remained unaltered, as generally considered, and the discrepancy will have to be explained by physical difference. The only way this is possible is that cold soda pulp is not made of 100 per cent individual discrete fibers.

It has been a long-known fact that cold soda pulp is a mixture of individual fibers and fiber bundles. The relative proportion of individual fibers to fiber bundles depends on the degree of the softening of the lignin and on the degree of refining. Usually a rather high percentage of fiber bundles are tolerated in order that the energy of refining be kept at a minimum and that fiber cutting be minimized.

In making cold soda pulp for the experiments, it was noticed that after steeping in alkali the shredded wood chips were not nearly as flexible as might be desired. This would indicate that the cementing lignin had not been sufficiently softened to bring about complete fiber separation during refining.
A microscopic examination of the Kraft and cold soda pulps showed that there were some fiber bundles in the cold soda pulp, while the Kraft pulp had all individual fibers. The diameters of the cold soda fibers appear to be about one and one-half times the diameter of Kraft fibers. The Kraft fibers were quite uniform in length, while the cold soda contained some short fibers caused by fiber cutting. There were also some fibers in the cold soda pulp, which were about twice as long as the Kraft fibers. These long fibers were probably made up of more than one individual fiber.

All these observations from the microscopic study indicate that the lignin surface in the cold soda pulp was considerably less than that in the Kraft pulp. Reaction rate equation with values of constants and exponents derived from this cold soda pulp with low lignin surface to weight ratio would naturally give higher values of L, as was found to be true.

This would appear to open an entirely new approach to the problem. The shredded wood should be steeped in alkali under various conditions of concentration of alkali, steeping time and temperature. These different steeped-wood samples should later be refined in an attrition mill. These refined samples may have different proportions of individual fibers and degrees of fiber cutting, depending on the conditions of steeping.

Each of these samples should be later chlorinated
at constant chlorine concentrations for various time intervals and the values of L determined. The values of constants in equation (XXIV) should be determined for each sample. Through the use of these constants and equation (XXIV), the values of L under conditions of falling concentration for the Kraft pulp should be calculated.

The sample for which the calculated values of L were equal to or possibly even less than those observed for the Kraft pulp would seem to have lignin surface similar to that of the Kraft pulp. Thus, this sample can be used to determine the mechanism of chlorination.

It may be concluded that lignin surface might be an important variable just as has been found in delignification by chemical pulping. This surface variable should be incorporated in equation (XXIV). In such a case, constants \( \beta_1 \) and \( \beta_2 \) may possibly, in reality, be a combination of another constant and the surface variable.
SUMMARY AND CONCLUSIONS

An investigation was made of the chlorination of pulps with a view to study the mechanism of lignin removal and the pulp degradation. The individual effects of chlorine concentration, chlorination time and temperature on the rate of delignification were also evaluated.

1. When the pulp was chlorinated under conditions of falling concentration, increases in pulp consistency and initial chlorine concentration increased the total chlorine consumption, as well as the consumption of chlorine by substitution.

2. Above a certain initial chlorine concentration there was no change in the rate of lignin removal with increase in initial chlorine concentration. At short-time intervals the degradation of the cellulose was independent of the initial chlorine concentration.

3. For the Kraft pulp used it was found that, for every gram of lignin removal, the pulp consumed about 1.30 grams of chlorine.

4. Two chlorination stages of short-time duration with immediate alkali extraction removed more lignin than a single chlorination stage of a time equal to the two chlorination stages. This indicated that the incrustations
of chlorinated products formed on the fiber hinder further reaction and hence should be removed.

5. The heat of reaction between the Kraft pulp and chlorine was found to be 360 BTU/# of pulp treated and corresponds to a temperature rise of 16.4°F at a pulp consistency of 9 per cent. The heat of reaction of sodium hypochlorite and pulp was found to be 375 BTU/# of pulp treated.

6. When the Kraft pulp was chlorinated under conditions of constant chlorine concentration and temperature, it was found that constancy of reaction rates was attained at higher chlorine concentrations.

7. The delignification data for the Kraft pulp after chlorination and for chlorination followed by alkali extraction fit very well an equation based on two apparent simultaneous or consecutive first order reactions. In addition to the lignin removed by these two apparent reactions, a certain percentage of the original lignin was assumed to be removed instantaneously.

8. The reaction velocity constants for both the apparent first order reactions have been shown to vary with chlorination temperature in accordance with the Arrhenius equation.

9. For the same quantity of lignin removed at different concentration levels, it was found that the degree of polymerization number of the cellulose was lower at
higher concentrations. However, it was also indicated that at very short-time intervals the decrease in the degree of polymerization number at higher concentration levels was not appreciable.

10. It was found that rates of delignification of the ground wood were slower as compared to those for the Kraft pulp. This might have been due to the small area of lignin surface exposed for reaction in the ground wood.

11. The rate of delignification of cold soda pulp was a function of chlorine concentration and no constancy of reaction rates was found. This substantiated the fact that for the Kraft pulp the constancy of the apparent reaction velocity constants at higher chlorine concentrations was possibly due to the low lignin concentration. Thus, it was the concentration of lignin and not the concentration of chlorine which was the controlling factor.

12. An equation similar to that derived from the Kraft pulp seemed to apply well to the delignification data for the cold soda pulp. The apparent reaction velocity constants for both the reactions were logarithmic functions of chlorine concentration. Hence the equation was developed which correlated $L$, chlorine concentration and chlorination time.

13. It was found that the values of $L$ calculated for the Kraft pulp through the use of equation derived for
the cold soda pulp were much higher than those observed.

14. A microscopic study of both the cold soda pulp and the Kraft pulp indicated that the ratio of surface to weight for the cold soda pulp was considerably less than the Kraft pulp.

15. It was concluded that in chlorination of pulps, the exposed surface is an important variable. Therefore, an attempt should be made to incorporate this variable in the general equation derived for delignification by chlorination.
TABLE 1

EFFECT OF CHLORINATION TIME ON CHLORINE CONSUMPTION

Weight of oven-dry sample = 16.5 gm.
Pulp consistency = 1.0 %
Initial Cl\(_2\) concentration in liquor = 1.63 g/l.
Total volume of liquor = 1635 ml.
Temperature = 77°F.

<table>
<thead>
<tr>
<th>Time min.</th>
<th>Res. Cl(_2) gm.</th>
<th>% Res. Cl(_2)</th>
<th>Total Cl(_2) used gm.</th>
<th>Cl(_2) used by Subs. gm.</th>
<th>Cl(_2) used by Oxid. gm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.897</td>
<td>33.6</td>
<td>1.77</td>
<td>0.92</td>
<td>0.85</td>
</tr>
<tr>
<td>5</td>
<td>0.839</td>
<td>31.4</td>
<td>1.83</td>
<td>0.90</td>
<td>0.93</td>
</tr>
<tr>
<td>10</td>
<td>0.669</td>
<td>25.0</td>
<td>2.00</td>
<td>0.90</td>
<td>1.10</td>
</tr>
<tr>
<td>20</td>
<td>0.572</td>
<td>21.4</td>
<td>2.20</td>
<td>0.89</td>
<td>1.31</td>
</tr>
<tr>
<td>40</td>
<td>0.357</td>
<td>13.3</td>
<td>2.31</td>
<td>0.87</td>
<td>1.44</td>
</tr>
<tr>
<td>60</td>
<td>0.312</td>
<td>11.6</td>
<td>2.36</td>
<td>0.87</td>
<td>1.49</td>
</tr>
</tbody>
</table>
TABLE 2

EFFECT OF CHLORINATION TIME ON CHLORINE CONSUMPTION

- Weight of oven-dry sample = 16.5 gm.
- Pulp consistency = 2.0 %
- Initial Cl₂ concentration in liquor = 3.33 g/1.
- Total volume of liquor = 810 ml.
- Temperature = 77°F.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Res. Cl₂ (gm.)</th>
<th>% Res. Cl₂</th>
<th>Total Cl₂ used (gm.)</th>
<th>Cl₂ used by Subs. (gm.)</th>
<th>Cl₂ used by Oxid. (gm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.784</td>
<td>29.4</td>
<td>1.89</td>
<td>0.94</td>
<td>0.95</td>
</tr>
<tr>
<td>5</td>
<td>0.660</td>
<td>24.7</td>
<td>2.01</td>
<td>0.92</td>
<td>1.09</td>
</tr>
<tr>
<td>10</td>
<td>0.553</td>
<td>20.7</td>
<td>2.12</td>
<td>0.93</td>
<td>1.19</td>
</tr>
<tr>
<td>20</td>
<td>0.460</td>
<td>17.2</td>
<td>2.21</td>
<td>0.94</td>
<td>1.27</td>
</tr>
<tr>
<td>40</td>
<td>0.320</td>
<td>12.0</td>
<td>2.35</td>
<td>0.93</td>
<td>1.42</td>
</tr>
<tr>
<td>60</td>
<td>0.273</td>
<td>10.2</td>
<td>2.40</td>
<td>0.93</td>
<td>1.47</td>
</tr>
</tbody>
</table>
TABLE 3

EFFECT OF CHLORINATION TIME ON CHLORINE CONSUMPTION

Weight of oven-dry sample = 25.0 gm.
Pulp consistency = 3.0 %
Initial Cl₂ concentration in liquor = 5.00 g/l.
Total volume of liquor = 810 ml.
Temperature = 77°F.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Res. Cl₂ (gm)</th>
<th>% Res. Cl₂</th>
<th>Total Cl₂ used (gm)</th>
<th>Cl₂ used by Subs. (gm)</th>
<th>Cl₂ used by Oxid. (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.134</td>
<td>27.7</td>
<td>2.92</td>
<td>1.70</td>
<td>1.22</td>
</tr>
<tr>
<td>5</td>
<td>0.967</td>
<td>23.9</td>
<td>3.08</td>
<td>1.74</td>
<td>1.34</td>
</tr>
<tr>
<td>10</td>
<td>0.788</td>
<td>19.4</td>
<td>3.26</td>
<td>1.76</td>
<td>1.50</td>
</tr>
<tr>
<td>20</td>
<td>0.660</td>
<td>16.2</td>
<td>3.39</td>
<td>1.77</td>
<td>1.62</td>
</tr>
<tr>
<td>40</td>
<td>0.446</td>
<td>11.0</td>
<td>3.60</td>
<td>1.82</td>
<td>1.78</td>
</tr>
<tr>
<td>60</td>
<td>0.371</td>
<td>9.2</td>
<td>3.68</td>
<td>1.84</td>
<td>1.84</td>
</tr>
</tbody>
</table>
TABLE 4

EFFECT OF CHLORINE CONCENTRATION AT 3.0% CONSISTENCY ON CHLORINE CONSUMPTION

Weight of oven-dry sample  =  25.0 gm.
Pulp consistency  =  3.0 %
Total volume of liquor  =  810 ml.
Temperature  =  77° F.
Chlorination time  =  5 min.

<table>
<thead>
<tr>
<th>No.</th>
<th>Init. Cl₂ Conc. gm.</th>
<th>Res. Cl₂ gm.</th>
<th>% Res. Cl₂</th>
<th>Total Cl₂ used gm.</th>
<th>Cl₂ used by Subs. gm.</th>
<th>Cl₂ used by Oxid. gm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.00</td>
<td>0.967</td>
<td>23.9</td>
<td>3.08</td>
<td>1.74</td>
<td>1.34</td>
</tr>
<tr>
<td>2</td>
<td>4.62</td>
<td>0.666</td>
<td>17.8</td>
<td>3.07</td>
<td>1.76</td>
<td>1.31</td>
</tr>
<tr>
<td>3</td>
<td>4.23</td>
<td>0.432</td>
<td>12.6</td>
<td>3.00</td>
<td>1.73</td>
<td>1.26</td>
</tr>
<tr>
<td>4</td>
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<td>0.291</td>
<td>9.3</td>
<td>2.84</td>
<td>1.64</td>
<td>1.20</td>
</tr>
<tr>
<td>5</td>
<td>3.08</td>
<td>0.025</td>
<td>1.0</td>
<td>2.46</td>
<td>1.36</td>
<td>1.10</td>
</tr>
</tbody>
</table>
TABLE 5

EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL AND DEGREE OF POLYMERIZATION NUMBER OF CELLULOSE

The experimental conditions are same as listed in Table 1.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Removed</th>
<th>% of Orig. L Remaining</th>
<th>D.P. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorination</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>100.0</td>
<td>11.50</td>
<td>0.0</td>
<td>100.0</td>
<td>1715</td>
</tr>
<tr>
<td>5</td>
<td>95.2</td>
<td>7.40</td>
<td>37.4</td>
<td>62.6</td>
<td>1690</td>
</tr>
<tr>
<td>20</td>
<td>94.0</td>
<td>6.25</td>
<td>47.8</td>
<td>52.2</td>
<td>1630</td>
</tr>
<tr>
<td>40</td>
<td>93.1</td>
<td>6.05</td>
<td>50.0</td>
<td>50.0</td>
<td>1603</td>
</tr>
<tr>
<td>60</td>
<td>92.2</td>
<td>5.81</td>
<td>52.4</td>
<td>47.6</td>
<td>1576</td>
</tr>
<tr>
<td>Chlorination and Alkali Extraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>88.5</td>
<td>1.92</td>
<td>84.5</td>
<td>15.5</td>
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<td>20</td>
<td>87.3</td>
<td>1.52</td>
<td>88.2</td>
<td>11.8</td>
<td>1625</td>
</tr>
<tr>
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<td>87.0</td>
<td>1.35</td>
<td>91.3</td>
<td>8.7</td>
<td>1580</td>
</tr>
<tr>
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<td>86.8</td>
<td>0.86</td>
<td>93.8</td>
<td>6.2</td>
<td>1535</td>
</tr>
</tbody>
</table>
TABLE 6

EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL AND DEGREE OF POLYMERIZATION NUMBER OF CELLULOSE

The experimental conditions are same as listed in Table 2.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Removed</th>
<th>% of Orig. L Remaining</th>
<th>D.P. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorination</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>94.3</td>
<td>6.54</td>
<td>45.0</td>
<td>55.0</td>
<td>1675</td>
</tr>
<tr>
<td>20</td>
<td>93.1</td>
<td>5.98</td>
<td>50.4</td>
<td>49.6</td>
<td>1632</td>
</tr>
<tr>
<td>40</td>
<td>92.2</td>
<td>5.63</td>
<td>54.0</td>
<td>46.0</td>
<td>1600</td>
</tr>
<tr>
<td>60</td>
<td>91.5</td>
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<td>58.9</td>
<td>41.1</td>
<td>1578</td>
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<tr>
<td>Chlorination and Alkali Extraction</td>
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<td></td>
<td></td>
</tr>
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<td>5</td>
<td>86.7</td>
<td>1.76</td>
<td>86.0</td>
<td>13.0</td>
<td>1659</td>
</tr>
<tr>
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<td>86.0</td>
<td>1.27</td>
<td>89.8</td>
<td>10.2</td>
<td>1605</td>
</tr>
<tr>
<td>40</td>
<td>85.3</td>
<td>1.15</td>
<td>93.5</td>
<td>6.5</td>
<td>1568</td>
</tr>
<tr>
<td>60</td>
<td>84.9</td>
<td>0.65</td>
<td>95.5</td>
<td>4.5</td>
<td>1540</td>
</tr>
</tbody>
</table>
TABLE 7

EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL AND DEGREE OF POLYMERIZATION NUMBER OF CELLULOSE

The experimental conditions are same as listed in Table 3.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Removed</th>
<th>% of Orig. L Remaining</th>
<th>D.P. No.</th>
</tr>
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<td>93.5</td>
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<td>0.65</td>
<td>95.5</td>
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TABLE 8

EFFECT OF CHLORINE CONCENTRATION AT 3 PER CENT
CONSISTENCY ON LIGNIN REMOVAL AND DEGREE OF
POLYMERIZATION NUMBER OF CELLULOSE

The experimental conditions are same as listed in
Table 4.

<table>
<thead>
<tr>
<th>Time(min.)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Removed</th>
<th>% of Orig. L Remaining</th>
<th>D.P. No.</th>
</tr>
</thead>
</table>
| Chlorination
| 5.00         | 91.3            | 6.51        | 48.4                 | 51.6                   | 1665    |
|             |          | 90.5            | 6.73        | 47.2                 | 52.8                   | 1665    |
|             |          | 91.4            | 6.89        | 45.3                 | 54.7                   | 1665    |
| Chlorination and Alkali Extraction
| 3.85         | 92.6            | 7.12        | 42.7                 | 57.3                   | 1695    |
| 5.00         | 85.7            | 1.76        | 86.0                 | 14.0                   | 1660    |
| 4.62         | 84.7            | 1.93        | 85.5                 | 14.5                   | 1645    |
| 4.23         | 85.6            | 2.36        | 82.6                 | 17.4                   | 1645    |
| 3.85         | 86.2            | 2.90        | 79.6                 | 21.4                   | 1665    |
### TABLE 9

**AMOUNTS OF CHLORINE CONSUMED PER GRAM OF TOTAL LIGNIN REMOVED**

Calculated from Tables 1 - 3 and Tables 5 - 7.

Basis: 100 grams of dry pulp.

<table>
<thead>
<tr>
<th>Chlorination Time (min.)</th>
<th>Final Lignin (gm.)</th>
<th>Lignin Removed (gm.)</th>
<th>% Cl₂ Res.</th>
<th>Cl₂ Consumed (gm.)</th>
<th>gm. Cl₂ Consumed per gm. of Lignin Removed</th>
</tr>
</thead>
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<tr>
<td><strong>Cons. = 1.0%</strong></td>
<td></td>
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<td>9.75</td>
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<td>1.14</td>
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<td>10.13</td>
<td>21.4</td>
<td>13.3</td>
<td>1.31</td>
</tr>
<tr>
<td>40</td>
<td>1.19</td>
<td>10.31</td>
<td>13.3</td>
<td>14.0</td>
<td>1.35</td>
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<tr>
<td>60</td>
<td>0.75</td>
<td>10.75</td>
<td>11.6</td>
<td>14.3</td>
<td>1.33</td>
</tr>
<tr>
<td><strong>Mean = 1.29</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| **Cons. = 2.0%**        |                    |                      |            |                   |                                          |
| 5                       | 1.56               | 9.94                 | 24.7       | 12.3              | 1.24                                     |
| 20                      | 1.16               | 10.34                | 17.2       | 13.4              | 1.29                                     |
| 40                      | 1.03               | 10.47                | 12.0       | 14.3              | 1.36                                     |
| 60                      | 0.59               | 10.91                | 10.2       | 14.6              | 1.34                                     |
| **Mean = 1.31**         |                    |                      |            |                   |                                          |

| **Cons. = 3.0%**        |                    |                      |            |                   |                                          |
| 5                       | 1.51               | 9.99                 | 23.9       | 12.3              | 1.23                                     |
| 20                      | 1.11               | 10.39                | 16.2       | 16.2              | 1.29                                     |
| 40                      | 1.02               | 10.48                | 11.0       | 14.3              | 1.37                                     |
| 60                      | 0.55               | 10.95                | 9.2        | 14.7              | 1.31                                     |
| **Mean = 1.31**         |                    |                      |            |                   |                                          |
TABLE 10.
AMOUNTS OF CHLORINE CONSUMED BY SUBSTITUTION AND
BY OXIDATION PER GRAM OF TOTAL LIGNIN REMOVED

Calculated from Tables 1 - 3 and 8.
Basis: 100 grams of dry pulp.

<table>
<thead>
<tr>
<th>Chlorination Time (min.)</th>
<th>Lignin Removed (gm.)</th>
<th>Cl₂ used by Subs. (gm.)</th>
<th>Cl₂ used by Oxid. (gm.)</th>
<th>gm Cl₂ used by Subs per gm. of L Removed</th>
<th>gm Cl₂ used by Oxid per gm. of L Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cons. = 1.0%</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>9.75</td>
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<td>5.63</td>
<td>0.56</td>
<td>0.57</td>
</tr>
<tr>
<td>20</td>
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<td>5.38</td>
<td>7.94</td>
<td>0.53</td>
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</tr>
<tr>
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<td>5.27</td>
<td>8.72</td>
<td>0.51</td>
<td>0.84</td>
</tr>
<tr>
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<td>10.75</td>
<td>5.27</td>
<td>9.03</td>
<td>0.49</td>
<td>0.84</td>
</tr>
<tr>
<td>Cons. = 2.0%</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>9.94</td>
<td>5.67</td>
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</tr>
<tr>
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<td>7.70</td>
<td>0.55</td>
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<tr>
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<tr>
<td>60</td>
<td>10.91</td>
<td>5.68</td>
<td>8.91</td>
<td>0.52</td>
<td>0.82</td>
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<td>6.96</td>
<td>5.36</td>
<td>0.69</td>
<td>0.54</td>
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<tr>
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<td>7.36</td>
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</table>
TABLE 11
RESIDUAL CHLORINE CONCENTRATION IN THE LIQUOR
Calculated from Tables 1, 2 and 3

<table>
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<tr>
<th>Time (min)</th>
<th>Cons. = 1.0 %</th>
<th>Cons. = 2.0 %</th>
<th>Cons. = 3.0 %</th>
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<td>0.683</td>
<td>0.971</td>
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<tr>
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<td>0.350</td>
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TABLE 12

EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL AND DEGREE OF POLYMERIZATION NUMBER OF KRAFT PULP

Weight of oven-dry sample = 66.0 gm.
Total volume of liquor = 33.0 l.
Chlorine concentration of the liquor = 0.36 g/l.
Temperature = 77°F.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig.L Removed</th>
<th>D.P. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorination</td>
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<td>7.1</td>
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</table>
TABLE 13
EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL AND DEGREE OF POLYMERIZATION NUMBER OF KRAFT PULP

Weight of oven-day sample  = 66.0 gm.
Total volume of liquor  = 33.0 l.
Chlorine concentration of the liquor  = 0.57 g/l.
Temperature  = 77°F.

<table>
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<th>Time (min.)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
<th>D.P. No.</th>
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</table>
TABLE 14

EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL AND
DEGREE OF POLYMERIZATION NUMBER OF KRAFT PULP

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
<th>D.P. No.</th>
</tr>
</thead>
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<td>94.5</td>
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</table>
### TABLE 15

EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL AND DEGREE OF POLYMERIZATION NUMBER OF KRAFT PULP

- **Weight of oven-dry sample** = 66.0 gm.
- **Total volume of liquor** = 33.0 l.
- **Chlorine concentration of the liquor** = 1.63 g/l.
- **Temperature** = 77°F.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L remaining</th>
<th>% of Orig. L Removed</th>
<th>D.P. No.</th>
</tr>
</thead>
<tbody>
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<td></td>
</tr>
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<tr>
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</table>
TABLE 16
EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL AND DEGREE OF POLYMERIZATION NUMBER OF KRAFT PULP

Weight of oven-dry sample = 66.0 gm.
Total volume of liquor = 33.0 l.
Chlorine concentration of the liquor = 0.57 g/l.
Temperature = 87°F.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
<th>D.P. No.</th>
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Chlorination and Alkali Extraction

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<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
<th>D.P. No.</th>
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TABLE 17

EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL AND DEGREE OF POLYMERIZATION NUMBER OF KRAFT PULP

Weight of oven-dry = 66.0 gm.
Total volume of liquor = 33.0 l.
Chlorine concentration of the liquor = 0.57 g/l.
Temperature = 66°F.

<table>
<thead>
<tr>
<th>Time min.</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
<th>D.P. No.</th>
</tr>
</thead>
<tbody>
<tr>
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TABLE 18
EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL FROM PINE

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% Wood Remaining</th>
<th>% L in Wood</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
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Chlorination and Alkali Extraction

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<th>Time (min)</th>
<th>% Wood Remaining</th>
<th>% L in Wood</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
</tr>
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<tbody>
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<td>19.10</td>
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</table>
### TABLE 19

**EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL FROM COLD SODA PULP**

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
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TABLE 20

EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL FROM COLD SODA PULP

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<th>Time min.</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
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<td>78.7</td>
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</table>
TABLE 21

EFFECT OF CHLORINATION TIME ON LIGNIN REMOVAL FROM COLD SODA PULP

Weight of oven-dry sample = 20.0 gm.
Total volume of liquor = 33.0 l.
Chlorine concentration in the liquor = 1.50 g/l.
Temperature = 77°F

<table>
<thead>
<tr>
<th>Time min.</th>
<th>% Pulp Remaining</th>
<th>% L in Pulp</th>
<th>% of Orig. L Remaining</th>
<th>% of Orig. L Removed</th>
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</table>
16.2% (based on pulp) Cl₂ applied in all cases

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<th>Initial conc.</th>
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<td>1.63 g/l</td>
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<tr>
<td>2%</td>
<td>3.33 g/l</td>
</tr>
<tr>
<td>3%</td>
<td>5.00 g/l</td>
</tr>
</tbody>
</table>

Figure 6. -- Percent Residual Chlorine at Various Consistencies versus Time.
Chlorine Consumed by Oxid. versus Time for the Kraft Pulp at Various Consistencies

- O - 1%
- x - 2%
- △ - 3%

Chlorine Consumed by Subs. versus Time for the Kraft Pulp at Various Consistencies

- O - 1%
- x - 2%
- △ - 3%

Figure 7
Figure 8

Percent Chlorine Consumed by Substitution versus Time by the Kraft Pulp at Various Consistencies

- ○ - 1%
- × - 2%
- △ - 3%
Figure 9

Percent of Original Lignin Removed by Chlorination versus Time for Kraft Pulp

<table>
<thead>
<tr>
<th>Pulp Cons.</th>
<th>Cl₂ Conc.</th>
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<tbody>
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<td>1.0%</td>
<td>1.63 g/l</td>
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<tr>
<td>2.0%</td>
<td>3.33 g/l</td>
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<tr>
<td>3.0%</td>
<td>5.00 g/l</td>
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</tbody>
</table>
Percent of Original Lignin Removed by Chlorination and Alk. Extn. versus Time for Kraft Pulp

Pulp Cons. Cl₂ Conc.

- 1.0% 1.63 g/l
- 2.0% 3.33 g/l
- 3.0% 5.00 g/l

Figure 10
D.P. No. After Chlorination versus Time for Kraft Pulp

Pulp Cons.  Cl₂ Conc.
⊙ - 1.0%  1.63 g/l
× - 2.0%  3.33 g/l
△ - 3.0%  5.00 g/l

Figure 11
D.P. No. After Chlorination and Alk. Extn. versus Time for Kraft Pulp

<table>
<thead>
<tr>
<th>Pulp Cons.</th>
<th>Cl₂ Conc.</th>
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<tbody>
<tr>
<td>○ - 1.0%</td>
<td>1.63 g/l</td>
</tr>
<tr>
<td>× - 2.0%</td>
<td>3.33 g/l</td>
</tr>
<tr>
<td>△ - 3.0%</td>
<td>5.00 g/l</td>
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</table>

Figure 12
Relation Between Maximum Chlorine Application versus Consistency at 760 mm Hg and Various Temperatures
Relation Between Lignin Removal and Consistency at 760 mm Hg and Various Temperatures

Figure 14
Percent of Original Lignin Removed by Chlorination versus Time for Kraft Pulp at 77°F

Cl₂ conc. g/l

- ○ 0.36
- △ 0.57
- × 0.90
- □ 1.62

Time (Minutes)

Figure 15
Percent of Original Lignin Removed by Chlorination and Alk. Extn. for Kraft Pulp at 77°F

Time (Minutes)

Figure 16
Figure 17

Percent of Original Lignin Removed from Kraft Pulp versus Time at 0.57 g/l Cl₂ Conc.

- △ - Chlorination at 66°F
- ○ - Chlorination at 87°F
- × - Chlorination and Alk. Extn. at 66°F
- □ - Chlorination and Alk. Extn. at 87°F
Figure 18. D.P. No. after Chlorination versus Time for Kraft Pulp at 77°F.
Figure 19.-- D.P. No. after Chlorination and Alk. Extm. versus Time for Kraft Pulp at 77°F.
Figure 20.-- D.P. No. after Chlorination versus Time For Kraft Pulp at 0.57 g/l Cl₂ Conc.
Figure 21. -- D.P. No. after Chlorination and Alk. Extn. versus Time for Kraft Pulp at 0.57 g/l Cl₂ Conc.
Percent of Original Lignin Removed versus Time for Ground Wood at 0.80 g/l Cl₂ Conc. and 77°F

○ - by Chlorination
△ - by Chlorination and Alk. Extn.

Figure 22
Percent of Original Lignin Removed by Chlorination versus Time for Cold Soda Pulp at 77°F

$\text{Cl}_2$ Conc. g/l

- $\text{O} - 0.80$
- $\times - 1.14$
- $\triangle - 1.50$

Figure 23
Percent of Original Lignin Removed by Chlorination and Alkali Extn. for Cold Soda Pulp at 77°F

\[ \text{Cl}_2 \text{ Conc. g/l} \]

- ⊗ - 0.80
- × - 1.14
- △ - 1.50

Time (Minutes)

Figure 24
Log \left( \frac{-dL}{dt} \right) \text{ versus } \Log L \text{ for Kraft Pulp at } 77^\circ \text{F}

Cl_2 \text{ Conc. } g/l

- \Large{\circ} \text{ - 0.36} \quad \Large{\times} \text{ - 0.90}

- \Large{\triangle} \text{ - 0.57} \quad \Large{\square} \text{ - 1.63}

Figure 25
Log L after Chlorination versus Time for Kraft Pulp at 77°F and 0.36 g/l

- Data Points
- Reaction A
- Reaction B

Figure 26
Log L after Chlorination versus Time for Kraft Pulp at 77°F and 0.57 g/l

Figure 27
Log L after Chlorination versus Time for Kraft Pulp at 77°F, 0.90 and 1.63 g/l

- x - 0.90 g/l
- □ - 1.63 g/l

- - - Reaction A
- - -Reaction B

Figure 28
Log L after Chlorination and Alk. Ext'n. versus Time for Kraft Pulp at 77°F

Cl₂ Conc. g/l

- 0.36
- 0.90
- 0.57
- 1.63

Percent of Original Lignin Remaining

Time (Minutes)

Figure 29
Log $L'$ and $L''$ after Chlorination and Alk. Ext'n. versus Time for Kraft Pulp at 77°F

- Reaction A, ($L'$)
- Reaction B, ($L''$)

Percent of Original Lignin Remaining

Time (Minutes)

Figure 30
Log L after Chlorination versus Time for Kraft Pulp at 66°F and 0.57 g/l

- O Data Points
- - - Reaction A
- -- - Reaction B

Fig. 31
Log L after Chlorination versus Time for Kraft Pulp at 87°F and 0.57 g/l

- Data Points
- Reaction A
- Reaction B
Reaction Velocity Constants $k_1$ and $k_2$ for Chlorination at 0.57 g/l versus Reciprocal of Absolute Temperature

Figure 33
Log L after Chlorination and Alk. Extn. versus Time for Kraft Pulp at 66°F and 0.57 g/l

Percent of Original Lignin Remaining

Time (Minutes)

Figure 34
Log L after Chlorination and Alk. Extnt. versus Time for Kraft Pulp at 87°F and 0.57 g/l

- Data Point
- Reaction A
- Reaction B

Percent of Original Lignin Remaining

Time (Minutes)

Figure 35
Figure 36.-- Reaction Velocity Constants \( k_1 \) and \( k_2 \) for Chlorination and Alk. Ext. at 0.57 g/l versus Reciprocal of Absolute Temperature
Log L after Chlorination versus Time for Cold Soda Pulp at 77°F and 0.80 g/l

- Data Points
- Reaction A
- Reaction B

Figure 37
Log L after Chlorination versus Time for Cold Soda Pulp at 77°F and 1.14 g/l

Percent of Original Lignin Remaining

Time (Minutes)

Figure 38
Log $L$ after Chlorination versus Time for Cold Soda Pulp at $77^\circ F$ and 1.50 g/l
Log L after Chlorination and Alk. Extn. for Cold Soda Pulp at 77°F

Cl₂ Conc. g/l

○ - 0.80
× - 1.14
△ - 1.50

Time (Minutes)

Percent of Original Lignin Remaining

Figure 40
Figure 41: Log $L'$ and $L''$ after Chlorination and Alk. Extn. for Cold Soda Pulp at 77°F.

Percent of Original Lignin Remaining vs. Time (Minutes).

- - - - - Reaction A, $(L')$
- - - - - Reaction B, $(L'')$

0.80 g/l
1.14 g/l
1.50 g/l

0 10 20 30 40 50 60

Time (Minutes)
Figure 42.— Log $k_1$ and $k_2$ for Chlorination versus Log Cl₂ Conc. for Cold Soda Pulp.
Figure 43. -- Log $k_1$ and $k_2$ for Chlorination and Alk. Extn. versus Log Cl₂ Conc. for Cold Soda Pulp.
BIBLIOGRAPHY


29. Davidson, G. F., Shirley Institute Memoirs, 12, 6 (1933).
BIOGRAPHICAL ITEMS

Vasant D. Chapnerkar was born in Bombay, India, on the twenty-fifth day of August, 1932. In 1952, he graduated in Chemistry from the University of Bombay. From the same University he received his B. Sc.(Tech.) degree in 1954, in Chemical Engineering. Before joining the University of Florida, he worked as Research Assistant in Atomic Energy Commission, Government of India. In August, 1958, he received his M. S. degree in Engineering from the University of Florida and has been studying for his Ph.D. degree in Chemical Engineering since then.
This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Ph.D with major in Chemical Engineering.

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