

Development of a predictive model
for the
Hypochlorite bleaching
of
CE-prebleached *Pinus Radiata* Kraft pulp

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*To my parents —
Their love, encouragement
and confidence in me have
been abundant and
unconditional*

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Abstract

A study was done to determine the kinetics and stoichiometry of hypochlorite bleaching of *pinus radiata* kraft pulp obtained from the extraction stage of a chlorine, caustic extraction and hypochlorite (CEH) bleaching sequence. The “differential method” of experimentation was used, where bleaching chemicals are charged at the start of the experiment and allowed to decrease as bleaching proceeds. The bleaching rate is found to be dependent on temperature, chromophore concentration (approximated by the specific light absorption coefficient), hypochlorite ion concentration (OCl^-) and hydroxide ion concentration (alkalinity, OH^-). Bleaching rate increases with chromophore concentration and hypochlorite ion concentration but decreases with increasing alkalinity. The bleaching rate, $\left\{\frac{dC_k}{dt}\right\}$, for the hypochlorite bleaching of CE-prebleached *pinus radiata* kraft pulp can be expressed by the following kinetic equation.

$$-\frac{dC_k}{dt} = k_1 * C_k^{2.629} * [\text{OH}^-]^{-0.043} * [\text{OCl}^-]^{0.383}$$

where

C_k : specific light absorption coefficient at 457 nm, $[\text{m}^2 \text{kg}^{-1}]$
 $[\text{OH}^-]$: hydroxide ion concentration, $[\text{mol l}^{-1}]$
 $[\text{OCl}^-]$: hypochlorite ion concentration, $[\text{mol l}^{-1}]$
 and the Arrhenius' activation energy is approximately 64 kJ mol^{-1}

The stoichiometry of the bleaching reaction can be described by the following two equations.

$$\frac{d\text{OCl}}{dC_k} = \frac{3.89 * C_{k_0}^{-1.25}}{C_k}$$

$$\frac{dpH}{d\text{OCl}} = 2.299 * \text{OCl}_0^{-0.493} * \text{OCl}^{-0.507}$$

where

C_{k_0} : initial specific light absorption coefficient, $[\text{m}^2 \text{kg}^{-1}]$
 OCl_0 : initial hypochlorite charge, $[\text{moles per kg O.D. pulp}]$
 OCl : hypochlorite charge at time = t, $[\text{moles per kg O.D. pulp}]$

CHAPTER 1

Introduction

1.1) GENERAL

Ever since the invention of the printing press, paper has become one of the most important manufactured products in our world today. Paper products are intimately linked into our lives each time we read a newspaper, pick up a novel, write a letter, wrap an object and last but not least, when we present our thesis. Even with the coming of the computer age, which was meant to herald the “paperless society”, the usage of paper has continued to increase as the ability to store and record information on paper is made easier.

Cellulose, a colourless substance, is the basic raw material for the manufacture of paper. An abundant naturally occurring compound, cellulose is a carbohydrate which can be found in all varieties of plants. It is the major component of the cell wall of all woods, straws and grasses. Cellulose is a straight chain polysaccharide with an empirical formula of $C_6H_{10}O_5$ and a molecular weight of up to 1,620,000. Bundles of cellulose molecules are grouped together as microfibrils, which in turn are bundled together to form fibrils and finally cellulose fibres.

Wood is one of the principle sources of cellulose and is the most widely used raw material in the paper industry. Apart from cellulose, which comprises about 40 - 45% of wood, wood also contains other compounds such as hemicellulose, lignins and other minor impurities.

Hemicelluloses are highly branched carbohydrates with a degree of polymerisation much lower than that of cellulose. Unlike cellulose, which is fibrous in nature, hemicelluloses are non-fibrous wood components. Comprising of between 20 - 30% of wood, hemicelluloses are more susceptible to chemical attack than cellulose.

Apart from cellulose and hemicellulose, lignin is the other major component of wood, comprising between 17 - 32% of wood. Little is known about the exact chemical structure of lignin but it is believed to be a tridimensional polymer of phenylpropane units. It should be noted however, that lignin is not a constitutionally defined compound but is a group of high molecular weight amorphous materials that are chemically closely related. Lignin and lignin

derivatives are the main light absorbing substances present in wood and it is these compounds that are removed during chemical pulping and bleaching.

Besides celluloses, hemicelluloses and lignins, a number of other minor substances such as resin, tannins, tall oils, turpentine and other aromatic hydrocarbons can also be found in wood. Most of these substances are either soluble in water or organic solvents and are collectively known as extractives. The amount of extractives present varies widely, depending on the wood species.

A simple representation of the chemical structure of wood is illustrated by Figure 1.1.

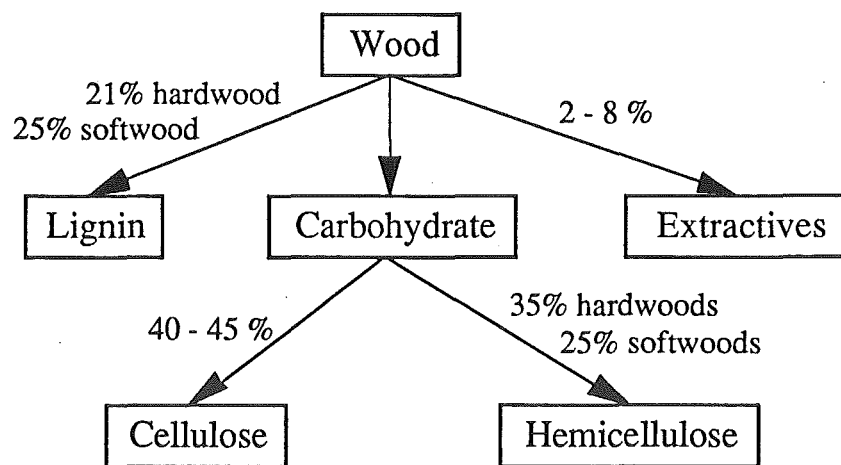


FIGURE 1.1: Simple representation of the chemical composition of wood.

1.2) PRINCIPLES OF PULPING

Before wood can be utilised for paper manufacture, it first necessary to reduce the wood to a fibrous state by a process known as pulping. There are basically two main types of pulping; mechanical pulping and chemical pulping.

In mechanical pulping, wood or wood chips are physically shredded and ground into a fibrous mass. An example of mechanical pulping is the groundwood process which defiberise wood by pressing a block of wood lengthwise against a revolving grinding stone. A more recent process involves feeding wood chips in between rotating discs in a device known as a refiner. Mechanical pulping has the advantage of high yields, converting up to 95% of the original wood into pulp. However, mechanical pulps usually have low brightness and poor strength qualities.

Separation of fibres in chemical pulping is achieved by the chemical degradation and dissolution of the bonding material in wood, leaving behind intact wood fibres. Lignin is the major

compound removed in chemical pulping, although a certain amount of cellulose and hemicellulose is also degraded. The resulting yield from chemical pulping is low compared to mechanical pulping, usually between 40 - 50 % of the original wood.

There exists, however, many other forms of pulping, most of which are a variation of mechanical pulping and/or chemical pulping. In semichemical pulping, chemical treatment is used to soften the wood before being ground mechanically. Thermo-mechanical pulping uses heat treatment to soften the wood chips before being defiberised mechanically. A combination of heat, chemical and mechanical treatment is used in chemical thermal mechanical pulping.

With chemical pulping, the Kraft process is one of the most widely used in the pulp and paper industry. Also sometimes called the "sulphate process", kraft pulping uses sodium hydroxide (NaOH) and sodium sulphide (Na_2S) as the cooking chemicals. In the Kraft pulping process, wood chips are "cooked" together with the cooking chemicals in a pressure vessel at high temperature for 2 - 4 hours. At the end of the cook, the contents are discharged into a blow tank where the sudden decrease in pressure literally causes the softened wood chips to explode into a fibrous mass. In a typical kraft pulping process, approximately 80% of the lignin, together with 50% of the hemicellulose and around 10% of the cellulose is removed.

1.3) PRINCIPLES OF BLEACHING

To obtain pulp of acceptable brightness, it is necessary to further treat the pulp to remove the coloured compounds. This is achieved by bleaching the pulp chemically. The colour of pulp is generally agreed to be due to the presence of strong light absorbing substances known as chromophores. Chromophores exist naturally in native lignin but may also be formed from chemical reactions during the pulping process. To increase the brightness of pulp, the chromophores can be removed by two different methods: (1) lignin preserving bleaching and (2) lignin removing bleaching (delignification).

Lignin preserving bleaching, also known as brightening, is mainly used for high yield pulps that have a high lignin content. In this process, the bleaching chemicals increases brightness by selective reaction with the chromophoric groups on the lignin, changing them into weaker light absorbing compounds, while leaving the bulk of the lignin intact. The advantage of this process is that high yields can be achieved. However, high brightness pulps are difficult to produce and brightness stability is often poor. The action of light and oxygen will cause certain groups in the pulp to be changed into coloured compounds. An example of a lignin-preserving chemical is sodium peroxide, commonly used in the bleaching of mechanical pulps.

To produce pulps of high brightness, lignin removing methods have to be used. This method is essentially a continuation of the pulping process although more selective chemicals are used

instead. For effective bleaching, the bleaching is usually done in a series of stages known as pulping sequences. The choice of bleaching sequence will depend on the pulp species, pulp treatment, bleaching method and the end use of the pulp. At Tasman Pulp and Paper, the production of semi-bleached pulp is bleached using the CEH bleaching sequence. Bleaching of this type consists of three kinds of reactions: (1) chlorination in an acidic medium, (2) alkaline extraction and (3) alkaline hypochlorite bleaching.

1.4) CHEMISTRY OF BLEACHING

1.4.1) CHLORINE - WATER SYSTEM

To understand the principles of chlorine and chlorine-related bleaching, it is important to understand the reaction between water and chlorine. The chlorine - water system plays an important role in determining the type of bleaching reaction that occurs in the bleaching stage. Chlorine gas, when dissolved in water, forms the following equilibrium:



This equilibrium in the chlorine-water system makes it possible to regulate the concentrations of the various components by changing the pH of the system.(Fig. 1.2)

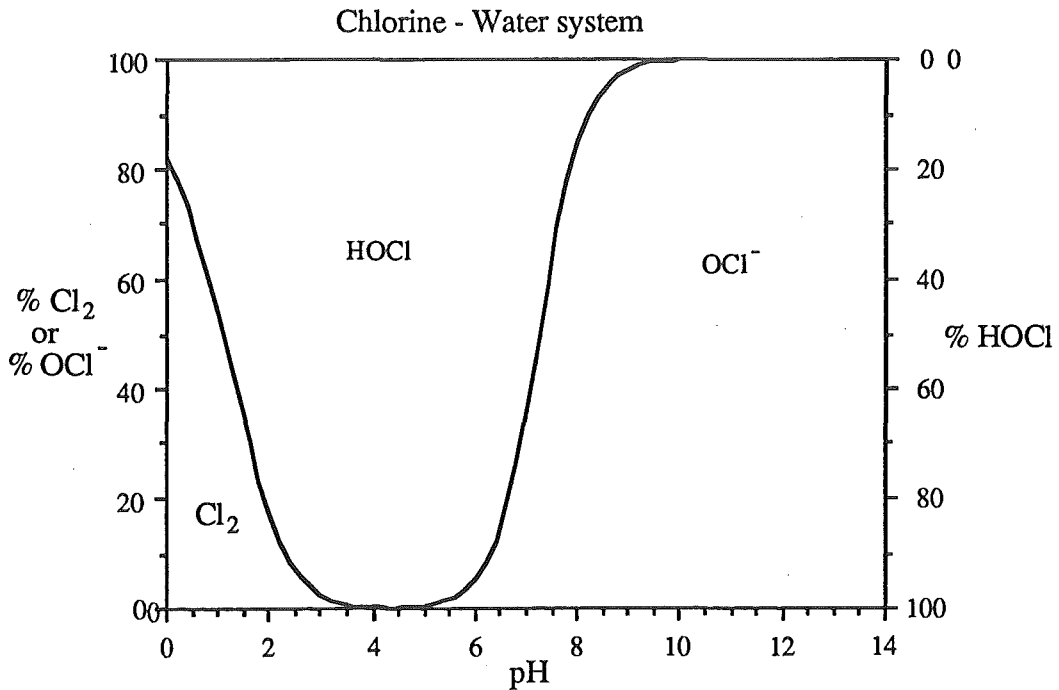


FIGURE 1.2: Composition of 0.01M chlorine and water at 25°C and different pH's

The relationship between molecular chlorine, hypochlorous acid and hypochlorite ion with pH is an important one. If bleaching is allowed to be carried out at a pH range of between 4 and 7, extensive cellulose degradation will occur. Outside this pH range, cellulose degradation is reduced. At low pH, the dominant species present is molecular chlorine whereas at pH above 9, hypochlorite ion is the dominant species. This relationship between pH and the chlorine-water system is utilised in both chlorination and hypochlorite bleaching.

1.4.2) CHLORINATION

Chlorination, although found as part of a bleaching sequence, is strictly speaking, not a true bleaching process. Although some lignin is removed, the main function of chlorination is to convert residual lignin and its derivatives from the pulping stage into alkali-soluble compounds, allowing it to be removed in a subsequent alkali extraction stage. Molecular chlorine has the advantage that it is considerably more selective in delignification than the cooking chemicals. As a true bleaching agent, however, molecular chlorine is ineffective in destroying the chromophoric groups. In fact, chlorination, followed by alkali extraction, results in a pulp of reduced brightness. For this reason, chlorination is never used by itself but is instead used in conjunction with hypochlorite or other bleaching agents.

1.4.3) ALKALINE EXTRACTION

Alkaline extraction is necessary after a chlorination stage to dissolve the chloro-lignins formed during chlorination. The extraction is carried out at high consistency (12 - 15%) and at temperatures of between 60 - 80°C. Sodium hydroxide is the most commonly used solvent. Besides removing chlorinated lignin, alkaline extraction also serves to expose more "fresh" lignin for subsequent bleaching stages.

1.4.4) HYPOCHLORITE BLEACHING

Hypochlorite is one of the first bleaching chemicals used in the pulp and paper industry. Initially used in single stage bleaching, hypochlorite bleaching can now be more commonly found as part of a multi-stage bleaching sequence such as CEH, CEHEH, CEHED etc. A true bleaching agent, hypochlorite preferentially destroys certain chromophoric groups of lignin.

Hypochlorite brightens the pulp by destroying and removing residual native lignin and lignin derivatives formed from the pulping and chlorination stages. The reaction between hypochlorite and lignin involves a series of complicated reactions, the mechanics of which have still not being fully understood. However, the reactions can basically be categorised into three types; 1) inorganic reactions, 2) lignin reactions and 3) carbohydrate reactions. The later two reactions are influenced by the first reaction, which in turn is determined by the pH of the reaction. At the pH that hypochlorite bleaching is usually carried out at (around pH 9), the

predominant ions present are hypochlorite ions with oxidation as the primary type of reaction taking place.

The final quality of the bleached pulp is dependent on the conditions under which hypochlorite bleaching is carried out at. Brightness is one of the quality looked for in bleached pulp and is dependent on the temperature, reaction time, chemical charge and pH of the reaction. Residual chlorine and the pH at the end of the reaction are also important factors which can determine the brightness stability of the pulp.

The amount of bleach chemical charged to the pulp is often reported as % active chlorine, which is a measure of the oxidising power of the bleach solution, expressed as weights of chlorine. The bleaching rate is dependent on the amount of hypochlorite added. In general, the higher the hypochlorite to pulp ratio, the faster the reaction rate and the higher the final pulp brightness. The reaction rate, however, does not stay constant throughout the reaction but decreases with time as more and more bleach chemicals are consumed. In hypochlorite bleaching, the consumption of bleach chemicals is never allowed to go to completion as a residual amount of chlorine (measured as residual active chlorine) charge is required to maintain a driving potential and prevent brightness reversion during the retention period. The correct bleach to pulp ratio used will depend on the type of pulp, the process conditions and the desired properties of the bleached pulp. In general, chemical charge of around 1 - 2% available chlorine is used.

The consistency at which bleaching is carried out is dependent on the type of bleaching process used and the bleaching equipment. High consistency bleaching is preferred because of its lower energy and equipment costs and increased productivity.

The pH of the pulp suspension has a small influence on the reaction rate, lowering the pH will increase the reaction rate slightly. However, in terms of cellulose degradation, pH is probably the most important of all the bleaching variables. Hypochlorite bleaching must be carried out at a pH value of around 9 and above. Below pH 9, hypochlorous acid becomes the predominant species (Figure 1.2) and excessive cellulose degradation can occur if caution is not taken. During bleaching, the alkalinity of the pulp suspension will drop due to the formation of organic acids and hydrochloric acid. Therefore, pH buffering or additional alkali must be added to maintain the pH level during hypochlorite bleaching.

The bleaching rate is also dependent on the reaction temperature. Doubling of the bleaching rate can be achieved for every 10°C increase in temperature. Reaction time of less than ten minutes have been achieved with the "hot hypo" concept with reaction temperatures of around 70°C (P.T. Milne, 1981). However, hot hypochlorite bleaching requires a very strict control on the bleaching conditions and an efficient mixing system to prevent overbleaching.

Hypochlorite bleach solution is supplied in the form of calcium or sodium hypochlorite solution and is usually generated on site at the paper mill by the reaction of chlorine with alkali.



The above reactions are reversible reactions and excess alkali is required to stabilise the hypochlorite ions.

Hypochlorite bleaching is generally carried out under the following conditions in table 1.1.

TABLE 1.1: Bleaching conditions

Chemical addition	1.5% as active Cl ₂
Consistency	10%
pH	10
Temperature	30°C
Time	3 hours

One of the major use of hypochlorite bleaching is in the production of semi-bleached pulp using the three stage (CEH) bleaching sequence.

Figure 1.3 shows a simple flow diagram of a CEH bleach plant.

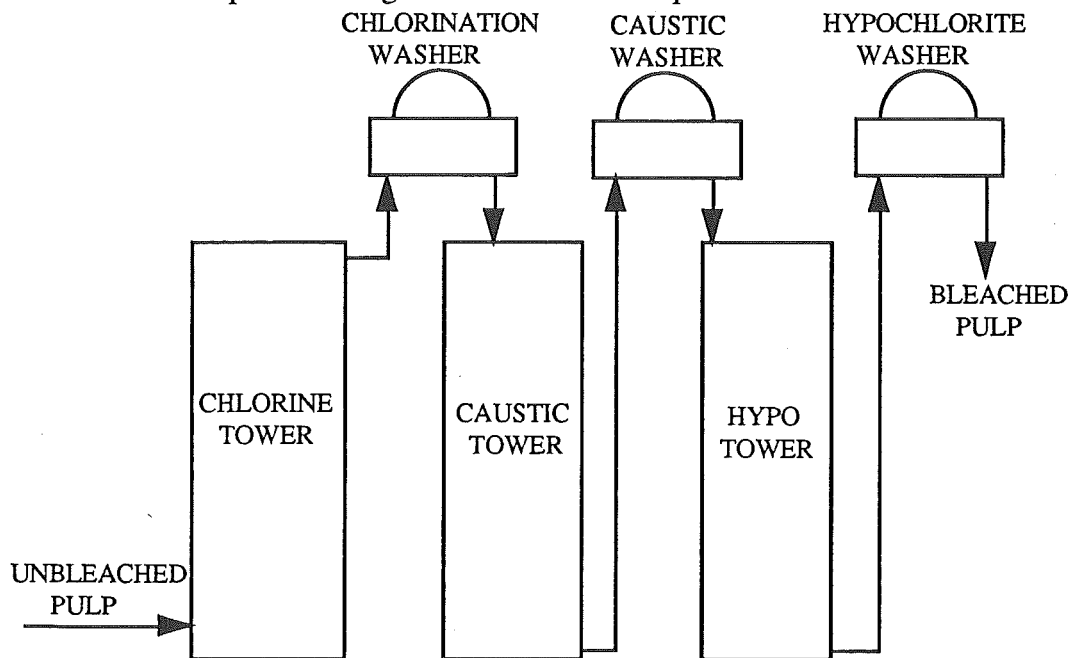


FIGURE 1.3: Flow diagram of a Chlorine, Extraction and Hypochlorite (CEH) bleach plant

A simplified illustration of the reactions taking place in a CEH bleaching sequence is shown in Figure 1.3.

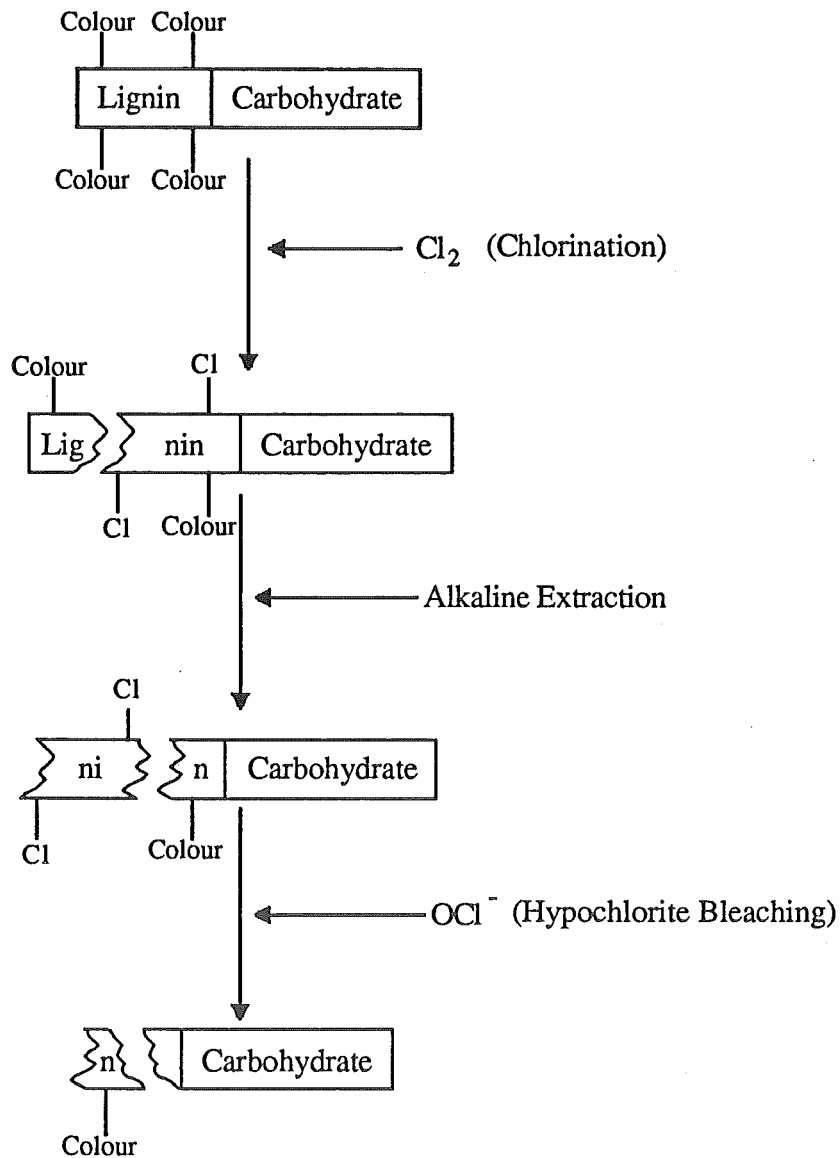


FIGURE 1.3: Simple representation of reactions taking place in a CEH bleaching sequence.

1.5) OPTICAL PROPERTIES OF PULP

1.5.1) GENERAL

One of the ways by which paper is graded is by its optical properties, the most important of which are opacity, colour, gloss and brightness.

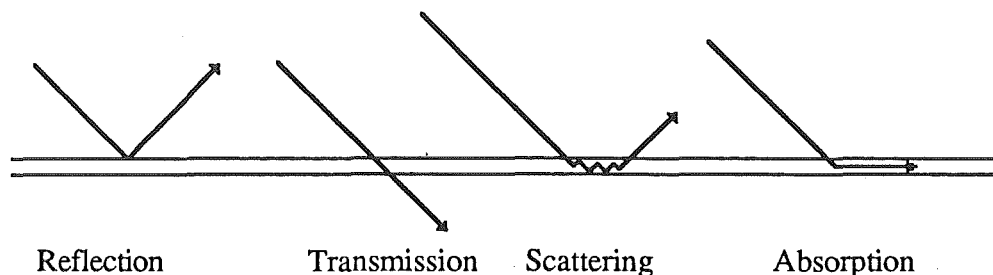


FIGURE 1.4: Behaviour of a light ray striking a sheet of paper.

Figure 1.4 illustrates the 4 possible ways that a ray of light can behave after striking a sheet of paper. Paper that has a high gloss will have a reflectance whereas the amount of light transmission will depend on the opacity of the paper.

With regard to brightness, the scattering and absorption ability of the sheet is of importance. The phenomenon of light scattering can be illustrated by comparing a sheet of glass with powdered glass. Although made from the same substance, a sheet of glass appears clear whereas powdered glass have a whitish appearance. This is because, in powdered glass, an extremely large number of reflecting surfaces is present. Thus, a ray of light shining into powdered glass may be reflected many times internally before it emerges. In a sheet of paper, the surfaces of individual pulp fibres serve as reflecting surfaces. The scattering power of a sheet of paper is therefore dependent on the physical properties of the paper, i.e. alignment of pulp fibres, density of paper and roughness of the paper surface.

Light absorption is described as the ability of the medium to absorb light. A dark object will absorb more light than a lighter coloured object. In a sheet of paper, light is absorbed as it passes through the pulp fibres. The amount of light absorbed depends on the concentration of the coloured compounds (chromophores) present in the pulp. The amount of light absorbed is also dependent on the wavelength of the light source. Light of 457 nm (blue wavelength) is the standard used in the paper industry.

The amount of light absorbed or scattered can be described by two independent variables, the light absorption coefficient and the light scattering coefficient respectively. These coefficients can be derived from the Kubelka-Munk theory.

1.5.2) THE KUBELKA - MUNK THEORY

Among the many optical theories available, the Kubelka-Munk model has been used almost exclusively to analyse or predict the optical properties of paper. The Kubelka-Munk theory defines two fundamental properties, the light scattering coefficient (S) and the light absorption coefficient (K), and uses the thickness of the medium as the independent variable. However, difficulties in measuring the thickness of a sheet of paper have resulted in the replacement of thickness with mass per unit area (basis weight) as the independent variable. (Van Der Acker, 1949). Light scattering and light absorption coefficients based on basis weight is called specific scattering coefficient and specific absorption coefficient and denoted by s and k respectively.

Figure 1.5 illustrates the Kubelka-Munk model.

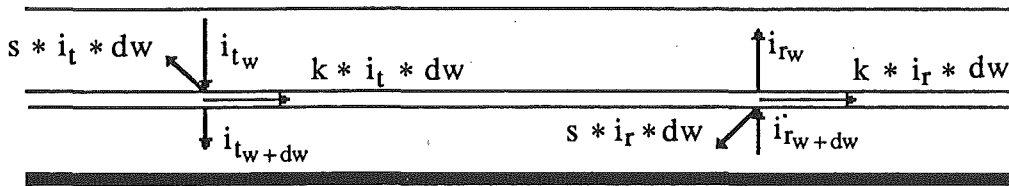


FIGURE 1.5: Behaviour of a light ray interacting with a medium, illustrating the Kubelka - Munk theory.

$$i_{t_w+dw} = i_{t_w} - (s + k) * i_t * dw + s * i_r * dw \quad (1.1)$$

$$i_{r_w} = i_{r_w+dw} - (s + k) * i_r * dw + s * i_t * dw \quad (1.2)$$

or $-di_t = -(s + k) * i_t * dw + s * i_r * dw \quad (1.3)$

$$di_r = -(s + k) * i_r * dw + s * i_t * dw \quad (1.4)$$

Defining $r = \frac{i_r}{i_t}$,

$$dr = \left(\frac{\delta r}{\delta i_t}\right) i_t * di_r + \left(\frac{\delta r}{\delta i_r}\right) i_r * di_t \quad (1.5)$$

$$= \frac{1}{i_t} * di_r + \left(\frac{-i_r}{i_t^2}\right) * di_t \quad (1.6)$$

$$= \frac{-(s + k) * i_r * dw + s * i_t * dw}{i_t} + \frac{-(s + k) * i_t * dw + s * i_r * dw}{i_t^2} * i_r$$

$$= -(s+k) * r * dw + s * dw + (-(s+k) * r * dw + s * r^2 * dw)$$

$$= (s * r^2 - 2 * (s + k) * r + s) * dw \quad (1.7)$$

$$= (r^2 - 2 * (1 - \frac{k}{s}) * r + 1) * s * dw \quad (1.8)$$

In the case where the layer is infinitely thick, $\frac{dr}{dw} = 0$

$$R_{\infty}^2 - 2 * (1 - \frac{k}{s}) * R_{\infty} + 1 = 0 \quad (1.9)$$

Solving the quadratic equation, (1.9):

$$R_{\infty} = (1 + \frac{k}{s}) - \sqrt{(1 + \frac{k}{s})^2 - 1} \quad (1.10)$$

When the layer is very thin and the backing is completely black (i.e. $r = 0$ when $w = 0$) we have

$$\int_0^{R_0} \frac{1}{1 - 2 * (1 + \frac{k}{s}) * r + r^2} * dr = \int_0^W s * dw \quad (1.11)$$

substituting $2 * (1 + \frac{k}{s}) = R_{\infty} + \frac{1}{R_{\infty}}$ from equation 8 into equation 1.11 and integrating

$$R_0 = \frac{\exp \left[sW * \left(\frac{1}{R_{\infty}} - R_{\infty} \right) \right]}{(1 - R_{\infty}) * \exp \left[sW * \left(\frac{1}{R_{\infty}} - R_{\infty} \right) \right]} \quad (1.12)$$

Equations 1.10 and 1.12 can be used for calculating R_0 and R_{∞} from the coefficients and the basis weight. However, R_0 and R_{∞} are generally measured values, and it is the values of the coefficients that are often required.

Therefore, from equation 1.10 and equation 1.12,

$$\frac{k}{s} = \frac{(1 - R_{\infty})^2}{R_{\infty}} \quad (1.13)$$

and

$$sW = \frac{1}{\left(\frac{1}{R_\infty} - R_\infty\right)} * \ln \left[\frac{(1 - R_\infty R_o)}{\left(1 - \frac{R_o}{R_\infty}\right)} \right] \quad (1.14)$$

In the case where the backing is not completely black, (i.e. $r = R_g$ when $w = 0$, $r = R$ when $w = W$)

$$\int_{R_g}^R \frac{1}{1 - 2*\left(1 + \frac{k}{s}\right)*r + r^2} * dr = \int_0^W s * dw \quad (1.15)$$

$$sW = \frac{1}{\left[\frac{1}{R_\infty} - R_\infty\right]} * \ln \left[\frac{(R*R_g*R_\infty - R*R_\infty^2 - R_g + R_\infty)}{(R*R_g*R_\infty - R - R_g*R_\infty^2 + R_\infty)} \right] \quad (1.16)$$

An important property of specific light absorption and specific light scattering coefficients is that they are additive, i.e. the following is true.

$$sW = s_1W_1 + s_2W_2 + s_3W_3 \dots\dots\dots + s_nW_n \quad (1.17)$$

$$kW = k_1W_1 + k_2W_2 + k_3W_3 \dots\dots\dots + k_nW_n \quad (1.18)$$

Therefore, it is possible to determine the brightness of a mixture of pulp if the k and s values of each individual pulp type is known.

TABLE 1.2: Definition of symbols used in the Kubelka - Munk theory

R_∞	=	Reflectivity of an infinite pile of paper
R_o	=	Reflectivity of a single sheet of paper backed by a black body
R	=	Reflectivity of a sheet of paper backed by a body with reflectance R_g
R_g	=	Reflectivity of a "black" body
s	=	Specific light scattering coefficient (based on weight per unit area)
k	=	Specific light absorption coefficient (based on weight per unit area)
W	=	Basis weight of paper (mass per unit area)

1.5.3) LIMITATIONS OF THE KUBELKA - MUNK THEORY

- 1) Diffuse and monochromatic light must be used.
- 2) Idealised representation of light interaction with medium
- 3) The assumption that the k and s are independent is not perfectly true.

- 4) Comparisons can only be made from measurements made with the same instrument, using the same light source and the same instrument geometry.

1.6) MATHEMATICAL MODELS

Mathematical representations of industrial processes have always been of interest to the chemical engineer. Mathematical modelling allows the simulation of industrial processes to be carried out economically and quickly on a computer. Mass and energy balance simulation packages are available for tasks such as process optimisation and process control, enabling the engineer to experiment with different process variables to obtain optimal process conditions and configuration. However, the quality of a manufactured product is usually not taken into account by most mass and energy balance simulation packages. What may be optimal in terms of mass and energy balance may have a negative effect on some product property. For example, operating a bleach plant at high temperature is favourable in terms of increased production rate. However, serious carbohydrate degradation can occur if the relationship between reaction time and reaction temperature is not known. Such relationship is usually non-linear (i.e. doubling reaction temperature does not necessarily mean halving the reaction time). Therefore, to be able to control the quality of the final product, it is important to know the relationship between the product quality and all relevant process variables. This is done by studying the kinetics and the stoichiometry of the process. In the paper industry, one such important product quality is the brightness of the paper.

The brightness of a sheet of paper is due to a combination of the physical properties of the paper and the chemical structure of the pulp fibres. To study the bleaching process, the specific light absorption coefficient (denoted as C_k to distinguish it from the rate constant, k_1) is a more appropriate variable to use instead of paper brightness. The following process parameters are of importance in the hypochlorite bleaching of pulp; (1) chemical charge, (2) reaction temperature, (3) pH, (4) reaction time and (5) chromophore concentration.

Kinetic and stoichiometric models have been developed for different bleaching stages such as the CE-prebleaching stage (Germgård & Klasson, 1985), chlorine dioxide bleaching stage (Teder & Tormund, 1980), hydrogen peroxide bleaching of mechanical pulps (Moldenius & Sjögren, 1982) and the hypochlorite bleaching stage (Axegård & Tormund, 1985).

Axegård and Tormund developed the kinetics and stoichiometric models for the hypochlorite bleaching of prebleached pine kraft pulp at the Swedish Forest Products Research Laboratory at Stockholm. The following rate, stoichiometric and pH models was developed by them:

1) Rate equation:

$$-\frac{dC_k}{dt} = k_1 * C_k^{3.5} * [OH^-]^{-0.1} * [OCl^-]^{0.6} \quad (1.19)$$

$$\text{where } E_a = 77 \frac{\text{kJ}}{\text{mole}}$$

2) Stoichiometric equation:

$$\frac{dOCl}{dC_k} = k_2 * [C_k]^n \quad (1.20)$$

where k_2 and n is dependent on bleaching conditions and pulp type.

3) pH equation:

$$\frac{dpH}{dOCl} = \text{const} \quad (1.21)$$

The above three equations (1.19, 1.20 & 1.21) are similar to the rate and stoichiometric models of other bleaching stages (Germgård *et al*, 1987).

For the hypochlorite bleaching of CE-prebleached *pinus radiata* kraft pulp, the models proposed are similar to those used by Axegård and Tormund.



$$-\frac{dC_k}{dt} = k_1 * C_k^a * [OH^-]^b * [OCl^-]^c \quad (1.22)$$

$$\frac{dOCl}{dC_k} = k_2 * [C_k]^n \quad (1.23)$$

$$\frac{dpH}{dOCl} = k_3 \quad (1.24)$$

However, the values of the exponents, coefficients and the rate constant are expected to be different due to differences in bleaching conditions, pulp type and experimental method. In their study, Axegård and Tormund used the “constant concentration” method where the concentration of the active reactants are kept constant throughout the experiment by either keeping the reactants in excess or by continuously adding reactants at the same rate as they are consumed. In this study, the “differential method” is used instead. The “differential method”

uses bleaching conditions that closely resemble that of an industrial bleaching mill, i.e. the chemicals are charged at the start and the concentration of the reactants decreases as bleaching proceeds. One disadvantage of the “differential method” is that it is not possible to isolate the effect of individual bleaching parameters on bleaching rate.

It should be noted that the reaction between chromophores and hypochlorite is not an elementary reaction, i.e. the rate equation does not correspond to the stoichiometric equation. The reaction mechanism is a highly complex one and has yet to be fully understood (Rydholm, 1965). As such, the proposed model is nothing more than a simple mathematical representation of a much more complex reaction and the values determined for the reaction orders in equation 1.22 should not be taken as an indication of the actual reaction mechanism.

CHAPTER 2

Experimental

2.1) OBJECTIVE

The objective of this study is to develop mathematical expressions that will describe the kinetics and stoichiometry of hypochlorite bleaching. Raw data were obtained from bleaching experiments using the “differential conditions” method. This method was used because of the similarities between experimental conditions and industrial conditions. Therefore, a model developed using the “differential method” would be more suited for industrial simulations. The bleaching experiments were carried out using the “polyethylene bag” method used in conventional laboratory bleaching. The CE-prebleached pulp used was obtained from after the caustic washer stage of the No. 1 (CEH) Semi-Bleached Plant at Tasman Pulp and Paper Co. Ltd., Kawerau, New Zealand. 100% *pinus radiata* wood pulp pulped by the kraft pulping process was used for the bleaching experiments. Two batches of pulp were used, one with an initial C_k value of $15.788 \text{ m}^2 \text{ kg}^{-1}$ and the other with an initial C_k value of $24.804 \text{ m}^2 \text{ kg}^{-1}$. Hypochlorite bleach liquor was also obtained from Tasman Pulp and Paper Co. Ltd. During the experimental phase of the study, the hypochlorite bleach liquor was analysed at least twice a week to check for hypochlorite decomposition. The extent of hypochlorite decomposition can be reduced by storing the bleach liquor in a dark coloured container and keeping it in a cool, dark cupboard.

To develop the proposed kinetic and stoichiometric models for hypochlorite bleaching, the values of the following variables, i.e. reaction temperature, specific light absorption coefficient, hypochlorite ion concentration, hydroxide ion concentration (pH) and reaction time, are required. These were obtained from measurements of: 1) reaction temperature, 2) reflectivity of the brightness pads at infinite thickness and single sheet thickness (R_∞ and R_o) for both bleached and unbleached pulp, 3) initial chemical charge (calculated from bleach strength and pulp consistency), 4) residual chlorine, 5) initial and final pH and 6) reaction time, for each individual bleaching run.

The conditions used for the bleaching experiments in this study are presented in table 2.1.

Experimental Conditions:

TABLE 2.1

Initial chemical charge (as available chlorine)	1.5%, 2.0%, 2.5%
Reaction temperature [°C]	30, 40, 50
Initial specific light absorption coefficient [m ² /kg]	15.788, 24.804
Reaction time [minutes]	0, 10, 30, 60, 120, 180
Consistency	10 %
Wood species	<i>Pinus Radiata</i>
Pulp type	CE-prebleached kraft pulp
Bleach chemical	Sodium hypochlorite

2.2) BLEACHING EXPERIMENTS

Before starting a bleaching experiment, the pulp is first prepared by washing on a Buchner funnel with excess water. This is to remove any residual CE filtrate which would otherwise interfere with the experiment through the consumption of hypochlorite ions. Approximately 10 grams O.D (oven dry) of pulp is used for each bleaching experiment. The amount of distilled water required to form a pulp suspension of 10% consistency is calculated and added together with the pulp into a polyethylene bag. To ensure that the pulp is at the right reaction temperature, the polyethylene bag is sealed and placed into a constant temperature water bath that has been preheated to the correct reaction temperature. After approximately half an hour, the correct amount of hypochlorite bleach liquor is added to the pulp suspension. The amount of bleach solution added will depend on the required bleaching conditions. Before the polyethylene bag is resealed and placed back into the water bath, the pH of the pulp suspension is measured. Frequent mixing of the pulp is required during the duration of the bleaching experiment to prevent uneven bleaching, especially in the initial ten or so minutes of the reaction. Mixing of the pulp with the bleach chemicals is achieved by “kneading” the pulp in the bag. After the required time has lapsed, the plastic bag is removed from the water bath and the filtrate squeezed into a clean beaker for pH and residual chlorine measurements. Further bleaching is stopped by dispersing and washing the pulp on a Buchner funnel with excess water.

2.3) BRIGHTNESS PADS

For every bleaching experiment, a total of three brightness pads are made. Each pad is made from approximately 1 gram O.D. of bleached pulp. The brightness pads are made by dispersing the pulp in excess water and draining onto a paper sheet mould. The pads are then

pressed to remove excess water before they are air-dried overnight in a closed cupboard with a circulating fan. An unused oven was used for this purpose.

There are several different instruments available with which the reflectivity of a sheet of paper can be measured, each giving slightly different reflectivity values for the same sheet of paper. This is due to the different methods of measurements used by different instruments and also because of the differences in the geometry of the different instruments. The Elrepho, one of the most common instrument used, uses diffuse light to illuminate the paper from all directions and measures the reflectivity at the normal. For this study, however, the only instrument available is the Photovolt reflectometer (Model 670). The Photovolt measures reflectivity by illuminating the paper at the normal with a photocell located at an angle to the paper surface. The differences between diffuse geometry and directional geometry is illustrated in figure 2.1.

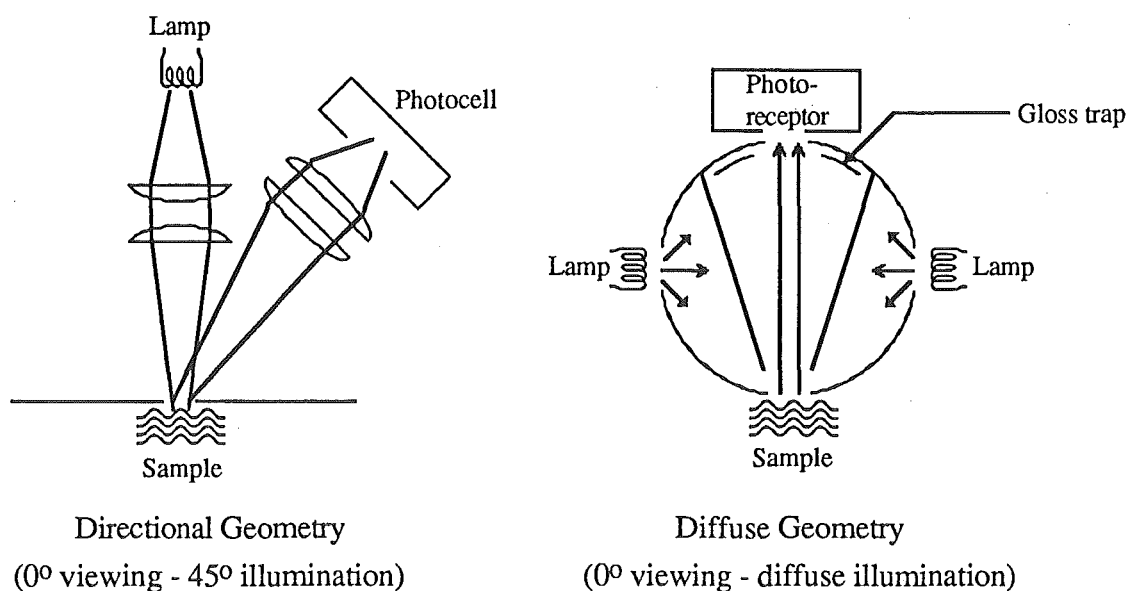


FIGURE 2.1: Comparison between directional geometry and diffuse geometry

The disadvantage of directional geometry is that it is susceptible to non-homogeneities in the paper whereas diffuse geometry tends to average out any non-uniformity in the sample.

To use the Photovolt reflectometer, it is first calibrated by placing the search unit over standard brightness pads and adjusting to the correct reading. The three standard brightness pads used for calibration were obtained from the Swedish Forest Products Research Laboratory at Stockholm, and have an ISO brightness of 27.9, 60.6 and 81.8 respectively. Frequent calibration of the reflection meter is required if reliable results are to be obtained. R_0 values are obtained by measuring the reflectance of a single sheet of brightness pad backed by a black body which has an ISO brightness of 0.6. Four R_0 readings are taken for each brightness pad. R_∞ values are obtained by folding the three brightness pads into quarters and measuring the

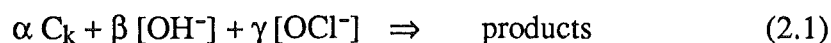
reflectance of each of the quarters. A total of twelve R_0 and R_∞ measurements are taken for each bleaching run.

To determine the C_k values of the bleached pulp, the reflectivity values (R_0 and R_∞) are first converted into their Elrepho equivalents using the correlations in Appendix A. Elrepho equivalents are required because the Kubelka-Munk theory requires that diffuse illumination be used to measure reflectivities. C_k is then calculated from the reflectivity values, the basis weight of the paper and the Kubelka - Munk theory.

2.4) DEVELOPMENT OF MATHEMATICAL MODELS

2.4.1) KINETIC MODEL

The bleaching of pulp is due to the chemical reactions between chromophores and the bleaching chemicals and can be represented by equation 2.1:



It is possible to express the reaction rate for the above reaction in common chemical terms such as activation energy, reaction orders and rate constant. In this study, the rate of bleaching is defined as the rate of chromophore removal (approximated by the decrease in specific light absorption coefficient, (C_k), per unit time). Thus, the rate of hypochlorite bleaching of pulp can be described by the following kinetic equation:

$$-\frac{dC_k}{dt} = k_1 * C_k^a * [OH^-]^b * [OCl^-]^c \quad (2.2)$$

The rate data, ($-\frac{dC_k}{dt}$), can be obtained by fitting experimental data of C_k and time using the following differential equation:

$$-\frac{dC_k}{dt} = k * C_k^z \quad (2.3)$$

Integrating

$$C_{k_t} = C_{k_0} * \exp [-k * t] \quad \text{when } z = 1 \quad (2.4)$$

$$C_{k_t} = \exp \left[\frac{\ln (C_{k_0}^{(1-z)} - k * (1-z) * t)}{(1-z)} \right] \quad \text{when } z \neq 1 \quad (2.5)$$

where

z = pseudo reaction order

k = pseudo rate constant = $k_1 * [OH^-]_{ave}^b * [OCl^-]_{ave}^c$

A plot of C_k versus time is characterised by a rapid initial reaction followed by progressively slower reactions. (Figure 2.1)

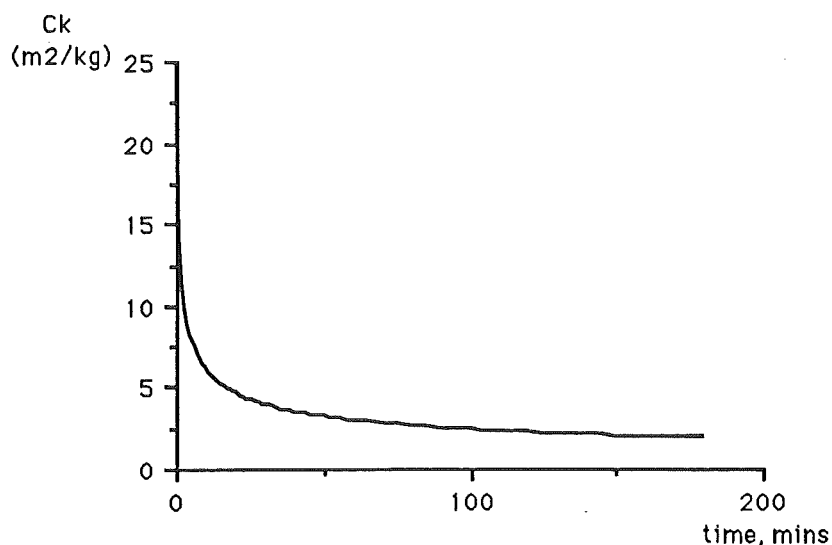


FIGURE 2.1: Plot of specific light absorption coefficient with time

A “best fit” curve can be obtained by using a least squares method to determine the values of the non-linear parameters, k and n , for each bleaching run. (Marquardt, 1963)

2.4.2) STOICHIOMETRIC MODELS

To be able to fully describe the bleaching reaction, it is not sufficient to know only the kinetics of the reaction. The stoichiometric relationship between the active reactants must also be known. For hypochlorite bleaching, the proposed stoichiometric model for the stoichiometry between hypochlorite ion concentration $[OCl^-]$ and specific light absorption coefficient, (C_k), can be mathematically described by equation 2.6.

$$\frac{dOCl}{dC_k} = k_2 * C_k^{-n} \quad (2.6)$$

Integrating

$$OCl_t = OCl_o + k_2 * \ln \left[\frac{C_{k_t}}{C_{k_o}} \right] \quad \text{when } n = 1 \quad (2.7)$$

$$OCl_t = OCl_o + k_2 * \left[\frac{C_{k_t}^{(1-n)} - C_{k_o}^{(1-n)}}{(1-n)} \right] \quad \text{when } n \neq 1 \quad (2.8)$$

Figure 2.2 shows a plot of hypochlorite consumption $-(OCl_t - OCl_o)$ versus change in chromophore concentration $-(C_{k_t} - C_{k_o})$. The plot shows that as the extent of bleaching

increases, (i.e. C_{k_t} becomes smaller, $-\Delta C_k$ becomes bigger), the amount of bleach required ($-\Delta OCl$) to obtain a given reduction in C_k is increased.

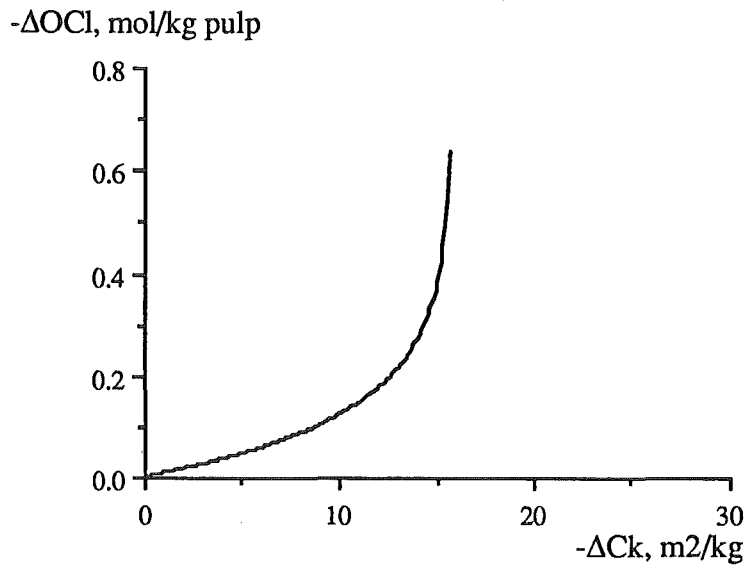


FIGURE 2.2: Plot of hypochlorite consumption versus chromophore elimination

For pH changes, the proposed model is as follows:

$$\frac{dpH}{dOCl} = \text{const} \quad (2.9)$$

Integrating

$$pH_t = pH_o + \text{const} * [OCl_t - OCl_o] \quad (2.10)$$

Thus a plot of pH versus hypochlorite ion consumption (mol/kg pulp) should give a straight line graph. (Figure 2.3)

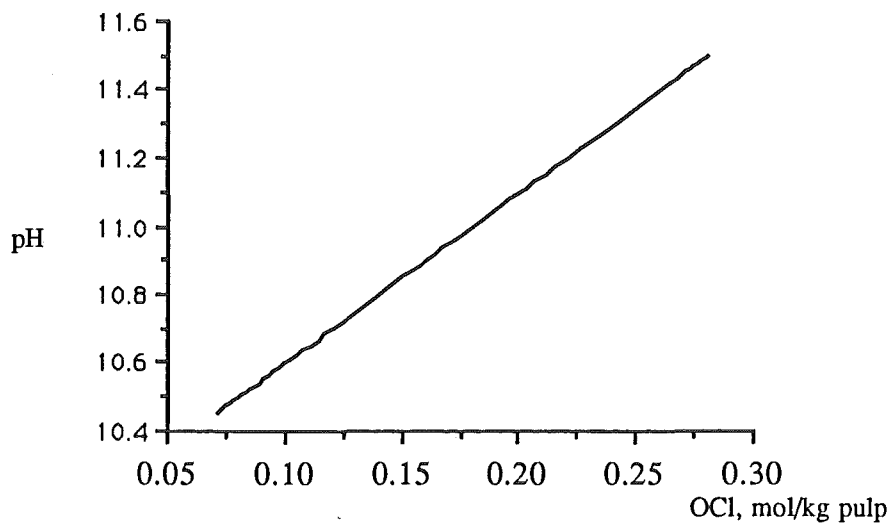


FIGURE 2.3: Plot of pH versus hypochlorite concentration (mol/kg pulp)

2.4.3) OVERALL KINETIC MODEL

To determine the values of the coefficients of the kinetic model, the model is first linearised by taking the natural logarithm, i.e.

$$-\frac{dC_k}{dt} = A * \exp\left[\frac{-E_a}{RT}\right] * C_k^a * [OH^-]^b * [OCl^-]^c \quad (2.11)$$

Taking ln

$$\ln\left(-\frac{dC_k}{dt}\right) = \ln(A) + \left[\frac{-E_a}{RT}\right] + a * \ln C_k + b * \ln [OH^-] + c * \ln [OCl^-] \quad (2.12)$$

Using multiple linear regression, the values of the reaction orders, (a,b,c), the activation energy, (E_a), and the frequency factor, (A), can be determined from the linearised equation.

Thus, the hypochlorite bleaching of pulp can be fully described by a simulation model consisting of the following three differential equations:

$$-\frac{dC_k}{dt} = A * \exp\left[\frac{-E_a}{RT}\right] * C_k^a * [OH^-]^b * [OCl^-]^c \quad (2.14)$$

$$\frac{dOCl}{dC_k} = k_2 * C_k^{-n} \quad (2.15)$$

$$\frac{dpH}{dOCl} = k_3 \quad (2.16)$$

It should be noted that for the kinetic equation (2.14), the hypochlorite term is expressed in units of concentration (i.e. moles per litre) whereas for equations 2.15 and 2.16, the hypochlorite term is expressed in terms of moles per kilogram of oven dry pulp.

CHAPTER 3

Results

3.1) EFFECT OF REACTION TIME ON REACTION RATE

The relationship between reaction time and chromophore concentration is shown by Figure 3.1. The relationship follows that described by the proposed model, showing a rapid initial reaction followed by progressively slower reactions. Such characteristic curve is also displayed by other types of bleaching processes.

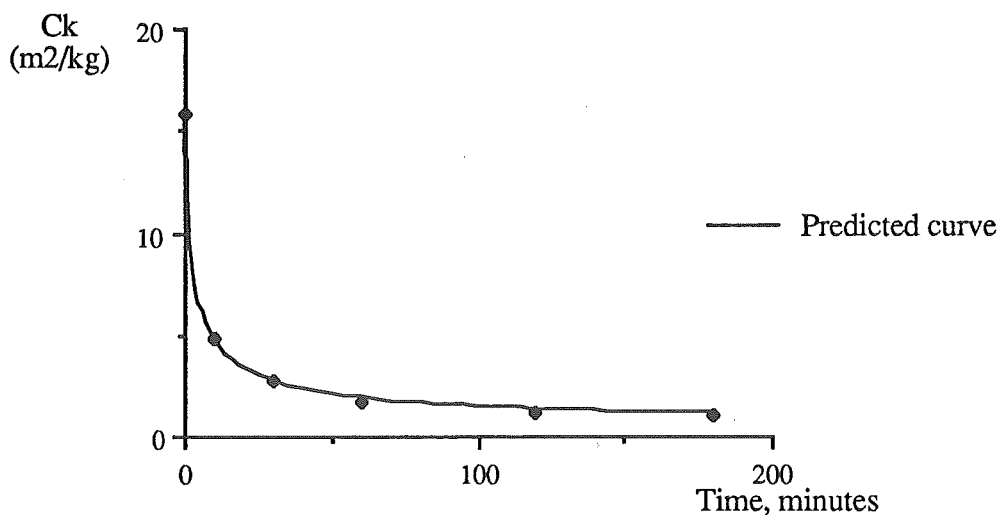


Figure 3.1: Specific light absorption coefficient versus time
Bleaching conditions: 40°C, 2.5% charge as available chlorine

Figure 3.2 shows a plot of the rate of reaction versus time, where the rate of reaction is defined as the reduction in chromophore concentration per unit time. The rapid reduction of the reaction rate in the initial stages of bleaching shows that the bulk of bleaching occurs in the first ten or so minutes. Experimental data shows that around 74% reduction in chromophore concentration is achieved in the first ten minutes whereas only a further 20% reduction in chromophore concentration is achieved if the reaction is allowed to carry on to the full three hours.

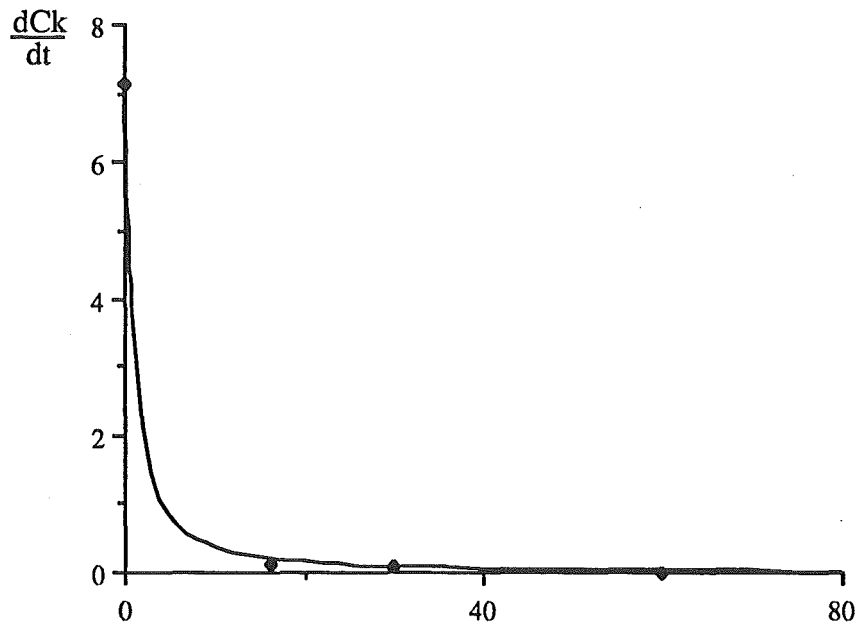


FIGURE 3.2: Chromophore elimination rate vs time
Bleaching conditions : 30°C, 2.0% charge as available chlorine

The bleaching rate is found to be dependent on the temperature, chromophore concentration, pH and chemical charge.

3.2) EFFECT OF REACTION TEMPERATURE ON REACTION RATE

The influence of temperature on the reaction rate is shown by Figure 3.3.

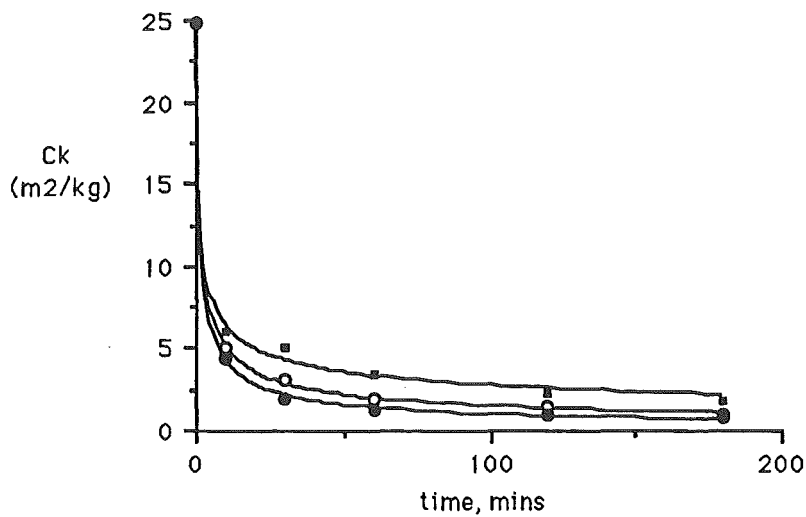


FIGURE 3.3: The effect of temperature on the rate of chromophore elimination

- 1.5% charge as available chlorine, 30°C
- 1.5% charge as available chlorine, 40°C
- 1.5% charge as available chlorine, 50°C

The results show that the reaction rate increases with increasing temperature. Experimental data showed that a twofold increase in reaction rate can be achieved for every 8 - 10 °C increase in reaction temperature.

The effect of temperature on the reaction rate is determined by the rate constant. The relationship between temperature and the rate constant can be described by the Arrhenius equation.

$$k_1 = A \exp\left(\frac{-E_a}{RT}\right) \quad (3.1)$$

Taking natural logarithm:

$$-\ln(k_1) = \left[\frac{E_a}{RT}\right] - \ln(A) \quad (3.2)$$

Therefore a plot of $-\ln(k_1)$ versus $\left[\frac{1}{T}\right]$ will give a straight line with gradient, $\left[\frac{E_a}{R}\right]$ (Figure 3.4)

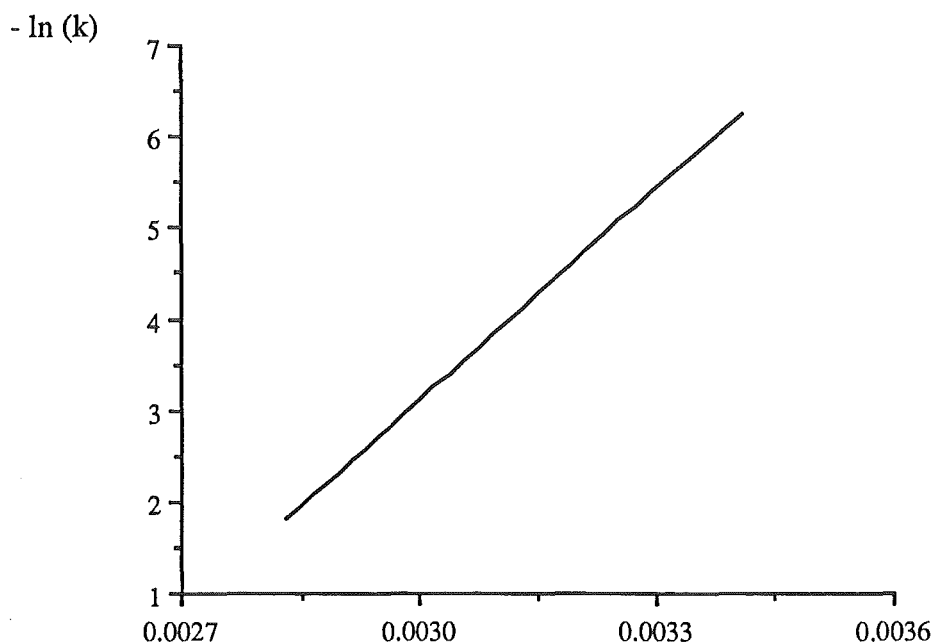


FIGURE 3.4: Plot of $-\ln(k_1)$ versus $\frac{1}{T}$, Kelvin

The rate constant, (k_1), is independent of the specific light absorption coefficient, the hypochlorite ion concentration and pH and is only dependent on the reaction temperature.

3.3) EFFECT OF ALKALINITY ON THE REACTION RATE

The influence of pH on the rate of chromophore removal is very small. The rate of reaction can be described by an apparent reaction order of -0.043 with respect to hydroxide ion concentration. The negative reaction order indicates that the reaction rate will increase slightly if the pH is decreased. A 10% increase in pH reduces the chromophore removal rate by approximately 10%. The hydroxide ion concentration is expressed in dimensions of moles per litre (mol/L). During the bleaching reaction, the pH decreases with time.

3.4) EFFECT OF HYPOCHLORITE ION CONCENTRATION ON REACTION RATE

The effect of hypochlorite ion on the reaction rate can be described by an apparent reaction order of 0.383 with respect to hypochlorite ion concentration. The positive reaction order indicates that the reaction rate increases if the chemical charge is increased. A doubling of the hypochlorite ion concentration will result in an increase in the reaction rate by as much as 30%. The hypochlorite ion concentration is expressed in dimensions of moles per litre (mol/L). Hypochlorite ions are consumed during the bleaching reaction.

3.5) EFFECT OF CHROMOPHORE CONCENTRATION ON REACTION RATE

Chromophore concentration has by far the greatest influence on the rate of chromophore removal. The rate of reaction can be described by an apparent reaction order of 2.629 with respect to the chromophore concentration. Halving the chromophore concentration will reduce the reaction rate by as much as 84%. This high dependence of reaction rate on the chromophore concentration is largely responsible for the characteristic bleaching curve (i.e. fast initial reaction, followed by progressively slower reaction) displayed by hypochlorite bleaching.

In this study, the chromophore concentration is approximated by the specific absorption coefficient (C_k), as determined from reflectance measurements of R_o (reflectivity of a single sheet of paper), R_∞ (reflectivity of paper of infinite thickness) and the Kubelka - Munk theory.

Figure 3.5 shows the relationship between rate of chromophore removal and the specific absorption coefficient. The chromophore removal rate decreases asymptotically as the absorption coefficient decreases. This means that the amount of time required to obtain a given reduction in the specific light absorption coefficient increases rapidly as the chromophore concentration decreases.

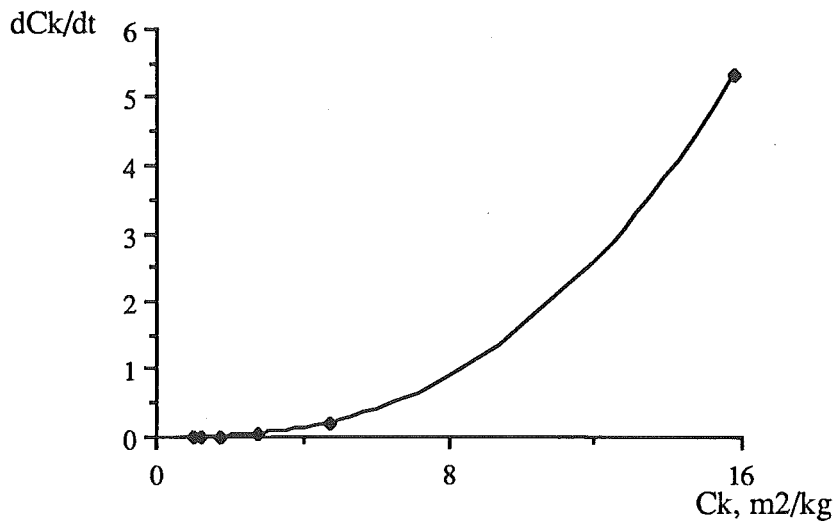


FIGURE 3.5: Chromophore elimination rate vs chromophore concentration
Bleaching conditions : 40°C, 2.5% charge as available chlorine

3.6) OVERALL KINETIC MODEL

Because of the nature of the experimental method used, the orders of the reaction with respect to the different bleaching chemicals cannot be determined independently. To determine the values of the reaction orders as well as the rate constant, the reaction rate has first to be estimated by fitting a 'best fit' curve (See Experimental) through the C_k versus time plot. The rate equation can then be calculated from experimental measurements of specific light absorption coefficient hypochlorite ion concentration and hydroxide ion concentration and from the estimated reaction rate, $\left[\frac{dC_k}{dt}\right]$.

A statistical computer package was used to determine the coefficients and exponents of the rate equation, using multiple linear regression. The proposed reaction rate model is first linearised by taking the natural logarithm, i.e.

$$-\frac{dC_k}{dt} = A \exp\left(\frac{-E_a}{RT}\right) C_k^a [OH^-]^b [OCl^-]^c \quad (3.3)$$

Taking natural log:

$$\ln\left(-\frac{dC_k}{dt}\right) = \ln(A) + \left[\frac{-E_a}{R}\right] * \left[\frac{1}{T}\right] + a \ln C_k + b \ln [OH^-] + c \ln [OCl^-] \quad (3.4)$$

Multiple linear regression can then be used to estimate the regression coefficients, $\beta_0, \beta_1, \beta_2, \beta_3, \beta_4$, for the linearised equation, i.e.

$$y = \beta_0 + \beta_1 * x_1 + \beta_2 * x_2 + \beta_3 * x_3 + \beta_4 * x_4 \quad (3.5)$$

The results of the regression analysis is summarised in the Table 3.1.

TABLE 3.1: Summary of multiple linear regression analysis

Multiple Regression Y₁:ln(-dC_k/dt) 4 X variables

DF:	R:	R-squared:	Adj. R-squared:	Std. Error:
124	.97	.941	.939	.697

Analysis of Variance Table

Source	DF:	Sum Squares:	Mean Square:	F-test:
REGRESSION	4	926.274	231.568	476.047
RESIDUAL	120	58.373	.486	p = .0001
TOTAL	124	984.646		

Beta Coefficient Table

Parameter:	Value:	Std. Err.:	Std. Value:	t-Value:	Probability:
INTERCEPT	20.004				
-1/(RT)	63997.734	7673.665	.205	8.34	.0001
ln(C _k)	2.629	.109	.931	24.205	.0001
ln(OH)	-.043	.055	-.048	.787	.4326
ln(OCl)	.383	.113	.15	3.385	.001

The results indicate that the apparent reaction order with respect to the chromophore concentration is of an order of 2.63 whereas the effect of alkalinity on the reaction rate is very small, with an apparent reaction order with respect to hydroxide ion concentration of only -0.04. The negative reaction order indicates that the reaction rate increases slightly with decreasing pH. The apparent reaction order with respect to hypochlorite ion concentration is 0.38. The Arrhenius activation energy is calculated to be 64 kJ/mol.

The rate equation can be summarised by equation 3.6.

$$-\frac{dC_k}{dt} = \exp[20.004] * \exp\left[\frac{-63998}{R*T}\right] * C_k^{2.629} * [OH^-]^{-0.043} * [OCl^-]^{0.383} \quad (3.6)$$

where both the hydroxide and hypochlorite terms are expressed in concentration units of moles per litre.

Figure 3.6 shows a plot between the predicted specific light absorption coefficient calculated using the above model against experimentally obtained specific light absorption coefficient.

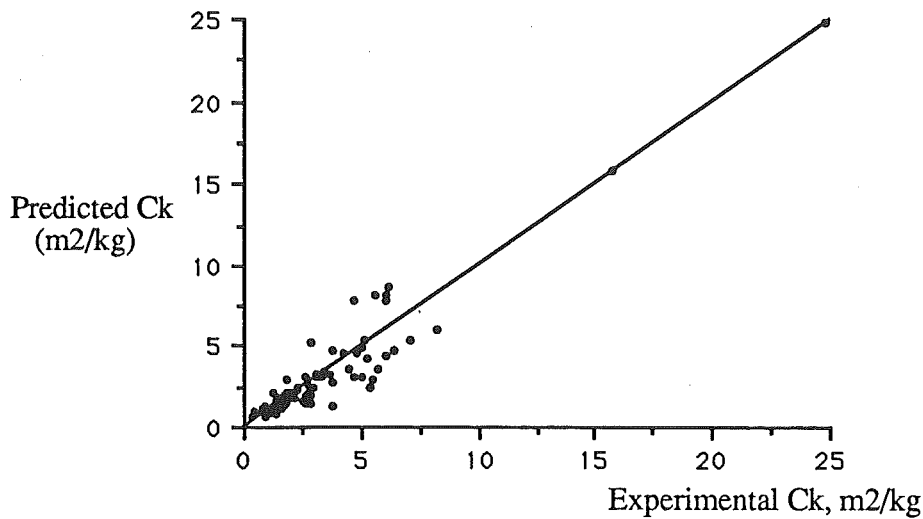


FIGURE 3.6: Predicted C_k vs experimental C_k

3.7) THE STOICHIOMETRY OF CHROMOPHORE REMOVAL IN HYPOCHLORITE BLEACHING

The stoichiometric relationship between hypochlorite ions and the specific light absorption coefficient can be described by equation 3.7.

$$\frac{dOCl}{dC_k} = k_2 * C_k^{-n} \quad (3.7)$$

The relationship independent of temperature and pH but dependent on the specific absorption coefficient. Hypochlorite is expressed in terms of moles per kilogram of O.D. pulp as opposed to the term used for the kinetic equation, which is expressed in concentration terms of moles per litre.

A plot of hypochlorite ion consumption, $-(OCl_t - OCl_o)$, versus chromophore elimination, $-(C_{k_t} - C_{k_o})$, displays a non-linear relationship (Figure 3.7). Figure 3.7 shows that, as well as being dependent on C_k , the stoichiometry is also dependent on the initial specific light absorption coefficient. The relationship can be expressed mathematically as follows:

$$\frac{dOCl}{dC_k} = k_x * C_{k_o}^x * C_k^{-n} \quad (3.8)$$

where

$$k_3 = k_x * C_{k_o}^x$$

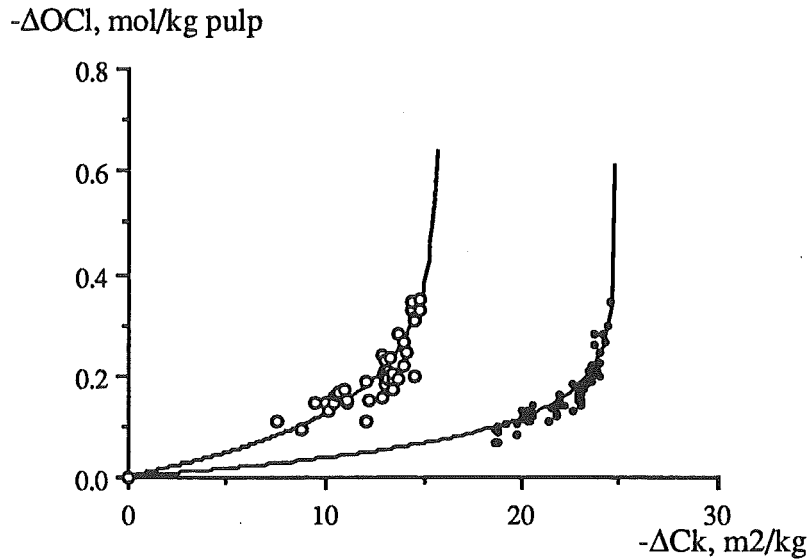


FIGURE 3.7: The effect of initial specific light absorption coefficient on hypochlorite consumption

- $C_{k_0} = 24.8038 \frac{m^2}{kg}$
- $C_{k_0} = 15.7881 \frac{m^2}{kg}$

The non-linear equation can be solved using the Levenberg Marquardt method for least squares fitting of non-linear equations. The results of the 'fit' is summarised by equation 3.9.

$$\frac{dOCl}{dC_k} = 3.89 * \frac{C_{k_0}^{-1.25}}{C_k} \quad (3.9)$$

or

$$OCl_t = OCl_0 + 3.89 * C_{k_0}^{-1.25} * \ln \left[\frac{C_{k_t}}{C_{k_0}} \right] \quad (3.10)$$

Figure 3.7 also shows that as the chromophore concentration decreases, the amount of bleach required to achieve a given reduction in C_k increases. From equation 3.10, it can be seen that the amount of bleach required to remove completely all traces of chromophores is infinitely large and is not physically possible. Experience has shown that, for kraft pulp, around 80 brightness is obtainable with a three stage (CEH) bleaching sequence. Higher brightness would require the use of other bleaching chemicals such as chlorine dioxide with sequences such as CEHD or CEHDED.

Figure 3.8 shows a typical plot of hypochlorite charge, OCl (in moles per kg O.D. pulp) versus chromophore concentration.

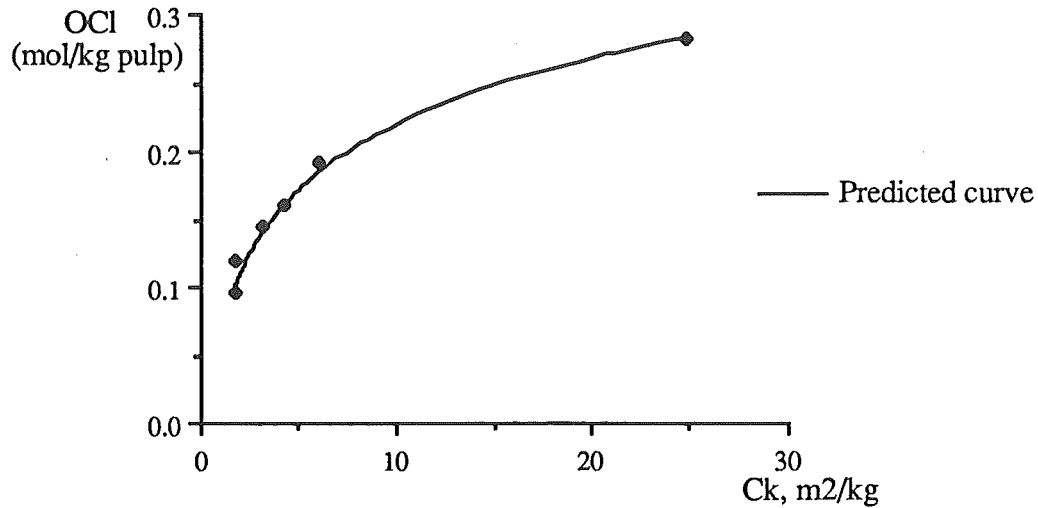


Figure 3.8: Hypochlorite charge versus chromophore concentration
Bleaching conditions: 30°C, 2% charge as available chlorine

Using equation 3.10, the minimum obtainable specific light absorption coefficient for which the pulp can be bleached to can be calculated. Minimum possible specific light absorption coefficient is obtained when all the hypochlorite ions have been consumed, i.e. $OCl_t = 0$. Therefore

$$C_{k_{min}} = C_{k_o} * \exp \left[\frac{-OCl_o}{3.89 * C_{k_o}^{-1.25}} \right] \quad (3.11)$$

However, in hypochlorite bleaching, the bleaching chemical is usually never allowed to be totally consumed as a residual amount of bleach is required to prevent brightness reversion.

By setting a target C_{k_t} and OCl_t and from the initial C_k , equation 3.10 can also be used to determine the required hypochlorite charge to be added to the pulp.

$$OCl_o = OCl_t + 3.89 * C_{k_o}^{-1.25} * \ln \left[\frac{C_{k_t}}{C_{k_o}} \right] \quad (3.12)$$

Figure 3.9 shows a plot of hypochlorite consumption predicted using the model versus experimental hypochlorite consumption.

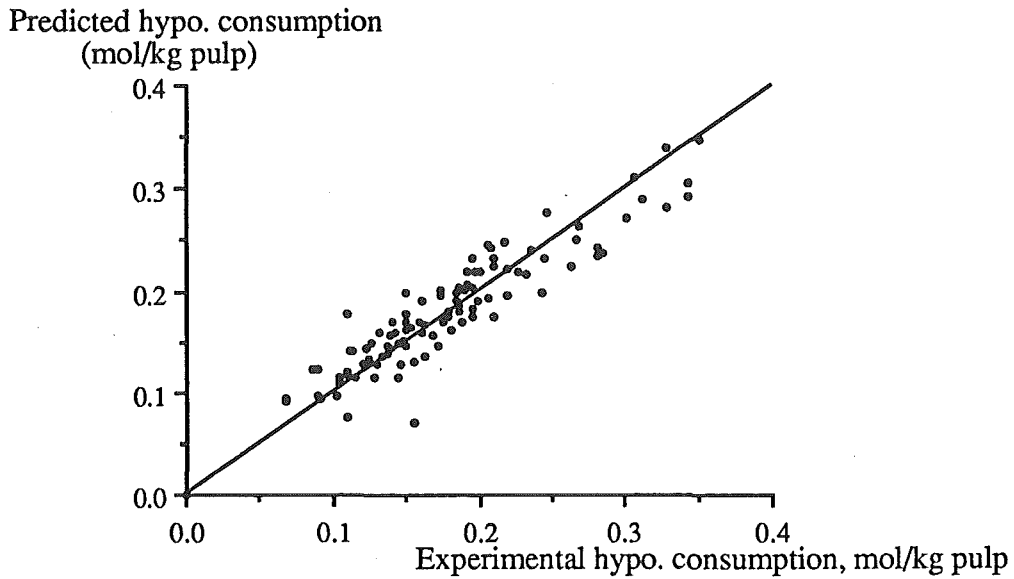


Figure 3.9: Predicted hypochlorite consumption vs experimental hypochlorite consumption

3.8) STOICHIOMETRIC RELATIONSHIP BETWEEN ALKALINITY AND HYPOCHLORITE CHARGE

The original model proposed for the relationship between pH and hypochlorite ions assumes that the relationship is a linear one. However, a plot of $-\Delta\text{pH}$, $-(\text{pH}_0 - \text{pH}_t)$, versus hypochlorite consumption, $-(\text{OCl}_0 - \text{OCl}_t)$, reveals that the relationship is a non-linear one (Figure 3.10)

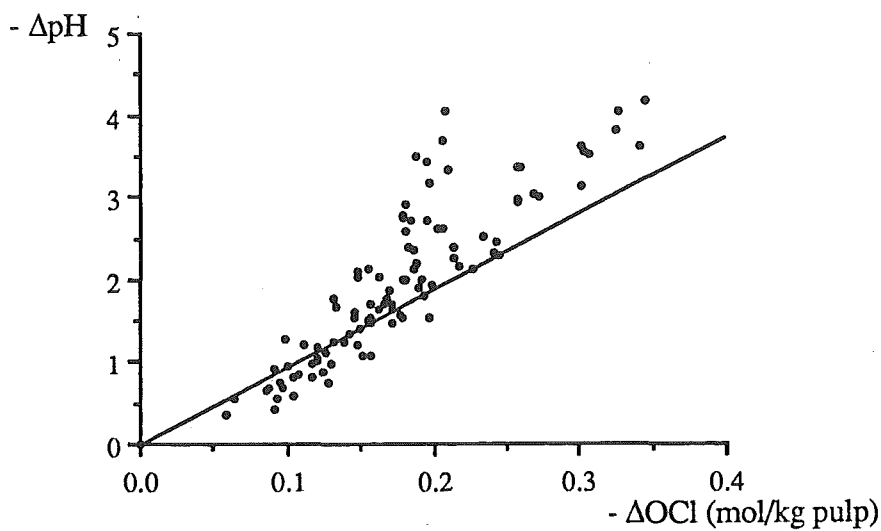


FIGURE 3.10: Plot of $-\Delta\text{pH}$ vs hypochlorite consumption

To describe the relationship between pH and hypochlorite consumption, a new model is proposed which can be expressed mathematically as follows:

$$\frac{dpH}{dOCl} = k_3 OCl^{-m} \quad (3.13)$$

or

$$pH_t = pH_o + k_3 * \left[\frac{OCl_t^{(1-m)} - OCl_o^{(1-m)}}{(1-m)} \right] \quad \text{when } m \neq 1 \quad (3.14)$$

$$pH_t = pH_o + k_3 * \ln \left[\frac{OCl_t}{OCl_o} \right] \quad \text{when } m=1 \quad (3.15)$$

where the coefficient, k_3 , is dependent on the initial hypochlorite charge.

The Levenberg Marquardt method is used to solve the above non-linear equation, giving the following results (3.10).

$$pH_t = pH_o + k_3 * \left[\frac{OCl_t^{0.493} - OCl_o^{0.493}}{0.493} \right] \quad (3.10)$$

where

$$k_3 = 2.299 * OCl_o^{-0.493}$$

A plot of predicted pH versus experimental pH is shown in Figure 3.11.

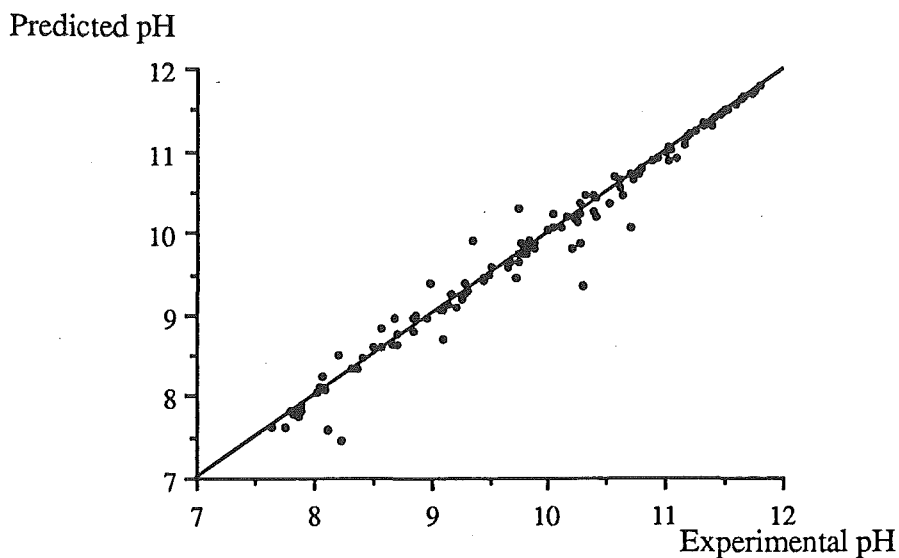


FIGURE 3.11: Plot of predicted pH versus experimental pH

CHAPTER 4

Discussion

4.1) EFFECT OF TEMPERATURE ON HYPOCHLORITE BLEACHING

To increase the production rate of an existing bleach plant, the operator can either increase the chemical charge or increase the reaction temperature. By increasing the chemical charge, reaction time will be reduced but the consequences are higher chemical costs and a higher residual chlorine with subsequent impact on water pollution. Increasing the temperature, however, suffers none of these effects. The study shows that the reaction rate can be doubled for every 8-10°C increase in the reaction temperature. From a production standpoint, this would mean operating the bleach plant at as high a temperature as possible. However, as the reaction temperature is increased, carbohydrate degradation becomes more severe. Studies by Axegård and Tormund (Axegård et al, 1985) on the hypochlorite bleaching of pine kraft pulp shows that the Arrhenius' activation energy for carbohydrate degradation is 113 kJ mol⁻¹ whereas the activation energy for chromophore elimination is only around 77 kJ mol⁻¹. This means that increasing the reaction temperature from 30°C to 40°C will increase the carbohydrate degradation rate by 265% (around 2½ times) whereas the same increase in temperature will increase the chromophore elimination rate by only 225%, keeping all other conditions constant. If the temperature increase is from 30°C to 60°C, the carbohydrate degradation rate will show an increase of around 1566% while the chromophore elimination rate only increase by 985%. By increasing the temperature, it can be seen that the reaction time can be drastically reduced but as the temperature gets higher, the advantage gained in shorter reaction time is offset by the increase in carbohydrate degradation. Reaction times of less than ten minutes have been reported for hypochlorite bleaching using temperatures of around 70°C (Milne, P.T., 1981). High temperature bleaching should be carried out with caution and a good knowledge of the relationship between chromophore elimination and carbohydrate degradation as well as a fairly strict control on process conditions is required. The rapid initial reaction rate for both chromophore elimination and carbohydrate degradation also means that an efficient mixing system is required to prevent uneven bleaching in the bleach tower.

In general, hypochlorite bleaching is usually carried out at temperatures of 30-40°C with reaction times ranging from two to as long as eight hours. The optimum operating temperature, however will depend on bleaching conditions such as bleach ratio and pH.

When the reaction temperature is kept constant throughout a bleach, the stoichiometry of hypochlorite bleaching was found to be independent of temperature. This means that the amount of bleach required to reach a target brightness at one temperature will be the same even if a different reaction temperature is used. This is as expected as the amount of hypochlorite ions consumed is dependent only on the amount of chromophores present and not on the temperature. This relationship can be made use of to increase the production rate by increasing the temperature, without incurring a cost in increased bleach consumption.

However, if the temperature is changed in the middle of a bleach, the temperature change will affect the character of the chlorine-water equilibrium. Increasing the temperature will shift the equilibrium towards an increase in the hypochlorite ion concentration and vice versa. Thus, pulp at 50°C charged with bleach chemicals at 30°C will have more hypochlorite ions present than pulp at 30°C charged with the same bleaching chemicals. In the same way, increasing the reaction temperature towards the end of the bleaching reaction can improve bleaching efficiency by shifting the chlorine-water equilibrium. However, too high a temperature will promote the decomposition of hypochlorites into chlorates. This represents a loss in bleaching efficiency as chlorates do not play an active role in hypochlorite bleaching.

The effect of temperature on the rate of chromophore elimination can be mathematically described by the Arrhenius equation.

4.2) EFFECT OF CHEMICAL CHARGE ON HYPOCHLORITE BLEACHING

At the bleach plant, the final brightness of the bleached pulp is controlled by varying the amount of bleach liquor charged into the pulp. The amount of bleach required will depend on factors such as bleaching conditions, wood species, pulping history of the pulp and the desired bleached pulp properties. Adding too much bleach could result in overbleaching with increased chemical costs and inferior paper strength while underbleaching will occur if too little bleach liquor is added, producing pulp of poor brightness qualities. The amount of bleach liquor required is usually determined by bleaching to a target residual chlorine. A small residual chlorine is required to maintain the driving potential during the retention period to prevent brightness reversion. At present, procedures for determining bleach liquor charge in a continuous bleach plant involves measuring the residual chlorine at the end of the bleach and charging the pulp accordingly. Considering the large lag time of around three hours, this is not an effective method of process control.

If, however, the kinetics of the bleaching reaction are known, the amount of bleach required to reach a target residual chlorine can be calculated, for different bleaching conditions. This would allow efficient use of bleaching chemicals, using only the required amount of bleach liquor to achieve the targeted brightness and residual chlorine at the end of the bleach. In the industry, hypochlorite bleach solution is usually charged to the pulp at 2% available chlorine with a target residual chlorine of around 0.05% available chlorine.

As mentioned, the hypochlorite charge can be used to increase the bleaching rate. This study shows that a 30% increase in reaction rate can be achieved if the hypochlorite ion concentration is doubled. However, as with temperature, operating with high hypochlorite charges requires that the bleaching conditions at the bleach tower be under strict control to prevent overbleaching.

As the chromophore concentration decreases, the amount of bleach required to achieve a given reduction in chromophore concentration increases, i.e. a lot more bleach is required to reduce C_k from, say, $4 \text{ m}^2 \text{ kg}^{-1}$ to $3 \text{ m}^2 \text{ kg}^{-1}$ than to reduce C_k from $10 \text{ m}^2 \text{ kg}^{-1}$ to $9 \text{ m}^2 \text{ kg}^{-1}$.

4.3) EFFECT OF ALKALINITY ON HYPOCHLORITE BLEACHING

The alkalinity of the reaction affects both the bleaching reaction and the amount of carbohydrate degradation occurring. pH has an inverse effect on the reaction rate, i.e. increasing the pH will decrease the bleaching rate. However, the alkalinity has only a small influence on the reaction rate. Doubling the hydroxide ion concentration will only reduce the bleaching rate by only 3%.

The importance of alkalinity in hypochlorite bleaching, however, is in its ability to control the degree of carbohydrate degradation occurring. Hypochlorite bleaching is best carried out at pH values of above 9. At these pH levels, the active bleaching agent is predominantly hypochlorite ions. As pH drops below a value of 9, hypochlorous acid becomes more predominant and serious carbohydrate degradation will occur if caution is not taken. Hypochlorous acid also has a catalytic effect on hypochlorite decomposition, reducing bleaching efficiency. Lowering of the pH during the bleach also reduces the bleaching efficiency by changing the chlorine-water equilibrium towards a reduction in hypochlorite ions.

In the study, unbuffered hypochlorite bleach solution was used. Initial pH is around 11 - 11.5. The pH decreases (characterised by a rapid initial reduction followed by slower reduction rate) as bleaching proceeds. This is due to the formation of carbon dioxide and organic acids and also the fact that hypochlorite (an alkaline salt) is being converted into sodium chloride (a neutral salt). The total reaction product of hypochlorite bleaching consists of around 75% carbon dioxide and 25% organic acids. At the end of the reaction, the final pH lies between 7.5

- 8, depending on the bleaching conditions. Therefore, to maintain a pH of above 8.5 throughout the bleaching reaction, either buffering of the hypochlorite bleach solution or the stepwise addition of alkali into pulp is required. Operating the bleach plant with a very high initial pH is not commonly practiced as reaction rate is retarded.

The pH of bleaching is also an important factor in terms of brightness stability. Pulp bleached at low pH levels will produce unstable carbonyl groups while high pH bleaching gives stable carbonyl groups. (Spinner, 1962). The best brightness stability for hypochlorite bleaching was found to be from pulps bleached at a pH value of around 10 - 10.5.

In general, most bleach plants uses sodium hypochlorite bleach liquor buffered with sodium hydroxide to ensure a terminal pH of around 9. The optimal pH, however, will depend on bleaching conditions such as temperature, chemical charge, wood species, etc.

4.4) THE ADVANTAGE OF A KINETIC MODEL

The advantage of a kinetic model as a tool to 'predict' bleaching behaviour can be illustrated by the following example.

Without the aid of a kinetic model, the operation of the bleach plant will be dependent on the experience of the operator. Decisions on whether to increase or decrease chemical charge will depend on brightness and residual chlorine measurements at the end of the bleach. If the pulp brightness is too low or if the residual chlorine is too low, then the chemical charge will be increased and vice versa. However, if the fluctuation was just a temporary, then the operator will be making unnecessary corrections to the chemical charge which would either result in overbleaching or underbleaching, both of which are undesirable. If the operator is experienced, he may choose to ignore the disturbance if he knows the process conditions upstream and realise that the disturbance is only a temporary one. However, automated process control would be virtually impractical, considering the large lag time involved.

On the other hand, with aid of the kinetic model as a tool in decision making, the correct amount of chemical charge could be calculated from variables such as the C_k of the incoming pulp, reaction temperature, reaction time and the desired brightness of the bleached pulp. As these variables can be predetermined from the input stream and set process conditions, the amount of bleaching chemicals required can be "predicted" before any actual bleaching takes place. This is especially important if automated process control is used, as the lag time has been effectively reduced to zero. Chemical costs will also be reduced as only the correct amount of bleach liquor is used.

Kinetic models are also useful aids for investigating new process configurations with different process conditions. A computer program can be written which can be used to determine bleaching behaviours under different bleaching conditions without having to perform expensive experimentation. Combined with a mass and energy software package such as GEMS, the whole bleach plant can be modelled to give optimal mass and energy configurations as well as optimal process conditions for product quality.

4.5) LIMITATION OF THE MODEL

The kinetics and stoichiometry for the hypochlorite bleaching of CE-prebleached *pinus radiata* kraft pulp can be adequately described by a rate equation, a stoichiometric equation and a pH equation:

$$-\frac{dC_k}{dt} = k_1 * C_k^{2.629} * [OH^-]^{-0.043} * [OCl^-]^{0.383}$$

$$\frac{dOCl}{dC_k} = \frac{3.89 * C_{k_0}^{-1.25}}{C_k}$$

$$\frac{dpH}{dOCl} = 2.299 * OCl_0^{-0.493} * OCl^{-0.507}$$

The three equations were determined from experiments performed under the following conditions:

TABLE 4.1: Bleaching conditions

Bleaching chemical	Sodium hypochlorite
Consistency	10%
Initial hypochlorite charge	1.5 - 2.5 % as available chlorine
pH	7.5 - 11.5
Pulp type	CE- prebleached kraft pulp
Specific light absorption coefficient (C_k)	24.804 - 0.31 m ² kg ⁻¹
Temperature	30 - 50 °C
Time	0 - 180 minutes
Wood species	<i>Pinus Radiata</i>

Care should be taken if the model is to be used to predict bleaching behaviour outside the range listed in table 4.1.

The effectiveness of a kinetic model as a tool can only be realised if the model is able to accurately predict the bleaching behaviour. Indeed, if the model fails in any way, the

consequences can be quite severe. The model developed in this study appears to correlate well with existing experimental data. However, to obtain full use of the model, it would have to be tested under industrial conditions. It is expected that some correction factors may be required because of differences between industrial bleaching and laboratory bleaching.

For example, the model was developed from experiments using unbuffered hypochlorite bleach solution while most industrial bleaching uses either buffered bleach liquor or stepwise addition of alkali to maintain a high pH. This is not expected to affect the bleaching rate because of the small effect hydroxide ion concentration has on bleaching rate. However, the stoichiometry of the reaction will be different. Constant pH bleaching can be simulated with the model by setting the exponents of the pH equation to zero and the value of the coefficient to the pH of the reaction.

Another area where the model differs from industrial bleaching is in the amount of CE filtrate carryover. CE filtrate, if present, will consume hypochlorite ions and increase bleach liquor consumption. In laboratory bleaching, the pulp was thoroughly washed on a Buchner funnel to remove CE filtrate. At the bleach plant, however, some CE filtrate carryover is inevitable and hypochlorite bleach consumption will be somewhat higher than that predicted by the model.

The model also does not take into account the possibility of hypochlorite decomposition. It assumes that the consumption of hypochlorite during the reaction is due entirely to the reaction between chromophores and hypochlorite ions. This is true at high pH and low temperatures as the decomposition of hypochlorite is retarded under these conditions. However, as pH drops or the reaction temperature increases, the decomposition of hypochlorite will become more pronounced.

4.6) ERRORS

One of the major source of error in the study is from the measurement of reflectances of the brightness pads. Reflectance was measured using a Photovolt reflectometer. To determine the specific light absorption coefficient (C_k), the Kubelka-Munk theory requires that diffuse light be used for reflectance measurements whereas the Photovolt reflection meter uses directional illumination. To obtain suitable reflectance values for use with the Kubelka-Munk theory, Photovolt reflectance readings were correlated to Elrepho equivalents using the correlation in Appendix A. (Elrepho is a brightness measurement instrument that is widely used in the paper industry). The Elrepho - Photovolt correlation was assumed to be linear.

The Photovolt reflectometer is also a fairly imprecise instrument that requires frequent recalibration. Standard brightness pads were used for calibration but frequent usage of the pads resulted in slightly soiled surfaces, contributing to errors in reflectance measurements.

Another possible source of error lies in the determination of the initial hypochlorite ion concentration (at time = 0). Hypochlorite ion concentration are normally determined from iodometric titrations with thiosulphate in the presence of iodide and starch. (See Appendix C). However, initial hypochlorite ion concentration cannot be determined by titration and has to be calculated from bleach liquor strength and pulp consistency. (See Appendix D). The oven dry (O.D.) weight of the pulp was determined by drying the pulp in a microwave oven until constant weight is achieved.

4.7) ASSUMPTIONS MADE BY THE MODEL

- 1) Hypochlorite consumption is due only to the reaction between chromophore and hypochlorite ions.
- 2) The chromophore concentration is proportional to the specific light absorption coefficient (C_k)
- 3) The bleaching rate is dependent only on the reaction temperature, reaction time, chromophore concentration, chemical charge and alkalinity.
- 4) Temperature is kept constant throughout a bleaching experiment.
- 5) The specific light absorption coefficient is dependent only on the chemical properties of the pulp and not on the physical structure of the brightness pads.
- 6) The correlations between Photovolt reflection readings and readings from the Elrepho are linear.

CHAPTER 5

Conclusions

The kinetics of hypochlorite bleaching of CE-prebleached pinus radiata kraft pulp can be described by the following rate equation:

$$-\frac{dC_k}{dt} = k_1 * C_k^{2.629} * [OH^-]^{-0.043} * [OCl^-]^{0.383}$$

where

Arrhenius activation energy is 64 kJ mol⁻¹

The rate of reaction ($\frac{dC_k}{dt}$), is defined as the reduction of chromophore concentration (approximated by the specific light absorption coefficient) per unit time.

Higher reaction temperatures, chromophore concentrations and hypochlorite concentrations will result in a higher reaction rate while increasing pH will decrease the reaction rate. During the bleaching reaction, the chromophore concentration, hypochlorite ion concentration and pH decreases with time.

The stoichiometry between hypochlorite ions and specific light absorption coefficient is independent of temperature and pH but dependent on the initial specific light absorption coefficient of the pulp. The stoichiometry, ($\frac{dOCl}{dC_k}$), is defined as the amount of hypochlorite consumed (in moles) per unit change in the specific light absorption coefficient and can be expressed mathematically as follows:

$$\frac{dOCl}{dC_k} = \frac{3.89 * C_{k_o}^{-1.25}}{C_k}$$

Hypochlorite consumption is defined as the amount of hypochlorite ions consumed per kilogram of oven-dry (O.D.) pulp.

The stoichiometric relationship between pH and hypochlorite ions is not constant as was proposed but is found to be dependent on the initial hypochlorite charge and hypochlorite

consumption. The relationship between pH and hypochlorite consumption can be described mathematically as follows:

$$\frac{dpH}{dOCl} = 2.299 * OCl_0^{-0.493} * OCl^{-0.507}$$

where the stoichiometry, $(\frac{dpH}{dOCl})$, is defined as the change in pH for a given change in hypochlorite consumption.

The mathematical model developed in this study to describe the bleaching mechanism of hypochlorite bleaching can be used as a tool to “predict” the brightness of bleached pulp from the hypochlorite stage of a three stage (CEH) bleaching sequence. It can also serve as a simulation tool to study hypochlorite bleaching under different bleaching conditions.

However, the objective of bleaching is not just to achieve a bleached pulp of a certain brightness. Other bleached pulp properties such as fiber strength, brightness stability and dirt content are also important qualities looked for in the bleached pulp and can sometimes be more critical than brightness. Therefore, if the bleaching reaction is to be fully simulated, the relationship between fiber strength, brightness stability and dirt removal efficiency with bleaching conditions should also be included in the predictive model. Such a model would be an invaluable tool in determining optimum bleaching conditions for achieving maximum brightness, maximum brightness stability, maximum dirt removal with minimal carbohydrate degradation.

However, when using the model developed in this study as a decision making tool, it is important that factors such as carbohydrate degradation, brightness reversion and dirt removal be taken into consideration. Failure to do so could result in bleached pulps of poor quality which will fail to meet the requirements of the consumers.

CHAPTER 6

Recommendations

Recommendations for future work include:

- 1) Investigation of the hypochlorite reaction with CE-prebleached pulp of other wood species.
- 2) Investigation of the hypochlorite reaction with CE-prebleached pulp using the “constant condition” experimental method. With the “constant condition” method, the bleaching conditions are kept constant by either having the bleaching chemicals in excess or adding the chemicals at the same rate as they are consumed. The advantage of the “constant condition” method is that the effect of the different bleaching variables on the bleaching behaviour can be examined individually.
- 3) Investigation of the carbohydrate degradation rate of hypochlorite bleaching with respect to the different bleaching variables. Carbohydrate degradation is a function of the degree of polymerisation of the cellulose which can be determined by measuring the viscosity. The extent of carbohydrate degradation gives an indication of the reduction in fiber strength due to the bleaching chemicals.
- 4) Investigation of the dirt removal efficiency of hypochlorite bleaching with respect to the different bleaching variables. Dirt removal (or shive removal) efficiency is a measure of the percentage of shives removed during the bleaching reaction. Good shive removal is important because any remaining shives will result in an unsightly paper.
- 5) Investigation of the brightness stability of hypochlorite bleaching with respect to the different bleaching variables. Brightness stability is a measure of the paper’s ability to retain brightness with time. Papers with good brightness stability are required for uses such as computer papers. Bleaching conditions such as pH and residual chlorine have an important influence on the brightness stability of the pulp.
- 6) Investigation of the kinetics and stoichiometry of chromophore elimination, carbohydrate degradation, dirt removal efficiency and brightness stability of other methods of bleaching. (Such as oxygen, chlorine dioxide, chlorine, peroxide, etc..)

Nomenclature

[OCl ⁻]	Hypochlorite ion concentration	[mol l ⁻¹]
[OH ⁻]	Hydroxide ion concentration	[mol l ⁻¹]
A	Arrhenius frequency factor	
a	Reaction order with respect to chromophore concentration	
b	Reaction order with respect to hydroxide ion concentration	
c	Reaction order with respect to hypochlorite ion concentration	
C _k	Specific light absorption coefficient (see also k)	[m ² kg ⁻¹]
C _{k₀}	Specific light absorption coefficient at time = 0	[m ² kg ⁻¹]
C _{k_t}	Specific light absorption coefficient at time = t mins	[m ² kg ⁻¹]
E _a	Arrhenius activation energy	[kJ mol ⁻¹]
K	Light absorption coefficient	[m ⁻¹]
k	Specific light absorption coefficient (see also C _k)	[m ² kg ⁻¹]
k ₁	Rate constant	
k ₂	Constant for hypochlorite stoichiometric equation	
k ₃	Constant for pH stoichiometric equation	
m	Exponent for pH stoichiometric equation	
n	Exponent for hypochlorite stoichiometric equation	
OCl	Hypochlorite charge	[mol per kg O.D pulp]
OCl ₀	Hypochlorite charge at time = 0	[mol per kg O.D pulp]
OCl _t	Hypochlorite charge at time = t mins	[mol per kg O.D pulp]
pH ₀	pH at time = 0	
pH _t	pH at time = t mins	
R	Universal gas constant = 8.3144	[kJ kmol ⁻¹ K ⁻¹]
R	Reflectance of a thin pad backed by a backing with a reflectance value of g	
R _g	Reflectance of the backing behind the pad whose reflectance is being considered	
R ₀	Reflectance of a thin pad backed with a backing of zero reflectance (R _g = 0)	
R _∞	Reflectance of a pad of infinite thickness	
S	Scattering coefficient	[m ⁻²]
s	Specific scattering coefficient	[m ² kg ⁻¹]
T	Temperature	[K]
W	Basis weight	[kg m ⁻²]

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Glossary

Active Chlorine

See Available chlorine

Available Chlorine

Measure of the oxidising power of the bleach solution expressed in terms of chlorine with a gram-equivalent weight of 35.46g.

Basis Weight

See Grammage

Bleaching

Chemical treatment of pulp to alter or remove the coloured material to obtain pulp of higher brightness.

Brightness

An indication of the degree of “whiteness” of a sheet of paper or pulp, measured using light with a wavelength of 457 nm (blue light).

Cellulose

A long chain polymer composing of glucose monomers. It is the main constituent of plant fibres.

Chemical charge

Weight percentage of chemicals added based on the amount of solids to be treated.

$$= \frac{\text{Dry weight of chemicals used}}{\text{Dry weight of solids(pulp)}} * 100\%$$

(also percent chemical)

Chromophore

Chemical groups attached to the lignin molecule. Generally considered as responsible for the colour in pulp.

Consistency

A measure of the amount of solid (pulp) in a pulp-water suspension, expressed as a percentage.

$$= \frac{\text{Dry weight}}{\text{Wet weight}} * 100\%$$

(also solids content)

Cooking

Chemical treatment of wood chips under heat and pressure to produce fibrous mass (pulp) for paper making.

Degree of Polymerisation (DP)

As applied to cellulose, refers to the average number of glucose monomers per cellulose molecule.

Fibrils

Thread like elements unraveled from the walls of native cellulose fibres.

Grammage

Weight per unit area of paper expressed in grams per square meter.

Light Absorption Coefficient

It is the fraction of light incident upon an infinitesimally thin layer of the material that is absorbed, divided by the basis weight of the layer. It is expressed in reciprocal basis weight units.

Light Scattering Coefficient

It is the fraction of light incident upon an infinitesimally thin layer of the material that is scattered backwards by that layer, divided by the basis weight of the layer.

Lignin

Generally defined as the incrusting material in which cellulose is imbedded, there is yet no definite chemical representation for native lignin. The definition of lignin varies according to the method with which it is extracted.

pH

A measure of the hydrogen ion concentration and the degree of acidity or alkalinity on a scale ranging from 0 to 14.

$$= - \ln [H^+]$$

Pulp

Wood broken down physically, chemically or both, to the extent that the fibres can be dispersed in water and reformed into a web.

Reflectance

A measure of the amount of light reflected from a sheet of pulp or paper.

R_{∞} = Reflectance of a pad of infinite thickness (also known as reflectivity)

R = Reflectance of a thin pad backed by a backing with a reflectance value of g

R_g = Reflectance of the backing behind the pad whose reflectance is being considered

R_o = Reflectance of a thin pad backed with a backing of zero reflectance ($R_g = 0$)

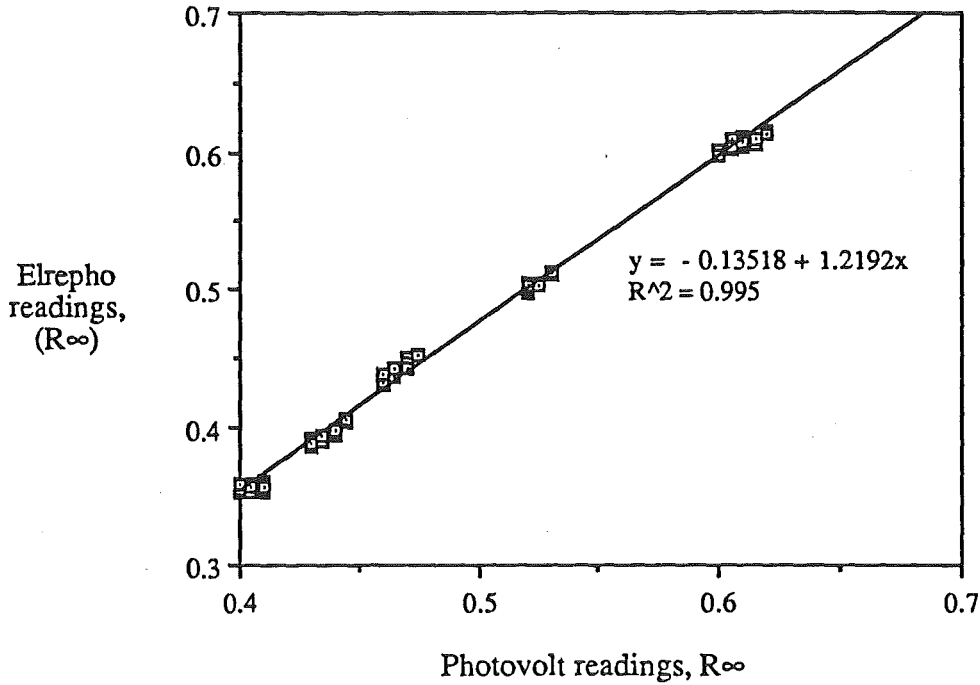
Reflectivity

See Reflectance

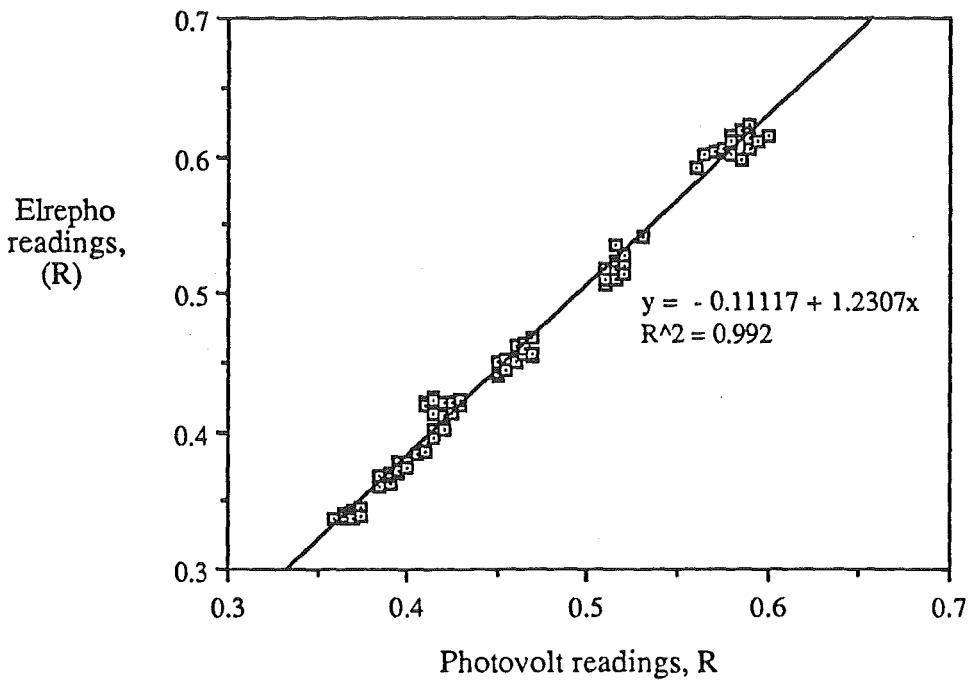
APPENDICES

Appendix A: Correlation between Elrepho readings and Photovolt readings

Correlation between Elrepho readings and Photovolt reflection meter readings



Correlation between Elrepho readings and Photovolt reflection meter readings



Appendix B: Preparation and Standardisation of Reagent Chemicals

1) Preparation of Sodium Thiosulphate (Na₂S₂O₃·5H₂O) solution

Sodium thiosulphate solution is used to analyse the hypochlorite strength and also residual chlorine test at the end of each run. Two different strengths of thiosulphate solution are used:

1.1) Preparation of 0.1M Sodium Thiosulphate solution

Weigh out approximately 12.41g of sodium thiosulphate crystals in 200ml of distilled water and make up to 500ml in a volumetric flask. ¹Use freshly boiled and cooled distilled water.

1.2) Preparation of 0.01M Sodium Thiosulphate solution

Weigh out approximately 2.482g of sodium thiosulphate crystals in 200ml of distilled water and make up to 1000ml in a volumetric flask. Use freshly boiled and cooled distilled water.

1.2) Standardisation of sodium thiosulphate solution

Sodium thiosulphate solution can be standardise against 0.01M potassium dicromate solution made by weighing accurately approximately 0.7355g K₂Cr₂O₇ and dissolving it in 250ml of distilled water in a volumetric flask. Using a pipette, measure 25ml of potassium dicromate solution for 0.1M Na₂S₂O₃ (or 10 ml of potassium dicromate solution for 0.01 M Na₂S₂O₃) of into a 250ml Erlenmeyer flask. Add approximately 20ml of 10% potassium iodide solution and 50ml of dilute sulphuric acid and allow to stand for 5 minutes. Stopper the flask during the standing period to reduce the loss of iodine. Titrate the liberated iodine with the thiosulphate solution, adding starch indicator solution near the endpoint. At the endpoint, the blue colour of the starch indicator will be replaced by the pale green colour of the dicromate ion. Strength of sodium thiosulphate solutions should be checked at least once a week.

1.3) Equations:



¹Bacterial action (and also light) can cause decomposition of thiosulphate ions.

1.4) Calculations:

MW of $K_2Cr_2O_7$ = 294.1838g per mole

MW of $Na_2S_2O_3 \cdot 5H_2O$ = 248.1737g per mole

$$\text{Molarity of } K_2Cr_2O_7 = \frac{\text{grams of } K_2Cr_2O_7 * \text{ml of solution}}{1000 * \text{MW of } K_2Cr_2O_7} \quad [=] \text{ mol l}^{-1}$$

$$\text{Molarity of } Na_2S_2O_3 = \frac{6 * \text{ml of } K_2Cr_2O_7 * \text{Molarity of } K_2Cr_2O_7}{\text{ml of } Na_2S_2O_3} \quad [=] \text{ mol l}^{-1}$$

- 2) Preparation of 10% Potassium Iodide solution (100 grams KI per 1000 ml solution)
Dissolve approximately 100 g of KI in 200 ml of distilled water and dilute to 1000 ml in a volumetric flask.
- 3) Related methods
TAPPI standard T610 pm-75

Appendix C: Analysis of bleach liquor

Available chlorine of bleach liquor

The strength of bleach liquors are generally reported in terms of available chlorine. This is a measure of the oxidising power of the bleach solution and is expressed in terms of chlorine with a gram-equivalent weight of 35.46 grams. Available chlorine is numerically equal to the weight of liquid or gaseous chlorine added during the preparation of the bleach liquor.

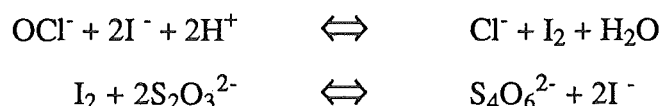
1) Analysis of hypochlorite bleach liquor

To 20ml of distilled water in a 250ml Erlenmeyer flask, add 10 ml of dilute H₂SO₄ and 10ml of 10% KI solution. Pipette 5ml of hypochlorite bleach liquor into the solution, keeping the tip of the pipette beneath the surface of the solution until drained. Titrate at once with 0.1M Na₂S₂O₃ to a pale yellow colour and complete the titration to the starch end point.

2) Analysis of spent liquor for residual chlorine

This test is similar to that for the determination of available chlorine in hypochlorite bleach liquor but is determined on a sample of filtrate taken from the pulp. A fibre free sample is obtained by passing the filtrate through a wire mesh. The sample volume depends on the amount of filtrate obtained and is typically around 25 to 50ml. 0.01M Na₂S₂O₃ is used rather than 0.1M Na₂S₂O₃.

3) Equations



4) Calculations

MW

Na = 22.98977 I = 126.9045 K = 39.098 S = 32.06
Cl = 35.453 O = 15.9994 H = 1.0079

$$\text{Available chlorine} = \frac{35.46 * \text{ml of Na}_2\text{S}_2\text{O}_3 * \text{Molarity of Na}_2\text{S}_2\text{O}_3}{\text{ml of NaOCl}} \quad [=] \text{ g l}^{-1}$$

$$\text{Molarity of NaOCl} = \frac{2 * \text{ml of Na}_2\text{S}_2\text{O}_3 * \text{Molarity of Na}_2\text{S}_2\text{O}_3}{\text{ml of NaOCl}} \quad [=] \text{ mol l}^{-1}$$

$$= \frac{2 * \text{Available chlorine}}{35.46} \quad [=] \text{ mol l}^{-1}$$

- 5) Related methods
 - i) TAPPI standard T611 os-75
 - ii) Canadian Pulp and Paper standard J.22P

Appendix D: Experimental procedures

1) Bleaching Experiments

1.1) For each bleaching experiment, a handful of pulp is thoroughly washed through a Buchner funnel and the excess water is removed. The moisture content of the pulp is determined and a sample size (wet sample wt), equivalent to approximately 10 gram oven dry pulp, is weighed out and placed into a polyethylene bag.

1.2) Depending on the required chemical charge, the amount of bleach required can be calculated according to equation 1.1a.

$$\text{hypo required} = \frac{\frac{\text{chemical charge}}{100} * \text{sample O.D. wt}}{\text{hypo strength}} \quad [\text{ml}] \quad 1.1a$$

1.4) A pulp suspension of 10% consistency was used for all the bleaching experiments. The amount of make-up water required can be calculated using equation 1.2a.

$$\text{make-up} = \frac{\text{sample O.D wt} * 100}{\text{Consistency}} - \text{wet sample wt} - \text{hypo required} \quad [\text{ml}] \quad 1.2a$$

Distilled water is used for the make-up.

1.5) The make-up water is added to the pulp sample and the polyethylene bag is sealed and submerged into a constant temperature water bath that has been preheated to the required reaction temperature.

1.6) After approximately 30 minutes, the bag is removed and the required amount of bleach is measured out and added to the sample. The bag is kneaded to ensure good mixing of the bleaching chemicals with the pulp. The pH is quickly taken before the bag is resealed and placed back into the water bath.

1.7) During the bleaching reaction, the bag is “kneaded” frequently to ensure proper mixing of the bleach liquor with the pulp.

1.8) After the required reaction time has lapsed, the polyethylene bag is removed from the water bath and the filtrate squeezed into a clean beaker. Further bleaching is stopped by dispersing the bleached pulp in a 5 litre bucket of water and washing through a Buchner funnel.

1.9) The filtrate is tested for residual chlorine and pH.

1.10) Table 1.1a shows the log-sheet for the bleaching experiments:

TABLE 1.1a: Experiment log sheet

Date: Date
 Run No: Run No
 Temperature: Temp °C
 Consistency: Consistency %
 Initial R: R m² kg⁻¹
 Initial R_{inf}: R_∞ m² kg⁻¹
 Initial pH: pH_i
 Chemical charge: chemical charge % as active chlorine
 Pulp O.D. weight: sample O.D. wt grams

Final pH		OCl [ml]		R	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆
pH ₁	pH ₂	OCl ₁	OCl ₂		R ₇	R ₈	R ₉	R ₁₀	R ₁₁	R ₁₂
ml Thio:		Thio ₁	Thio ₂	R _{inf}	R _{∞1}	R _{∞2}	R _{∞3}	R _{∞4}	R _{∞5}	R _{∞6}
Thio conc:		Thio conc [mol/l]			R _{∞7}	R _{∞8}	R _{∞9}	R _{∞10}	R _{∞11}	R _{∞12}

Wet weight: Wet sample wt grams
 Solid fraction: solid fraction
 Amt. of hypo added: hypo required ml
 Hypo strength: hypo strength grams l⁻¹
 Amt. of water added: make-up ml
 Time ended: end time mins
 Time started: start time mins Total time = end time - start time mins

Weight of brightness pads: [grams]

1	2	3
W ₁	W ₂	W ₃

2) Moisture content determination

2.1) The weight of a sample of moist pulp, (Wet wt) is measured before it is dried in a microwave oven, using the defrost option. Repeated weighing of the sample is then taken and the sample is considered oven dry, (O.D. wt) when the difference between two consecutive measurements is less than 0.005 grams. The moisture content is calculated as follows:

$$\text{moisture content} = \frac{\text{Wet wt} - \text{O.D. wt}}{\text{Wet wt}} * 100 \%$$

$$\text{solid fraction (consistency)} = \frac{\text{O.D. wt}}{\text{Wet wt}} * 100 \%$$

3) Brightness pads

3.1) Making brightness pads

3.1.1) The moisture content of the washed bleached pulp is determined and a pulp sample equivalent to approximately one gram O.D pulp is used for each brightness pad. A total of three brightness pads are required for each bleaching trial.

3.1.2) To make the brightness pads, the paper mould (appendix F) is first half filled with water. Care should be taken not to trap any air bubbles beneath the wire mesh. If air bubbles are present, these should be removed to ensure an even distribution of pulp fibres on the mesh.

3.1.3) The pulp sample is first dispersed in approximately 3.5 litres of water. A good dispersion is required to separate clumps of fibres. After dispersion, the pulp suspension is poured into the paper mould. The vacuum is then turned on and turned off when all the water have being removed.

3.1.4) The mesh unit is removed from the mould and a 150 mm filter paper is placed on top of the pulp fibre pad. Excess water is removed by pressing a 150 mm diameter piece of aluminium plate on top of the filter paper. The pad can then be removed by turning the mesh unit upside down and applying a sharp knock. The aluminium plate/filter paper/fibre pad should drop cleanly out without any fibres left sticking on the wire mesh. A glass plate is then placed on top of the fibre pad. Two more brightness pads are made in the same way (procedure 3.1.2 - 3.1.4) before the mould is washed thoroughly for the next experiment.

3.2) Pressing

3.2.1) To further remove more water, the pads are placed in a hydraulic press in the following arrangement.

3.2.2) A piece of blotting paper is first placed on the bottom piece of the press template to serve as a cushion. The gloss plate/test specimen/filter paper is then placed on top of the blotting paper with the filter paper side facing up. Two pieces of blotting paper are then laid on top of the filter paper.

3.2.3) Further test specimens are placed in the same order, i.e. gloss plate, test specimen, filter paper, two blotting paper, gloss plate,etc. The blotting paper used must have a bigger area than the brightness pads.

3.2.4) After the final test specimen has been laid down (with the two blotting paper on top), a piece of gloss plate is added and the upper half of the press template is placed on top of the stack. The final arrangement is as follows (figure 3.1a):

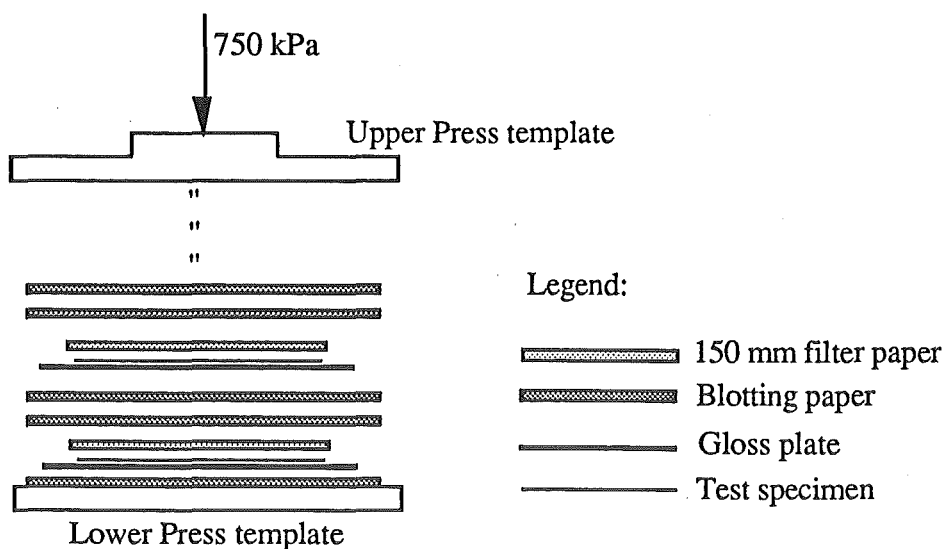


Figure 3.1a: Press arrangements

3.2.5) When the stack is completed, it is placed in a hydraulic press and a pressure of approximately 750 kPa is applied. After one minute, the pressure is released and the stack is removed for drying.

3.2.6) Related methods

TAPPI standard T218 os-75

3.3) Drying

3.3.1) As each gloss plate is removed from the stack, the two pieces of blotting paper together with the filter paper are discarded. The filter paper can be removed by holding down the gloss plate and test specimen at one edge and peeling the filter paper back from the test specimen at an acute angle.

3.3.2) To dry the test specimens, the gloss plate, with the test specimen facing up, is placed on top of a drying ring and a 180 mm filter paper is laid on top of the test specimen before the next drying ring is stacked. This arrangement is repeated for every test specimen. When the pile of rings have been completed, a piece of weight is placed on the top ring to clamp the pile together. The arrangement for the drying pile, from bottom to top, is as follows: drying ring, gloss plate, test specimen, 180mm filter paper, drying ring

3.3.3) Drying is achieved in an unused oven with the circulating fan turned on. When the test specimens are dried, they can be easily removed from the gloss plates and prepared for reflectance measurements.

3.3.4) Related methods

TAPPI standard T402 om-83

Note 1: Some blotters contain fluorescent fillers. The blotters used should be checked with an ultraviolet lamp to ascertain that such fillers are absent.

4) Brightness measurements

4.1) With the “Suppressor” knob turned to the “Off” position, switch on the “Lamp” and “Power” switches on the Photovolt reflection meter about an hour before use. (Refer figure 4.1a)

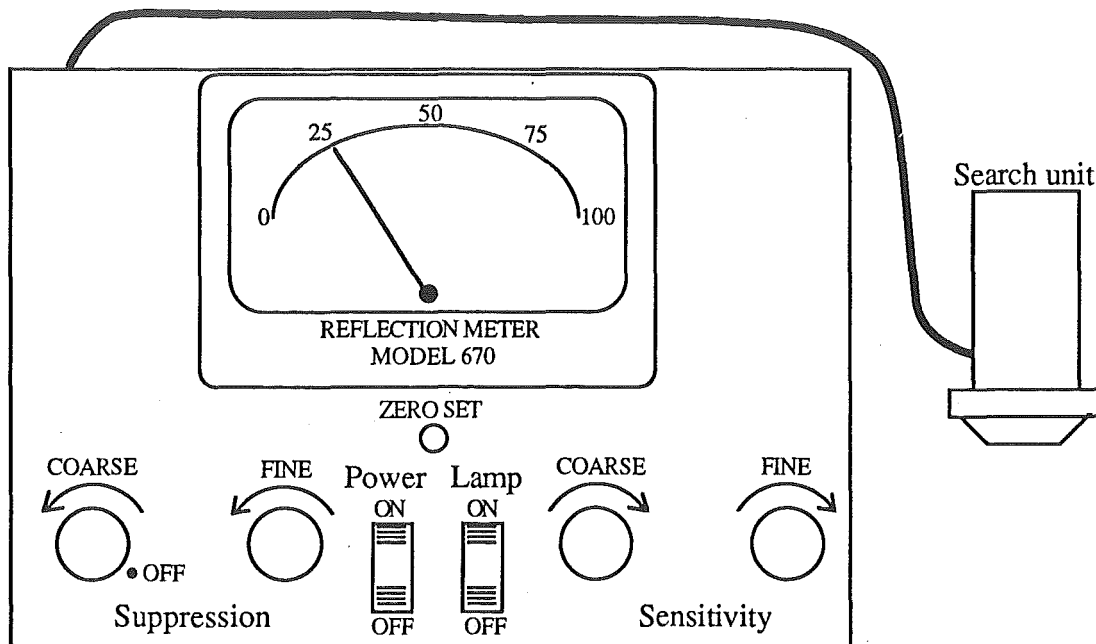


FIGURE 4.1a: Diagram of the Photovolt reflection meter, model 670

4.2) To calibrate, determine the approximate brightness of the test specimen(s) and calibrate accordingly using the appropriate standard brightness tabs and backing plate.

eg. If the brightness of the sheet is between 28 and 62%

- 1) Set the pointer to the lower scale (i.e. 27.9) using the “Zero set” knob and with the search unit on the 27.9 standard brightness tab.
- 2) Next, set the pointer to the upper scale (i.e. 60.6) using the “Sensitivity” knob with either the coarse or fine adjustment and with the search unit on the 60.6 standard brightness tab.
- 3) Repeat steps 1 and 2 alternately until the calibration is correct.

4.3) For R, place the individual test specimens, with the gloss side facing up, over the backing plate and record a reading for each quadrant of the sheet.

4.4) For R_∞, stack the three test specimens together and fold into halves, with the gloss side facing outwards. Record a reading from each quadrant of the three sheets.

Note 2: For R_∞, to check if the pad is “infinitely thick”, place a bright surface behind the pad of sheets and see if the reading changes. If reading changes, further fold the test specimens into quarters.

4.5) Determine the basis weight, (W), by dividing the oven-dry weight of the test specimen by the area of the sheet.

4.6) To determine the k and s values, the following equations are used:

$$\frac{k}{s} = \frac{(1 - R_{\infty})^2}{R_{\infty}}$$

$$sW = \frac{1}{\left[\frac{1}{R_{\infty}} - R_{\infty}\right]} * \ln \left[\frac{(R * R_g * R_{\infty} - R * R_{\infty}^2 - R_g + R_{\infty})}{(R * R_g * R_{\infty} - R - R_g * R_{\infty}^2 + R_{\infty})} \right]$$

4.7) Related methods

TAPPI standard T452 os-77

Appendix E: Fortran source code for predict hypochlorite bleaching behaviour

```

C*****
C   THIS PROGRAM IS USED TO ESTIMATE BLEACHING BEHAVIOUR IN ALKALINE
C   HYPOCHLORITE BLEACHING OF CE-PREBLEACHED PINUS RADIATA KRAFT PULP. IT
C   CAN ALSO BE USED TO ESTIMATE BLEACHING RESPONSE WITH OTHER FORMS OF
C   BLEACHING PROVIDED THE EQUATIONS USED ARE SIMILAR. THE THREE EQUATIONS
C   USED, ONE KINETIC AND TWO STOICHIOMETRIC, RELATES THE BLEACHING
C   VARIABLES, TIME, TEMPERATURE, ABSORPTION COEFFICIENT, CHEMICAL CHARGE
C   AND pH WITH EACH OTHER. THE THREE EQUATIONS ARE
C
C   1) -dCk/dt      =      k1 [Ck]**a1 [OH]**b1 [OCI]**c1
C   2) dOCI/dCk     =      k2 [Ck(t)]**(-n)
C   3) dpH/dOCI     =      k3 [OCI(t)]**(-m)
C
C   THE MAIN PROGRAM BLOCK HANDLES MOST OF THE SCREEN MANAGEMENT
C   ROUTINES AND DATA INITIALISATION. IT RELIES HEAVILY ON USE OF ANSI ESCAPE
C   SEQUENCES WHICH CAN BE FOUND IN DOS. FOR THE COMPUTER TO UNDERSTAND
C   THESE ESCAPE SEQUENCES, THE COMPUTER MUST READ IN THE ANSI.SYS FILE WHEN
C   IT BOOTS. (ANSI.SYS CAN BE FOUND IN ANY ORIGINAL DOS DISK) THE FOLLOWING
C   LINE MUST BE PLACE IN THE CONFIG.SYS FILE ON YOUR BOOT DISK.
C
C           DEVICE=[D:][PATH]ANSI.SYS
C
C   Example: DEVICE=C:\DOS\ANSI.SYS
C
C   THE SUBROUTINE, EQT, PERFORMS ALL THE NECESSARY CALCULATIONS FOR THE
C   SIMULATION.
C*****

```

```

PROGRAM HypoSim
COMMON/COM1/a1,b1,c1,n,m,k(3)
COMMON/COM2/Ck(3),pH(3),OCI(3),OH(3),OCIL(3),SL,IFLAG
DIMENSION EN(20),STRMI(3)

REAL*4 n,m,k
CHARACTER ESC*1,ANS*1

ESC=CHAR(27)
60 CALL CLEARSCR()
DO 70 I=1,20
    EN(I)=0
70 CONTINUE
CALL OPTION()
10 CALL MESS(21,1,'SELECT OPTION REQUIRED:',23)
WRITE(*,'(A3,A)')ESC,'[K'
READ(*,*,ERR=10)IOPTION
IF (IOPTION.LT.1.OR.IOPTION.GT.16) GOTO 10
EN(1)=IOPTION
CALL CHOICE()
CALL ME(24,1,'Bleaching consistency [%] =',27,SL,9)
CALL INPUT(IOPTION,EN)
CALL DEF(IOPTION,EN)
ANS='Y'
30 CALL MESS(24,1,'Are the above values correct [Y]? ',34)

```



```

20 READ(*,20,ERR=30)ANS
   FORMAT(A1)
   IF (ANS.EQ.'n'.OR.ANS.EQ.'N')THEN
       CALL CORR(EN,IOPTION)
       GOTO 30
   ENDIF
   SL=SL/(100-SL)
   CALL EQT(EN)
   DO 40 I=9,20
       CALL WRIT(I,EN(I))
40 CONTINUE
50 CALL MESS(24,1,'Do you want another run [N]? ',29)
   WRITE(*,'(A3,A\)' )ESC,'[K'
   READ(*,20,ERR=50)ANS
   IF (ANS.EQ.'Y'.OR.ANS.EQ.'y')GOTO 60
   CALL CLEARSCR()
   END

```

C+++++ Corrections subroutine

```

SUBROUTINE CORR(EN,IO)
COMMON/COM1/a1,b1,c1,n,m,k(3)
COMMON/COM2/Ck(3),pH(3),OCI(3),OH(3),OCIL(3),SL,IFLAG
DIMENSION EN(20)
CHARACTER ESC*1
REAL*4 n,m,k

ESC=CHAR(27)
10 CALL MESS(24,1,'Enter the line number you want to change:',41)
   WRITE(*,'(A3,A\)' )ESC,'[K'
   READ(*,*,ERR=10)I
   IF (I.LT.1.OR.I.GT.20)GOTO 10
   IF (I.EQ.1) THEN
       CALL ME(24,1,'Rate constant =',15,k(1),1)
   ELSEIF (I.EQ.2)THEN
       CALL ME(24,1,'Reaction order w.r.t Ck =',25,a1,2)
   ELSEIF (I.EQ.3)THEN
       CALL ME(24,1,'Reaction order w.r.t OH =',25,b1,3)
   ELSEIF (I.EQ.4)THEN
       CALL ME(24,1,'Reaction order w.r.t OCI =',26,c1,4)
   ELSEIF (I.EQ.5)THEN
       CALL ME(24,1,'Constant for hypochlorite equation =',36,k(2),5)
   ELSEIF (I.EQ.6)THEN
       CALL ME(24,1,'Exponent for hypochlorite equation =',36,n,6)
   ELSEIF (I.EQ.7)THEN
       CALL ME(24,1,'Constant for pH equation =',26,k(3),7)
   ELSEIF (I.EQ.8)THEN
       CALL ME(24,1,'Exponent for pH equation =',26,m,8)
   ELSEIF (I.EQ.9)THEN
       CALL ME(24,1,'Bleaching consistency [%] =',27,SL,9)
   ELSEIF (I.EQ.10) THEN
       CALL ME(24,1,'Ck of unbleached pulp [m2/kg] =',31,EN(10),10)
   ELSEIF (I.EQ.11) THEN
       CALL ME(24,1,'Hypochlorite concentration [mol/l] =',36,EN(11),11)
   ELSEIF (I.EQ.12) THEN
       CALL ME(24,1,'Initial pH =',12,EN(12),12)
   ELSEIF (I.EQ.13) THEN
       CALL ME(24,1,'Required residence time [mins] =',32,EN(13),13)
   ELSEIF (I.EQ.14) THEN
       CALL ME(24,1,'Required Ck of bleached pulp [m2/kg] =',38,EN(14),14)
   ELSEIF (I.EQ.15) THEN
       CALL ME(24,1,'Required residual hypo. conc. [mol/l] =',39,EN(15),15)
   ELSEIF (I.EQ.16)THEN
       CALL ME(24,1,'Required final pH =',19,EN(16),16)
   ELSEIF (I.EQ.17) THEN

```

```

      CALL ME(24,1,'Residence time [mins] =',23,EN(17),17)
ELSEIF (I.EQ.18) THEN
      CALL ME(24,1,'Ck of bleached pulp [m2/kg] =',29,EN(18),18)
ELSEIF (I.EQ.19) THEN
      CALL ME(24,1,'Residual hypochlorite concentration [mol/l] =',45,EN(19),19)
ELSEIF (I.EQ.20) THEN
      CALL ME(24,1,'Final pH =',10,EN(20),20)
ENDIF
RETURN
END

```

C+++++ Defining default values

```

SUBROUTINE DEF(IO,EN)
COMMON/COM1/a1,b1,c1,n,m,k(3)
DIMENSION EN(20)
REAL*4 k,n,m

```

```

20  FORMAT(F8.4,\)
      CALL ME(24,1,'Reaction temperature =',22,TEMP,100)
      k(1)=EXP(20.004-63997.734/(8.3144*(273.15+TEMP)))
      CALL WRIT(1,k(1))
      a1=2.629
      b1=-0.043
      c1=0.383
      CALL WRIT(2,a1)
      CALL WRIT(3,b1)
      CALL WRIT(4,c1)
      k(2)=3.37*(EN(10)**(-1.2099))
      n=1.0
      IF (IO.EQ.16) EN(11)=EN(15)-k(2)*ALOG(EN(14)/EN(10))
      k(3)=2.299*(EN(11)**(-0.493))
      m=0.507
      IF (IO.EQ.16) THEN
          EN(12)=EN(16)-k(3)*(EN(15)**(1-m)-EN(11)**(1-m))/(1-m)
          EN(1)=14
      ENDIF
      CALL WRIT(5,k(2))
      CALL WRIT(6,n)
      CALL WRIT(7,k(3))
      CALL WRIT(8,m)
      RETURN
      END

```

C+++++ Accepting input data

```

SUBROUTINE INPUT(I,EN)
DIMENSION EN(20)

      CALL ME(24,1,'Ck of unbleached pulp [m2/kg] =',31,EN(10),10)
      IF (I.LE.15) THEN
          CALL ME(24,1,'Hypochlorite concentration [mol/l] =',36,EN(11),11)
          CALL ME(24,1,'Initial pH =',12,EN(12),12)
      ENDIF
      IF (I.GE.4.AND.I.LE.7.OR.I.GE.11.AND.I.LE.13.OR.I.EQ.15) THEN
          CALL ME(24,1,'Residence time [mins] =',23,EN(13),13)
      ENDIF
      IF (I.EQ.1.OR.I.EQ.5.OR.I.EQ.8.OR.I.EQ.9.OR.I.EQ.11.OR.I.EQ.12.
*OR.(I.GE.14.AND.I.LE.15)) THEN
          CALL ME(24,1,'Ck of bleached pulp [m2/kg] =',29,EN(14),14)
      ENDIF
      IF (I.EQ.2.OR.I.EQ.6.OR.I.EQ.8.OR.I.EQ.10.OR.I.EQ.11.OR.(I.GE.13.AND.I.LE.15)) THEN
          CALL ME(24,1,'Residual hypo. conc. [mol/l] =',30,EN(15),15)
      ENDIF
      IF (I.EQ.3.OR.I.EQ.7.OR.I.EQ.9.OR.I.EQ.10.OR.(I.GE.12.AND.I.LE.15)) THEN
          CALL ME(24,1,'Final pH =',10,EN(16),16)
      ENDIF

```

```

ENDIF
IF (I.EQ.16)THEN
    CALL ME(24,1,'Ck of bleached pulp [m2/kg] =' ,29,EN(14),18)
    CALL ME(24,1,'Residual hypo. conc. [mol/l] =' ,30,EN(15),19)
    CALL ME(24,1,'Final pH =' ,10,EN(16),20)
ENDIF
RETURN
END

```

```

C+++++++ Processing input data for subroutine WRIT
SUBROUTINE ME(IX,IY,A,I,ANS,J)
CHARACTER*1 A(80),ESC

```

```

10    ESC=CHAR(27)
    CALL POS(IX,IY)
    WRITE(*,'(A3,A)' )ESC,'[2K'
    CALL MESS(IX,IY,A,I)
    READ(*,*,ERR=10)ANS
    IF(J.EQ.100)RETURN
    CALL WRIT(J,ANS)
    RETURN
END

```

```

C+++++++ Determining screen coordinates for input data
SUBROUTINE WRIT(J,ANS)

```

```

IF (J.EQ.1) THEN
    CALL WR(3,48,ANS)
ELSEIF (J.EQ.2) THEN
    CALL WR(4,48,ANS)
ELSEIF (J.EQ.3) THEN
    CALL WR(5,48,ANS)
ELSEIF (J.EQ.4) THEN
    CALL WR(6,48,ANS)
ELSEIF (J.EQ.5) THEN
    CALL WR(7,48,ANS)
ELSEIF (J.EQ.6) THEN
    CALL WR(8,48,ANS)
ELSEIF (J.EQ.7) THEN
    CALL WR(9,48,ANS)
ELSEIF (J.EQ.8) THEN
    CALL WR(10,48,ANS)
ELSEIF (J.EQ.9) THEN
    CALL WR(11,48,ANS)
ELSEIF (J.EQ.10) THEN
    CALL WR(12,48,ANS)
ELSEIF (J.EQ.11) THEN
    CALL WR(13,48,ANS)
ELSEIF (J.EQ.12) THEN
    CALL WR(14,48,ANS)
ELSEIF (J.EQ.13) THEN
    CALL WR(15,48,ANS)
ELSEIF (J.EQ.14) THEN
    CALL WR(16,48,ANS)
ELSEIF (J.EQ.15) THEN
    CALL WR(17,48,ANS)
ELSEIF (J.EQ.16) THEN
    CALL WR(18,48,ANS)
ELSEIF (J.EQ.17) THEN
    CALL WR(19,48,ANS)
ELSEIF (J.EQ.18) THEN
    CALL WR(20,48,ANS)
ELSEIF (J.EQ.19) THEN
    CALL WR(21,48,ANS)

```

```

ELSEIF (J.EQ.20) THEN
    CALL WR(22,48,ANS)
ENDIF
RETURN
END

```

```

C+++++++ Writing input data to screen
SUBROUTINE WR(IX,IY,ANS)

```

```

    CALL POS(IX,IY)
    WRITE(*,10)ANS
10  FORMAT(F8.4,*)
    RETURN
    END

```

```

C+++++++ Printing program options to screen

```

```

SUBROUTINE OPTION()
CALL BOX(79,19)
CALL MESS(3,10,'Option',6)
CALL MESS(4,13,'1 Bleach to a given Ck',23)
CALL MESS(5,13,'2 Bleach to a given OCl',24)
CALL MESS(6,13,'3 Bleach to a given OH',23)
CALL MESS(7,13,'4 Bleach to a given time',25)
CALL MESS(8,13,'5 Bleach to a given time or Ck',31)
CALL MESS(9,13,'6 Bleach to a given time or OCl',32)
CALL MESS(10,13,'7 Bleach to a given time or OH',31)
CALL MESS(11,13,'8 Bleach to a given Ck or OCl',30)
CALL MESS(12,13,'9 Bleach to a given Ck or pH',29)
CALL MESS(13,12,'10 Bleach to a given OCl or pH',31)
CALL MESS(14,12,'11 Bleach to a given time, Ck or OCl',37)
CALL MESS(15,12,'12 Bleach to a given time, Ck or pH',36)
CALL MESS(16,12,'13 Bleach to a given time, OCl or pH',37)
CALL MESS(17,12,'14 Bleach to a given Ck, OCl or pH',35)
CALL MESS(18,12,'15 Bleach to a given time, Ck, OCl or pH',41)
CALL MESS(19,12,'16 Determine initial conditions from final conditions',53)
RETURN
END

```

```

C+++++++ Defining input data on screen

```

```

SUBROUTINE CHOICE()
CALL CLEARSCR()
CALL BOX(79,22)
CALL MESS(3,3,' 1) RATE CONSTANT FOR KINETIC EQUATION.....=',42)
CALL MESS(4,3,' 2) REACTION ORDER w.r.t Ck.....=',42)
CALL MESS(5,3,' 3) REACTION ORDER w.r.t OCl .....=',42)
CALL MESS(6,3,' 4) REACTION ORDER w.r.t OH .....=',42)
CALL MESS(7,3,' 5) CONSTANT FOR HYPO. EQUATION .....=',42)
CALL MESS(8,3,' 6) EXPONENT OF HYPO. EQUATION.....=',42)
CALL MESS(9,3,' 7) CONSTANT FOR pH EQUATION .....=',42)
CALL MESS(10,3,' 8) EXPONENT FOR pH EQUATION.....=',42)
CALL MESS(11,3,' 9) BLEACHING CONSISTENCY [%] .....=',42)
CALL MESS(12,3,'10) Ck OF UNBLEACHED PULP [m2/kg].....=',42)
CALL MESS(13,3,'11) HYPOCHLORITE CONCENTRATION [mol/l] .....=',42)
CALL MESS(14,3,'12) INITIAL pH OF THE REACTION.....=',42)
CALL MESS(15,3,'13) REQUIRED RESIDENCE TIME [mins] .....=',42)
CALL MESS(16,3,'14) REQUIRED Ck OF BLEACHED PULP [m2/kg]....=',42)
CALL MESS(17,3,'15) REQUIRED RESIDUAL HYPO. CONC. [mol/l] ...=',42)
CALL MESS(18,3,'16) REQUIRED FINAL pH.....=',42)
CALL MESS(19,3,'17) RESIDENCE TIME.....=',42)
CALL MESS(20,3,'18) FINAL Ck OF BLEACHED PULP [m2/kg].....=',42)
CALL MESS(21,3,'19) FINAL HYPO. CONC. [mol/l].....=',42)
CALL MESS(22,3,'20) FINAL pH .....=',42)
WRITE(*,A)
RETURN

```

END

C+++++++ Subroutine to draw a box on screen given width, (IX) and height, (IY)

```
SUBROUTINE BOX(IX,IY)
CHARACTER*1 TL,TR,TOP,BL,BR,SIDE

TL=CHAR(201)
TR=CHAR(187)
TOP=CHAR(205)
BL=CHAR(200)
BR=CHAR(188)
SIDE=CHAR(186)

10  FORMAT(1X,A1,\)
60  FORMAT(A1,\)
70  FORMAT(A1)
WRITE(*,10)TL
DO 20 I=1,IX-2
    WRITE(*,60)TOP
20  CONTINUE
WRITE(*,70)TR
DO 30 I=1,IY-2
    WRITE(*,10)SIDE
    DO 40 J=1,IX-2
        WRITE(*,60)' '
40  CONTINUE
WRITE(*,70)SIDE
30  CONTINUE
WRITE(*,10)BL
DO 50 I=1,IX-2
    WRITE(*,60)TOP
50  CONTINUE
WRITE(*,70)BR
RETURN
END
```

C+++++++ Subroutine to move cursor to coordinates IX, IY on the screen

```
SUBROUTINE POS(IX,IY)
CHARACTER ESC*1

ESC=CHAR(27)
WRITE(*,10)ESC,IX,IY
10  FORMAT(1X,A1,'I',I2.2,',',I2.2,'H',\)
RETURN
END
```

C+++++++ Clears screen

```
SUBROUTINE CLEARSCR()
CHARACTER ESC*1

ESC=CHAR(27)
WRITE(*,*)ESC,'[2J'
RETURN
END
```

C+++++++ Subroutine to write M of length, I characters, to coordinates IX, IY on the screen

```
SUBROUTINE MESS(IX,IY,M,I)
CHARACTER*1 M(80)

CALL POS(IX,IY)
WRITE(*,10)' '
DO 20 L=1,I
```

```
        WRITE(*,10)M(L)
20    CONTINUE
10    FORMAT(A1,\)
        RETURN
        END]
```

C+++++ Error subroutines

```
SUBROUTINE ERRR(I)
CHARACTER BELL*1,ESC*1
```

```
BELL=CHAR(7)
ESC=CHAR(27)
CALL POS(24,1)
WRITE (*,'(A1,A1,A1,A\)'BELL,BELL,BELL
CALL POS(24,1)
WRITE(*,'(A3,A\)'ESC,'[K'
IF(I.EQ.1)THEN
    CALL MESS(24,1,'ALL BLEACHING CHEMICALS CONSUMED',32)
ELSEIF (I.EQ.2) THEN
    CALL MESS(24,1,'NO PULP IN INPUT STREAM',23)
ELSEIF (I.EQ.3) THEN
    CALL MESS(24,1,'REACTANTS NOT DECREASING WITH TIME',34)
ELSEIF (I.EQ.4) THEN
    CALL MESS(24,1,'INITIAL Ck,OCI OR pH IS ZERO. PLEASE CHECK DATASET',50)
ENDIF
READ(*,*)
RETURN
END
```

```

C*****
C THIS SUBROUTINE PERFORMS THE CALCULATIONS REQUIRED TO ESTIMATE
C BLEACHING BEHAVIOUR IN ALKALINE HYPOCHLORITE BLEACHING. THREE
C EQUATIONS ARE USED, ONE KINETIC AND TWO STOICHIOMETRIC, RELATES THE
C BLEACHING VARIABLES, TIME, TEMPERATURE, ABSORPTION COEFFICIENT, CHEMICAL
C CHARGE AND pH WITH EACH OTHER. THE THREE EQUATIONS ARE
C
C 1) -dCk/dt = k1 [Ck]**a1 [OH]**b1 [OCI]**c1
C 2) dOCI/dCk = k2 [Ck(t)]**(-n)
C 3) dpH/dOCI = k3 [OCI(t)]**(-m)
C*****

```

```

SUBROUTINE EQT(EN)
COMMON/COM1/a1,b1,c1,n,m,k(3)
COMMON/COM2/Ck(3),pH(3),OCI(3),OH(3),OCIL(3),SL,IFLAG

```

```

DIMENSION EN(20)

```

```

REAL*4 DT,T,TEMP,n,m,k
REAL*4 Ck3,OCI3,pH3

```

```

C EN(1) = OPTION NO 1 THRU 15 AS FOLLOWS:
C 1 BLEACH TO CERTAIN Ck
C 2 BLEACH TO CERTAIN OCI
C 3 BLEACH TO CERTAIN pH
C 4 BLEACH TO CERTAIN TIME
C 5 BLEACH TO CERTAIN TIME OR Ck
C 6 BLEACH TO CERTAIN TIME OR OCI
C 7 BLEACH TO CERTAIN TIME OR pH
C 8 BLEACH TO CERTAIN Ck OR OCI
C 9 BLEACH TO CERTAIN Ck OR pH
C 10 BLEACH TO CERTAIN OCI OR pH
C 11 BLEACH TO CERTAIN TIME, Ck OR OCI
C 12 BLEACH TO CERTAIN TIME, Ck OR pH
C 13 BLEACH TO CERTAIN TIME, OCI OR pH
C 14 BLEACH TO CERTAIN Ck, OCI OR pH
C 15 BLEACH TO CERTAIN TIME, Ck, OCI OR pH
C 16 DETERMINE INITIAL OCI AND pH GIVEN TERMINATING CONDITIONS
C EN(2) = RATE CONSTANT [k(1)]
C EN(3) = REACTION ORDER WITH RESPECT TO Ck [a]
C EN(4) = REACTION ORDER W.R.T OH [b]
C EN(5) = REACTION ORDER W.R.T OCI [c]
C EN(6) = CONSTANT FOR OCI/Ck STOICHIOMETRIC EQN. [k(2)]
C EN(7) = EXPONENT FOR OCI/Ck STOICHIOMETRIC EQN. [n]
C EN(8) = CONSTANT FOR pH/OCI STOICHIOMETRIC EQN. [k(3)]
C EN(9) = EXPONENT FOR pH/OCI STOICHIOMETRIC EQN. [m]
C EN(10)= INITIAL Ck [Ck(1)]
C EN(11)= INITIAL OCI [OCI(1)]
C EN(12)= INITIAL pH [pH(1)]
C EN(13)= RESIDENCE TIME [MINUTES]
C EN(14)= FINAL Ck [Ck(t)]
C EN(15)= FINAL OCI [OCI(t)]
C EN(16)= FINAL pH [pH(t)]
C EN(17)= REACTION TIME
C EN(18)= FINAL ABSORPTION COEFFICIENT [Ck(3)]
C EN(19)= FINAL HYPOCHLORITE ION CONCENTRATION [OCI(3)]
C EN(20)= FINAL pH [pH(3)]

```

```

C+++++ INITIALISATION ++++++
C Ck(1)=EN(10)
C OCI(1)=EN(11)

```

```

pH(1)=EN(12)
IEN=NINT(EN(1))
IFLAG=0
T=0.1
Ck(2)=Ck(1)
OCI(3)=OCI(1)
pH(3)=pH(1)
OH(3)=10**(pH(3)-14)
Q=0.000001
IF (SL.LE.Q.OR.Ck(1).LE.Q.OR.OCI(1).LE.Q.OR.pH(1).LE.Q)THEN
    IF (SL.LE.Q) THEN
        CALL ERRR(2)
    ELSE
        CALL ERRR(4)
    ENDIF
    Ck(3)=Ck(2)
    GOTO 50
ENDIF
OCIL(3)=OCI(3)*SL
DT=0.1
C+++++ BEGIN CALCULATIONS ++++++
CALL NEWVALUES(DT,Ck(3),OCI(3),pH(3))
IF (Ck(3).GT.Ck(1).OR.OCI(3).GT.OCI(1).OR.pH(3).GT.pH(1))THEN
    CALL ERRR(3)
    GOTO 50
ENDIF
DO 40 I=1,500
C##### TESTING FOR TERMINATING CONDITION #####
IF (IEN.EQ.1) THEN
    IF (Ck(3).LE.EN(14))CALL SUB1(T,1,DT,EN(14))
ELSEIF (IEN.EQ.2) THEN
    IF (OCI(3).LE.EN(15))CALL SUB1(T,2,DT,EN(15))
ELSEIF (IEN.EQ.3) THEN
    IF (pH(3).LE.EN(16))CALL SUB1(T,3,DT,EN(16))
ELSEIF (IEN.EQ.4) THEN
    IF ((T+DT).GE.EN(13))CALL SUB5(T,DT,EN(13))
ELSEIF (IEN.EQ.5) THEN
    IF (Ck(3).LE.EN(14)) THEN
        CALL SUB1(T,1,DT,EN(14))
    ELSEIF ((T+DT).GE.EN(13)) THEN
        CALL SUB5(T,DT,EN(13))
        CALL NEWVALUES(DT,Ck3,OCI3,pH3)
        IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
    ENDIF
ELSEIF (IEN.EQ.6) THEN
    IF (OCI(3).LE.EN(15))THEN
        CALL SUB1(T,2,DT,EN(15))
    ELSEIF ((T+DT).GE.EN(13)) THEN
        CALL SUB5(T,DT,EN(13))
        CALL NEWVALUES(DT,Ck3,OCI3,pH3)
        IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
    ENDIF
ELSEIF (IEN.EQ.7) THEN
    IF (pH(3).LE.EN(16)) THEN
        CALL SUB1(T,3,DT,EN(16))
    ELSEIF ((T+DT).GE.EN(13)) THEN
        CALL SUB5(T,DT,EN(13))
        CALL NEWVALUES(DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
    ENDIF
ELSEIF (IEN.EQ.8) THEN
    IF (OCI(3).LE.EN(15)) THEN
        CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
        IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
    ENDIF

```



```

ELSEIF (Ck(3).LE.EN(14)) THEN
    CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
    IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
ENDIF
ELSEIF (IEN.EQ.9) THEN
    IF (pH(3).LE.EN(16)) THEN
        CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
        IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
    ELSEIF (Ck(3).LE.EN(14)) THEN
        CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
    ENDIF
ENDIF
ELSEIF (IEN.EQ.10) THEN
    IF (pH(3).LE.EN(16)) THEN
        CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
        IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
    ELSEIF (OCI(3).LE.EN(15)) THEN
        CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
    ENDIF
ENDIF
ELSEIF (IEN.EQ.11) THEN
    IF (OCI(3).LE.EN(15)) THEN
        CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
        IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
    ELSEIF (Ck(3).LE.EN(14)) THEN
        CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
        IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
    ELSEIF ((T+DT).GE.EN(13)) THEN
        CALL SUB5(T,DT,EN(13))
        CALL NEWVALUES(DT,Ck3,OCI3,pH3)
        IF (Ck3.LE.EN(14)) THEN
            CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
            IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
        ELSEIF (OCI3.LE.EN(15)) THEN
            CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
            IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
        ENDIF
    ENDIF
ENDIF
ELSEIF (IEN.EQ.12) THEN
    IF (pH(3).LE.EN(16)) THEN
        CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
        IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
    ELSEIF (Ck(3).LE.EN(14)) THEN
        CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
    ELSEIF ((T+DT).GE.EN(13)) THEN
        CALL SUB5(T,DT,EN(13))
        CALL NEWVALUES(DT,Ck3,OCI3,pH3)
        IF (Ck3.LE.EN(14)) THEN
            CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
            IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
        ELSEIF (pH3.LE.EN(16)) THEN
            CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
            IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
        ENDIF
    ENDIF
ENDIF
ELSEIF (IEN.EQ.13) THEN
    IF (pH(3).LE.EN(16)) THEN
        CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
        IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
    ELSEIF (OCI(3).LE.EN(15)) THEN
        CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
    ELSEIF ((T+DT).GE.EN(13)) THEN

```

```

        CALL SUB5(T,DT,EN(13))
        CALL NEWVALUES(DT,Ck3,OCI3,pH3)
    IF (OCI3.LE.EN(15)) THEN
        CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
    ELSEIF (pH3.LE.EN(16)) THEN
        CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
        IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
    ENDIF
ENDIF
ELSEIF (IEN.EQ.14) THEN
    IF (pH(3).LE.EN(16)) THEN
        CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
        IF (Ck3.LE.EN(14)) THEN
            CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
            IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
        ELSEIF (OCI3.LE.EN(15)) THEN
            CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
            IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
        ENDIF
    ELSEIF (OCI(3).LE.EN(15)) THEN
        CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
        IF (Ck3.LE.EN(14)) THEN
            CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
            IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
        ELSEIF (pH3.LE.EN(16)) THEN
            CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
            IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
        ENDIF
    ELSEIF (Ck(3).LE.EN(14)) THEN
        CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) THEN
            CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
            IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
        ELSEIF (OCI3.LE.EN(15)) THEN
            CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
            IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
        ENDIF
    ENDIF
ELSEIF (IEN.EQ.15) THEN
    IF (pH(3).LE.EN(16)) THEN
        CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
        IF (OCI3.LE.EN(15)) THEN
            CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
            IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
        ELSEIF (Ck3.LE.EN(14)) THEN
            CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
            IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
        ENDIF
    ELSEIF (OCI(3).LE.EN(15)) THEN
        CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) THEN
            CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
            IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
        ELSEIF (Ck3.LE.EN(14)) THEN
            CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
            IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
        ENDIF
    ELSEIF (Ck(3).LE.EN(14)) THEN
        CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) THEN
            CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
            IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
        ELSEIF (OCI3.LE.EN(15)) THEN

```

```

        CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
    ENDIF
ELSEIF ((T+DT).GE.EN(13)) THEN
    CALL SUB5(T,DT,EN(13))
    CALL NEWVALUES(DT,Ck3,OCI3,pH3)
    IF (pH3.LE.EN(16)) THEN
        CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
        IF (OCI3.LE.EN(15)) THEN
            CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
            IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
        ELSEIF(Ck3.LE.EN(14)) THEN
            CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
            IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
        ENDIF
    ELSEIF (OCI3.LE.EN(15)) THEN
        CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
        IF (pH3.LE.EN(16)) THEN
            CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
            IF (Ck3.LE.EN(14)) CALL SUB1(T,1,DT,EN(14))
        ELSEIF (Ck3.LE.EN(14)) THEN
            CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
            IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
        ENDIF
    ELSEIF (Ck3.LE.EN(14)) THEN
        CALL SUB4(T,1,EN(14),DT,Ck3,OCI3,pH3)
        IF (OCI3.LE.EN(15)) THEN
            CALL SUB4(T,2,EN(15),DT,Ck3,OCI3,pH3)
            IF (pH3.LE.EN(16)) CALL SUB1(T,3,DT,EN(16))
        ELSEIF (pH3.LE.EN(16)) THEN
            CALL SUB4(T,3,EN(16),DT,Ck3,OCI3,pH3)
            IF (OCI3.LE.EN(15)) CALL SUB1(T,2,DT,EN(15))
        ENDIF
    ENDIF
ENDIF
ENDIF
ENDIF
ENDIF
IF (IFLAG.EQ.1) THEN
    CALL NEWVALUES(DT,Ck(3),OCI(3),pH(3))
    GOTO 50
ENDIF
IF (OCI(3).EQ.0) THEN
    CALL SUB1(T,2,DT,0)
    CALL SUB2(T,DT)
ENDIF
IF (IFLAG.EQ.0) THEN
    CALL SUB2(T,DT)
    CALL NEWVALUES(DT,Ck(3),OCI(3),pH(3))
ENDIF
40 CONTINUE
50 EN(17)=T
   EN(18)=Ck(3)
   EN(19)=OCI(3)
   EN(20)=pH(3)
   IF (OCI(3).EQ.0) CALL ERRR(1)
   RETURN
   END

```

```

SUBROUTINE SUB1(TIME,IEN,DELTAT,X)
COMMON/COM1/a1,b1,c1,n,m,k(3)
COMMON/COM2/Ck(3),pH(3),OCI(3),OH(3),OCIL(3),SL,IFLAG
REAL*4 O,C,DELTAT,X,n,m,k,TIME

```

```

TIME=TIME-DELTAT

```

```

IF (IEN.EQ.2) THEN
    O=X
    GOTO 1
ELSEIF (IEN.EQ.1) THEN
    C=X
    GOTO 2
ENDIF
p=X
IF (m.EQ.1.0) THEN
    O=OCI(1)*EXP((p-pH(1))/k(3))
ELSE
    O=EXP((ALOG((p-pH(1))*(1-m)/k(3)+OCI(1)**(1-m)))/(1-m))
ENDIF
1 IF (n.EQ.1.0) THEN
    C=Ck(1)*EXP((O-OCI(1))/k(2))
ELSE
    C=EXP(ALOG(Ck(1)**(1-n)+(O-OCI(1))*(1-n)/k(2)))/(1-n)
ENDIF
2 DELTAT=(Ck(2)-C)/(k(1)*(Ck(2)**a1)*(OH(3)**b1)*(OCIL(3)**c1))
TIME=TIME+DELTAT
IFLAG=1
RETURN
END

```

```

SUBROUTINE SUB2(T,DT)
COMMON/COM2/Ck(3),pH(3),OCI(3),OH(3),OCIL(3),SL,IFLAG
REAL*4 T,DT,MIN

```

```

MIN=0.000001
IF (ABS(T-1.0).LT.MIN)DT=1.0
IF (ABS(T-60.0).LT.MIN)DT=5
IF (ABS(T-180.0).LT.MIN)DT=30
IF (ABS(T-480.0).LT.MIN)DT=60
Ck(2)=Ck(3)
OH(3)=10**(pH(3)-14)
IF (OCI(3).LE.MIN)OCI(3)=0
OCIL(3)=OCI(3)*SL
T=T+DT
RETURN
END

```

```

SUBROUTINE SUB4(T,IEN,X,DT,Ck3,OCI3,pH3)
CALL SUB1(T,IEN,DT,X)
CALL NEWVALUES(DT,Ck3,OCI3,pH3)
RETURN
END

```

```

SUBROUTINE SUB5(T,DT,X)
COMMON/COM2/Ck(3),pH(3),OCI(3),OH(3),OCIL(3),SL,IFLAG
REAL*4 T,DT,X
DT=X-T
CALL SUB2(T,DT)
IFLAG=1
RETURN
END

```

```

SUBROUTINE NEWVALUES(DT,Ck3,OCI3,pH3)
COMMON/COM1/a1,b1,c1,n,m,k(3)
COMMON/COM2/Ck(3),pH(3),OCI(3),OH(3),OCIL(3),SL,IFLAG
REAL*4 TEMP,Ck3,OCI3,pH3,n,m,k

```

```

Ck3=Ck(2)-k(1)*(Ck(2)**a1)*(OH(3)**b1)*(OCIL(3)**c1)*DT
IF (n.EQ.1.0) THEN

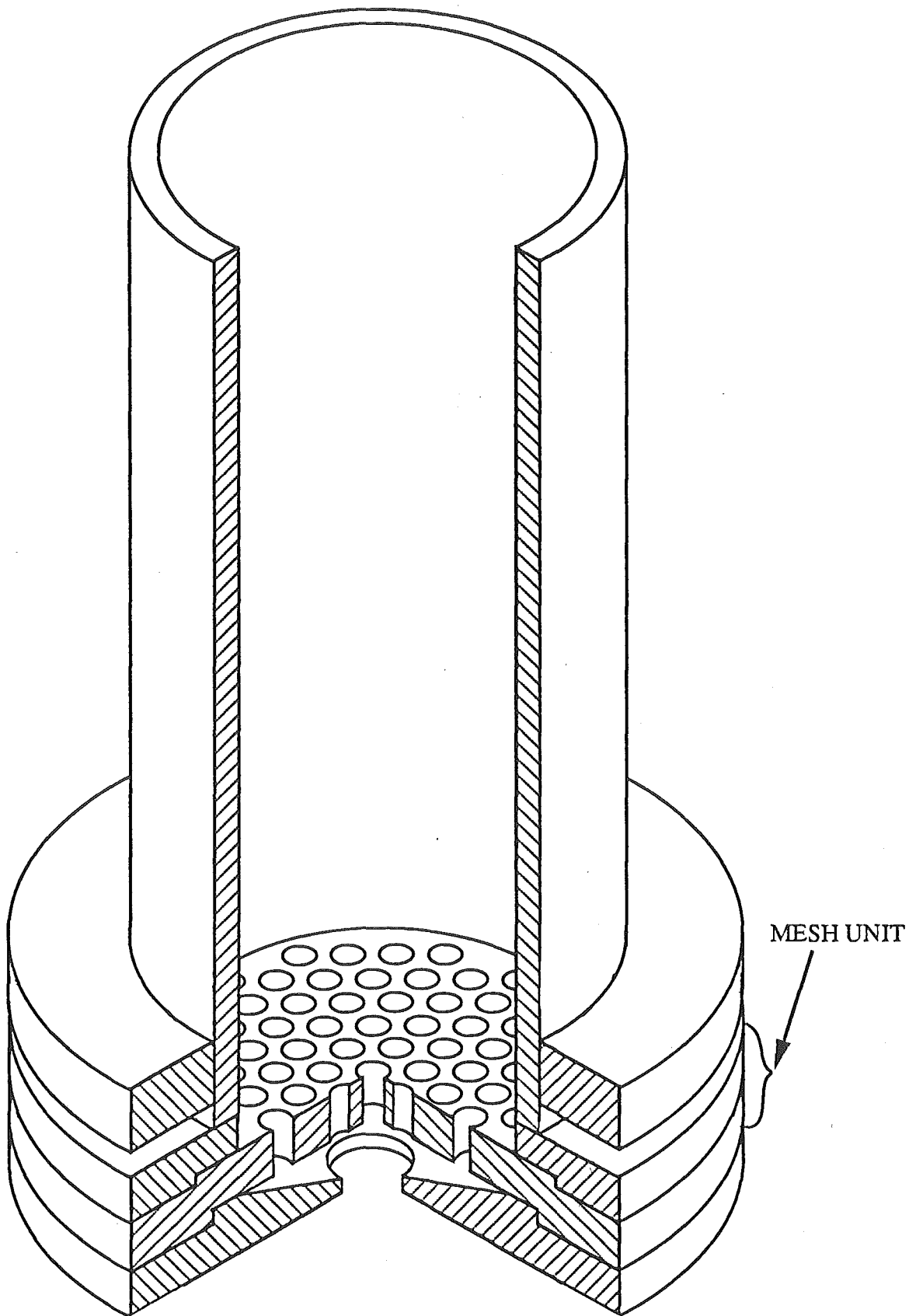
```

```

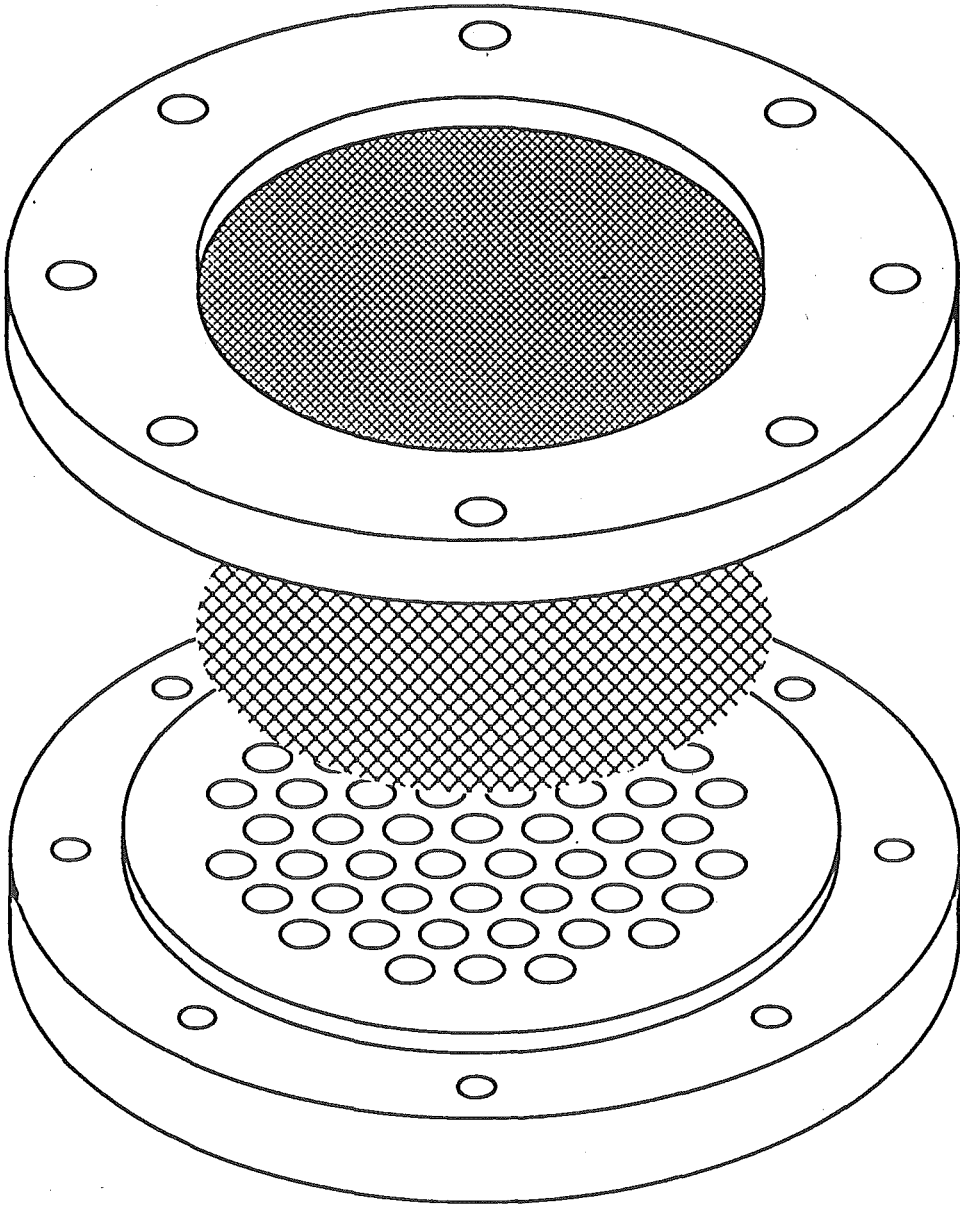
      TEMP=OCL(1)+k(2)*ALOG(Ck3/Ck(1))
ELSE
      TEMP=OCl(1)+k(2)*(Ck3**(1-n)-Ck(1)**(1-n))/(1-n)
ENDIF
IF (TEMP.LE.1E-10) THEN
      OCL3=0
      RETURN
ELSE
      OCI3=TEMP
ENDIF
IF (m.EQ.1.0) THEN
      pH3=pH(1)+k(3)*ALOG(OCI3/OCl(1))
ELSE
      pH3=pH(1)+k(3)*((OCI3**(1-m))-(OCl(1)**(1-m)))/(1-m)
ENDIF
RETURN
END

```

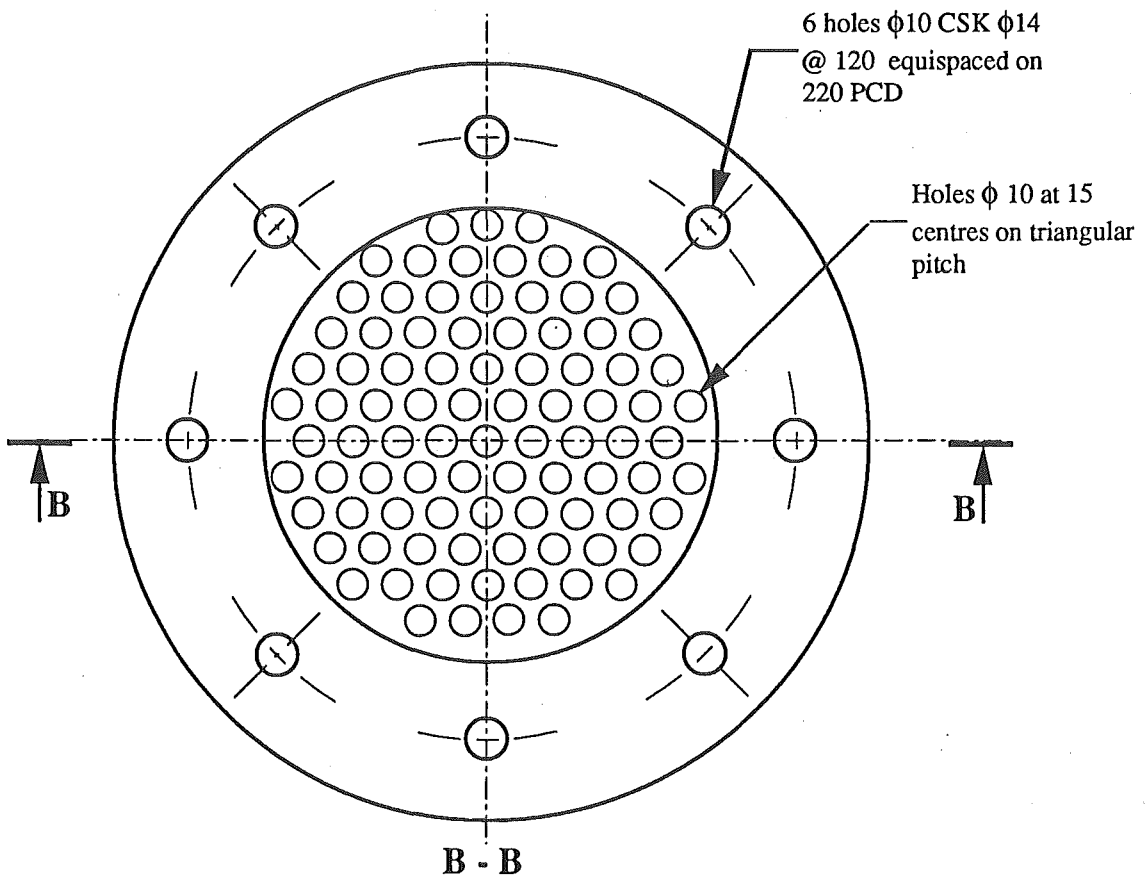
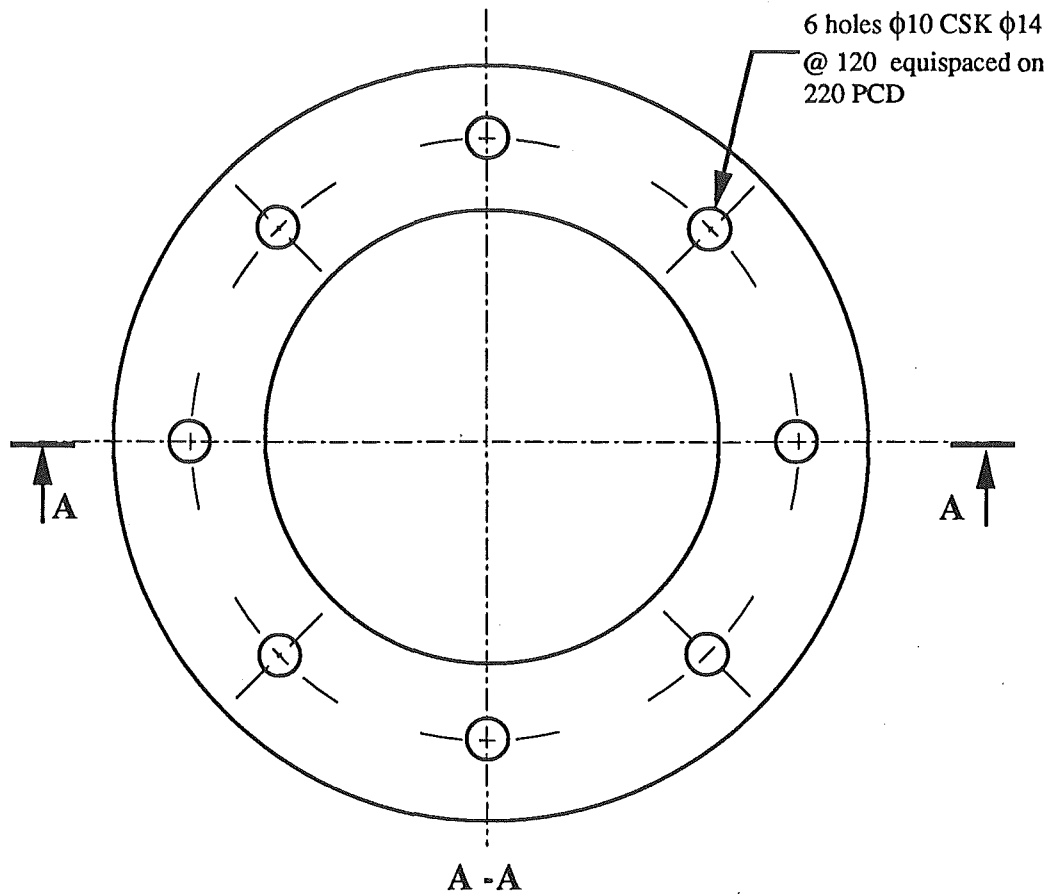
Appendix F: Paper mould design



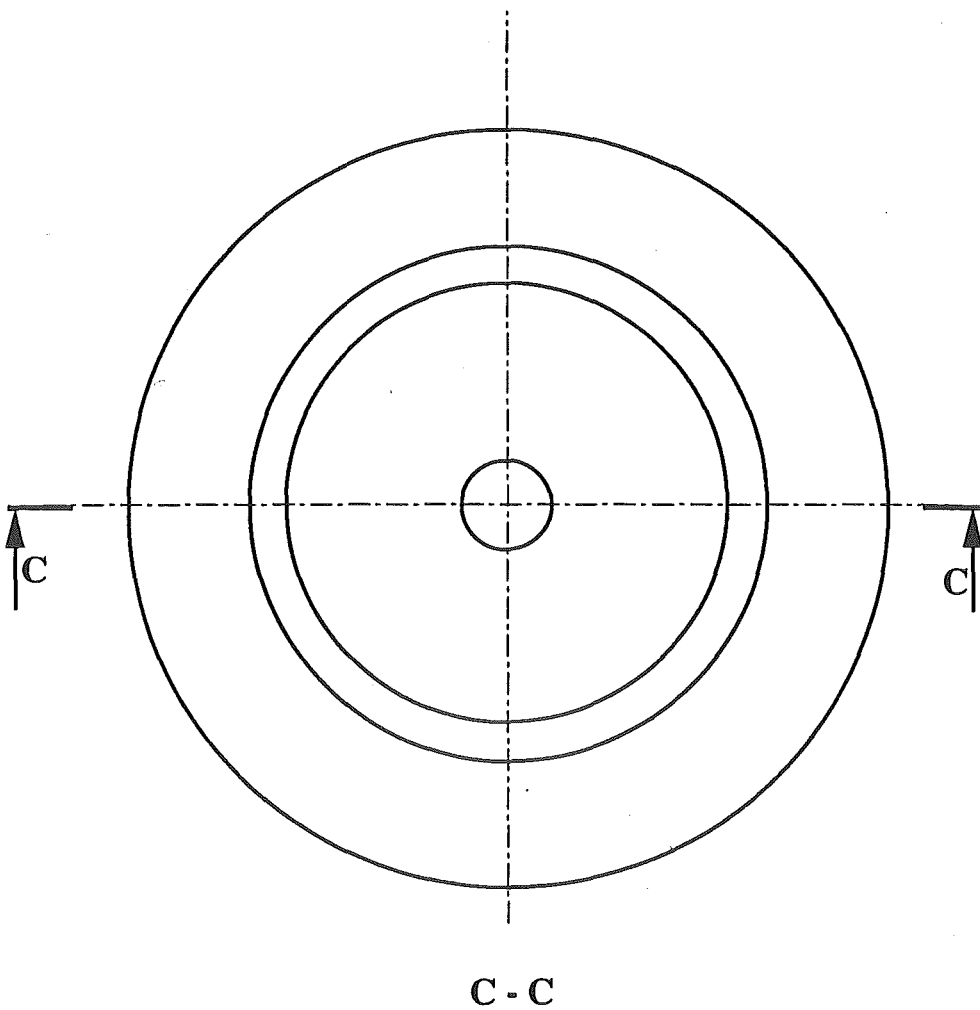
ISOMETRIC VIEW OF PAPER MOULD



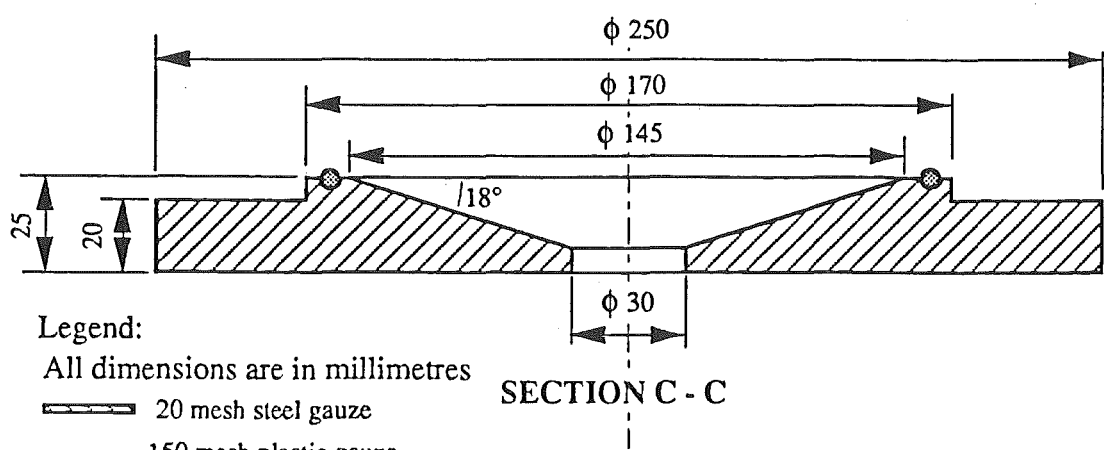
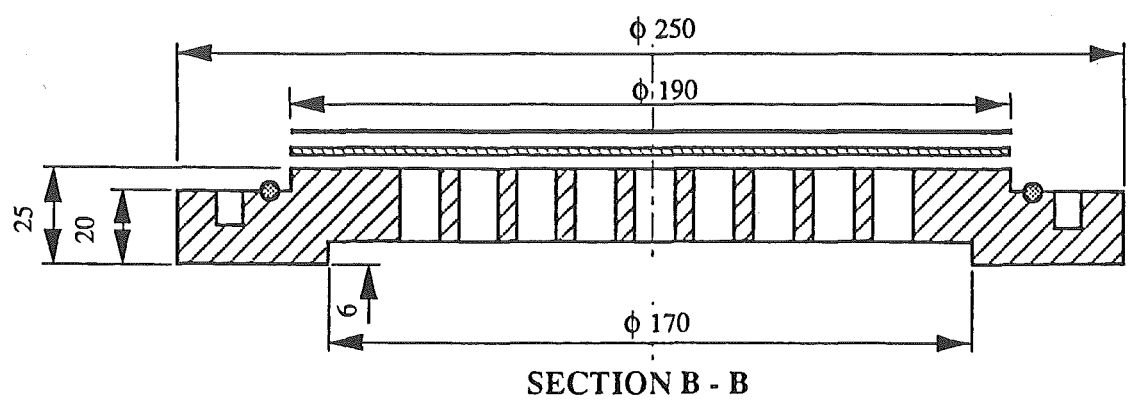
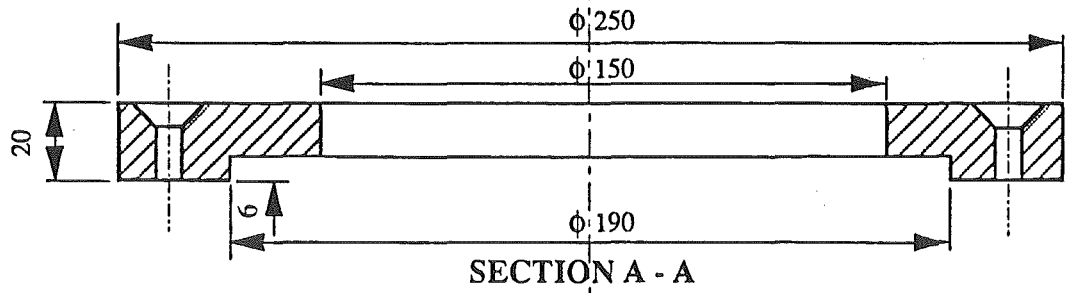
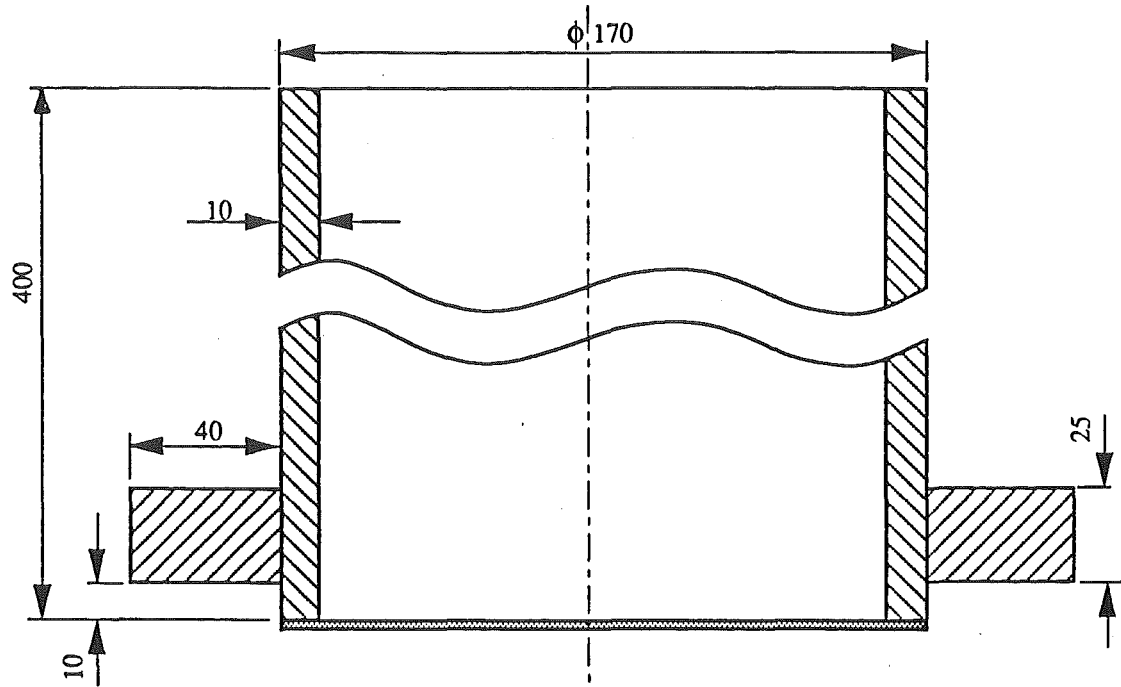
EXPLODED ISOMETRIC VIEW OF MESH UNIT






All dimensions are in millimetres
SCALE: 1: 2.5



All dimensions in millimetres
Scale 1:2.5



Legend:
 All dimensions are in millimetres
 20 mesh steel gauze
 150 mesh plastic gauze
 'O' rings
 Scale 1:2

Paper mould specifications

Time	Temp	Consis.	O.D. wt	Wet wt	Hypo. added	Hypo. strength	Water added	pH	Thio1	Thio2	Hypo1	Hypo2	Thio. Conc.	Photovolt Ro	Photovolt R ∞	Basis Wt of pads
mins	°C	%	g	g	ml	g l-1	ml		ml	ml	ml	ml	mol/l			g m-2
0								11.40						0.349	0.360	56.456
10	30	10	5.86	38.68	2.13	41.510	17.750	10.00	14.1	13.3	10	10	0.0100	0.501	0.550	50.930
30	30	10	9.27	47.65	3.38	41.165	41.650	10.00	58.6	21.6	25	10	0.0100	0.543	0.586	58.097
60	30	10	10.00	52.75	3.61	41.510	43.590	9.30	3.4	3.5	25	25	0.0992	0.557	0.598	56.966
120	30	10	10.00	56.50	3.64	41.165	39.860	8.55	11.2	11.0	25	25	0.0100	0.352	0.415	29.049
180	30	10	9.89	58.42	3.57	41.510	36.980	8.18	1.4	0.6	40	15	0.0992	0.585	0.646	55.457
0								11.18						0.349	0.360	56.456
10	40	10	10.07	60.54	3.67	41.165	36.470	9.21	32.4	30.6	25	25	0.0100	0.548	0.606	57.154
30	40	10	10.11	58.12	3.68	41.165	39.300	9.20	31.9	31.2	25	25	0.0100	0.551	0.599	63.002
60	40	10	9.99	39.82	3.64	41.165	56.390	8.43	8.6	8.4	25	25	0.0100	0.583	0.667	63.002
120	40	10	10.10	70.77	3.68	41.165	26.560	7.88	1.2	1.8	25	50	0.0100	0.562	0.665	51.307
180	40	10	10.00	64.14	3.64	41.165	32.260	8.10	1.0		25		0.0100	0.567	0.653	53.570
0								11.64						0.349	0.360	56.456
10	40	10	10.10	53.77	6.12	41.165	40.900	9.85	100.4	99.6	25	25	0.0100	0.546	0.611	54.514
30	40	10	9.54	55.79	5.79	41.165	33.790	9.30	67.4	66.4	25	25	0.0100	0.593	0.671	63.945
60	40	10	10.10	56.82	6.14	41.165	38.070	8.60	46.8	46.6	25	25	0.0100	0.596	0.713	57.343
120	40	10	10.04	64.58	6.10	41.165	29.700	8.05	26.0	25.4	25	25	0.0100	0.610	0.746	57.909
180	40	10	9.99	66.68	6.07	41.165	27.180	7.75	13.2	13.0	25	25	0.0100	0.617	0.762	57.720
0								11.66						0.349	0.360	56.456
10	40	15	10.03	38.94	7.63	32.880	20.300	10.25	34.0	33.3	5	5	0.0100	0.543	0.600	56.400
30	40	15	9.93	45.19	7.49	33.120	13.500	9.28	58.6	57.7	15	15	0.0100	0.553	0.658	49.609
60	40	15	9.93	52.17	7.55	32.880	6.460	9.10	61.8	61.6	15	15	0.0100	0.578	0.676	56.568
120	40	15	10.05	39.96	7.64	32.880	19.400	8.03	20.4	20.2	25	25	0.0100	0.587	0.729	54.891
180	40	15	9.94	58.21	7.56	32.880	0.530	7.98	7.8	4.7	25	15	0.0100	0.596	0.732	56.570
0								11.50						0.349	0.360	56.456
10	40	15	9.75	36.07	4.41	33.120	24.510	9.45	24.4	23.8	10	10	0.0100	0.535	0.580	59.229
30	40	15	9.98	40.99	4.52	33.120	21.010	8.63	13.1	21.2	15	25	0.0100	0.551	0.633	52.816
60	40	15	10.32	42.31	4.67	33.120	21.790	8.18	6.5	8.3	10	10	0.0100	0.579	0.670	60.738
120	40	15	9.78	30.65	4.43	33.120	30.090	8.10	2.8	0.9	15	10	0.0100	0.571	0.669	55.834
180	40	15	9.95	44.52	4.65	33.120	17.170	8.15	0.6	0.6	25	25	0.0100	0.561	0.637	55.834

Time	Temp	Consis.	O.D. wt	Wet wt	Hypo. added	Hypo. strength	Water added	pH	Thio1	Thio2	Hypo1	Hypo2	Thio. Conc.	Photovolt Ro	Photovolt R ∞	Basis Wt of pads
mins	°C	%	g	g	ml	g l-1	ml		ml	ml	ml	ml	mol/l			g m-2
0								11.31						0.349	0.360	56.456
10	40	5	10.11	37.07	4.65	32.627	160.495	10.38	27.2	27.1	25	25	0.0098	0.506	0.544	59.229
35	40	5	9.91	42.08	4.56	32.627	151.600	9.85	18.2	16.8	25	25	0.0098	0.537	0.591	56.023
60	40	5	10.26	35.77	4.72	32.627	164.800	9.50	17.6	15.9	25	25	0.0098	0.558	0.605	63.756
120	40	5	10.25	58.67	4.64	33.120	141.690	9.08	28.9	13.7	100	50	0.0100	0.566	0.664	55.834
180	40	5	9.69	38.00	4.45	32.627	151.310	8.50	15.6	7.2	100	50	0.0098	0.574	0.671	56.211
0								11.39						0.349	0.360	56.456
10	40	5	10.05	57.98	7.70	32.627	135.350	10.50	41.9	41.7	15	15	0.0098	0.518	0.561	58.663
30	40	5	10.10	69.75	7.74	32.627	124.620	9.80	48.0	51.0	25	25	0.0098	0.557	0.610	60.550
60	40	5	8.35	40.65	6.52	31.995	119.770	9.65	42.8	41.4	25	25	0.0099	0.574	0.664	59.418
120	40	5	9.93	42.63	7.61	32.627	148.350	9.25	34.3	37.6	25	25	0.0098	0.591	0.706	57.532
180	40	5	9.96	43.75	7.63	32.627	147.800	9.15	28.6	27.9	25	25	0.0098	0.542	0.715	41.875
0								11.80						0.349	0.360	56.456
10	50	10	10.32	47.52	8.39	30.734	47.280	10.20	45.2	47.0	10	10	0.0098	0.546	0.609	56.777
30	50	10	10.10	71.44	8.20	30.734	21.350	8.58	16.1	39.2	10	25	0.0098	0.581	0.686	60.172
60	50	10	9.76	32.17	7.94	30.734	57.450	8.08	13.4	13.3	15	15	0.0098	0.591	0.730	58.663
120	50	10	9.23	41.06	7.51	30.734	43.760	7.75	0.7	0.8	25	25	0.0098	0.616	0.755	63.379
180	50	10	9.88	44.23	8.03	30.734	46.490	7.65	0.8	1.6	25	50	0.0098	0.614	0.758	62.813
0								11.51						0.349	0.360	56.456
10	50	10	10.06	51.11	3.57	42.312	45.940	9.80	44.8	43.3	25	25	0.0099	0.546	0.596	59.229
30	50	10	9.99	44.86	4.87	30.734	50.137	8.73	21.8	21.5	25	25	0.0098	0.576	0.677	57.154
60	50	10	9.90	53.58	4.83	30.734	40.580	7.85	3.3	3.0	25	25	0.0098	0.588	0.680	63.945
120	50	10	10.05	44.58	4.90	30.734	50.980	7.95	0.4	1.0	25	50	0.0098	0.556	0.697	48.855
180	50	10	10.03	61.74	4.89	30.734	33.620	8.23	1.6	0.8	25	15	0.0098	0.564	0.665	54.514
0								11.17						0.350	0.368	55.457
10	50	10	10.02	54.74	4.74	42.312	40.730	10.28	91.0	90.9	25	25	0.0094	0.545	0.606	59.229
30	50	10	10.01	54.68	4.73	42.312	40.687	9.60	59.8	59.5	25	25	0.0094	0.574	0.680	60.927
60	50	10	9.84	55.02	4.65	42.312	38.736	8.90	44.6	44.1	25	25	0.0094	0.589	0.723	59.041
120	50	10	8.86	57.94	4.19	42.312	26.430	7.85	10.8	10.7	25	25	0.0094	0.604	0.751	60.738
180	50	10	10.00	59.84	4.72	42.312	35.360	7.73	0.8	0.8	25	25	0.0094	0.560	0.742	49.798

Time	Temp	Consis.	O.D. wt	Wet wt	Hypo. added	Hypo. strength	Water added	pH	Thio1	Thio2	Hypo1	Hypo2	Thio. Conc.	Photovolt Ro	Photovolt R ∞	Basis Wt of pads
mins	°C	%	g	g	ml	g l-1	ml		ml	ml	ml	ml	mol/l			g m-2
0								11.58						0.350	0.368	55.457
10	40	10	9.98	37.83	4.72	42.312	57.248	11.10	10.2	9.9	25	25	0.0995	0.516	0.565	62.770
30	40	10	9.99	62.20	4.72	42.312	32.594	10.25	88.4	87.8	25	25	0.0099	0.544	0.613	57.343
60	40	10	10.09	47.22	4.54	43.698	47.365	10.20	79.7	79.8	25	25	0.0099	0.544	0.609	60.927
120	40	10	10.00	62.25	4.73	42.312	32.984	9.50	57.0	56.8	25	25	0.0099	0.564	0.705	55.630
180	40	10	10.01	62.35	4.73	42.312	33.033	8.90	34.3	34.4	25	25	0.0099	0.580	0.731	58.286
0								11.75						0.350	0.368	55.457
10	30	10	9.92	47.26	4.54	43.698	47.400	11.25	54.0	53.6	25	25	0.0199	0.508	0.565	55.513
30	30	10	9.91	47.22	4.54	43.698	47.365	10.75	45.0	44.8	25	25	0.0199	0.544	0.609	60.927
60	30	10	9.99	52.68	4.57	43.698	42.678	10.35	40.4	40.4	25	25	0.0199	0.554	0.641	57.105
120	30	10	10.01	47.69	4.58	43.698	47.838	9.95	33.4	33.5	25	25	0.0199	0.568	0.691	59.418
180	30	10	10.75	56.68	4.92	43.698	45.912	9.75	27.0	27.0	25	25	0.0199	0.581	0.695	62.279
0								11.74						0.350	0.368	55.457
10	30	10	10.00	52.70	5.72	43.698	41.547	11.35	72.8	72.7	25	25	0.0199	0.503	0.558	55.574
30	30	10	9.92	44.29	5.68	43.698	49.224	10.95	62.0	62.0	25	25	0.0199	0.537	0.599	60.504
60	30	10	9.86	49.02	5.64	43.698	43.969	10.70	57.4	57.3	25	25	0.0199	0.562	0.646	64.215
120	30	10	10.06	49.97	5.75	43.698	44.527	10.15	49.7	49.6	25	25	0.0199	0.567	0.682	58.471
180	30	10	10.01	49.72	5.72	43.698	44.601	9.80	43.8	43.9	25	25	0.0199	0.580	0.719	61.530
0								11.59						0.350	0.368	55.457
16	30	10	10.09	51.86	4.62	43.698	44.377	11.05	49.8	49.7	25	25	0.0199	0.510	0.567	58.841
30	30	10	10.11	52.00	4.63	43.698	44.492	10.75	47.1	47.0	25	25	0.0199	0.534	0.594	61.295
60	30	10	9.82	45.07	4.49	43.698	48.588	10.30	38.7	38.8	25	25	0.0199	0.557	0.655	58.741
120	30	10	9.65	44.29	4.41	43.698	47.750	9.85	28.5	29.0	25	25	0.0199	0.562	0.681	58.169
180	30	10	9.73	44.68	4.45	43.698	48.167	9.50	26.9	26.8	25	25	0.0199	0.573	0.710	58.030
0								11.72						0.350	0.368	55.457
10	30	10	10.05	44.84	5.87	42.787	49.817	11.50	72.6	72.7	25	25	0.0219	0.515	0.570	54.891
30	30	10	9.91	55.46	5.67	43.698	38.011	10.95	66.7	66.8	25	25	0.0219	0.548	0.586	65.186
60	30	10	9.89	55.33	5.66	43.698	37.918	10.65	59.5	59.2	25	25	0.0199	0.559	0.693	56.375
120	30	10	9.50	53.12	5.43	43.698	36.409	10.20	50.8	50.7	25	25	0.0219	0.547	0.643	59.612
180	30	10	10.01	55.24	5.73	43.698	39.107	9.85	39.6	39.6	25	25	0.0199	0.581	0.717	60.800

Time	Temp	Consis.	O.D. wt	Wet wt	Hypo. added	Hypo. strength	Water added	pH	Thio1	Thio2	Hypo1	Hypo2	Thio. Conc.	Photovolt Ro	Photovolt R ∞	Basis Wt of pads
mins	°C	%	g	g	ml	g l-1	ml		ml	ml	ml	ml	mol/l			g m-2
0								11.46						0.350	0.368	55.457
10	30	10	9.94	49.09	3.48	42.787	43.804	11.05	37.8	37.8	25	25	0.0219	0.499	0.554	57.532
30	30	10	10.07	49.76	3.53	42.787	47.443	10.50	32.0	32.0	25	25	0.0219	0.524	0.587	56.211
60	30	10	9.93	49.07	3.48	42.787	46.788	10.15	25.4	25.4	25	25	0.0219	0.541	0.623	59.418
120	30	10	10.16	50.19	3.56	42.787	47.851	9.70	20.4	20.4	25	25	0.0219	0.550	0.668	56.588
180	30	10	9.98	44.52	3.50	42.787	51.798	9.55	15.7	15.6	25	25	0.0219	0.581	0.698	61.870
0								11.46						0.350	0.368	55.457
10	40	10	9.95	41.87	4.65	42.787	52.944	10.75	48.1	48.1	25	25	0.0199	0.530	0.596	60.137
30	40	10	10.02	42.20	4.69	42.787	53.350	10.15	38.8	38.7	25	25	0.0199	0.558	0.652	62.059
60	40	10	10.08	48.42	4.71	42.787	47.689	9.80	36.0	36.2	25	25	0.0219	0.554	0.642	61.893
120	40	10	10.09	48.43	4.71	42.787	47.706	9.30	21.0	21.0	25	25	0.0219	0.579	0.720	62.323
180	40	10	10.03	48.14	4.69	42.787	47.420							0.585	0.741	60.842
0								11.38						0.350	0.368	55.457
10	40	10	10.01	44.14	5.85	42.787	50.140	10.90	66.8	66.5	25	25	0.0199	0.536	0.594	63.502
30	40	10	9.92	52.68	5.76	42.787	40.675	9.50	53.4	53.3	25	25	0.0199	0.548	0.646	57.779
60	40	10	9.85	43.43	5.76	42.787	49.329	9.80	47.0	47.0	25	25	0.0199	0.555	0.710	51.418
120	40	10	10.01	44.13	5.85	42.787	50.128	9.10	35.0	35.2	25	25	0.0199	0.594	0.753	64.747
180	40	10	10.03	42.22	5.86	42.787	52.216	8.45	19.1	18.9	25	25	0.0199	0.594	0.769	64.715
0								10.89						0.350	0.368	55.457
10	40	10	9.88	40.90	3.64	42.787	54.397	10.25	31.6	31.9	25	25	0.0199	0.515	0.575	59.923
30	40	10	10.11	41.87	3.55	42.787	55.694	9.75	24.4	24.5	25	25	0.0199	0.553	0.640	60.791
60	40	10	10.01	41.47	3.51	42.787	55.156	9.30	17.9	17.7	25	25	0.0199	0.568	0.686	61.108
120	40	10	10.24	54.39	3.59	42.787	44.383	8.22	7.4	7.3	25	25	0.0199	0.574	0.715	59.772
180	40	10	10.03	51.55	3.51	42.787	45.182	7.80	3.8	3.6	25	25	0.0199	0.590	0.752	63.117
0								11.20						0.350	0.368	55.457
10	50	10	9.79	45.82	4.84	40.440	47.213	10.45	43.7	26.2	25	15	0.0204	0.558	0.641	62.059
30	50	10	9.86	46.16	4.88	40.440	47.558	9.65	33.1	33.1	25	25	0.0204	0.572	0.689	60.380
60	50	10	9.80	39.25	4.85	40.440	53.939	8.70	17.2	17.0	25	25	0.0204	0.578	0.753	55.664
120	50	10	9.98	39.95	4.93	40.440	54.889	7.90	4.1	4.0	25	25	0.0204	0.598	0.796	59.852
180	50	10	10.00	40.05	4.95	40.440	55.040	7.65	0.4	0.3	25	25	0.0204	0.587	0.804	54.891

Time	Temp	Consis.	O.D. wt	Wet wt	Hypo. added	Hypo. strength	Water added	pH	Thio1	Thio2	Hypo1	Hypo2	Thio. Conc.	Photovolt Ro	Photovolt R ∞	Basis Wt of pads
mins	°C	%	g	g	ml	g l-1	ml		ml	ml	ml	ml	mol/l			g m-2
0								11.24						0.350	0.368	55.457
10	50	10	9.99	48.78	6.17	40.440	44.918	10.65	59.0	58.6	25	25	0.0204	0.544	0.628	60.167
30	50	10	9.98	51.26	6.17	40.440	42.358	10.25	48.8		25		0.0204	0.581	0.707	61.927
60	50	10	9.99	46.75	6.17	40.440	46.935	8.85	29.4	29.3	25	25	0.0204	0.597	0.762	61.832
120	50	10	10.05	51.60	6.21	40.440	42.639	8.10	14.3	14.0	25	25	0.0204	0.600	0.804	60.568
180	50	10	10.09	51.81	6.24	40.440	42.814	7.65	2.3	2.3	25	25	0.0204	0.615	0.827	61.002
0								10.93						0.350	0.368	55.457
10	50	10	10.21	50.88	3.79	40.440	47.450	10.25	28.1	27.8	25	25	0.0204	0.533	0.597	61.266
30	50	10	10.09	50.26	3.74	40.440	46.871	9.25	14.7	14.4	25	25	0.0204	0.563	0.686	59.342
60	50	10	10.00	48.86	3.71	40.440	47.467	8.35	5.8	5.7	25	25	0.0204	0.575	0.723	60.469
120	50	10	10.01	48.88	3.71	40.440	47.482	8.00	0.4	0.4	25	25	0.0204	0.573	0.743	56.413
180	50	10	10.05	50.09	3.73	40.440	46.709	8.00	0.3	0.4	25	25	0.0204	0.573	0.749	56.387