

**The Computer Simulation of  
NZFP No. 2 Bleach Plant**

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*Dedicated to my friends, my sisters, my brothers.....*

*but most of all to*

*my parents*

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## Abstract

A steady state descriptive GEMS computer model, established by Edwards et al, 1988, for the simulation of NZFP No.2 bleach plant was further tuned to match the existing plant conditions. The initial GEMS model incorporated assumptions estimated by Edwards, for chlorine chemical adjustment which resulted from the accumulation of recycled organics.

Laboratory studies, applied to organics generated from bleaching of Pinus Radiata pulp were carried out to verify these assumptions. Bench scale experiments were conducted in D/C-stage and E1-stage filtrates for both laboratory generated filtrates and mill samples, whereas for the D1-stage filtrate, only the generated filtrate was investigated.

Chlorine consumption of the generated D/C-stage and E1-stage filtrates was measured as 0.33kg and 0.20kg active chlorine per kg of organics, at the temperatures of 50°C and 70°C, respectively. The quantity of organics in each filtrate was determined as Total Volatile Solids. For the D/C-stage filtrate, the organics-chlorine reaction was shown to be temperature dependent with a maximum consumption occurring at approximately 50°C, whereas for the E1-stage filtrate, the organics-chlorine reaction as a function of temperature was not investigated.

For the mill filtrate samples, chlorine consumption measured as kg active chlorine per kg of organics was 0.38 and 0.14 for D/C-stage and E1-stage organics, respectively.

The chlorine consumption of D1-stage organics was negligible compared to the D/C-stage and the E1-stage organics, due to only a minor concentration of volatile solids present in the effluent, i.e., approximately 20-30mg per litre of effluent.

The generated D/C-stage and E1-stage filtrates were also found to consist of 17.8kg and 17.0kg of organics per tonne of O.D. pulp, respectively.

The measured chlorine consumption values were incorporated into the fine tuned GEMS model (total closure case) to assess the effect of various amounts of fresh water substitution, by recycling D/C-stage and E1-stage effluents, on the economics of

bleach plant operation with respect to chemical, water, and steam usage. The studies indicated a lowering of the total cost of these utilities, with increasing amounts of recycled effluent. Using the existing bleach plant model (open case) as a base case, the annual savings in cost of utilities for total mill closure was estimated to be NZ\$0.2 million.

Experience gained from this study has been applied to the formation of a GEMS model for a proposed bleach plant expansion with double capacity, using two three stage short sequences in parallel, and using recycled effluent. Initial runs with this model predict potential savings of utilities of approximately NZ\$1.04 million p.a. compared to the existing open case configuration.

# 1 - Introduction

## 1.1 - General

Wood is by far the most important raw material for the production of pulp. Its main component groups are cellulose, hemicellulose, lignin and extractives. Cellulose is a carbohydrate which comprises the major portion of the wall tissue of most plant cells. It is a linear polysaccharide consisting of  $\beta$ -D-glucopyranose units, which are linked by (1-4)-glucosidic bonds, Figure 1.1. The cellulose molecules are bundled together in wood to form microfibrils. These in turn build up fibrils and finally, cellulose fibres. About 40% of most wood is cellulose that has a molecular weight in excess of 10,000.

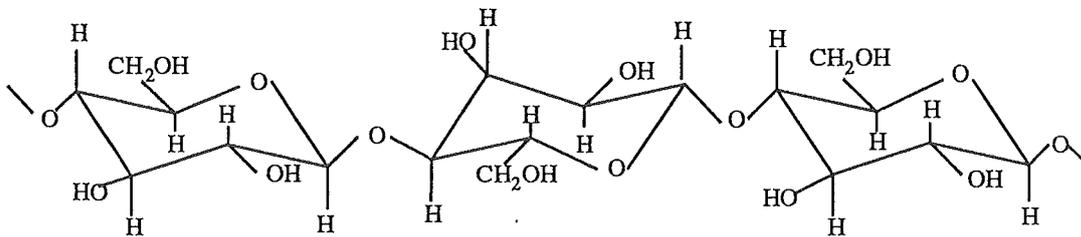


Fig. 1.1 - The linear structure of cellulose

The wood hemicelluloses are the principal noncellulosic polysaccharides present in wood. It consists of different carbohydrate units, and are branched to various extents. Their relative molecular masses are much lower. The most common content and types of hemicellulose in softwood are galacto-glucomannans (15-20%), arabino-glucuronoxylan (5-10%) and arabinogalactan (2-3%), Kringstad et al, 1984.

Lignin is one of the major substances present in wood, ranging from about 17-32% of the weight of moisture-free wood. Unfortunately, the highly complex chemical nature of lignin which, so far, still remains a mystery seems to vary in wood of different species and also varies according to the age of the wood in the same species. All the physical properties reported in the literature have been determined on

isolated lignin or lignin derivatives, whose structure may be different from the native or natural lignin in the original wood.

Lignin is essentially believed to be an aromatic polymer. It is formed in wood by an enzyme-initiated dehydrogenative polymerization of a mixture of three different 4-hydroxyarylpropenyl alcohols as illustrated in Figure 1.2. The proportions of these alcohols vary with different wood species.

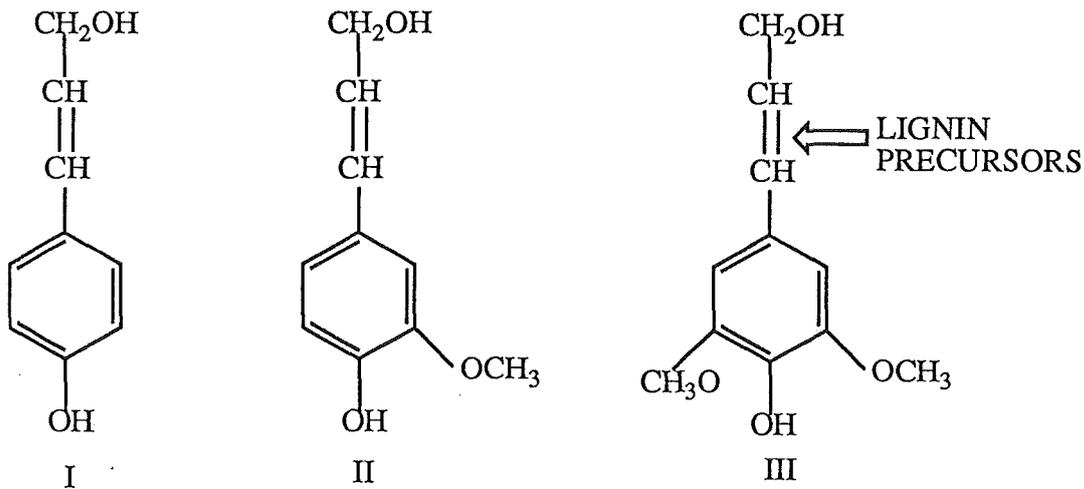


Fig. 1.2

Softwood lignin is largely a polymerization product of coniferyl alcohol (Figure 1.2, II). It is a branched molecule in which the phenylpropane-based units are linked by different types of bonds. These include ether bonds of alkyl-aryl, alkyl-alkyl, and aryl-aryl configurations. Lignin performs such functions as imparting rigidity to the fibre walls, and acting as a bonding agent between fibres.

Extractives include aliphatic extractives, which consist mainly of fats and waxes; terpenoid compounds which are present only in softwood and phenolic extractives which include hydrolyzable tannins, flavonoids, lignans, stilbenes and tropolines. Total content of extractives in wood varies greatly from 1.5-5.0% depending on the species, place of growth, and the age of the tree.

## 1.2.- Principle of Pulping

One of the major objectives of all pulping processes is to liberate the fibers of the wood. This involves the cooking of raw material i.e., wood chips in suitable

chemicals in a digester under controlled conditions of temperature, pressure, time, and liquor composition, or reducing the raw material to the fibrous state by mechanical or semimechanical means. The pulping process is then followed by pulp purification, whereby the pulp is subjected to bleaching and purifying agents to render the pulp more suitable for its intended use.

Pulping processes are of three principal types: mechanical, chemical and semichemical. The mechanical process involves the reduction of wood to the fibrous state by mechanical means, generally by grinding wood to a pulp against a large grindstone. Chemical processes involve cooking of the wood with chemicals which selectively remove lignin and other impurities, thereby isolating and partially purifying the individual fibers; whereas the semichemical pulping consists of an initial chemical treatment for softening the wood, followed by mechanical reduction to the fibrous state.

There are three major chemical processes of commercial importance, namely, the sulfite, soda and kraft. The sulfite process is one of the oldest pulping processes. It involves the cooking of wood in cooking liquor, called acid which, contains bisulfite, sulfurous acid and sulfur dioxide. The rate of delignification in the sulfite process is proportional to the concentration of sulfurous acid in the cooking liquor.

The soda and kraft processes are two principal alkaline processes. Sodium hydroxide is the major cooking chemical for the soda process, whereas the kraft process entails treating wood chips with a liquor that contains both the sodium hydroxide and sodium sulfide, which promotes cleavage of the various ether bonds in the lignin. The lignin degradation products so formed dissolve in the alkaline pulping liquor. Depending on pulping conditions, as much as 90-95% of the lignin is removed from wood at this stage.

During the pulping operation, portions of the wood polysaccharides, especially those of the hemicelluloses, are dissolved. This is because cellulose and hemicelluloses are sensitive to alkali through their aldehydic end groups, and will thus degrade by a mechanism known as the peeling reaction. As a result, isosaccharinic acid and a number of other organic acids are formed and dissolved in the pulping liquor. The peeling reaction is ended by the so-called stopping reaction, in which the end group rearranges to an alkali-stable m-saccharinic end group.

Wood extractives are also dissolved or dispersed in the kraft pulping liquor. For softwood pulping, the extractives are to a large degree recovered as important by-products such as sulfate, turpentine and tall oil.

### 1.3 - Principle of Bleaching

The main objective of bleaching is to increase the pulp brightness, cleanliness, brightness stability and chemical purity by removal or modification of some of the constituents of the unbleached pulp, mainly the lignin and its degradation products, resins, metal ions, non-cellulosic carbohydrate components, pitch content and bark fragments of various kinds. These characteristics are important in maintaining the marketing value of pulp. For most purposes it is desired not only to make the pulp whiter and brighter, but also to make it stable so that it will not lose its brightness in ageing.

There has been some debate over the boundary between delignification and bleaching or brightening, and there are a number of options now available for extending delignification below normal Kappa number 32. This enhances the reduction in chemical costs and also makes short-sequence bleaching possible, which in turn lowers the bleach plant capital cost. However, there are some common problems among extended delignification options. As lignin removal is extended, carbohydrate degradation can increase, leading to lower strength and lower yield. In addition, lignin can condense, making it much more difficult to remove in subsequent bleaching stages and increasing the burden on the recovery system.

To obtain a pulp of very high brightness and brightness stability, the final lignin delignification is, therefore, performed in the bleaching process with certain oxidizing agents, and the conditions of the reactions are adjusted so as to prevent the carbohydrate degradation and protect the pulp strength properties. The delignification in the pulping processes used today leaves some 5-10% of the original lignin in the pulp. The residual can be removed by multistage bleaching.

Bleaching of chemical pulp differs fundamentally from of bleaching mechanical pulps. In the case of chemical pulps, e.g., sulfite or kraft, very little of the lignin component remains in the pulp as a result of the corresponding pulping process, whereas for mechanical pulp bleaching, the lignin fraction, which in softwood species comprises 25-30% of the wood, is retained and constitutes an important part of the total yield. Therefore, the bleaching of mechanical pulp must not involve delignification, since this would result in a serious loss in yield and excessive consumption of bleaching chemicals. For this reason, the bleaching agents are limited to those which extract the groundwood component to only a minor extent such as hydrosulfites and peroxides.

On the other hand, chemical pulp bleaching can be accomplished by a series of treatments involving chlorine, caustic, and oxidizing agents, such as hypochlorites, chlorine dioxide and sometimes peroxides. Yield loss due to bleaching may be as high as 10% for high brightness kraft pulp. The bleaching of pulp is done through chemical reactions of bleaching agents with the lignin and coloring matter of the pulp. In this study, only the bleaching of chemical pine kraft pulp will be investigated.

The bleaching of chemical pulps is usually performed in a series of different bleaching stages, known as bleaching sequences. The exact choice of the bleaching sequence depends upon the type of pulp to be bleached and the level of brightness to be achieved. In modern pulp bleaching technology, kraft pulp bleaching is normally carried out in five or six stages, employing either CEDED, CEHDED or OCEDED sequence for the production of high quality pulp at low cost. Other sequences commonly practiced primarily in older mills in North America, such as CEHD, CEHDE and CEHED, are not especially economical in either capital or chemical use and do not yield pulps of high quality.

The sequence CEHDED offers the benefit of being an efficient chemical user although it is more expensive in terms of capital investment. It has a great flexibility in simultaneously offering a spectrum of pulp brightness compared to the CEDED bleaching sequence. However, the CEDED bleaching sequence adapts better to countercurrent washing with less corrosion problems than CEHDED. In addition lower bleaching cost can be achieved by the introduction of small amounts of chlorine in the second alkaline extraction stage.

In recent years, the pulp and paper industry has been spending large sums of money on research and development in the area of pulping and bleaching. More and better approaches are being tried out to meet rapidly changing demands of the industry, particularly with respect to the following:

- a) Increasingly stringent requirements for pollution control.
- b) Increasing restrictions on water usage.
- c) Demands to recycle the down stream effluent for replacing upstream water usage.
- d) Greater concern of safety.
- e) Rapidly mounting costs of new plants.

Bleaching effluents are known to be the main contributors of toxicity, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Chlorine (TOCl), Dioxins and colour. Typically, about 90% of the colour in combined

mill effluent originates in the bleach plant; most of the organic material is dissolved from the pulp during the first chlorination and extraction stages.

There has been growing interest in the identification and analysis of specific chlorinated organic compounds in bleach plant effluents since the early 1970s. Research in this area has been particularly concerned with acute toxicity and mutagenicity. The dissolved organic material includes various non-chlorinated and chlorinated aliphatic and aromatic acids, chlorinated phenolic compounds and various chlorinated neutral compounds such as alkanes, alkenes, thiophenes, acetones, aldehydes and furans (Kringstad et al, 1984). According to Lindstrom et al, 1981, 70% of the total organically bound chlorine (TOCl) in the chlorination stage and 95% in the extraction stage consist of components of high relative molecular mass ( $M_r > 1000$ ), which are not easily identified or even characterized. This material provides much of the colour associated with the bleach plant effluents, but is thought to be biologically inactive because of the size of the molecules. However, it is possible that these high molecular weight compounds might be broken down in recipient waters or in sediments, and converted into smaller, more biologically-active compounds (Annergren et al. 1986).

From an environmental point of view there is an increasing interest in compounds with relative molecular masses lower than 1000. These compounds are suspected as being the main sources of problems since they are relatively lipophilic and can penetrate the cell membranes, causing bioaccumulation in the fat of aquatic organisms and possibly resulting in toxic and mutagenic effects. As the organic matter dissolved in the bleaching treatment is partly coloured, the bleach plant effluent therefore decreases the light penetration in the receiving stream, thereby disturbing the photosynthetic processes which are essential for some aquatic life and, which to a great extent contribute to the oxygenation of the water. Moreover, the colour of the effluent is not reduced completely in the biodegradation process.

As there has been increasing concern within the pulp and paper industry about the environmental impact of chemical compounds created in the pulping and bleaching process, many advances have been made in pulping and bleaching technology through work designed to minimize the formation of toxic chemical compounds believed to be deleterious to the environment.

One commonly used approach to eliminate pollution from kraft mill bleacheries is the reuse of derived effluents. This involves washing the pulp countercurrently through the various bleaching stages and brown stock washers. This measure is believed to be economical as it enables savings to be effected in the

bleaching process itself, by the reuse of heat and the lowered cost of effluent treatment due to the reduction in effluent volume. However, a higher degree of effluent reuse introduces unfavourable side effects, such as increases in chlorination temperature, which promotes radical formation with subsequent loss of pulp viscosity, and the risk of corrosion (Reeve et al, 1980) due to the accumulation of recycled inorganics, such as chloride ion ( $\text{Cl}^-$ ). The bleaching chemical consumption will also increase due to the presence of organic matter in the recycled effluent.

#### 1.4 - (D/CE<sub>0</sub>DED) Multi-stage Bleaching

The bleach plant of New Zealand Forest Products Ltd.(NZFP), is a five stage plant employing a D/CE<sub>0</sub>DED sequence. A general flowsheet of the bleach plant at Kinleith pulp and paper mill is given in Figure 1.3. Approximately 320 air dry tonnes per day (ADTPD) of kraft pulp produced from *Pinus Radiata* soft wood enters the bleaching process after passing through a high-density storage chest at about 11% consistency. The pulp is diluted to about 3.4% consistency before entering a buffer tank. It is then pumped as a slurry with consistency and flow control devices to the chlorine dioxide ( $\text{ClO}_2$ ) and chlorine ( $\text{Cl}_2$ ) premixers, whereby the incoming pulp is pretreated with  $\text{ClO}_2$  for a short period, prior to application of  $\text{Cl}_2$ , i.e., the sequential mode (denoted D/C). The  $\text{ClO}_2$  water and  $\text{Cl}_2$  gas, usually dispersed as gas bubbles in water are injected into the premixers, which rapidly mixes the heterogeneous water-pulp-gas system. The injector water comes from fresh Waikato river water. The mixing operation is crucial to the success of the chlorination with regard to homogeneity, chlorine consumption, and carbohydrate degradation.

Chlorination is the first stage of bleaching and is preceded by pulping, washing and screening. Pulping usually dissolves more than 90% of the lignin and transfers half of the wood substance to the spent liquor. The balance between cooking and bleaching is an important consideration with regard to both minimizing cost and maintaining pulp quality. A large amount of the spent cooking liquor i.e., black liquor is separated from the pulp in the washing operation, but even a small amount of residual liquor in the pulp may influence considerably the consumption of chlorine and the characteristics of the bleach plant effluent. It also decreases the chemical reaction rate by increasing the chlorination pH.

The bleaching chemicals used in the chlorination stage are  $\text{ClO}_2$  and chlorine water for lignin degradation, and are expressed as kg of active chlorine per tonne of air dry unbleached pulp (kg/t90) or as a percentage charge. The total active chlorine charge

varies from 5.0 to 5.5% for the D/C-stage and is set as a multiple of Kappa number (i.e.,  $0.22 \times$  Kappa number), based on the properties and the amount of incoming pulp. An approximate average of 25 to 35% of  $\text{ClO}_2$  substitution is usually maintained. After the pre-mixer, the pulp passes to the chlorination tower, an upflow tower with a retention time of 45 minutes, at a consistency of around 3.0% and a temperature near  $50^\circ\text{C}$ . The net changes occurring during chlorination are assessed by measuring the lignin content and the average degree of polymerisation (e.g., Kappa number, viscosity and colour). As a general rule sufficient chlorine is applied to maintain about 0.1 to 0.2% residual chlorine, based on the pulp, at the end of the chlorination stage. After this D/C tower, the pulp is washed in a rotary drum washer using a combination of fresh Waikato river water and filtrate from the second extraction stage (E2). The pulp mat from the D/C washer is diluted to approximately 11-12% consistency, and is sprayed with sodium hydroxide (NaOH) solution before entering the  $\text{E}_0$  steam mixer, where 65-psig steam is added to raise the temperature to about  $70^\circ\text{C}$ , prior to oxygen-enriched extraction. The pulp stock is then pumped with a thick stock pump to the oxygen gas mixer, a high-shear-mixer to get the desired amount of the gas dispersed into the pulp suspension. The oxygen gas is applied at approximately 0.5% based on air dry pulp, which increases the delignification efficiency prior to entering the first extraction tower (E1), where approximately 3.0% of NaOH is added for dissolving the chlorinated, and partially oxidized products of the first stage chlorination reaction. The NaOH charge controls tower pH, and the pulp extract Kappa number is measured. This extraction stage allows the pulp to achieve 55-60% brightness (% ISO).

The subsequent process is pulp washing with warm water and filtrate from the first  $\text{ClO}_2$  tower (D1). All the effluent from the E1-stage is sewered. The washed pulp mat is then diluted to approximately 10-12% consistency before entering the D1 tower. Sufficient NaOH is added as buffer to the entering pulp mat to control tower pH. This is desirable since the pH of D1-stage has an optimum for which both the chemical consumption and the viscosity decrease are at a minimum. The tower pH and residual chlorine are measured at one third of tower height. Pulp brightness of 80+ % ISO is achieved before entering the second extraction (E2), and final  $\text{ClO}_2$  (D2) stages. The controlled parameters of both E2- and D2- stages are very similar to the previous E1- and D1- stages, except for the D2-stage, with a lower dosage of  $\text{ClO}_2$  controlled at approximately 0.4-0.5%, which brings the pulp to market brightness of 88+ % ISO.

## 1.5 - Computer Simulation of NZFP No.2 Bleach Plant

A steady state descriptive computer simulation model for the bleaching sequence of D/CE<sub>0</sub>DED, of the NZFP No.2 bleach plant at Kinleith mill, was established by Edwards et al, 1988. This model is based on the GEMS (General Energy and Material Balance System) computer software package, a data driven simulator, which was developed by the University of Idaho for pulp and paper processing application.

GEMS contains prediction models to estimate the condition of the pulp, dynamic models to track the pulp condition as it moves through the bleach plant, and stoichiastic models to adjust these estimates. It is available in microcomputer version, and it is capable of tracking up to thirty three dissolved and suspended solids subspecies; performing sodium sorption calculations around the rotary diffusion washers; calculating steam requirements for heaters and tracking stream variables such as temperature, flow rates, consistency and enthalpy. The computer simulation model is useful for predicting performance assessing mass and energy flows, optimising effluent recycled and making some quantitative judgements on the bleaching chemicals and utilities usage of the bleach plant.

## 1.6 - Aims

The major aims of this thesis are divided into the following goals:

- 1) Subsequent tuning of NZFP No.2 bleach plant computer model, which was established by Edwards et al, 1988, to match the existing plant conditions. Further enhancement of the model to simulate various degrees of mill closure, i.e.:
  - a) Closed D/C-stage, open E1-stage
  - b) Closed E1-stage, open D/C-stage
  - c) Total closure of both D/C- & E1-stages

The fine tuned computer model enables feasibility studies to be done for various degrees of mill closure for different levels of D/C filtrate reuse, i.e., 100 & 50% fresh water substitution for

upstream water replacement at the high density storage tank as illustrated in Figure 1.3.

- 2) Verification of the assumptions which were incorporated in the original GEMS model for chlorine chemical adjustment due to the accumulation of recycled organics. The assumptions were as follows:
  - a) 0.75kg extra chlorine consumed per kg D/C- stage organics
  - b) 1kg extra chlorine consumed per kg E- stage organics
- 3) To establish a computer model to simulate a proposed expansion for the existing bleach plant, Figure 1.4.
- 4) Experimental determination of the sodium sorption constants for incorporation into the GEMS package specifically for Pinus Radiata pulp. Due to the shortage of time, this work was not accomplished. The details of this proposed study are detailed in Appendix D.1.

### 1.7 - Technical Work

Bench scale bleaching tests were first required for the investigation of the effect of 100% reuse of D/C filtrate on pulp properties, while maintaining the market pulp brightness and quality. Experimental details are listed in Experiments 3.1 & 3.2. The results will help determine the feasibility of mill closure.

A laboratory study was also required on the chlorine consumption of organic matters, which build up due to the reuse of effluent from the D/C and the E1 bleaching stages, in order to verify the assumptions inherent in GEMS computer package. Total Organic Carbon (TOC), COD and Total Volatile Solids methods were used to assist the measurement of chlorine consuming potential of the organic matters.

The active chlorine consumption potential of D1-stage filtrate was also studied. For the effluents from the subsequent E2 and D2 bleaching stages, the active chlorine consumption was assumed to be insignificant due to only minor concentration of organics.

A fine tuned model of the existing No.2 bleach plant was then established, and subsequently used to generate data to assess mass and energy flows for the expansion of the bleach plant, to a maximum capacity of 660 air dry tonnes of unbleached pulp per day. This is to be achieved by doubling the D1-stage capacity at

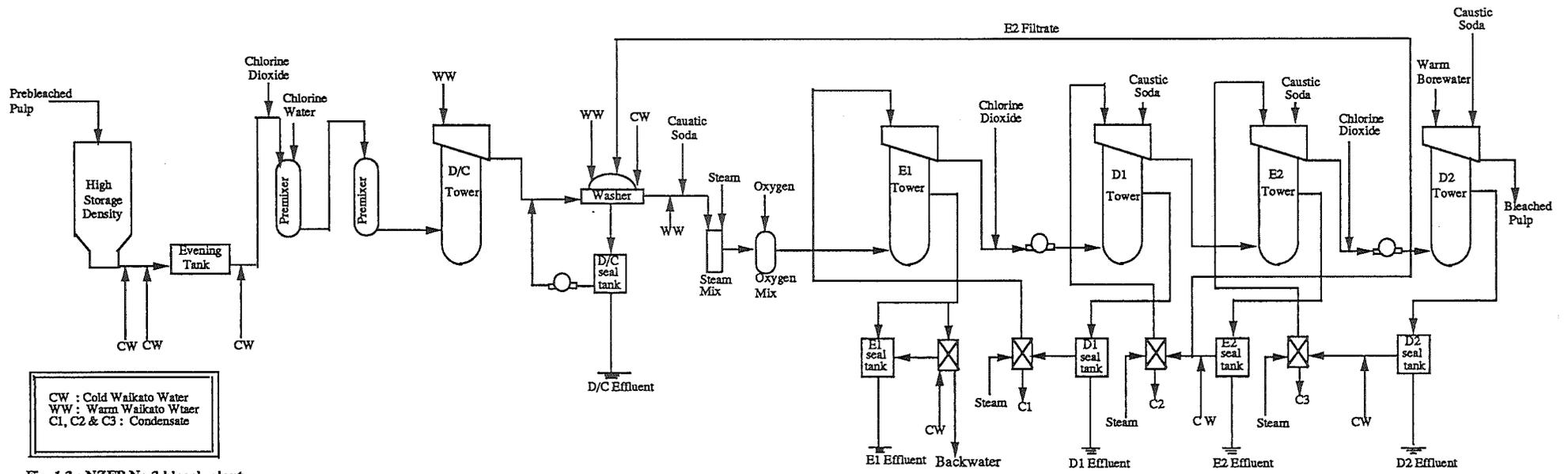


Fig. 1.3 : NZFP No.2 bleach plant

the front end, and splitting the subsequent bleaching sequence into two parallel lines, each with a stream rate of 330 ADTPD. Each line will also have E<sub>0</sub> and D<sub>2</sub> stages as detailed in Figure 1.4

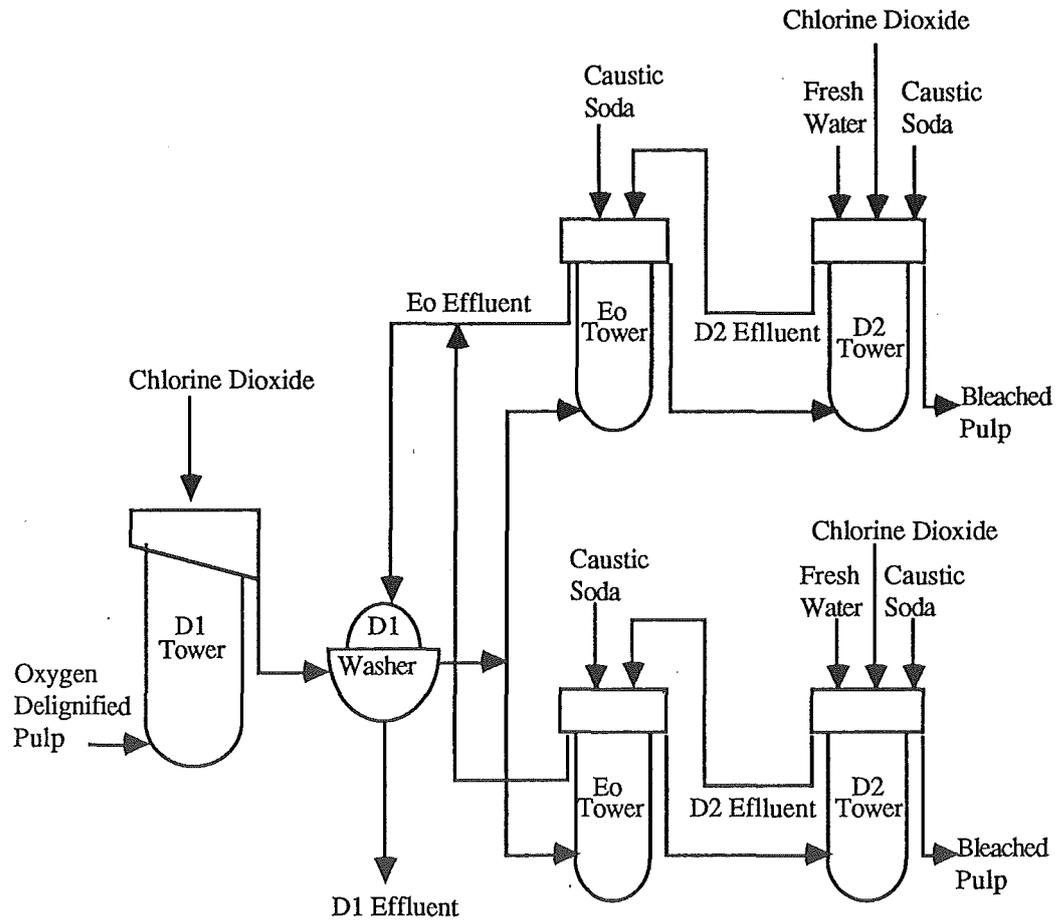
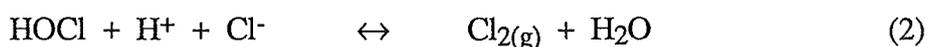


Fig 1.4 - No.2 bleach plant expansion

## 2 - Chemistry of Bleaching

### 2.1 - Chemistry of Chlorine-Water System

The chlorine water was prepared from the mixture of sulphuric acid and sodium hypochlorite produced by the on-site chemical plant. The chemistry underlying the process is first reviewed (Aylward et al, 1974):



Chlorine in water hydrolyses to form hypochlorous acid and in alkaline conditions hypochlorite ion. Hydrochloric acid is completely dissociated in dilute aqueous solution, whereas the hypochlorous acid is dissociated only slightly according to the equilibrium of reaction (3). It was claimed that at 25°C, chlorine is soluble in water to the extent of nearly 1 mole per 10 liters (Dence et al, 1979).

At the pH observed during pulp chlorination ca 1.5-3.0, the chlorinating medium is comprised of a mixture of elemental chlorine and hypochlorous acid. In a chlorine solution of pH 2, 20% of the oxidizing power is in the form of elemental chlorine and 80% is in the form of hypochlorous acid as illustrated in Figure 2.1. The hypochlorous acid increases as the pH increases. It is important to keep the pH below 2 in the chlorination stage because the hypochlorous acid degrades in the cellulose and results in strength loss. Chlorine consumption is a function of lignin removal requirement. It is also important to maintain a residual chemical concentration throughout the full retention time for all stages. This maintains a chemical potential or driving force for the penetration and bleaching of the shives and dirt for the longest possible time.

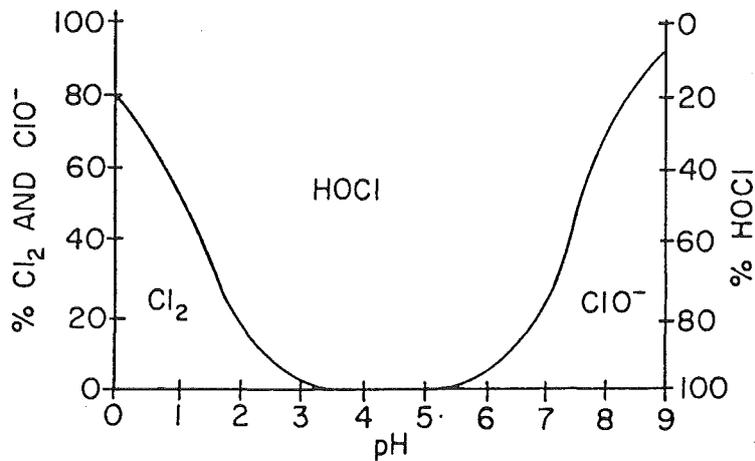


Fig. 2.1 - The composition of an 0.01N aqueous chlorine solution as a function of pH, after Rydholm (1965, p.921).

## 2.2 - Chemistry of Chlorine Dioxide System

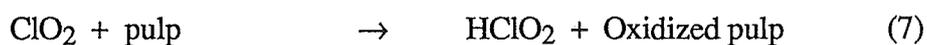
As with all other bleaching agents, the solution pH has a very important bearing on the results obtained with chlorine dioxide.

Chlorine dioxide reacts with hydroxyl ions in water to form chlorate,  $\text{ClO}_3^-$ , and chlorite,  $\text{ClO}_2^-$  ions:



At pH 4, the rate of the reaction with water is very slow and the loss of  $\text{ClO}_2$  was less than 10% in 3 hours, while at pH 7, in the same time at the same temperature, 90% of the  $\text{ClO}_2$  was converted to  $\text{ClO}_3^-$  and  $\text{ClO}_2^-$ , in equimolar ratio within the experimental error of the analytical methods (McCullough, 1961 & Wilkinson, 1961).

At pH 4 the decomposition in water alone is very slow, but in the presence of pulp the consumption of  $\text{ClO}_2$  is about as fast as at pH 7. In the presence of pulp, the oxidizing equivalent made available by the reduction of a mole of  $\text{ClO}_2$  to chlorous acid,  $\text{HClO}_2$ , is taken up by the pulp instead of by oxidizing another mole of  $\text{ClO}_2$  to  $\text{ClO}_3^-$  ion:



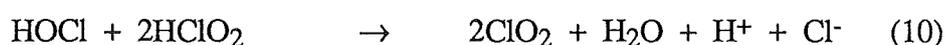
The  $\text{HClO}_2$  which forms very rapidly establishes equilibrium with its dissociation products, chlorite ion and hydrogen ion, the position of equilibrium being dependent on the pH of the solution:



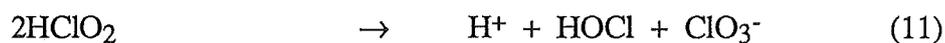
As the pH becomes higher, the concentration of  $\text{HClO}_2$  becomes lower. The  $\text{ClO}_2^-$  ion is unreactive towards lignin, but  $\text{HClO}_2$  is very reactive. It oxidizes lignin and is thereby reduced to hypochlorous acid,  $\text{HOCl}$ , which in the presence of chloride ( $\text{Cl}^-$ ) ion, enters into the following equilibrium which is also pH dependent.



In the absence of  $\text{Cl}^-$  ion,  $\text{HClO}$  reacts with  $\text{HClO}_2$  to form  $\text{ClO}_2$  and  $\text{HCl}$ :



Simultaneously  $\text{HClO}_2$  reacts with itself to form  $\text{ClO}_3^-$ ,  $\text{HOCl}$ , and hydrogen ion:



The  $\text{HOCl}$  is then available to form  $\text{ClO}_2$  by reaction (10), which is then available to react with lignin to form more  $\text{HClO}_2$ . Eventually, the chlorine dioxide is converted to  $\text{ClO}_3^-$ ,  $\text{ClO}_2^-$  and  $\text{Cl}^-$ , the proportions of which are highly dependent on the pH of the solution and on the lignin concentration in the pulp.

The sum of  $\text{ClO}_3^-$  and  $\text{ClO}_2^-$  is a minimum at end pH 3.8, for the chlorine dioxide stage of kraft pulp bleaching.

### 2.3 - Chlorine Dioxide Bleaching System

Chlorine dioxide has very high selectivity in destroying lignin without significantly degrading cellulose or hemicellulose, thus preserving strength while giving high brightness and minimizing "colour reversion", or yellowing with age.

The lignin present in the unbleached brown pulp and many components of wood resin are oxidized and chlorinated by a large enough excess of  $\text{ClO}_2$ . Only part of the lignin dissolves in the water, most of the remainder being dissolved in a subsequent hot alkaline extraction stage. In the range pH 3-7,  $\text{ClO}_2$  has relatively little effect on the carbohydrate components of pulp, unless a large excess of  $\text{ClO}_2$  is provided, an excessively high temperature is used, and the reaction time is unduly

prolonged. However, degradation increases sharply as the pH is increased above 7. With softwood kraft pulps,  $\text{ClO}_2$  cannot efficiently replace chlorine completely under the ordinary conditions of water temperature (4-27°C), consistency (3-4%), and time (30-60 minutes) normally used in the chlorination stage of bleaching.

It has been well established by operation in many mills that, inclusion of a very small proportion of  $\text{ClO}_2$  with the chlorine (2-4% of the equivalent oxidizing power), effectively decreases the viscosity loss. The benefit is even more important when chlorination is carried out at a higher temperature by recycling chlorination washer effluent to dilute the stock from high consistency storage to the 3-4 % normally used in the chlorination stage.

#### **2.4 - Bleaching Systems with Chlorine and Chlorine Dioxide**

The fundamental chemistry of combined systems with chlorine and chlorine dioxide has not been extensively studied due to the complexity of the reaction mixture. During sequential chlorinations, lignin oxidation reactions with chlorine are promoted by the initial pulp treatment with chlorine dioxide. Chlorine dioxide oxidizes reactive phenols to aliphatic structures and thereby suppresses aromatic substitution reactions with chlorine (Dence et al, 1979). Increased oxidation over substitution with chlorine dioxide results in greater lignin removal and less formation of chlorinated organic compounds.

#### **2.5 - Reactions of Chlorine with Lignin Model Compounds and Lignin**

Pulp chlorination is the first-stage treatment in the multi-stage bleaching of kraft pulp, and is preceded by pulping, washing and screening. It is normally performed in an aqueous solution of dissolved chlorine gas. Chlorine selectively chlorinates, oxidizes and depolymerizes the residual pulp lignin, resulting in its partial dissolution in the chlorinated liquor, and facilitates its removal during subsequent alkaline extraction.

There has been much controversy in the literature as to the characterization of the structure of residual lignin. It was pictured as high molecular weight structure, rich in phenolic hydroxyl groups, which is uniformly distributed throughout the cell wall and probably linked to carbohydrate moieties (Allison, 1985).

Lignin model compound studies have indicated that in aqueous chlorine solution, the residual lignin structures participate in a few types of reactions as

illustrated in Figure 2.2. Oxidation and electrophilic substitution are the major types of reactions.

Electrophilic substitutions chlorinate aromatic nuclei and displace side chains as an aldehyde. It is a very rapid reaction and occurs at various sites around the aromatic nuclei, which results in the scission of the aromatic and aliphatic moieties of the compound. Side chain displacement occurs to the greatest extent in the chlorination of benzyl alcohols (Figure 2.2, R=H).

The aromatic substitution patterns exhibited by the aromatic moieties of the lignin like structure in Figure 2.2 are controlled by the nature, number and positions of the substituents attached to the phenolic rings, as well as by the amount of applied chlorine. In the case of uncondensed softwood guaiacyl units, three sites i.e., carbons 2, 5 and 6 (Figure 2.2), are available for substitution by chlorine, and trisubstitution occurs when sufficient chlorine is available (Gess et al, 1971 & Gierer et al, 1971).

Substitution of chlorine on the phenolic ring of lignin model compounds does not proceed in a step-wise uniform manner, even under the most favorable conditions-homogeneous reaction system, good mixing and portion-wise application of chlorine. Thus, unsubstituted and polychlorinated phenolic residues are often found to coexist in chlorination product mixtures (Gess et al, 1971).

The oxidation reactions dealkylate and open aromatic ring structures, which result in the transformation of phenolic nuclei to nonaromatic structures incapable of undergoing substitution and electrophilic displacement reactions under normal chlorination conditions. Oxidation reactions during pulp chlorination are considered the major contributors to lignin removal (Dence et al, 1979).

Oxidative dealkylation of etherified phenolic units causes the rupture of interunitary ether linkages (i.e., the 4-O-lignin linkage in Figure 2.2) (Gierer et al, 1971), producing O-benzoquinonoid structures which are oxidized further to dicarboxylic acid fragments. The oxidative breakdown of the model compound also causes an extensive cleavage of methoxyl groups, yielding methanol (Sarkanen et al, 1969 & Dence et al, 1965). The intermediate O-benzoquinones are unstable in aqueous solution and may be further oxidized to open the ring, or in the absence of excess oxidant, reduced to the corresponding catechol (Simson et al, 1978).

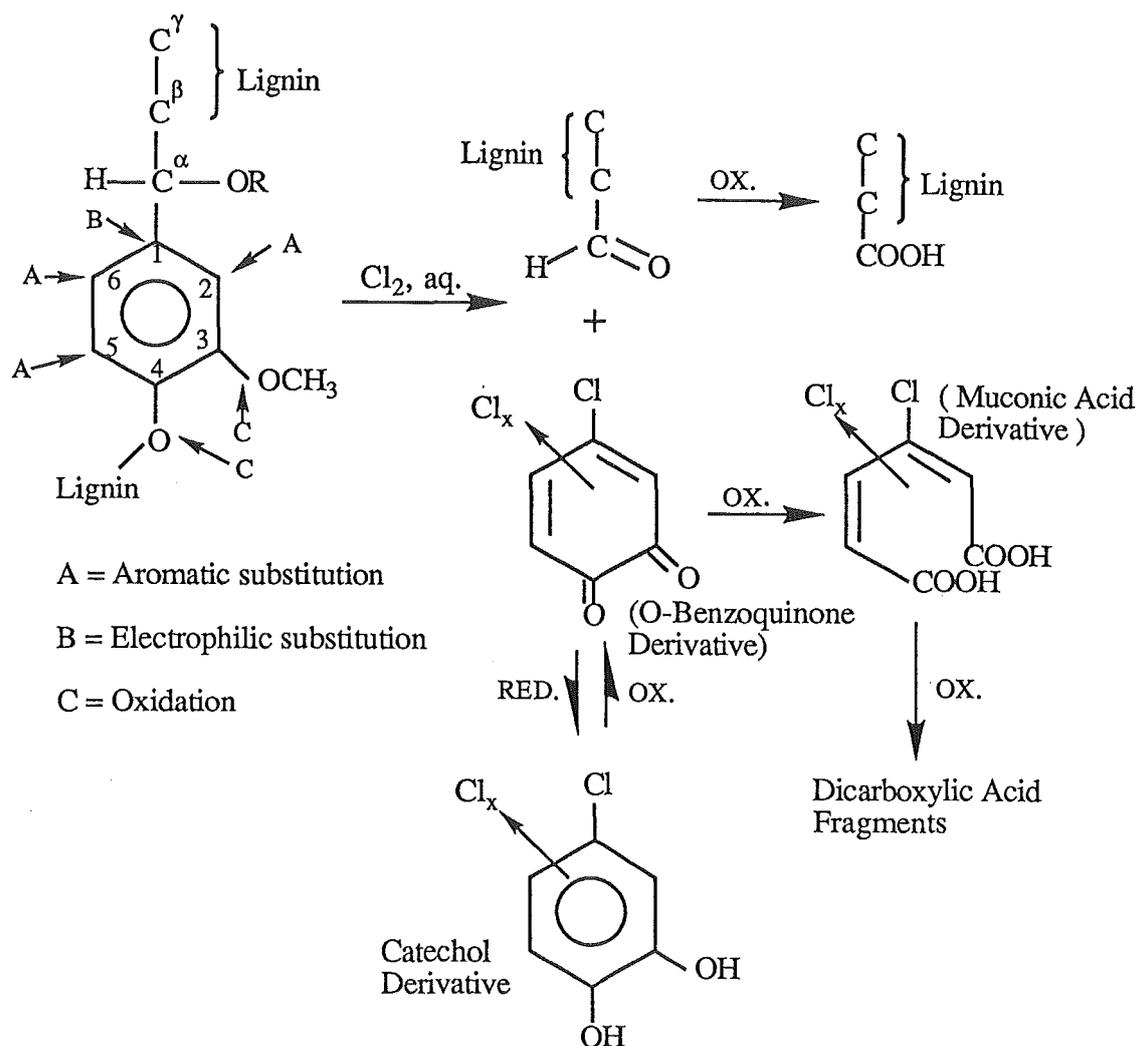


Fig. 2.2 - The reactions of chlorine with a representative lignin fragment.

Direct substitution reactions during pulp chlorination are extensive but not uniform. Some aromatic rings may be poly-chlorinated while others may remain completely unchlorinated. Direct substitution in itself does not fragment lignin nor increase lignin solubility in water. However, the resulting side chain displacement represents degradative interruption of the extended lignin network and thus leads to lignin fragmentation and dissolution. The subsequent alkali extraction causes the displacement of chloro groups by hydroxyl groups which do enhance water solubility and lability toward further reaction (Braddon et al, 1968). The average chlorine content after chlorination is about one chlorine atom per aromatic nucleus (Dence et al, 1979).

## **3 - Experimental**

### **3.1 - The Evaluations of the Effect of Chlorine Charge on Pulp Properties for zero and 100% D/C Filtrate Recycling**

The evaluations of the effect of chlorination charge at zero & 100% filtrate recycling in the D/C-stage, subjected to the standard D/C-stage and E1-stage bleaching conditions were carried out. Samples of unbleached pulp and filtrate from D/C bleaching stage were collected simultaneously from the brown stock decker, and the D/C washer seal tank of the NZFP. No.2 bleach plant. The pulp was rescreened prior to the determination of its Kappa number and oven dry content. Both the wet pulp and the effluent were then stored at 4°C until required. The stock dilution system prior to stock entering the bleach plant was simulated, i.e., the pulp with approximately 25% consistency was diluted down to 11% consistency with deionized water and D/C filtrate, in accordance with the percentage of recycle to depict stock exit from the No. 5 & 6 high density storage towers. It was then further diluted to 3% consistency with the appropriate amount of filtrate prior to the D/C bleaching stage.

#### **Procedures**

A thermostat water bath was used for temperature control and all the bleaches were carried out using the normal laboratory technique of manual mixing in thick plastic bags. The chlorine water was prepared from concentrated sulphuric acid and sodium hypochlorite (NaOCl). NaOCl was supplied by the chemical plant of Kinleith pulp and paper mill. It was diluted to half of its original concentration prior to the chlorine water preparation. Two levels of recycled filtrate at different levels of chlorine charges which, cover only the chlorination and extraction stages were carried out using 100 & 50g O.D. pulp samples. The concentration of chlorine dioxide was determined before addition to the pulp 30 seconds prior to adding the chlorine water, as it is the minimum time which, could be achieved due to limitations in the speed of chemical addition and mixing. This set procedure was retained throughout the test work. The amount of filtrate used was selected to relate to its association with pulp in the bleach plant. The concentration of chlorine water was determined before use, the amount



Analytical methods :

Kappa number	APPITA
Brightness	APPITA
Residual chlorine	Laboratory Standard Method, Kinleith Technical Department .
TOC	Dohrmann DC-90 Combustion/Infrared Laboratory Total Organic Carbon Analyzer (Xertex, 1986).
COD	Standard Methods For the Examination of Water and Wastewater (Rand et al, 1975).

### 3.2 - The Effect of Various Levels of Fresh Water Replacement by D/C Filtrate on Pulp Properties

The effect of replacing varying amounts of dilution water with D/C-stage filtrate at a fixed active chlorine charge of (0.22 x incoming pulp Kappa number) was investigated. The stock dilution system prior to the stock entering the No.2 bleach plant, and the bleaching conditions were simulated as for Experiment 3.1. Five different levels of water replacement were studied i.e., 0, 25, 50, 75 and 100%, and only three measured parameters were considered i.e., residual chlorine, pulp brightness and pulp extract Kappa number.

### 3.3 - The Investigation of Active Chlorine Consumption Potential of Organics in Bleaching Effluents

The objective is to investigate the active chlorine consumption potential, of the organics generated in the effluents of D/C chlorination, E1 extraction and D1 chlorine dioxide bleaching stages. Effluents from these bleaching stages were generated from bench scale bleaching experiments. The bleaching procedures, conditions, chemicals and measured parameters were as follows:

Prebleached pulp properties:	Kappa No. = 19.27	% O.D.= 17.85	
Bleaching chemicals:	<b>D/C-stage</b>	<b>E1-stage</b>	<b>D1-stage</b>
	NaOCl (~70g/l)	NaOH	ClO <sub>2</sub>
	H <sub>2</sub> SO <sub>4</sub>		
	ClO <sub>2</sub>		
Measured parameters:	Residual chlorine of D/C filtrate		
	Residual pH of D/C, E1 and D1 filtrates		

Bleaching conditions:

**D/C-stage**

Active chlorine charge =  $0.22 \times \text{Kappa}$

Sequential replacement (%) = 35

Residence time (minute) = 45

Consistency (%) = 3

Temperature (°C) = 25

pH =  $1.9 \pm 0.1$

**E1-stage**

Caustic charge (%) =  $0.5 \times \text{active chlorine charge}$

Residence time (minute) = 90

Consistency (%) = 10

Temperature (°C) = 75

pH =  $11.0 \pm 0.1$

**D1-stage**

Residence time (minute) = 180

Consistency (%) = 10

Temperature (°C) = 70

pH =  $4.0 \pm 0.1$

Distilled water was used to make up to the required pulp consistency to simulate the D/C, E1, and D1 bleaching stages. Filtrates generated from these bleaching stages were separated into two portions. One portion was used to determine the extent, to which the dissolved organics affect the total active chlorine consumption, while the other portion was analysed for "Total Dissolved Solids" and COD tests. Similar procedures were repeated for D/C and E1 filtrates collected from their corresponding seal tanks of the bleach plant.

### **3.3.1 - Measurement of Total Active Chlorine Consumption by Organics of D/C Bleaching Effluent**

The effluent was filtered using a grade 2 pyrex Gooch crucible prior to the experiment to provide an effluent free of suspended solids. Various amounts of chlorine water, which correspond to known amounts of active chlorine were added to a litre of sample effluent in a reaction flask. The whole system was sealed with vacuum grease applied on the surface of all the conical joints to provide a complete closed system. The chlorine water was prepared as in the previous Experiments (3.1 & 3.2), and its pH was adjusted to 2.0. Residual chlorine tests were conducted at 5 minute

intervals for the first hour, followed by 20 minute intervals for another hour and 2<sup>1</sup>/<sub>2</sub> hours intervals thereafter until the equilibrium state was reached. 45ml of sample was withdrawn from the reaction flask by a sampling pipette for the residual chlorine test. A blank test with distilled water was conducted on each set of filtrates. The amount of active chlorine added to both D/C and E1 effluents was based on past model predictions for a closed bleach plant operation (Appendix, B.9). The experimental layout is illustrated in Figure 3.1.

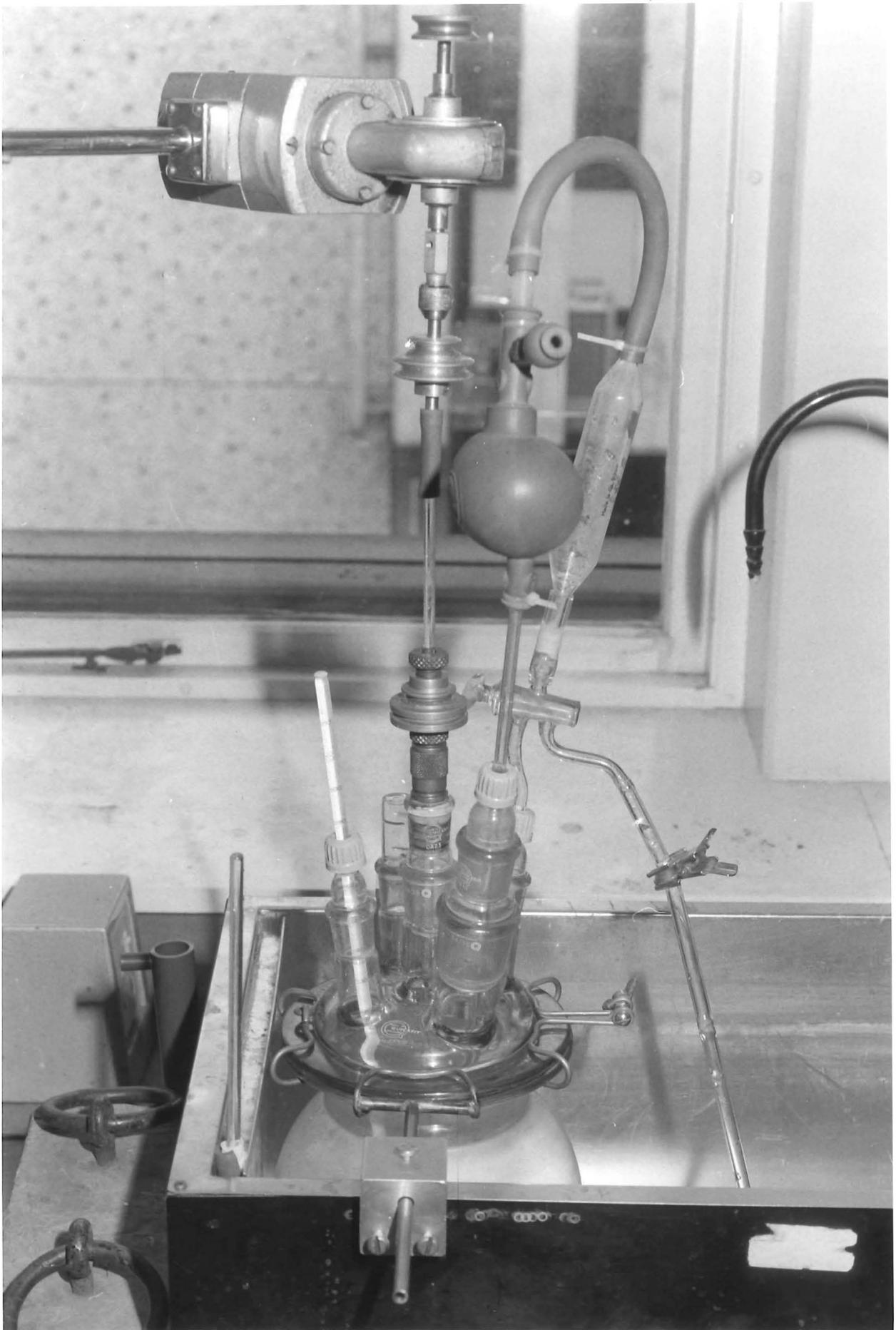
### Apparatus:

- 1) A two litre wide neck reaction flask fitted with multi-socket/flat flange lid and standard Quickfit equipment for stirring and temperature measurement.
- 2) A modified two ways stopcock pipette for sampling system with calibrated volume of  $45.0 \pm 0.5\text{ml}$ .
- 3) A stuffing box gland for sealing to prevent the escape of chlorine gas from the closed system.
- 4) Screwcap adaptors with silicone rubber ring inside the cap for thermometer and glass tube fitting.
- 5) Glass paddle stirrer.
- 6) Stirrer motor.
- 7) Rubber squeeze bulb.
- 8) Two metal clamps to clamp the reaction flask to the water bath.
- 9) Water bath with proportional temperature control, 0-100°C.
- 10) Metal clip to fit the flask and the flat flange lid.
- 11) Digital stop watch with an accuracy of  $\pm 0.01\text{second}$ .

### Experimental Conditions

#### For generated effluents:

Types of effluent:	D/C	E1	D1
Levels of active chlorine (g):	1.58	5.73	1.58
Volume of effluent (ml):	1000	1000	1000
Temperature (°C):	50	70	70



**Figure 3.1 - Apparatus for the Determination of Chlorine Consumption Potential of Effluent Organics**

For mill effluents:

Types of effluent:	D/C	E1
Levels of active chlorine (g):	1.58	5.73
Volume of effluent (ml):	1000	1000
Temperature (°C):	50	70

**3.3.2 - The Determination of Total Volatile Solids**

The total organics generated in the D/C, E1 and D1 bleaching stages was analysed according to the "Total Volatile Solids" method quoted from (Rand et al, 1975). A triplicate was carried out for each effluents. The effluents used were assumed suspended solids free.

**Apparatus:**

- 1) Platinum evaporating dishes
- 2) Muffle furnace for operation at  $550 \pm 50^{\circ}\text{C}$
- 3) Drying oven for operation at  $103-105 \pm 2^{\circ}\text{C}$
- 4) Desiccator, provided with a desiccant containing a colour indicator of moisture concentration.
- 5) Analytical balance, capable of weighing to 0.1mg.
- 6) Gooch crucible, pyrex, grade 2.

**Procedure**

Heat clean evaporating dish to 103 to 105°C for one hour. Store in desiccator until needed. Weigh immediately before use. Evaporate the filtrate in a round bottom triple neck distilling flask with condenser attached at 103 to 105°C. Evaporate the filtrate until approximately 10 to 20ml before transferring into preweighed dried platinum dish and evaporate to dryness in the drying oven. When evaporating in the drying oven, lower temperature to approximately 2°C below boiling to prevent splattering. Dry evaporated sample for at least one hour in the oven at 103 to 105°C, cool dish in desiccator to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until weight loss is less than 4% of previous weight or 0.5mg, whichever is less.

Calculation

$$\text{mg total solids per litre} = \frac{(A-B) \times 100}{\text{sample volume in ml}}$$

Where:

A = [weight of dried residue + dish] (mg), and

B = weight of dish (mg).

Ignite the fixed residue produced to constant weight in a muffle furnace at a temperature of  $550 \pm 50^\circ\text{C}$  for 15 to 20min. Have furnace up to temperature before inserting sample. Let dish cool partially in air until most of the heat has been dissipated. Transfer to a desiccator for final cooling in a dry atmosphere. Weigh dish as soon as it has cooled to balance temperature. Repeat cycle of igniting, cooling, desiccating, and weighing until weight loss is less than 4% of previous weight.

Calculation

$$\text{mg volatile solids per litre} = \frac{(A - B) \times 1000}{\text{sample volume in ml}}$$

where:

A = [weight of residue + dish before ignition] (mg),

B = [weight of residue + dish or filter after ignition] (mg) and

C = weight of dish or filter (mg).

### **3.4 - The Effect of Temperature on Active Chlorine Consumption by Organics of D/C Bleaching Effluent**

The effect of temperature on active chlorine consumption by organics in the D/C filtrate was studied. Similar bleaching procedures, conditions, chemicals and measured parameters as described in Experiment 3.3 earlier were repeated for D/C filtrate generation. Four temperatures were studied i.e., 30, 50, 60 &  $70^\circ\text{C}$  on the generated filtrate. A blank test with distilled water was conducted with each set of temperatures. The experimental set-up and procedures of measuring the active chlorine consumption of D/C organics and Total Volatile Solids determination were similar to that of Experiments 3.3.1 and 3.3.2. A summary of the experimental conditions for both Experiments 3.3 & 3.4 is illustrated in Table 3.1.

Table 3.1:

	Generated filtrate			Mill filtrate	
Sample	A	C	E	B	D
Bleaching stage	D/C	E1	D1	D/C	E1
Chlorine addition (g/l)	1.58	5.73	1.58	1.58	5.73
Temperature (°C)	30, 50, 60 & 70	70	70	50	70

## 4 - NZFP No.2 Bleach Plant Simulation

### 4.1 - GEMS Computer Model of No.2 Bleach Plant

Figure 4.1 and 4.2 show the GEMS block diagram, adopted for both the open and closed case model, which corresponds to the existing plant configuration. All liquid streams are defined according to the following set of stream variables:

Liquor (Mt/hr)  
Pulp fraction (Mt/Mt)  
Temperature (°C)  
C-stage organics (Kg/Mt)  
E-stage organics (Kg/Mt)  
D-stage organics (Kg/Mt)  
Oxidized organics (Kg/Mt)  
Black liquor organics (Kg/Mt)  
Chlorine dioxide (ClO<sub>2</sub>) (Kg/Mt)  
Chloride ion (Cl<sup>-</sup>) (Kg/Mt)  
Active chlorine (ICLA) (Kg/Mt)  
Hydroxyl ion (OH<sup>-</sup>) (Kg/Mt)  
Sodium ion (Na<sup>+</sup>) (Kg/Mt)  
Dissolved inorganics (ICO<sub>3</sub>) (Kg/Mt)  
Oxygen (O<sub>2</sub>) (Kg/Mt)

Note: Mt = metric ton

Model development for the existing bleach plant (Open case, Figure 4.1) is discussed below with particular reference to each of the five bleaching stages.

#### D/C-stage:

The brown stock from No.5 and 6 high density storage tank is taken to be 320 ADTPD, and of consistency 11%. All the chemicals are added based on air dry tonne of pulp. For this portion of flowsheet, three MIXER blocks are used for water dilution and chemicals addition. The D/C chlorination tower is simulated by four

REACT blocks and one MIXER block in series, followed by two washing stages. The basic chemistry involved in the REACT blocks is described by the following reactions:

- |   |   |                   |
|---|---|-------------------|
| 1) 47% ClO <sub>2</sub>                 | → | C-stage organics  |
| 2) 53% ClO <sub>2</sub>                 | → | Cl <sup>-</sup>   |
| 3) 50% Cl <sub>2</sub> H <sub>2</sub> O | → | ICLA              |
| 4) 50% Cl <sub>2</sub> H <sub>2</sub> O | → | Cl <sup>-</sup>   |
| 5) 100% Black liquor organics           | → | Oxidised organics |
| 6) 100% C-stage organics                | → | Oxidised organics |
| 7) 100% E-stage organics                | → | Oxidised organics |
| 8) 1.78% Pulp                           | → | C-stage organics  |

Black liquor organics are carried over from the previous pulping process and are assumed to include lignin. The conversion here is defined as the percentage of original reactant which converts to product. Four REACT blocks are required for simulating the D/C-stage due to the fact that, there is provision for only two components per block for chemical conversion. The 1.78% pulp which degrades to C-stage organics is based on the data supplied by the mill. The total active chlorine charge is 5.0% i.e., 3.25% is attributed by chlorine water (ClO<sub>2</sub>H<sub>2</sub>O), and 1.75% by ClO<sub>2</sub> based on 35% sequential replacement.

Chlorination is an exothermic reaction, and the overall heat of reaction i.e., 3000kcal/kg pulp is incorporated in one of the REACT blocks to account for the exothermic effect. The exit pH of the tower is set at 1.9. The MIXER block has the ability to turn sorption on and off. It is of particular interest in bleaching where the pH swings back and forth between acid and base conditions. The MIXER also simulates the scraper at the top of the tower where dilution water is added.

The D/C washer is simulated by two WASH blocks. Each block is equipped with a Norden efficiency of 2.0. This number is defined as the number of ideal mixing stages in series that would be necessary to obtain the same wash result, as in the actual wash plant. The displacement ratio, DR, for each washing stage differs because the first stage has fresh shower water, whereas the second stage has recycled shower liquor from E2-stage, which contains dissolved solids. The DR for both stages are 0.27 and 0.19, which gives the total DR of 0.46. The Cl<sup>-</sup> ion displacement ratio is 0.2 and the specific efficiency factor for temperature is 6.0, and it is assumed to be constant for the rest of the following washing stages of the bleach plant. The outlet pulp consistency is at 12.5%, and 100% of the fiber was assumed to be retained on the mat.

**E<sub>0</sub>-Stage:**

The E<sub>0</sub> bleaching tower is simulated by a MIXER, STMIX, CHARGE, REACT and WASH blocks. The pulp is mixed with 3.03% NaOH of concentration 100g/l prior to being heated to 75°C by live steam of pressure 4121.7mmHg. It is then charged with oxygen at 0.5% based on air dry pulp. Complete dissociation of NaOH into hydroxyl (OH<sup>-</sup>) and sodium (Na<sup>+</sup>) ions is assumed and this assumption holds for all the NaOH streams.

The conversion of pulp to E-stage organics is 2.45% and the exit pH from the tower is 10.5. No heat of reaction is assumed in this stage. The washing parameters are; Norden efficiency 2.6, pulp consistency 11%, Cl<sup>-</sup> ion displacement ratio 0.8 and DR of the washer is 0.815.

**D1-stage:**

This bleaching stage includes a MIXER, WASH and two REACT blocks in series. 0.9% of ClO<sub>2</sub> of concentration 22.93g/l is charged to the pulp, and the exit pH of pulp is adjusted to 4.0 with NaOH. 47% of ClO<sub>2</sub> is assumed to convert to D-stage organics while the residual is converted to Cl<sup>-</sup> ion. Conversion of pulp to D-stage organics is 1.17%. Washing parameters are; Norden efficiency 2.0, pulp consistency 11% and Cl<sup>-</sup> ion displacement ratio 0.8.

**E2-stage:**

Again this stage is represented by a MIXER, REACT and WASH blocks in series. The NaOH charge to the pulp is 0.8% and of concentration 100g/l. The conversion of pulp to E-stage organics is 1.87%. No heat of reaction is assumed and tower exit pH is 9.8. The E2 washing parameters are; Norden efficiency 2.6, pulp consistency 11%, Cl<sup>-</sup> ion displacement ratio 0.8 and the washer DR is 0.815.

**D2-stage:**

The conversion of pulp to D-stage organics is 1.10%. The ClO<sub>2</sub> charge to the pulp is 0.4% and the exit pH is adjusted to 4.0 by NaOH after the washing stage. The Norden efficiency is 2.4, pulp consistency 11%, Cl<sup>-</sup> ion displacement ratio 0.2 and the washer DR is 0.8.

The target pH values for all stages are provided by the mill. Washer displacement ratios DR are averaged from the mill data, and then input for each washer as an independent variable. This enables the computation of Norden efficiency which is then entered as the independent variable for each washer.

In the open case, the excess filtrate from the D/C washer and all the E1 filtrate are sewered. However, filtrates from D1, E2 and D2 bleaching stages are recycled partially to enable the exchange of heated shower water in three heat exchangers, one per stage. These heat exchangers are simulated by STMIX blocks.

#### 4.2 - Computer Simulation of Partially and Total Closure cases with Recycled of Acid and Alkali Effluents

A total closure model is derived from the fine tuned and well developed open case model as illustrated in Figure 4.2. The acid effluent from D/C seal tank of the bleach plant is recycled to a point upstream of D/C tower, for pulp dilution to reduce fresh water consumption and to prevent pulp degradation by maintaining pulp pH at about 1.9, whereas the alkaline effluent from E1 extraction stage is recycled to D/C washer which reduces the caustic effluent. Simulations are done for:

- a) Open case.
- b) Partial closure, with closed D/C-stage, open E1-stage.  
Two different percentages of D/C filtrate recycled are investigated, i.e, 50 and 100% substitution of fresh water.
- c) Partial closure with open D/C-stage, closed E1-stage.
- d) Total closure, with totally closed D/C and E1 stages.

The maximum quantity of liquor which can be recycled without altering pulp consistency is determined by the quantity of fresh water dilution added prior to the D/C stage (stream 2, Figure 4.2). For this reason, the 100% substitution of fresh water with D/C filtrate is limited to 49% of the original effluent, whereas 50% substitution is equivalent to 24.5% of the original effluent. The recycle percentage for acid effluent is defined as follows:

$$\frac{(\text{mass flowrate of stream 16})}{\text{mass flowrate of stream 15}} \times 100\%$$

For the open case, ICLA represents the actual active chlorine consumed by the bleach plant, and in the partial and total closure cases, ICLA is derived as base case rate plus additional ICLA consumed by dissolved organics of D/C and E1 stages. The recycling of E1 caustic effluent for total closure case is restricted to a maximum flow of

13.02 Mt/hr (10% recycle), as a replacement for the repulper fresh water flow (stream 26, Figure 4.2) at the D/C washer.

Two extra GPMOD blocks are incorporated into the total closure model to enhance the prediction of extra chlorine water requirement, to compensate for the consumption of extra active chlorine by the dissolved organics build up in the effluent due to recycling. The first GPMOD block (block 41, Figure 4.2) calculates the total amount of active chlorine consumed by both the D/C-stage and E1-stage organics. This result is then fed into second GPMOD block (block 42, Figure 4.2) which calculates the extra chlorine water flow required.

The amount of active chlorine consumed by organics of D/C and E1 stages at equilibrium state is established by carrying out Experiments 3.3.1 & 3.3.2 as described in Chapter 3. The active chlorine consumed by D1-stage organics was not included as it was found that, there were only minor amounts of volatile solids present in the effluent which consumed negligible amounts of chlorine.

### **4.3 - Computer Simulation of No.2 Bleach Plant Expansion**

A computer model for the proposed future revamped bleach plant configuration (Figure 1.4), designed to increase productivity by doubling D/C-stage capacity at the front end, splitting the subsequent bleaching sequence into two parallel lines is developed as illustrated in Figure 4.3.

Model development for the expansion of bleach plant is as follows:

#### **D1-stage**

The capacity of incoming brown stock from No.5 and 6 high density storage tank is taken to be 660 ADTPD and of 10% consistency. Again, all the chemicals are added based on air dry pulp. The unbleached pulp is mixed with 1.0% of  $\text{ClO}_2$  in a MIXER block prior to entering a heat exchanger, which is simulated by a HEATD block. The heat exchanger serves the purpose of recovering the heat loss through the D1 effluent from the D1 drum washer in order to maintain the D1 tower temperature at approximately 70°C. The D1 reaction tower and drum washer are represented by two REACT, one DILUTE and two D1 WASH blocks in series.

As only the 100% sequential replacement by  $\text{ClO}_2$  is considered, this simplified the chemistry involved in the reaction tower. The basic assumptions made are as follows:

- |    |                            |   |                   |
|----|----------------------------|---|-------------------|
| 1) | 47% ClO <sub>2</sub>       | → | D1-stage organics |
| 2) | 53% ClO <sub>2</sub>       | → | Cl <sup>-</sup>   |
| 3) | 100% Black liquor organics | → | Oxidized organics |
| 4) | 4% pulp                    | → | D1-stage organics |

The overall heat of reaction i.e., 3000kcal/kg pulp is incorporated in one of the REACT blocks to account for the exothermic effect, and the tower pH is set at 3.5. Two D1 WASH blocks are required to simulate the D1 drum washer due to the fact that, there are two equivalent recycled shower flows from each of the parallel E<sub>O</sub> diffuser washer. Each D1 WASH block is equipped with a Norden Efficiency of 2.0. The DR for each stage is approximately 0.58. The Cl<sup>-</sup> ion displacement ratio is 0.2, and the specific efficiency factor for temperature is taken to be 6.0. Both of these values are assumed to be constant for the following D2 washing stage of the bleach plant. The pulp outlet consistency from the drum washer is fixed at 10%, and 100% of the fiber is assumed to be retained on the mat.

### **E<sub>O</sub>-stage**

This part of the flow sheet is simulated by a MIXER, STMIX, CHGE, REACT and E<sub>O</sub> WASH blocks in series. NaOH of concentration 100g/l is added to the pulp stream after the SPLIT block prior to being heated to 80°C by steam of pressure 4121.7mmHg. Then follows a 0.5% oxygen charge on to the pulp before entering the E<sub>O</sub> reaction tower. Again, complete dissociation of NaOH into OH<sup>-</sup> and Na<sup>+</sup> ions is assumed, and this assumption holds for all the NaOH streams.

The conversion of pulp to E-stage organics is assumed to be approximately 2%, and the exit pH from the tower is 11. No heat of reaction applies in this stage. The washing parameters are; Norden efficiency 2.6, exit pulp consistency 10%, Cl<sup>-</sup> ion displacement ratio 0.8 and DR of the washer is 0.865.

### **D2-stage**

This final bleaching stage includes a MIXER, STMIX, D2 WASH and two REACT blocks in series. Similar assumptions as for the D1-stage are made, except that only 2% of pulp is assumed to convert to D2-stage organics. 0.7% of ClO<sub>2</sub> of concentration 22.93g/l is charged to the pulp, the exit pH of pulp is adjusted to 3.5 with NaOH, and the tower temperature is controlled at 70°C. The washing parameters are; Norden efficiency 2.0, exit pulp consistency 10%, Cl<sup>-</sup> ion displacement ratio 0.8

and washer DR 0.847. Total pulp loss through the whole bleach plant due to pulp degradation is estimated to be approximately 8%.

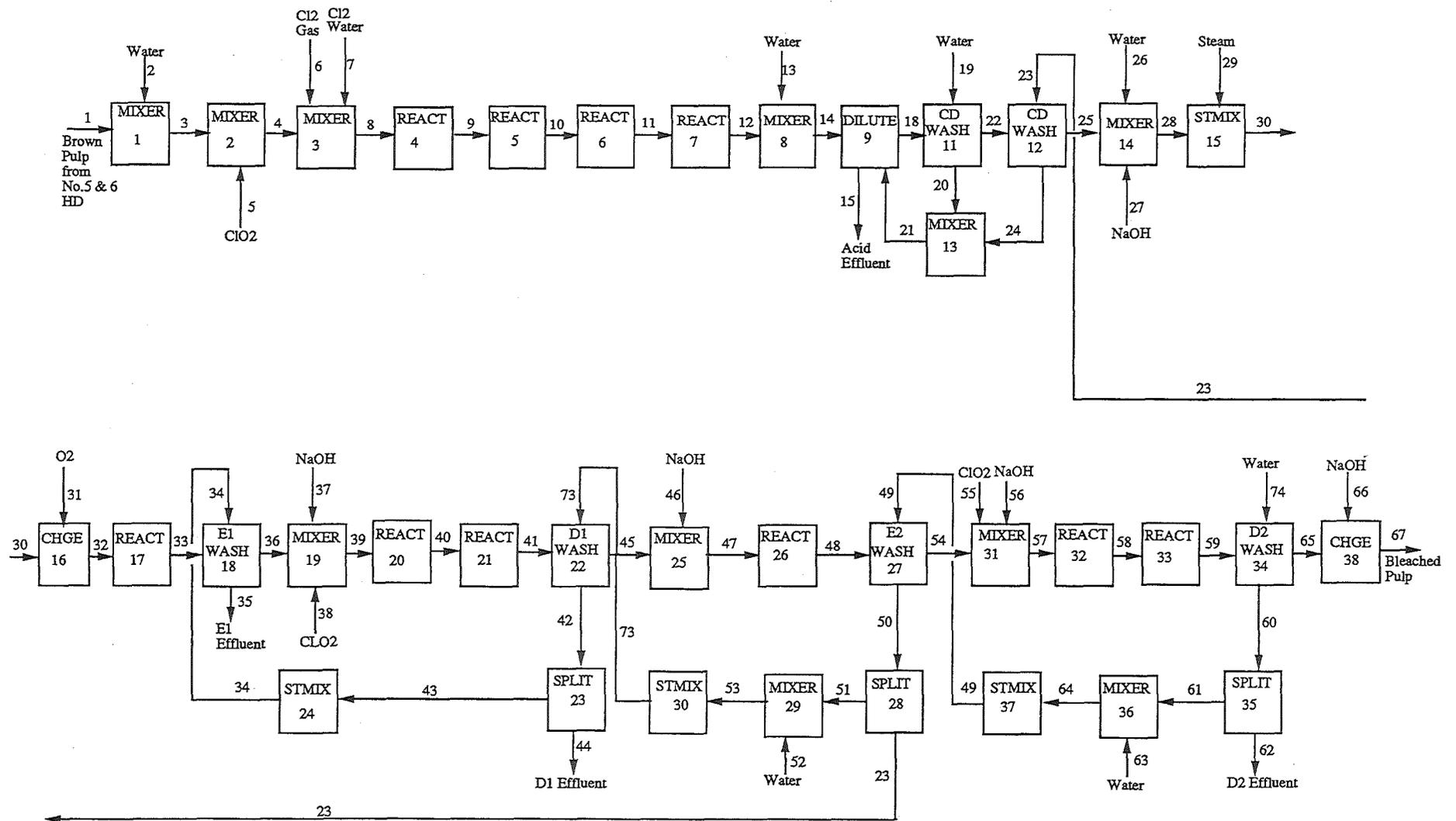


Fig. 4.1: Flow chart of the computer model of No. 2 bleach plant - Open case

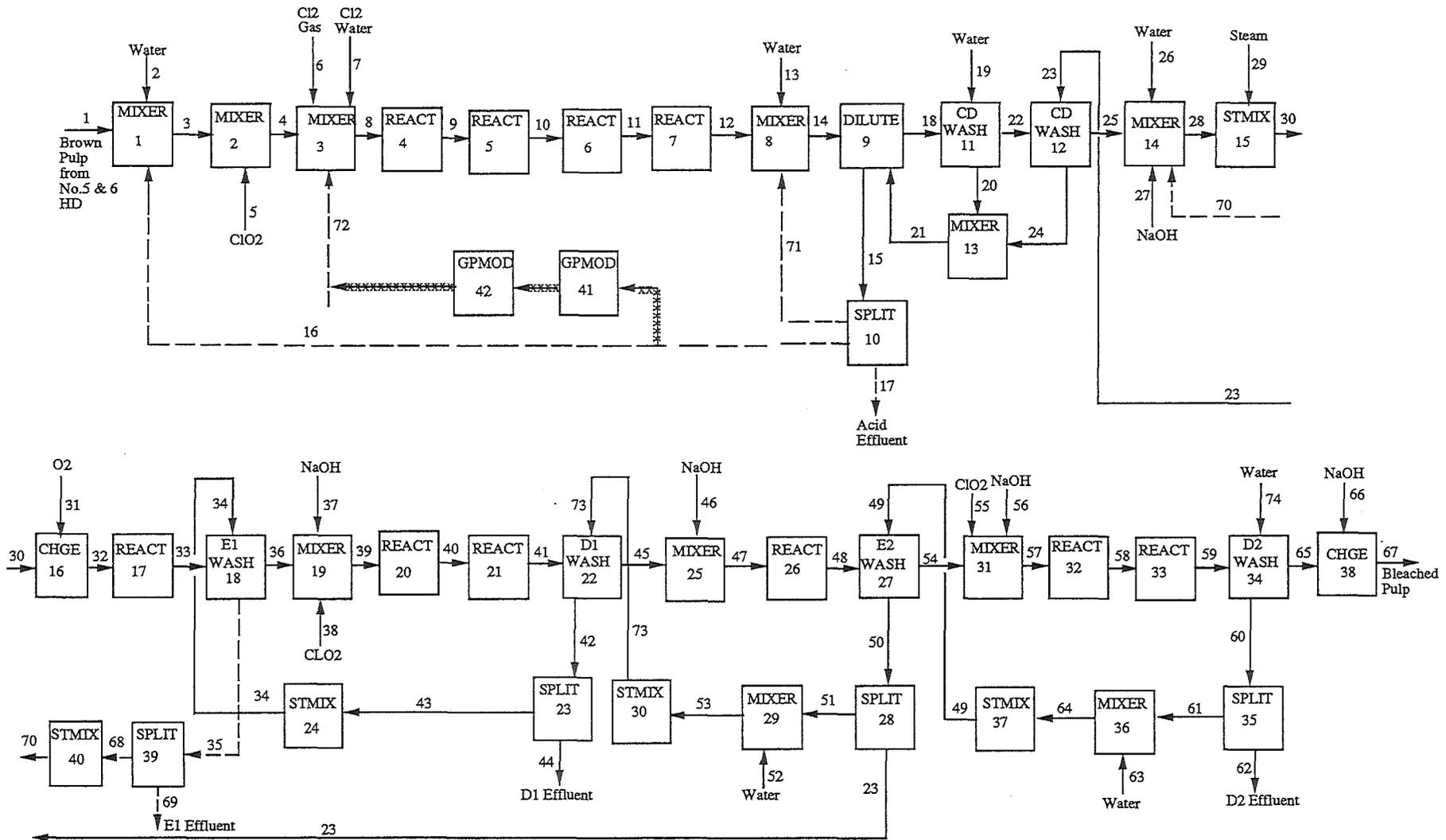


Fig. 4.2 : Flow chart of the computer model of No. 2 bleach plant  
 with :- a) Closed D/C-stage, Open E1-stage  
 b) Open D/C-stage, Closed E1-stage  
 c) Closed D/C-stage & E1-stage

----- Mill closure  
 alternatives

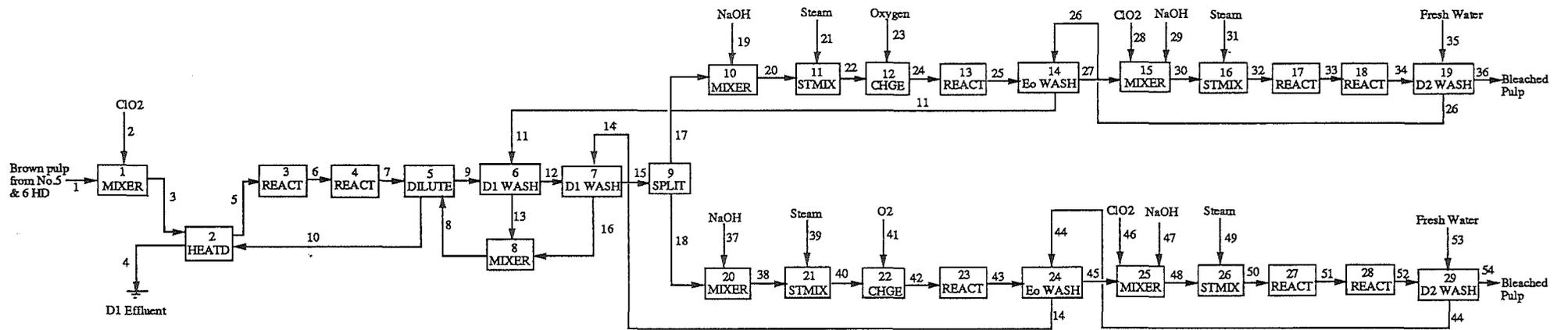


Fig. 4.3: Flow chart of the computer model of No.2 bleach plant expansion

## 5 - Results

### 5.1 - The Evaluations of the Effect of Chlorine Charge on Pulp Properties for zero & 100% D/C Filtrate Recycling

Figures 5.1.1, 5.1.2 and 5.1.3 indicate the effect of chlorine charge on pulp brightness, pulp Kappa number after E1 bleaching stage (CE extract Kappa number), and residual chlorine of the effluent concerned. The results of TOC and COD of the D/C effluent subjected to various chlorine charge are also presented in Figures 5.1.4 and 5.1.5.

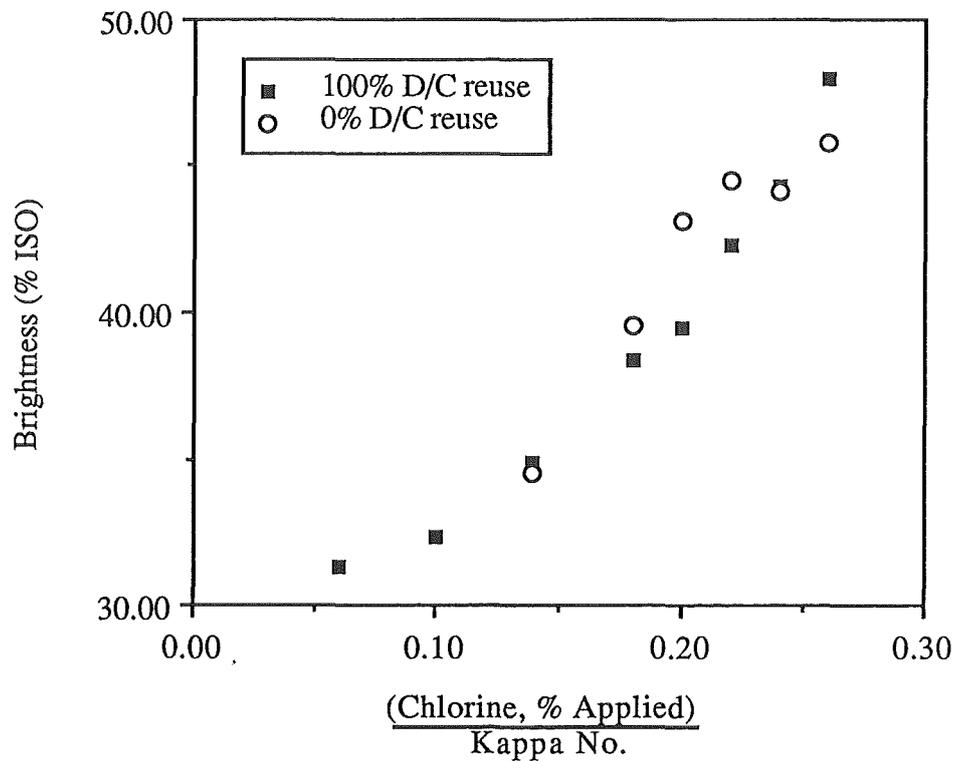


Fig. 5.1.1

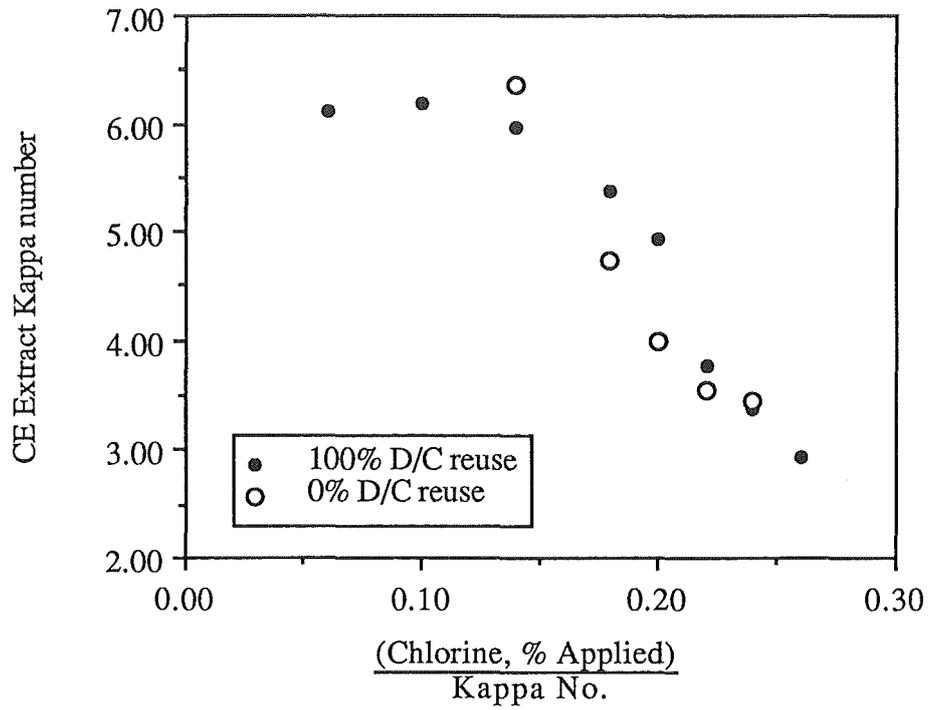


Fig. 5.1.2

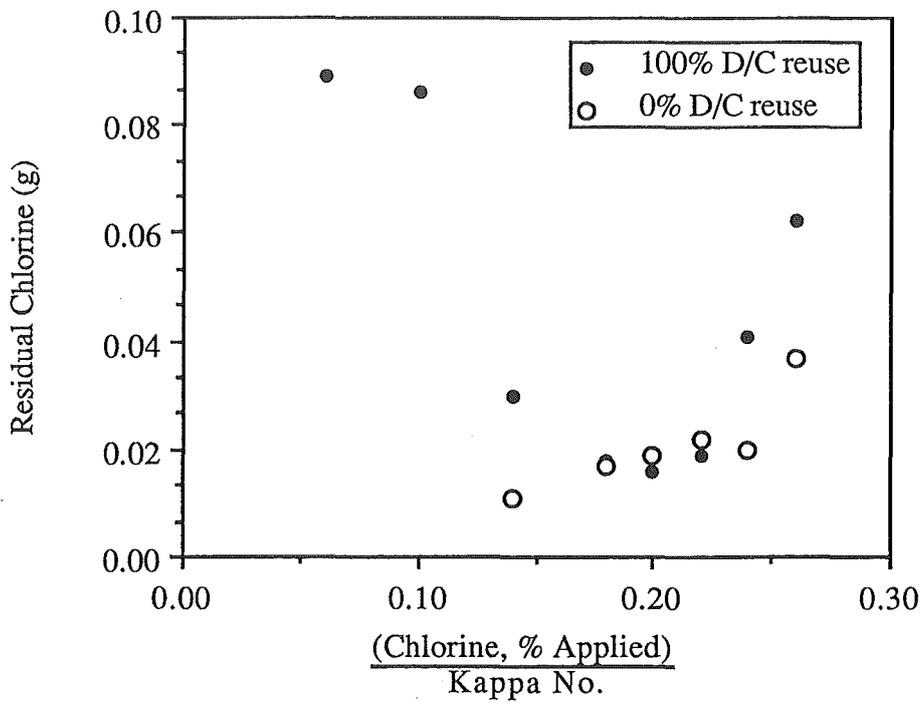


Fig. 5.1.3

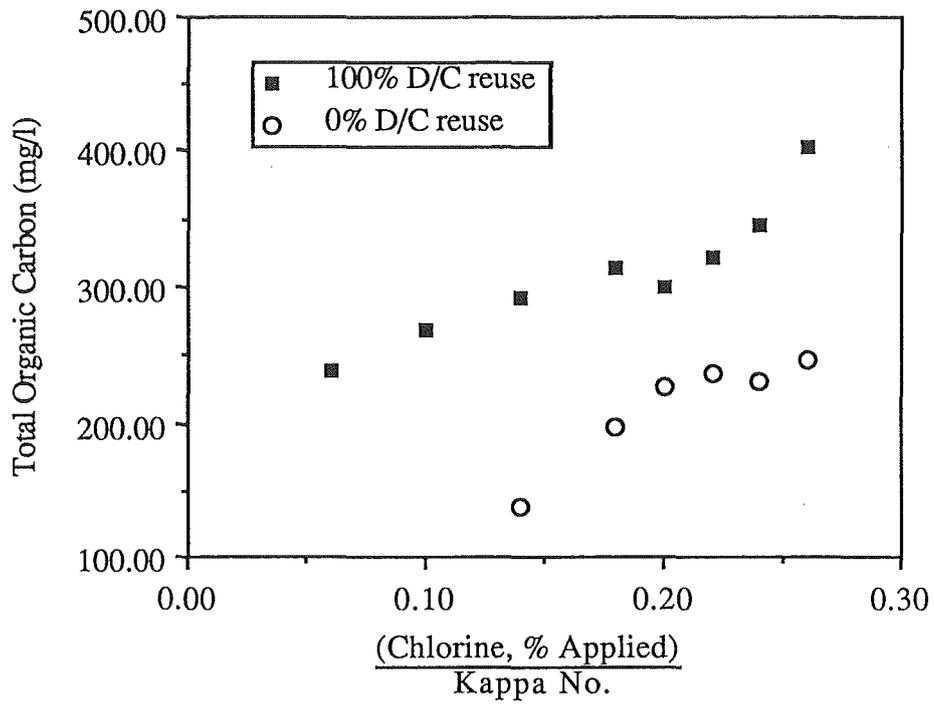


Fig. 5.1.4

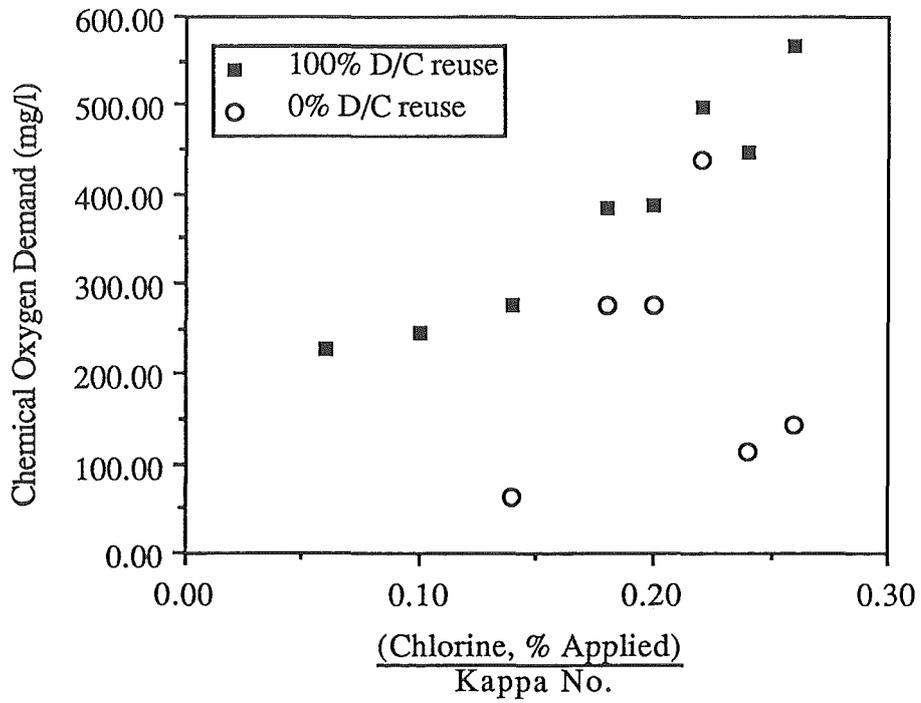


Fig. 5.1.5

## 5.2 - The Effect of Various Levels of Fresh Water Replacement by D/C Filtrate on Pulp Properties

The residual chlorine, CE extract Kappa number and brightness are plotted against different levels of D/C filtrate replacement as shown in Figures 5.2.1, 5.2.2 and 5.2.3.

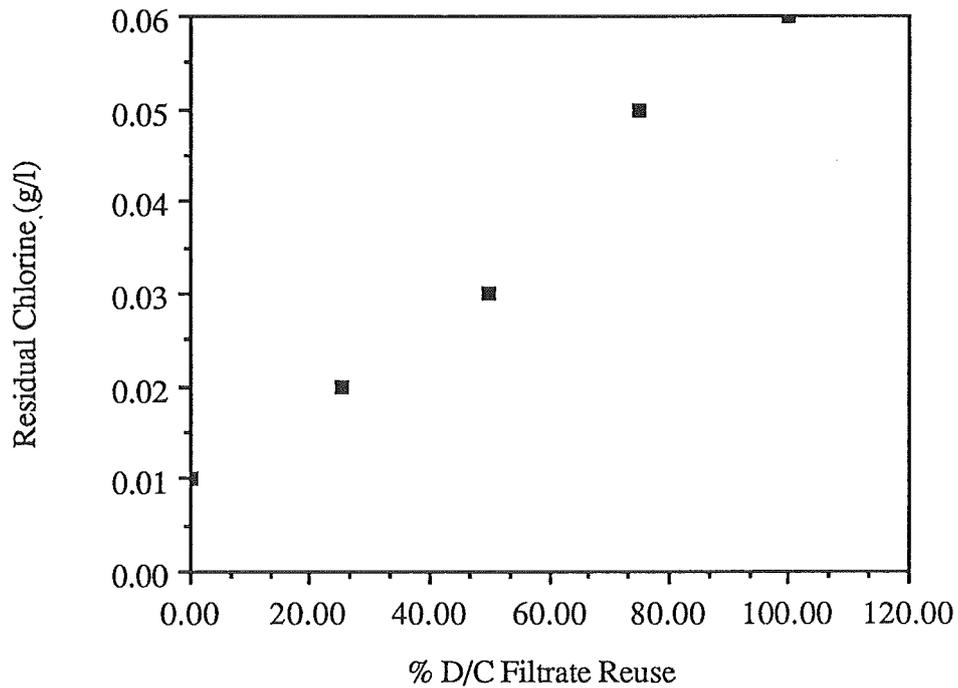


Fig. 5.2.1

Note: % D/C filtrate reuse means % water replacement by D/C filtrate.

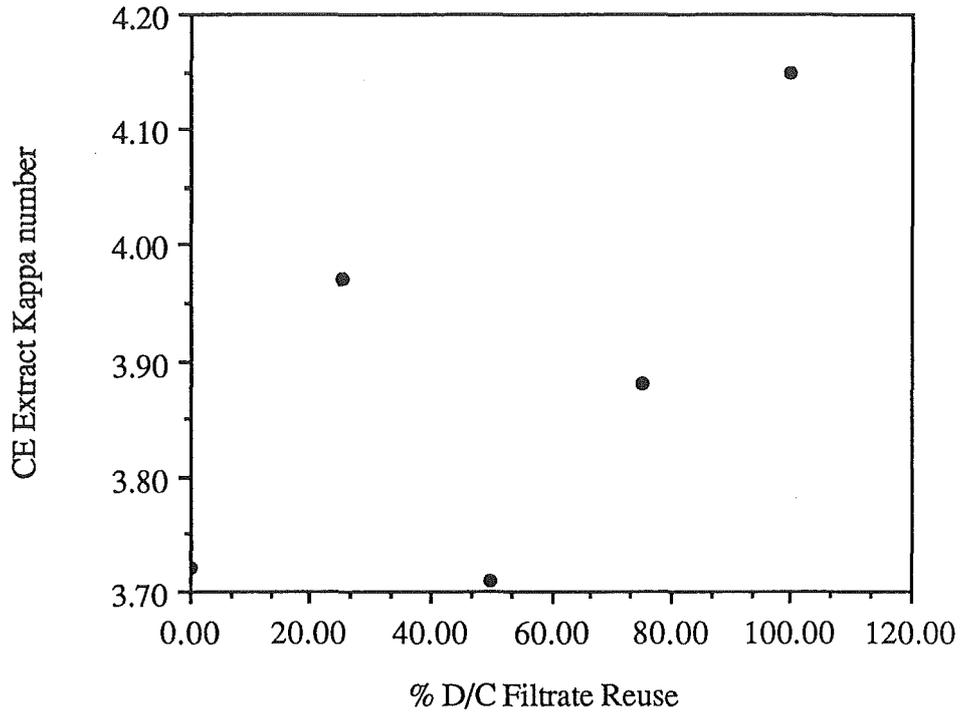


Fig. 5.2.2

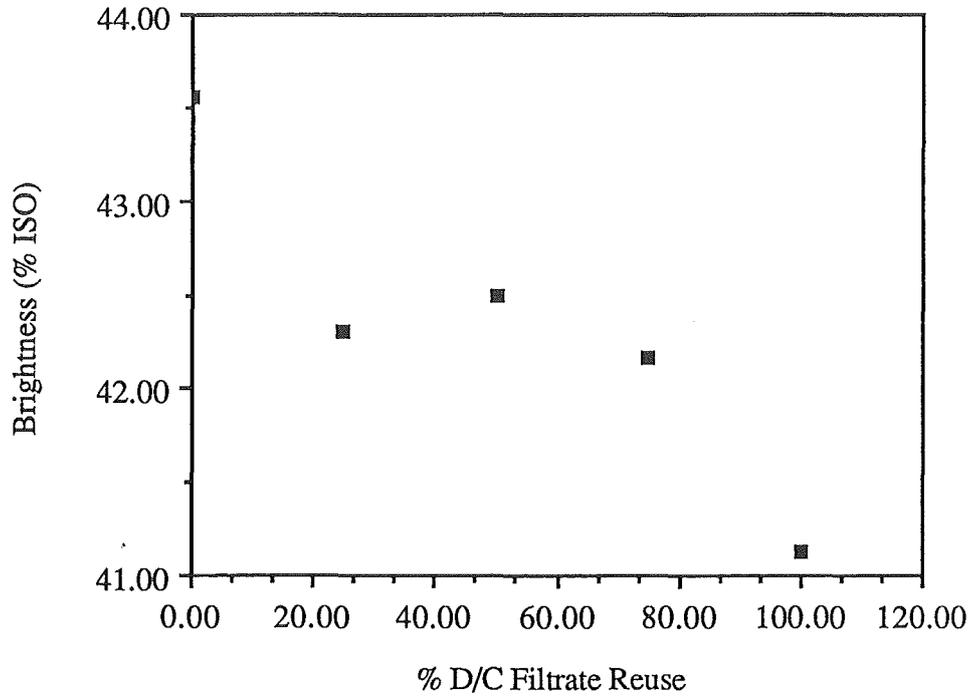


Fig. 5.2.3

### 5.3 - The Investigation of Active Chlorine Consumption Potential of Organics in Bleaching Effluents.

The results of COD and volatile solids for both the generated and mill D/C, E1 effluents are presented in Tables 5.3.1 and 5.3.2, whereas Table 5.3.3 shows the COD and volatile solids of only the generated D1 effluent.

Table 5.3.1: COD and volatile solids in D/C effluent

	Generated effluent	Mill effluent
COD (mg/l)	300-500	300-500
volatile solids (mg/l)	300-800	350-550

Table 5.3.2: COD and volatile solids in E1 effluent

	Generated effluent	Mill effluent
COD (mg/l)	2700-3000	3000-3400
volatile solids (mg/l)	1500-1900	2700-3100

Table 5.3.3: COD and volatile solids in D1 effluent

	Generated effluent
COD (mg/l)	15-30
volatile solids (mg/l)	20-30

The residual chlorine versus time curves for both the generated and mill effluents of D/C, E1 and D1 bleaching stages, with their corresponding blank test are illustrated in Figures 5.3.1, 5.3.2 and 5.3.3.

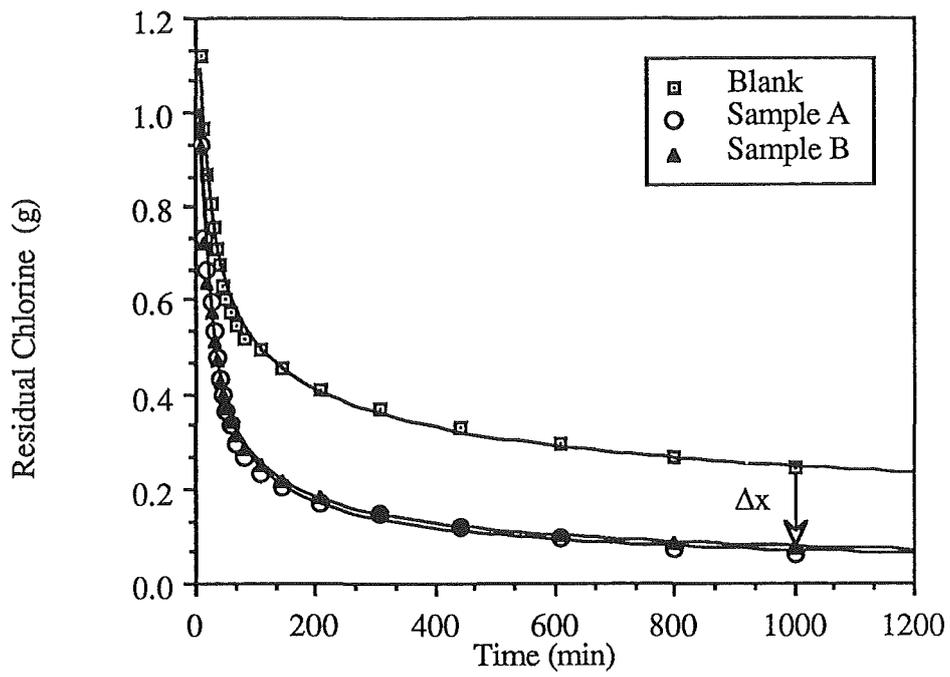


Fig. 5.3.1

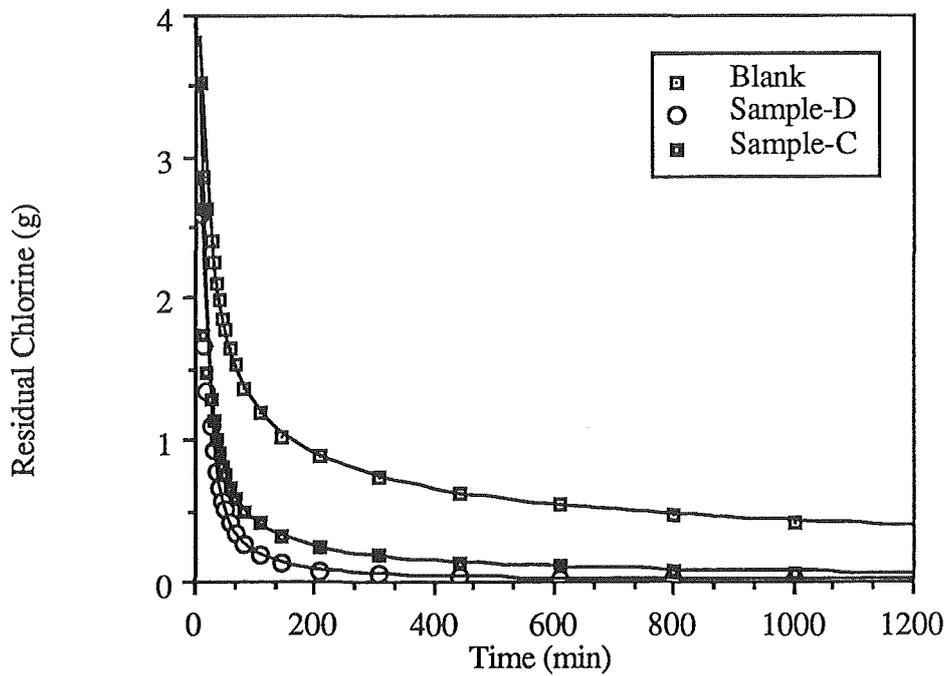


Fig. 5.3.2

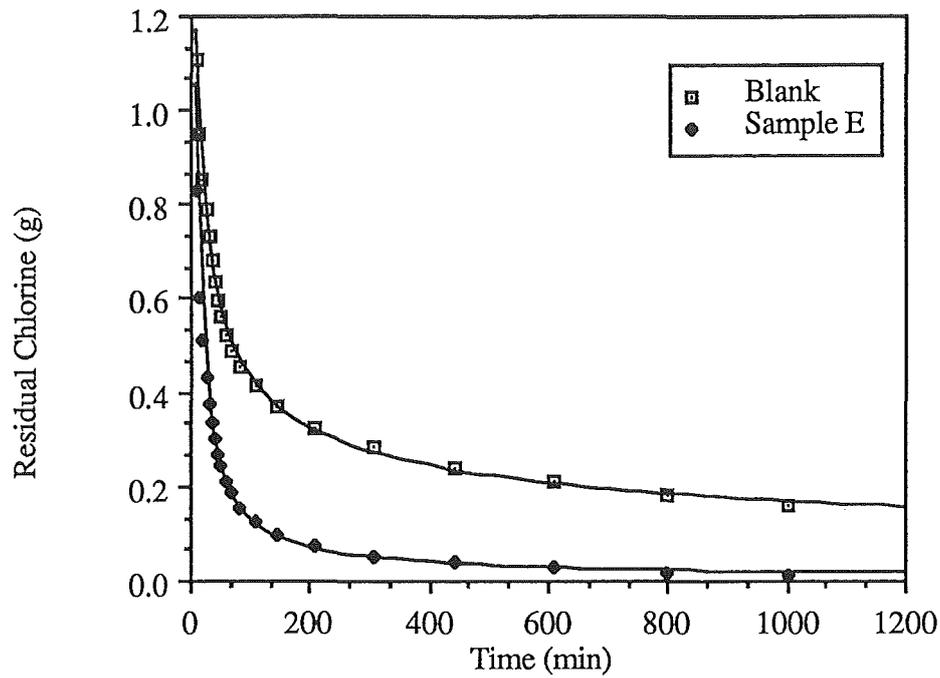


Fig. 5.3.3

#### 5.4 - The Effect of Temperature on Active Chlorine Consumption by Organics of D/C Bleaching Effluent.

Figure 5.4.1 indicates the effect of various temperatures on chlorine-water system (i.e., blank test), whereas Figure 5.4.2 indicates the temperature effect on active chlorine consumption of D/C effluent system. Four different temperature levels (i.e., 30, 50, 60 and 70°C) were investigated. The amount of active chlorine consumed by the D/C-stage organics at different temperatures, is also illustrated in Figure 5.4.3.

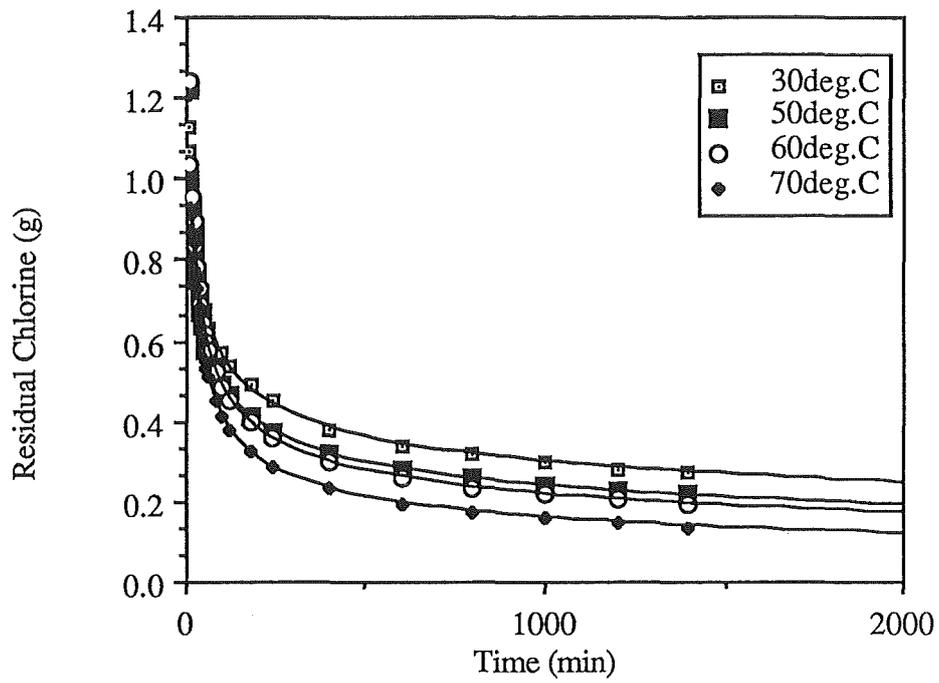


Fig. 5.4.1

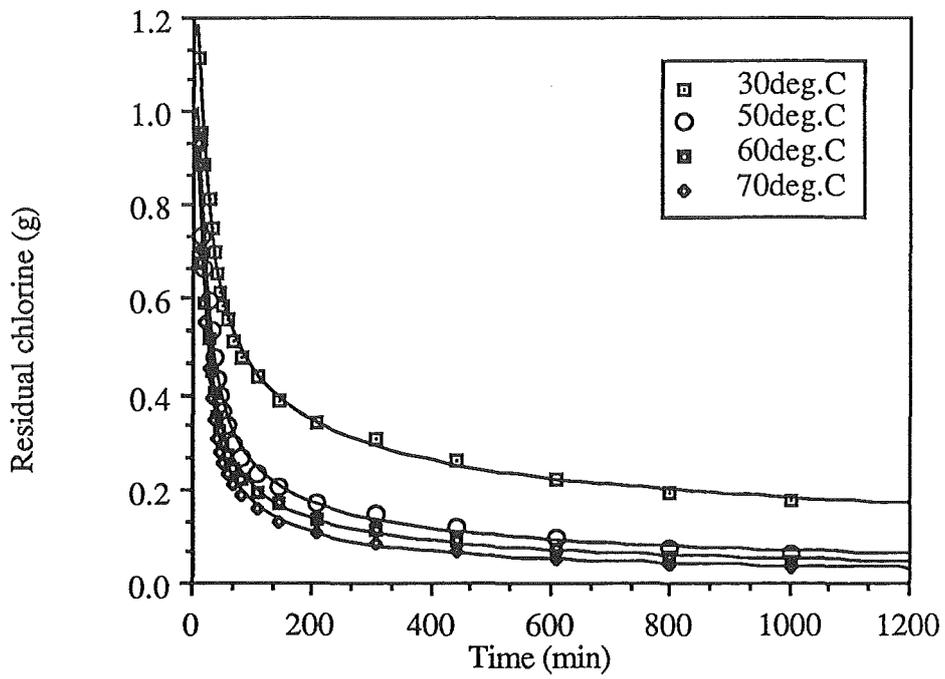


Fig. 5.4.2

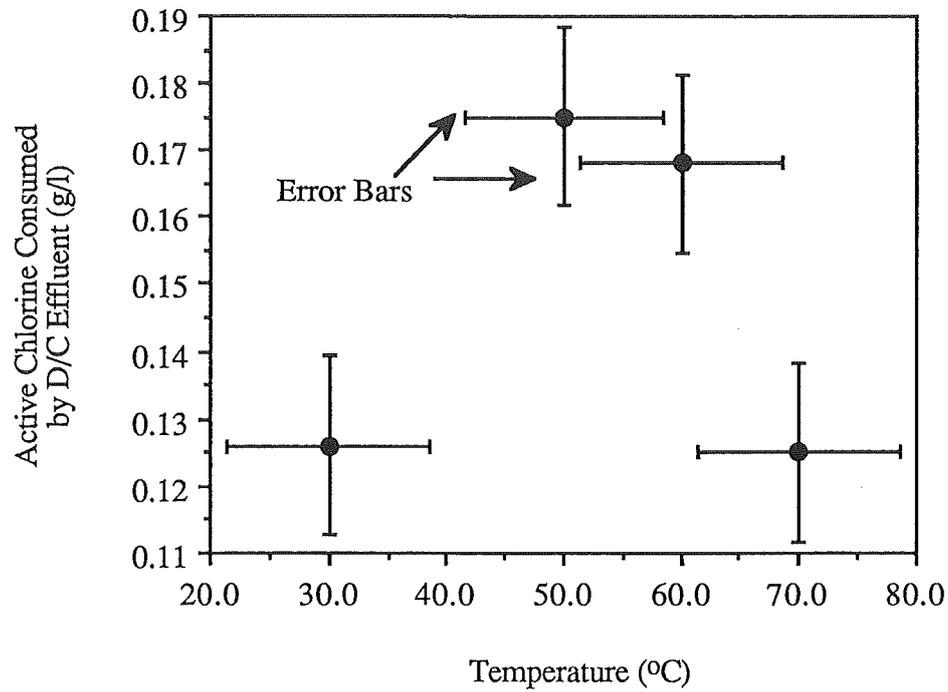


Fig. 5.4.3

### 5.5 - Computer Simulation of No.2 Bleach Plant

The dissolved solids from each bleaching stage and effluent volumes generated from all the five different cases of mill closure are presented in Table 5.5.1, whereas Tables 5.5.2 and 5.5.3 give the detail of the total steam, water and bleaching chemicals usage, and the annual cost for all the five cases.

Table 5.5.1

	Kg organics/tonne unbleached O.D. pulp			Effluent Volume Mt/hr
	D/C-stage	E-stage	D-stage	
open case	16.323	0.146	0.077	484.853
closed D/C, open E1 ( 100% D/C recycle )	13.544	0.103	0.158	70.729
closed D/C, open E1 ( 50% D/C recycle )	6.468	0.052	0.040	187.554
open D/C, closed E1	16.321	0.141	0.072	484.786
total closure	13.544	0.104	0.159	70.729

Table 5.5.2:

	Steam Mt/hr	Water Mt/hr	Chlorine Kg/hr	Oxygen Kg/hr	Chloride Kg/hr
open case	7.088	635.040	2.511	37.676	27.486
closed D/C, open E1 (100% D/C recycle)	6.847	211.730	56.173	43.327	238.530
closed D/C, open E1 (50% D/C recycle)	7.385	211.730	28.136	42.530	90.867
open D/C, closed E1	6.345	622.020	2.511	60.082	27.486
total closure	6.029	198.710	56.173	67.434	238.530

Table 5.5.3:

	\$ / tonne unbleached O.D. pulp				Total cost \$/year
	Steam	Water	Chlorine	Oxygen	
open case	11.81	3.18	0.06	0.78	1,550100
closed D/C, open E1 (100% D/C recycle)	11.41	1.06	1.31	0.90	1,437500
closed D/C, open E1 (50% D/C recycle)	12.31	1.06	0.66	0.89	1,461000
open D/C, closed E1	10.57	3.11	0.06	1.25	1,467800
total closure	10.04	0.99	1.31	1.40	1,345400

## 5.6 - Computer Simulation of No.2 Bleach Plant Expansion

The required utilities, bleaching chemicals and generated dissolved solids species of the No.2 bleach plant expansion as predicted by computer simulation are detailed in Table 5.6.1, whereas Table 5.6.2 lists the basic cost of utilities and bleaching chemicals.

Table 5.6.1

Steam	Water	Chlorine dioxide	Caustic soda	Chloride	D-stage organics	E-stage organics
*Mt/Mt	Mt/Mt	Kg/Mt	Kg/Mt	Kg/Mt	Kg/Mt	Kg/Mt
0.179	13.831	0.433	2.101	1.357	39.006	36.500

\* All the values listed above are based on metric ton of O.D.unbleached pulp.

Table 5.6.2

\$ / tonne unbleached O.D. pulp				Total cost steam + water \$/ year
Steam	Water	Chlorine dioxide	Caustic soda	
3.58	0.83	866.00	1890.00	890,600

## 6 - Discussion

### 6.1 - The Evaluations of the Effect of Chlorine Charge on Pulp Properties for zero and 100% D/C Filtrate Recycling

The results of the 100% D/C filtrate reuse in D/C and E1 bleaching, gave lower brightness readings than the fresh water bleaching. The chlorine charge for both series of experiments ranged from 0.14 to 0.24 x Kappa, as illustrated in Figure 5.1.1. At a higher chlorine charge of 0.24 x Kappa, the pulp brightness gradually levelled off with fresh water bleaching. This is understandable as more chlorine applied to the pulp will provide greater delignification until maximum delignification is achieved. This would also imply that the residual lignin in the pulp was highly condensed, with the result that only a few sites were available for aromatic substitution.

A more important consideration, however, was the effect of decreasing pH on the amount of lignin removed during chlorination. In the pH range applied to pulp chlorination (1.7-1.9), the increased acidity in this chlorinating medium leads to an increase in the overall rate of chlorine consumption (Hisey et al, 1936). This effect is most likely due to the increasing proportion of the elemental chlorine resulting from a shift in the chlorine hydrolysis equilibrium (Equation 2, Chapter 2, Figure 2.1). With the application of increasing amounts of chlorine until a point was eventually reached i.e., when the residual lignin was inaccessible to chlorine molecules after a certain extent of reaction, with the result that the chlorination products then required removal by an alkali treatment in order to expose fresh lignin surface for continued reaction.

Additional applied chlorine above 0.24 x Kappa appears to have a more pronounced effect on brightness, for the 100% D/C filtrate reuse than compared with fresh water bleaching (Figure 5.1.1). This may be due to the lowering in pH, as filtrate reuse in the chlorination stage always increases the acidity of the chlorinated pulp, which in turn facilitates the consumption of chlorine until the residual lignin is inaccessible to chlorine molecules after a certain extent of reaction. The pulp brightness would be expected to level off gradually with further chlorine charge. This was supported by the results of CE extract Kappa number after the E1-stage, plotted versus the percentage of active chlorine used in the first bleaching stage (Figure 5.1.2). Also

note that the CE extract Kappa number for both cases decreases with an increase in chlorine charge.

The utilization of D/C-stage effluent was shown to increase the COD and TOC loadings of the effluent concerned as shown in Figures 5.1.4 and 5.1.5. The TOC and COD content of the pulp is also believed to increase even though these values were not measured. Both the TOC and COD loadings for the zero & 100% D/C filtrate reuse were seen to increase with increase in chlorine charge, except at the chlorine charge of  $0.24 \times \text{Kappa}$ , where the TOC and COD loadings dropped slightly for both cases before increasing further. This again may be due to the pH effect, where the lowering in pH of the system at a higher chlorine charge encourages the generation of more elemental chlorine, according to Equation 2, Chapter 2, which enhances further delignification to generate more total organic bound chlorine until the lignin molecules are saturated with chlorine.

The recycling of D/C filtrate also affects the residual chlorine content of the effluent. Interestingly, for the case with 100% D/C filtrate reuse, the residual chlorine reduced gradually with increased chlorine charge from  $0.06$  to  $0.20 \times \text{Kappa}$ , and increased steadily thereafter as shown in Figure 5.1.3. Again, this may be attributed to the variation in pH of the system. Initially, as more chlorine is added to the pulp, the pulp acidity increases which then drives the reaction of Equation 2, Chapter 2 (Figure 2.1), to the left to produce more elemental chlorine. This elemental chlorine chlorinates the lignin until the maximum chlorination is reached, any further increment of chlorine charge would only contribute to an excess of active chlorine.

## **6.2 - The Effect of Various Levels of Fresh Water Replacement by D/C Filtrate on Pulp Properties.**

The present finding portrayed the trend that the residual chlorine increased linearly with the levels of D/C filtrate replacement at the chlorine charge of  $0.22 \times \text{Kappa}$  number, as illustrated in Figure 5.2.1.

In Figure 5.2.3, it was obvious that the pulp brightness dropped for about 2.4 units from zero to 100% D/C filtrate replacement, whereas Figure 5.2.2 implied that the CE extract Kappa number did not show any significant trend with different levels of D/C filtrate reuse.

### 6.3 - Total Volatile Solids and COD of D/C, E1 and D1 Effluents

The composition of bleaching effluent is very complex. The effluent contains large amounts of chlorinated compounds of both high and low relative molecular mass, and there has been a growing interest in the identification and analysis of specific chlorinated organic compounds in waste water since the early 1970s.

To the author's knowledge, several methods for the determination of total organically bound chlorine compounds in municipal and drinking water have been described, see reference Keith, 1976, for a comprehensive review. However, most of these methods involve one or more concentration steps followed by some suitable quantification technique. Among the concentration methods used are purge techniques, solvent extraction and resin sorption. For the quantification of the volatile organic chlorinated compounds, a gas chromatography/mass spectrometry technique or gas chromatography with a halogen-specific detector has been used.

The conventional laboratory methods commonly used to characterize and quantify the organic content of bleaching effluents are BOD, COD, TOC and Total Volatile Solids. The BOD test measures the portion of the organic content of the effluent, which is oxidizable by microorganisms. The major disadvantages of this test are the long time required for analysis, the poor precision and the inaccuracy of the method. On the other hand, the COD test provides an advantage over the BOD test, as it has greater accuracy, greater precision and requires much less time for analysis. It is a measure of the oxygen equivalent of organic and inorganic substances in waste water, that are susceptible to oxidation by a strong chemical oxidizing agent in an acidic medium.

The TOC analysis is based on the catalytic conversion of the total carbon in the sample to carbon dioxide, which is measured by a non-dispersive infrared-analyser, whereas the inorganic carbon is measured independently in a separate low temperature combustion tube containing an acid-salt catalyst. The total organic carbon is then given by the difference between the total carbon and inorganic carbon. Although this method produces rapid results, reliable and free from many variable effects that confound the BOD and COD tests, it does not differentiate between compounds with the same number of carbon atoms, but which are in different stages of oxidation and, hence, have different oxygen demanding potentials. In addition, as it measures only the carbon portion of a sample, the total organic compound of the sample cannot be estimated directly.

In view of the shortcomings of both the BOD and TOC methods, it was decided that the Total Volatile Solids and COD methods were the most suitable for characterizing and quantifying the organics of bleaching effluents. The volatile solids measurement is based on the sample weight loss on ignition (Rand et al, 1975).

### 6.3.1 - Total Volatile Solids

The volatile solids of the generated D/C effluent were found to be in between the range of 0.70 to 1.00g per litre of effluent, whereas for the mill effluent, it ranged from 0.35 to 0.55g. The high value of volatile solids in the generated D/C effluent may be attributed to the formation of sodium salts which decompose at temperature below 600°C.

The formation of sodium salts is confirmed by the presence of residue solids formed from the results of the evaporation of chlorine water. These residue solids were ignited, and the measured volatile solids were given by the decomposition of inorganic sodium salts, which were found to be in between 0.20 and 0.40g. These values have to be taken into account for the calculation of the exact amount of volatile solids present in the D/C effluent. Hence, the amount of organics present in the generated D/C effluent are between 0.30 and 0.80g as illustrated in Table 5.3.2, which gave the average value of 0.55g of organics per litre of the generated D/C effluent. Major errors in the volatile solids test arose from the wide temperature fluctuation of the muffle furnace and sample weighing. The total error was approximately 11.2%, and the volatile solids of the mill D/C effluent agreed with the generated D/C effluent within experimental error.

For E1 effluent, the volatile solids of the generated effluent ranged from 1500 to 1900mg, whereas the mill effluent provides higher volatile solids i.e., between 2800 and 3200mg per litre of effluent. This may be due to the assumption made in this experiment that the effluent is suspended solids free, which may not hold for the mill effluent, as there is approximately 8% of pulp loss by degradation through the bleach plant, which may have contributed to the high volatile solids.

For D1 effluent, it was found that only a minor amount of organics were present in the generated effluent. The average volatile solids were approximately 25mg per litre of effluent. This was supported by the fact that only 5 to 10% of the original lignin remains in the prebleached pulp, and cannot be removed by extended pulping without seriously degrading the polysaccharide fraction. During the conventional bleaching of a softwood kraft pulp, approximately 7% of material will dissolve from the pulp into the bleaching liquor as illustrated in Table 6.3.1. From most of this

material, 75-90% of organic material is produced in the first D/C and E1 bleaching stages (Kringstad, 1984).

Table 6.3.1:

Yield loss in kg/tonne of pulp in the bleaching of softwood kraft pulp:

<u>Sources of yield loss</u>	<u>Yield loss</u>
Lignin	50
Polysaccharides	19
Extractives	1
Total	70

### Sources of Errors and Variability

The temperature at which the residue is dried has an important bearing on the measured volatile solids of the effluent. This is mainly due to the fact that the weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating. The loss of organic matter by volatilization usually will be very slight. The large temperature fluctuation encountered by the muffle furnace ( $550 \pm 50^{\circ}\text{C}$ ) contributes to an error of approximately 9.1%, whereas the error estimated from evaporating and drying samples in the oven is approximately 1.9% ( $104 \pm 2^{\circ}\text{C}$ ). However, the accuracy in sample weighing contributes very little error i.e., approximately 0.2%. The total estimated error is 11.2%.

Determination of low concentrations of volatile solids in the presence of high fixed solids concentrations may well be subjected to considerable error. The volatile solids method does not distinguish precisely between organic and inorganic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts.

### 6.3.2 - Chemical Oxygen Demand

The COD results for generated D/C and D1 effluent agreed well with the corresponding volatile solids results within the experimental error. The COD of the generated E1 effluent is approximately two times higher than the volatile solids results.

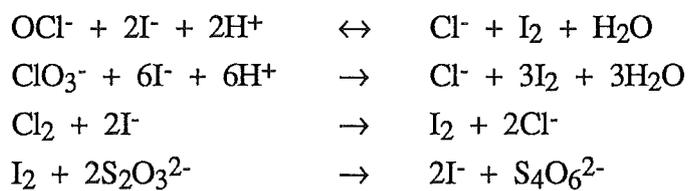
This can be explained by the fact that the generated effluent contains a higher inorganic portion, which consumes extra oxygen, and this is consistent with the volatile solids results of the generated D/C effluent, where a wider range of volatile solids results were encountered. Tables 5.3.1, 5.3.2 and 5.3.3 present data for COD and volatile solids of the effluents concerned.

### 6.3.3 - Active Chlorine Consumption Potential of D/C, E1 and D1 Effluents

The results obtained from the blank tests for all the samples investigated showed the instability of the chlorine water system, with a higher observed residual chlorine compared to the effluent with the same added active chlorine charge. The active chlorine decayed rapidly for the first 200 minutes and gradually reached equilibrium as illustrated in Figures 5.3.1, 5.3.2 and 5.3.3.

The asymptotic curves can be explained by two factors:

- a) There were multiple reactions taking place in the chlorine water system, which caused the variation in the concentration of chlorine species. The chemistry underlying the process was explained in Chapter 2.
- b) The reaction between chlorine species and iodide. The active chlorine was measured by the indirect iodometric titration method, where iodide was oxidized by chlorine species to iodine, and it was then reduced back to iodide by thiosulphate ion. The total concentration of chlorine species remained constant at equilibrium. The chemistry of the process is as follows:



Parallel to the blank test for each set of effluents, sample experiments were carried out under the same conditions as the corresponding blank tests. It was found that the residual chlorine results were lower than the results of the corresponding blank test as illustrated in Figures 5.3.1, 5.3.2 and 5.3.3.

In this study, both the blank and the corresponding sample systems were assumed to have achieved equilibrium at time 1000mins, and the actual consumption of

active chlorine by organics was given by the difference of residual chlorine between the blank and the sample i.e.,  $\Delta x$ , as shown in Figure 5.3.1.

By analysing the data collected, the results showed that process effluents have a 'chlorine demand' of their own. This justified the findings of Shera, 1968 and Sprout et al, 1947. The extent of chlorine consumption by organics in D/C, E1 and D1 bleaching effluents resulting from the bleaching of Pinus Radiata pulp has not been measured quantitatively. The generated D/C effluent was found to consist of 18kg of volatile solids per tonne of O.D. prebleached pulp. (Each kilogram of D/C volatile solids from the generated effluent consumed approximately 0.33kg of active chlorine, which is 14% higher than the value obtained from the mill effluent.)

The dissolution of organic material in the alkaline extraction stage was 17kg per tonne of O.D. pulp. The dissolved organic material is believed to be mainly lignin degradation products of high molecular mass. One kilogram of the E1-stage organics consumes 0.2kg of active chlorine, and this value is 30% higher than the value analysed from the mill data. (Both of the D/C and E1 effluents generated from bench scale bleaching experiments indicated higher uptake of active chlorine compared to the corresponding mill effluents. This may be caused by chemical changes, which occur with ageing due to the delay during transportation of effluent samples from Kinleith mill to Christchurch.)

A test on D1 effluent indicated only a minor concentration of volatile solids as shown in Table 5.3.3. Therefore, it is assumed that chlorine consumption by D1 organics would be negligible compared with D/C and E1 filtrates.

#### 6.4 - The Effect of Temperature on Active Chlorine Consumption by Organics of D/C Bleaching Effluent

From both Figures 5.4.1 and 5.4.2, it was obvious that an increase in temperature from 30 to 70°C resulted in a decrease of residual chlorine throughout the time period investigated. For the chlorine-water system, raising the temperature of the system caused a shift to the right of the following equilibrium reaction, which produced more active chlorine species, i.e., HOCl.



The main effect of higher temperature in the chlorination is reported to be an increase in the rate of chlorine consumption with respect to lignin removal, which is doubled for an increase of about 8°C (Rydholm, 1965). In this study it was found that

with a fixed application of chlorine charge on generated D/C chlorination effluent, the consumption of active chlorine by D/C dissolved organics first increased then decreased with increasing temperature as illustrated in Figure 5.4.3. The maximum consumption of active chlorine by D/C organics occurred at temperature 50°C. This finding could probably be of technical value for optimising temperature with respect to bleaching agent, and steam consumption for total mill closure conditions.

The observed trend of decreasing active chlorine consumption thereafter at still higher temperature, could be attributed to the reversible effect of chemical reactions between the chlorine and the organics. High temperature appeared to inhibit the chlorination reaction. This phenomenon requires further investigation.

## **6.5 - Computer Simulation of No.2 Bleach Plant**

### **6.5.1 - Effect of closing the chlorination stage and the extraction stage of existing NZFP No.2 bleach plant**

One of the most effective in-plant strategies to reduce soda, fiber and dissolved lignin contaminants in effluent is greater reuse or recycling of mill process water. The effects of a closed water system can be studied only when the filtrate has achieved a state of equilibrium. Favourable impacts on effluent properties are reduction in colour, BOD, COD, TOC, TOCl, toxicity, mutagenicity and production of chlorinated organics.

There are a few practical limitations on the degree of "closure" caused by build up of temperature and impurities such as chloride ion and organic load. The results of the active chlorine consumption potential by the D/C-stage and E1-stage organics from the previous Experiment 3.3, were incorporated in the computer model for the simulation of partial and total closure cases. It was found that each kilogram of the D/C-stage and E1-stage organics, consumed 0.33kg and 0.20kg of active chlorine, respectively. The active chlorine added to the pulp in the laboratory study was solely from chlorine water. It can be seen from Table 5.5.1 that the closure of both the D/C and E1 stages caused an increase in the concentration of dissolved solids subspecies, i.e., the organics of D/C, E and D stages, which increased in the acid effluent overflow stream (stream 16, Figure 4.2). The sum of total individual species was also increased. The results also confirmed the fact that closed E1-stage with open D/C-stage, incurred only a slight increase in the total dissolved solids with most of the dissolved solids attributed to the D/C-stage organics, as tabulated in Table 5.5.1.

The utilities investigated were steam, water and bleaching chemicals. The total steam usage for each case was the sum of all the steam calculated in each STMIX block of the computer models, whereas the water usage was calculated from the sum of all the corresponding input water streams. Only the oxygen and chlorine consumption were adjusted, whereas the caustic soda and chlorine dioxide consumption were assumed to remain unchanged for all the cases. The oxygen adjustment to the D/C-stage and E-stage organics was made according to the rule of thumb used by Edwards, i.e., one kilogram of each D/C- and E-stage organics consumes 0.5kg of extra oxygen. These values of oxygen adjustment were based on the results from stream 30, Figures 4.1 & 4.2 for all the cases investigated. As for the chlorine usage, the total chlorine required was taken to be the amount added to the D/C-stage (stream 7, Figures 4.1 & 4.2) together with the extra amount consumed by both the D/C- and E-stage organics.

The unit costs of chemicals, water and steam were quoted from an internal technical report of NZFP Technology Limited, 1988. These values were assumed for a 100% concentration basis and are presented in Table C.1. The yearly estimation of utilities consumption for all the cases was based on 340 operating days per year and 288 tonnes of O.D. unbleached pulp per day. The temperature of the D/C tower increased from 24 to 27.4°C due to the recycled enthalpy in the acid effluent. The Cl<sup>-</sup> ion build up was estimated based on the stream variable Cl<sup>-</sup> of stream 14, Figures 4.1 & 4.2 for all the cases investigated.

### 6.5.2 - Economic Analysis

The values in Table 5.5.3 showed that the partial closure of D/C-stage, open E1-stage for both 100 and 50% D/C filtrate recycled, and the partial closure of E1-stage with open D/C-stage were less economic than the total closure case. The annual saving in utilities for total mill closure was estimated to be approximately NZ\$0.2 million, compared to the open case. This is mainly due to the fact that saving in steam and water consumptions override the cost of extra bleaching chemicals incurred due to the dissolved organics build up in the bleach plant.

However, it was found that the concentration of Cl<sup>-</sup> ion for the total closure case increased adversely i.e., approximately 9 times more than the concentration of the open case, as shown in Table 5.5.2. The effect of Cl<sup>-</sup> ion concentration on the corrosion aspect was not investigated. If this aspect is judged to be significant, then appropriate protection would need to be considered as part of the civil works cost component for the project.

Some saving of fresh caustic would be expected due to excess unreacted caustic recycled in the E1-stage effluent. This aspect was not investigated or taken into account in the closed case model.

## 6.6 - Computer Simulation of No.2 Bleach Plant Expansion

The objective of expanding and upgrading the existing No.2 bleach plant is to increase the production of market grade bleached kraft softwood pulp, with the intention of reducing utilities consumption, and volume of bleaching effluent due to the recycling of liquors. The reuse of bleach plant filtrates is a common practice in any modernization, not only to save water and heat but also to improve the bleaching process. This is no exception for the modernization of the existing NZFP No.2 bleach plant, as the study showed that the reuse of D2 and E<sub>0</sub> stage filtrates enabled a reduction in fresh water and steam consumption compared to the case of the existing bleach plant. Annual savings from the decreased utilities (steam & water) consumption amounts to approximately NZ\$1.04 million based on the unbleached pulp capacity of 288 O.D. tonnes per day.

The total steam usage was the sum of all the steam calculated in each STMIX block of each parallel E<sub>0</sub>-D2 sequence (Figure 4.3). As for fresh water usage, there was only one fresh water shower temperature of 42°C to each of the D2 reaction towers (streams 35 & 53, Figure 4.3).

This bleach plant expansion using 3-stage short bleaching sequences necessitates a greater degree of chlorine dioxide substitution in the first stage. In this study, the simulation of the 100% sequential replacement by chlorine dioxide at the first D1-stage was carried out. However, as the laboratory studies on chlorine dioxide bleaching and the chlorine dioxide consumption potential of both D- and E-stage organics were not conducted, the extra amount of chlorine dioxide consumed by these organics cannot be estimated, and also the oxygen adjustment cannot be made to account for the extra amount consumed by the organics. Both the values of D- and E-stage organics tabulated in Table 5.6.1 were based on the values given by streams 11 & 14, Figure 4.3. These two streams were assumed to have achieved a state of equilibrium. The caustic soda consumption was calculated from the summation of all the input streams i.e., streams 19, 29, 37 and 47, Figure 4.3.

The extraction stage filtrate yields the greatest source of water pollutants from the bleach plant. If this filtrate is used on the first D1-stage showers, and if some of it

passes through the sheet, severe foaming can occur and a general upset of the chlorine dioxide stage can result. Therefore only limited amounts of E<sub>O</sub> filtrate can be used and this requires further investigation. Moreover, the build up of the dissolved solids concentration can be so high that poor washing and filtrate carryover into the next stage can result. This can be avoided by maintaining adequate fresh water on the showers of the second stage i.e., D2-stage.

The temperature at both D1 and D2 towers was found to increase approximately 6.5°C due to the recycling of the D2-stage and E<sub>O</sub>-stage filtrates, which caused the accumulation of recycled enthalpy. The assumed heat of reaction i.e., 3000kcal/kg of pulp incorporated in the computer model requires further investigation. If this amount is reasonable, then the removal of the excess heat generated in the D1 and D2 towers is necessary to protect further pulp degradation.

## 6.7 - Approaches to Future Work

The relatively open attitude of the paper industry in the past has allowed an evolution of technology resulting in substantial improvements. The industry needs to attack its problems on many fronts. As the present bleaching process continues to be used, there should be a search for opportunities to improve and modify it to make it more effective in meeting future needs.

Further investigations should be undertaken to improve the robustness of the GEMS computer simulation of the revamped No.2 bleach plant. Firstly, more laboratory studies on the chlorine dioxide and oxygen consumption potential of D-stage and E-stage organics are required. Secondly, the effect of temperature may have very important impact on the consumption rate of bleaching chemicals by effluent organics. This temperature dependency observed in Experiment 3.4 showed that the maximum rate of active chlorine consumed by the D/C-stage organics occurred at approximately 50°C. The rate decreased below and above this temperature.

Thirdly, in view of the importance of the heat release from the reaction between pulp and chlorine dioxide affecting the temperature in the reaction tower, the assumed value i.e., 3000kcal/kg pulp, needs to be justified. This again requires a laboratory study to be conducted specifically for Pinus Radiata kraft pulp.

Fourthly, a more precise way of characterizing the organics of bleaching effluents should be encouraged. The conventional method of characterizing bleaching

effluents such as COD may not fully include the total chlorine bound organics, as it relates only to the amount of oxygen required in the receiving water to react with the effluent, whereas recently, the total organically bound chlorine measurement has been proposed by Swedish environmental authorities as a monitoring and pollution control parameter. The aim of the TOCl test is to account for all the chlorine that has reacted with lignin to form chlorinated organic material. This test involves extensive sample preparation and does measure highly volatile chlorinated organics such as chloroform.

Alternatively, the AOX (adsorbable organic halide) test has also been considered as a regulatory guideline. This test involves no storage of liquor, it is not specific for chlorine, but it does encompass any halide such as, fluoride, chloride, bromide, or iodide. Therefore, both of the above suggested methods should be looked into for future characterization of bleach plant effluent.

Finally, although analytical and simulation technologies have made giant steps over the last decade, this study seems to have highlighted certain drawbacks in the existing tool when it comes to defining and simulating bleach plant chemistry. The increase of internal recycle in a pulp and paper mill can reduce energy costs, and the volume of effluent streams, it also results in higher temperatures and chemical concentrations, as discussed in section 6.5.1. These changes affect the rates of chemical reactions occurring within the mill such as, the reactions between the bleaching chemicals and pulp, and corrosion rate of the process equipment. It would be very useful to be able to predict how these reactions are affected at different levels of internal recycling. GEMS, a modular material-and-energy-balance software program does not account for chemical equilibria. It is not designed to provide the information required to formulate these predictions. Accurate predictions of chemical concentrations are needed to estimate the kinetics of bleaching reactions (Edwards et al, 1973, Ackert et al, 1975 and Germgerd, 1979).

The prediction of corrosion rates for process equipment also requires estimates of pH, temperature, and concentrations of chlorine and chloride ion (Rushton et al, 1980 and Beetham, 1986). Therefore, the present GEMS computer software package requires to be modified to enable the modeling of the interconversions of chemical species that are described by equilibrium relationships. The simulation results can then be used to estimate the initial kinetics of the chlorination reaction, or the corrosivity of process streams at various recycle ratios.

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# Appendix

## A - Raw Data

### A.1 - The Evaluations of the Effect of Chlorine Charge on Pulp Properties for zero & 100% D/C Filtrate Recycling

Table A.1.1: Effect of active chlorine charge on pulp brightness

% Active Cl on O.D. pulp	Brightness ( % ISO )	
	% D/C filtrate 100	0
1.71	31.30	
2.84	32.33	
3.98	34.88	34.47
5.12	38.33	39.52
5.69	39.49	43.08
* 6.26	42.33	44.45
6.82	44.33	44.09
7.39	47.97	45.80

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\* Current active chlorine charge at No.2 bleach plant, Kinleith.

Pulp Kappa number = 28.43

% active chlorine = 0.22 x Kappa number

Table A.1.2: Effect of active chlorine charge on pulp extract Kappa number

% Active Cl on O.D. pulp	Extract Kappa No.	
	% D/C filtrate	
	100	0
1.71	6.12	
2.84	6.18	
3.98	5.96	6.36
5.12	5.38	4.74
5.69	4.92	3.99
*6.26	3.78	3.56
6.82	3.38	3.45
7.39	2.93	

Table A.1.3: Effect of active chlorine charge on residual chlorine of D/C filtrate

% Active Cl on O.D.pulp	Residual Cl ( g/l )	
	% D/C filtrate	
	100	0
1.71	0.089	
2.84	0.086	
3.98	0.030	0.011
5.12	0.018	0.017
5.69	0.016	0.019
*6.26	0.019	0.022
6.82	0.041	0.020
7.39	0.062	0.037

Table A.1.4: Effect of active chlorine charge on COD of D/C filtrate

% Active Cl on O.D. pulp	COD ( mg/l )	
	% D/C filtrate	
	100	0
1.71	228.32	
2.84	246.27	
3.98	277.23	64.06
5.12	384.90	275.00
5.69	388.08	275.07
*6.26	499.50	437.09
6.82	447.48	113.04
7.39	566.94	145.07

Table A.1.5: Effect of active chlorine charge on TOC of D/C filtrate

% Active Cl on O.D. pulp	TOC ( mg/l )	
	% D/C filtrate	
	100	0
1.71	237.94	
2.84	267.50	
3.98	292.16	138.14
5.12	313.81	196.13
5.69	299.21	226.92
*6.26	321.19	236.54
6.82	345.49	231.47
7.39	402.29	246.63

**A.2 - The Effect of Various Levels of Fresh Water  
Replacement by D/C Filtrate on Pulp Properties**

Table A.2.1

% distilled water	% D/C filtrate	Residual Cl (g/l)	Extract Kappa No.	Brightness (% ISO)
100	0	0.01	3.72	43.55
75	25	0.02	3.97	42.30
50	50	0.03	3.71	42.49
25	75	0.05	3.88	42.16
0	100	0.06	4.15	41.13

### A.3 - The Investigation of Active Chlorine Consumption Potential of Organics in Bleaching Effluents

Table A.3.1

Time (min)	Blank Residual Cl (g)	Sample A Residual Cl (g)	Sample B Residual Cl (g)
0.00	1.58	1.58	1.58
5.00	1.22	0.89	0.93
10.00	1.01	0.80	0.78
15.00	0.93	0.75	0.73
20.00	0.86	0.65	0.62
25.00	0.80	0.59	0.56
30.00	0.75	0.53	0.50
35.00	0.70	0.47	0.46
40.00	0.67	0.42	0.43
45.00	0.64	0.39	0.40
50.00	0.61	0.35	0.35
55.00	0.58	0.35	0.36
60.00	0.57	0.30	0.32
80.00	0.53	0.28	0.27
100.00	0.49	0.20	0.25
120.00	0.47	0.22	0.22
180.00	0.41	0.18	0.18
240.00	0.37	0.15	0.15
400.00	0.32	0.11	0.12
600.00	0.28	0.08	0.10
800.00	0.26	0.07	0.08
1000.00	0.24	0.06	0.07
1200.00	0.23	0.06	0.06
1400.00	0.22	0.05	0.06

Experimental conditions:

Active chlorine: 1.58g, Sample A denotes generated effluent.  
 Type of Effluent: D/C, Sample B denotes mill effluent.  
 Temperature: (50.0 ± 1.0)°C

Table A.3.2

Time (min)	Blank Residual Cl (g)	Sample-D Residual Cl (g)	Sample-C Residual Cl (g)
0.00	5.73	5.73	5.73
5.00	3.40	2.47	2.42
10.00	3.12	1.98	1.97
15.00	2.82	1.52	1.67
20.00	2.55	1.26	1.41
25.00	2.40	1.08	1.27
30.00	2.27	0.93	1.12
35.00	2.04	0.70	0.96
40.00	2.00	0.69	0.91
45.00	1.80	0.51	0.79
50.00	1.82	0.52	0.76
55.00	1.64	0.39	0.67
60.00	1.64	0.41	0.65
80.00	1.33	0.23	0.49
100.00	1.21	0.16	0.39
120.00	1.04	0.11	0.31
180.00	0.76	0.06	0.20
240.00	0.80	0.06	0.20
400.00	0.63	0.03	0.13
600.00	0.51	0.02	0.09
800.00	0.44	0.01	0.07
1000.00	0.40	0.01	0.06
1200.00	0.36	0.01	0.05
1400.00	0.34	0.01	0.05

Experimental conditions:

Active chlorine: 5.73g  
Type of Effluent: E1  
Temperature: (70.0 ± 1.0)°C  
Sample C: Effluent generated from bench scale bleaching.  
Sample D: Mill effluent from E1 seal tank.

Table A.3.3

Time (min)	Blank Residual Cl (g)	Sample E Residual Cl (g)
0.00	1.58	1.58
5.00	1.21	0.83
10.00	0.99	0.70
15.00	0.92	0.61
20.00	0.84	0.43
25.00	0.78	0.43
30.00	0.73	0.38
35.00	0.68	0.32
40.00	0.64	0.31
45.00	0.59	0.25
50.00	0.55	0.26
55.00	0.53	0.21
60.00	0.51	0.19
80.00	0.45	0.15
100.00	0.41	0.12
120.00	0.38	0.10
180.00	0.32	0.07
240.00	0.29	0.05
400.00	0.23	0.03
600.00	0.19	0.02
800.00	0.17	0.02
1000.00	0.16	0.01
1200.00	0.15	0.01
1400.00	0.14	0.01

Experimental conditions:

Active chlorine: 1.58g

Type of Effluent: D1

Temperature:  $(70.0 \pm 1.0)^{\circ}\text{C}$ 

Sample E: Effluent generated from bench scale bleaching

**A.4 - The Effect of Temperature on Active Chlorine  
Consumption by Organics of D/C Bleaching Effluent**

Table A.4.1

Time (min)	Temperature (°C)			
	30	50	60	70
0.00	1.58	1.58	1.58	1.58
5.00	1.11	0.89	0.87	1.14
10.00	1.05	0.80	0.76	0.82
15.00	0.96	0.75	0.67	0.62
20.00	0.88	0.65	0.56	0.50
25.00	0.79	0.59	0.52	0.44
30.00	0.75	0.53	0.45	0.37
35.00	0.69	0.47	0.39	0.34
40.00	0.64	0.42	0.34	0.30
45.00	0.62	0.39	0.31	0.27
50.00	0.56	0.35	0.28	0.25
55.00	0.57	0.35	0.29	0.24
60.00	0.55	0.30	0.25	0.21
80.00	0.49	0.28	0.23	0.18
100.00	0.38	0.20	0.17	0.16
120.00	0.41	0.22	0.18	0.14
180.00	0.35	0.18	0.14	0.11
240.00	0.31	0.15	0.12	0.09
400.00	0.25	0.11	0.08	0.06
600.00	0.21	0.08	0.06	0.05
800.00	0.18	0.07	0.05	0.04
1000.00	0.17	0.06	0.05	0.03
1200.00	0.16	0.06	0.04	0.03
1400.00	0.15	0.05	0.04	0.03

Experimental conditions:

Active chlorine: 1.58g

Type of effluent: D/C

Table A.4.2

Time (min)	Temperature ( °C )			
	30	50	60	70
0.00	1.58	1.58	1.58	1.58
5.00	1.13	1.22	1.24	1.21
10.00	1.07	1.01	1.03	0.99
15.00	0.98	0.93	0.96	0.92
20.00	0.92	0.86	0.90	0.84
25.00	0.86	0.80	0.84	0.78
30.00	0.82	0.75	0.78	0.73
35.00	0.75	0.70	0.73	0.68
40.00	0.72	0.67	0.69	0.64
45.00	0.72	0.64	0.64	0.59
50.00	0.66	0.61	0.62	0.55
55.00	0.68	0.58	0.60	0.53
60.00	0.63	0.57	0.58	0.51
80.00	0.57	0.53	0.52	0.45
100.00	0.57	0.49	0.48	0.41
120.00	0.54	0.47	0.45	0.38
180.00	0.49	0.41	0.40	0.32
240.00	0.45	0.37	0.36	0.29
400.00	0.38	0.32	0.30	0.23
600.00	0.34	0.28	0.26	0.19
800.00	0.32	0.26	0.23	0.17
1000.00	0.30	0.24	0.22	0.16
1200.00	0.28	0.23	0.20	0.15
1400.00	0.27	0.22	0.19	0.14

Experimental conditions:

Active chlorine: 1.58g

Blank tests: Chlorine water system at different temperatures.

Table A.4.3: Active chlorine consumption potential of generated D/C effluent at different temperature levels.

Temperature (°C)	Active chlorine consumption (g/l)
30.00	0.126
50.00	0.175
60.00	0.168
70.00	0.125

Experimental conditions:

Active chlorine (g)	1.58
Sample vol. (mls)	1000
Temperature levels (°C)	30, 50, 60 & 70

## **B - Analytical Reagent Preparation**

### **B.1 - Starch Indicator**

Boil approximately 900 ml of distilled water in a 2 litre beaker. Weigh out, into a small tared beaker, 10g of soluble starch and 1g of salicylic acid. Add a small volume of luke warm distilled water and gently stir until the starch becomes a smooth paste. Carefully add the contents of the beaker to the boiling water and allow the solution to boil gently for about 5 minutes. Make up to approximately one litre when cool.

### **B.2 - Potassium Iodide (KI)**

Add 166g of laboratory grade chemical into a tared beaker. Add this to a one litre volumetric flask and after thorough mixing, make up to the mark.

### **B.3 - 4N Sulphuric Acid**

Carefully measure out 112ml of concentrated sulphuric acid into a measuring cylinder (250ml). Place a 2 litre beaker into a sink half full of cold water, and to the beaker add approximately 750ml of cold distilled water. Slowly and carefully (wearing safety glasses or safety face mask) add the 112ml of concentrated sulphuric acid while stirring. After the solution has cooled sufficiently, add the contents of the beaker to a one litre measuring cylinder and use distilled water to rinse out the beaker, and make the measuring cylinder up to the one litre mark. (Sulphuric acid container will hold 5 litres, so usually make up 4 litres of 4N at a time).

### **B.4 - 0.2N Sodium Thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ )**

Weigh out 49.64g of A.R. sodium thiosulphate crystals and dissolve in boiled-out distilled water, and make up to one litre in a graduated flask with boiled-out water. If the solution is to be kept for more than a few days, add 0.1g sodium carbonate or 3 drops of chloroform. For 5 litres stock, (49.64 x 5)g required.

#### **B.4.1 - Standardization of 0.2N Sodium Thiosulphate Solution**

Transfer all the contents of the Dr Shilling burette into the stock container and mix thoroughly. Fill the burette. Take 3 clean conical flasks (250ml), pipette exactly 50.0ml of 0.1N  $\text{KIO}_3$  into each flask. Add about 2g of KI (2 spatulas full) into each flask. Pipette about 3ml of 4N  $\text{H}_2\text{SO}_4$  into the flasks. Titrate each with the sodium

B-2

thiosulphate solution to a pale yellow colour. Add a few drops of starch indicator and continue the titration to a colourless end-point (approximately 25ml).

Equivalent wt. = 248.2

$$\text{Normality of Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = \left( \frac{0.1\text{N KIO}_3 \times 50.0}{\text{titre}} \right)$$

### B.5 - 0.1N Potassium Iodate (KIO<sub>3</sub>)

Weigh accurately 7.1334g of the A.R. salt which has been previously dried at 120°C, for a few hours. Dissolve in 2dm<sup>3</sup> water in a graduated flask.

Equivalent wt. = 35.6667

$$\begin{aligned} \text{Amount required} &= 0.0001\text{N} \times 2.0000 \text{ litre} \times 35.6667 \\ &= 0.71334\text{g} \end{aligned}$$

### B.6 - 1.0N Potassium Permanganate (KMnO<sub>4</sub>)

To make 1 litre of 1.0N KMnO<sub>4</sub>, weigh approximate 33g of potassium permanganate into a tared beaker. Transfer into a 1500ml beaker with 1 litre of water. Cover with a watch glass and bring to boil. Simmer for 15 to 30 minutes. Allow to cool to room temperature, and filter through a clean glass crucible. Store in a dark brown bottle. Dilute by 10 times and standardize for Kappa Number test.

#### B.6.1 - Standardization of 0.1N Potassium Permanganate

Dry some A.R. sodium oxalate at 105°C for at least 2 hours. Allow to cool in a dessicator. Weigh out approximately 0.17g of the sodium oxalate into a small 10ml beaker and carefully transfer into a clean 250ml flask, rinsing the beaker of all its contents into the flask. Add approximately 25ml of 4N sulphuric acid into the 250ml sodium oxalate solution. Titrate the solution with the permanganate from a burette. After about 10ml have been added, heat the solution to about 60°C over a bunsen or hot plate (the colour will disappear). Complete the titration by adding more permanganate until a faint pink persists for 30 seconds. Repeat the above, twice more to obtain an average normality - must be between 0.0995 and 0.1005.

Equivalent wt. of sodium oxalate = 67.01

$$\text{Normality of KMnO}_4 = \left( \frac{\text{sodium oxalate wt.}}{67.01} \right) \times \left( \frac{1000}{\text{titre}} \right)$$

\* For a less accurate but quicker determination, weigh out 1.7g exactly of the dried oxalate and transfer into a 250ml volumetric flask, make up to the mark after dissolving all the oxalate. Use 25ml of this solution per titration and add 25ml of 4N H<sub>2</sub>SO<sub>4</sub>. Carry out the titration as of above. If this is used, the following calculation is used:

$$\text{Normality of KMnO}_4 = \frac{(\text{sodium oxalate wt./10})}{67.01} \times \left( \frac{1000}{\text{titre}} \right)$$

NB: Permanganate may have to be strengthened or weakened.

### **B.7 - Sodium Hydroxide (100g/l)**

Weigh out 100g of pellets of sodium hydroxide and transfer it into a 1500ml beaker, covered and allow to stand, the carbonate remains insoluble; the clear supernatant liquid is then transferred into a one litre volumetric flask, and made up to the mark.

### **B.8 - Residual Chlorine Test**

This method is used by NZFP technical laboratory to determine the residual chlorine, and is a modification of the test for available chlorine in sodium hypochlorite.

#### **Apparatus**

Erlenmeyer flask with stopper 250ml

Measuring cylinders 100ml and 50ml

Wash bottle

Pipettes 5ml and 10ml

#### **Reagents**

Potassium Iodide solution, 1.0M (160g/l)

Sulphuric acid, 1.0M (2N)

Sodium Thiosulphate approximately 0.2M, standardized to within  $\pm 0.0005N$ .

Starch indicator solution, 0.2%

### Procedure

Transfer 25ml of KI into an Erlenmeyer flask. Pipette a known amount of aliquot into the flask. Add 40ml of 2N H<sub>2</sub>SO<sub>4</sub>, and titrate with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> until the solution is pale yellow. Add starch indicator and continue titrating until clear.

### Calculation

$$(\text{Titre}) \times (\text{Normality of Na}_2\text{S}_2\text{O}_3) \times \frac{35.45}{(\text{Sample volume})} = \text{active Cl (g/l)}$$

### B.9 - Derivation of Initial Active Chlorine Charge to be added to D/C Effluent for Purpose of Determining Chlorine Consumption by Organics

In experiment 3.3.1, the amount of active chlorine added to the D/C filtrate i.e., 1.58g, was derived from the results predicted by the computer model of the closure of No.2 bleach plant as illustrated in Figure 4.2.

According to the prediction of the model, the maximum amount of D/C-stage effluent generated from the bleach plant was 484.77Mt/hr (stream 15), and the amount of recycled effluent was based on the total fresh water substitution, which was the sum of 243.31 and 180Mt/hr, respectively, for both streams 16 & 71, Figure 4.2. The active chlorine addition to the unbleached pulp at the D/C-stage was of the multiple of 0.22 x Kappa number, and was based on the air dry (AD) pulp.

$$\text{Production rate of prebleached pulp} = 320 \text{ AD tonnes pulp} = 222.22\text{kg/min}$$

$$\text{Total \% of active chlorine added} = 5\% = 11.11\text{kg/min}$$

$$\text{Total D/C effluent recycled} = (180 + 243.31) = 423.31\text{Mt/hr}$$

$$\text{The specific gravity of D/C effluent is assumed} = 1$$

$$\text{Therefore, total D/C effluent recycled} = 7055.17 \text{ litres/min}$$

$$\text{Basis} = 1 \text{ minute}$$

11.11kg of active chlorine was added to the D/C chlorination stage and generates 7055.17 litres of D/C recycled effluent.

Hence, 1.58g of active chlorine is added for each litre of D/C effluent generated. This provided a starting point for the experiments.

For the determination of active chlorine consumption by E1-stage and D1-stage organics, arbitrary amounts of chlorine i.e., 5.73g were added to both the E1 and D1 effluents. This was judged by experience and initial trials to be sufficient excess for more detailed experimental determination.

## C - Current Cost of Bleaching Chemicals & Utilities

Table C.1

Utilities & Chemicals	Unit Cost (\$ / tonne)
steam	20.00
water	0.06
oxygen	250.00
chlorine	280.00
chlorine dioxide	2000.00
sodium hydroxide	900.00

\* The unit cost of chemicals are based on 100% concentration basis.

## D - Sodium Sorption

When the liquor systems in a mill are closed, the concentration levels of the circulating liquors are increased. Consequently, the amount of the various cations sorbed on to the pulp will also be increased. The liquor systems in a kraft pulp mill generally contain Mg, Ca and Na ions. The concentrations of these ions in the various liquor streams, in a pulp mill can be predicted by the understanding of sorption phenomena that takes place between the fibres and the surrounding liquors.

Good washing is the key to a successful closure of the water system in a pulp production line. It was well recognized that the washing of pulp fibres is a highly complex phenomenon involving interfiber mass transfer, diffusion, and adsorption mechanisms.

The adsorption of sodium on kraft pulp fibers during washing plays a significant role in the pulp washing process, and it can be the direct cause of almost half the total sodium losses in a well run wash plant. It was reported that the quantity of sorbed sodium is influenced only by the type of pulp, the degree of cooking, and the pH leaving the washers, and cannot be affected by changing wash water flow, water quality, or washing temperature.

When the pulp is washed in the wash plant and in the screen room, the sodium component tends to desorb to an extent, described largely by the Langmuir adsorption isotherm (Hartler et al, 1975). This desorption effect was speculated to have resulted from a shift in the equilibrium between the sodium bound by the carboxyl groups in the pulp and the sodium in the wash water. The Langmuir sorption isotherm is given by:

$$S = \frac{ABC_{Na}}{1+BC_{Na}} \quad (1)$$

Where:

$S$  = amount of sorbed Na (mg Na/g O.D. pulp)

$C_{Na}$  = concentration of Na in the surrounding liquor (mg/l)

$A$  = maximum amount of sorbed Na (mg Na/g O.D. pulp)

$B$  = a constant (l/mg)

The constants  $A$  and  $B$  reflect a specific property of the particular pulp tested at a particular pH. These two values that are currently incorporated in GEMS computer software package i.e.,  $A=2.4$ ,  $B=53$  are not specific for *Pinus Radiata* kraft pulp, hence the intent of this study is to establish these values. This can be achieved by experiment. However, this work was not accomplished due to lack of time. An outline of the design of experiments follows for future reference.

### D.1 - Experiment

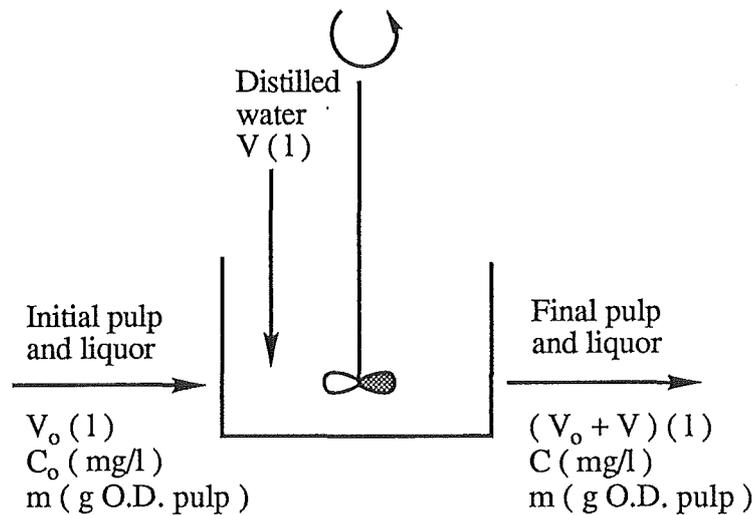
Batches of a litre of pulp samples of approximately 10% consistency, and of different Kappa number are collected from both the brown stock decker washer, and at the exit of high density storage tank. The pulp Kappa number and pH are determined prior to the experiment. Without squeezing the pulp, 100ml of the filtrate is collected from each batch for initial sodium concentration analysis by flame spectrophotometry.

The initial consistency of the pulp is determined by drying the pulp at 105°C. This enables the measurement of pulp O.D. weight and the initial volume of liquor. The O.D. pulp sample is then rediluted to the measured initial consistency, prior to further dilution to various degrees with distilled water. The amount of distilled water added for each dilution is recorded.

The pulp suspensions are then stored in polyethylene flasks for 48 hours to allow equilibrium to be reached. The process is assisted by shaking the flasks periodically. After each dilution, the pulps are dewatered by using a buchner funnel to approximately 10% consistency, before drying the pulp mat at 105°C. The collected filtrate is again analysed with respect to sodium. Duplicate experiments are performed for each dilution.

## D.2 - Theory

The washing stage is shown schematically as follows:



**Figure D.1 - Schematic drawing of dilution washing stage**

A simple material balance for a dilution and washing stage gives the following expression for the equilibrium concentration:

$$V_o C_o = (V + V_o) C \quad (2)$$

This simple material balance for this operation predicts that, the concentration of the dissolved components decreases in inverse proportion to the increase in liquor volume. However, in most cases the final concentration is higher than calculated. This is assumed that the desorption phenomenon plays an important effect, and it should be taken into account. Thus, if the sorption term in equation (1) is included, the material balance for the washing stage becomes:

$$V_o C_o + \frac{mABC_o}{1+BC_o} = (V+V_o) C + \frac{mABC}{1+BC} \quad (3)$$

Where:

$V_o$  = Initial volume of liquor (l)

$C_o$  = Initial concentration of sodium (mg/l)

$m$  = pulp O.D. weight (g)

$V$  = Volume of distilled water added for dilution (litre)

$C$  = Final concentration of sodium (mg/l)

The equation (3) can be arranged with the concentration  $C$  as the subject, i.e.,  $C = f(V_0, V, A, B, m)$ , where the desired parameters  $A$  and  $B$  remain unknown. These two parameters for each pulp Kappa number can be determined from the experimental data, using a computer program for non-linear regression analysis (Hartler et al, 1975). Finally, the parameter  $A$  and  $B$  will be the average values of  $A$  and  $B$  calculated from each pulp Kappa number.

## E - GEMS Computer Programs

### E.1 - No.2 Bleach Plant Simulation, Open Case (existing bleach plant model)

NO2 BLEACH PLANT SIMULATION 6/12/89 OPEN CASE

```
100 200 1 0 10000/LOOPS,MAXERR,IREAD,NFILE,NPRINT
2 0 0 60 0 0 0/KOP,KPORT,KPWIDE,NRLINE,IBUG,IDCHK,IFPR
0 0 0/DYNA,MACRO,INCRA,IPL0T
0 0 10000 1 -150 0/KEND,ITSTRT,IAUTO,FACT1,FACT2
0/NSACC
.01/DELS
41 74 27 15/NEB,NSN,NSVS,NEP
4 4 15 15 1 3 2 0 /II,JJ,KK,LL,ILIQ,ITEM,IPULP
13 12 0 0 0 10 11 0 0 14/INA,IOH,IDIS,IS2,ISO4,ICL,ICLA,IMG,IK,ICO3
0 0 0 0 0 0 0 0/ISO3,IHSO3,IS2O3,ICAO,ICACO3,ICAOH2,ICASO4,IINERT
0 0 0 0 0 0 0/IPR,IKAP,ID1,ID2,ID3,ID4,ID5
0 0 0 0 15 0 0 0 0 0 0/IAIR,IWV,IN2,ICO2,IO2,ITWB,ITDP,IPII,IW,IH,IV
0 0 0 0 0 0 0 0 0 0/IGT,IGPR,INS,INC,INCL,ISO2,ITRS,IHCL,ICO,ICH4
/
/
/
```

1/ Pulp from N0.5 & 6 HD tank is diluted to 3.45% consistency, sorption.

MIXER

```
1 2 16 -3 / STREAM ORDER
0 3 0 / EQUIPMENT PARAMETERS
```

2/ 0.67% ClO<sub>2</sub> addition based on the AD pulp, sorption.

MIXER

```
3 5 -4 /
0 2 0 /
```

3/ Chlorine gas and chlorine water are mixed, further dilution to 2.84% consistency,

MIXER / sorption in, no sorption out.

```
4 6 7 72 -8 /
0 4 3 /
```

E-2

4/ No sorption, existing target pH 1.9, 100% of black liquor & C-Orgs

REACT / convert to Oxidised-Orgs.

8 -9 /

0 0 1 1.9 0 0 7 8 7 4 0 /

5/ 47% ClO<sub>2</sub> convert to C-Orgs, 100% of E-Orgs convert to Oxidised-Orgs.

REACT

9 -10 /

0 0 1 1.9 0 0 4.47 9 7 5 /

6 / 100% ClO<sub>2</sub> (i.e., 53% of the ClO<sub>2</sub> residual) converts to Cl<sup>-</sup> and

REACT / 50% active Cl<sub>2</sub> converts to C-Orgs.

10 -11 /

0 0 1 1.9 0 0 10 9 4.5 11 /

7/ 1.78% pulp degrades to C-Orgs, 100% active Cl<sub>2</sub> (i.e., 50% of Cl<sub>2</sub> residual) converts to Cl<sup>-</sup>.

REACT

11 -12 /

3000 0 1 1.9 4.0178 0 10 11 0 0 /

8/ Dilution with warm water, no sorption.

MIXER

12 13 -14 /

0 2 1 /

9/ Dilute to 1% consistency with wash water from D/C washer,

DILUTE / excess acidic flow is sewerred, no sorption,

14 21 -18 -15 / no additional liquor make-up if short.

2 0.01 1 1 /

10 / Direct substitution of acid filtrate for brown stock dilution before D/C tower.

SPLIT

15 -16 -71 -17 /

7 3 243.31 180 64.25 /

11/ Norden factor 2, outlet pulp consistency 12.5%, DR 0.46,

WASH / specific efficiency factor for temperature & Cl<sup>-</sup> are 6 & 0.2.

18 19 -22 -20 /

2 0.125 1 0 3 6 10 0.2 0.46 /

12/ D/C wash with E2 filtrate, simulated with 2 WASH blocks, no sorption.

WASH

22 23 -25 -24 /

2 0.125 1 0 3 6 10 0.2 0.46 /

13/ No sorption due to mixing of only the liquid streams.

MIXER

24 20 -21 /

0 2 1 /

14/ Dilution with warm water, caustic to E1 tower, no sorption in, sorption out.

MIXER

25 26 27 70 -28 /

0 4 2 /

15/ Sorption, outlet temperature 75°C, saturated steam pressure 4121.7mmHg.

STMIX

28 29 -30 /

3 0 0 75 4121.7 /

16/ 0.5% of O<sub>2</sub> based on pulp flow is charged, sorption.

CHARGE

30 31 -32 /

5 0 0 15.005 /

17/ E1 tower reaction, 2.45% pulp converts to E-Orgs, exit pH 10.5, sorption.

REACT

32 -33 /

0 0 0 10.5 5.0245 0 0 0 0 0 /

18/ E1 wash with D1 filtrate, Norden factor 2.6, pulp outlet consistency 11%,

WASH / Cl<sup>-</sup> DR 0.8, DR 0.815, sorption.

33 34 -36 -35 /

2.6 0.11 0 0 3 6 10 0.8 0.815 /

19/ Caustic buffer after E1 & ClO<sub>2</sub> addition to D1, sorption in, no sorption out.

MIXER

36 37 38 -39 /

0 3 3 /

E-4

20/ D1 tower reaction, exit pulp pH 4, 53% ClO<sub>2</sub> converts to Cl<sup>-</sup>,

REACT / 1.17% of pulp degrades to D-Orgs, no sorption.

39 -40 /

3000 0 14 6.0117 0 10.53 9 0 0 /

21/ 100% of ClO<sub>2</sub> (i.e., 47% of residual ClO<sub>2</sub>) converts to D-Orgs.

REACT

40 -41 /

0 0 1 4 0 0 6 9 0 0 /

22/ D1 wash with E2 filtrate, Norden factor 2, 11% outlet pulp consistency,

WASH / Cl<sup>-</sup> DR 0.2, no sorption in, sorption out.

41 73 -45 -42 /

2 0.11 2 0 3 6 10 0.2 0.8 /

25/ Caustic flow to E2 tower, sorption in all streams.

MIXER

45 46 -47 /

0 2 0 /

23/ D1 seal tank overflow (S40), D1 filtrate (S41).

SPLIT

42 -43 -44 /

1 0 125 /

24/ D1 filtrate is exchanged with live steam before recycled back to E1 wash,

STMIX / no sorption.

43 -34 /

4 0 1 70 4121.7 /

26/ E2 tower reaction, exit pulp pH 9.8, 1.87% pulp converts to E-Orgs, sorption.

REACT

47 -48 /

0 0 0 9.8 5.0187 0 0 0 0 0 /

27/ E2 wash, Norden efficiency 2.6, outlet pulp consistency 11%, Cl<sup>-</sup> DR 0.8, DR 0.815,

WASH / sorption.

48 49 -54 -50 /

2.6 0.11 0 0 3 6 10 0.8 0.815 /

28/ E2 seal tank overflow (S23) or E2 filtrate.

SPLIT

50 -51 -23 /

1 0 106 /

29/ E2 filtrate mixes with E1 heat exchanger make-up water, no sorption.

MIXER

51 52 -53 /

0 2 1 /

30/ E2 filtrate is exchanged with live steam before recycled back to D1 tower,

STMIX / no sorption.

53 -73 /

4 0 1 71 4121.7 /

31/ Caustic buffer after E2, ClO<sub>2</sub> addition to D2 tower, sorption in, no sorption out.

MIXER

54 55 56 -57 /

0 3 3 /

32/ D2 tower reaction, exit pulp pH 4, 53% ClO<sub>2</sub> converts to Cl<sup>-</sup>,

REACT / heat of reaction 3000kcal/kg pulp, 1.10% pulp degrades to D-Orgs.

57 -58 /

3000 0 1 4 6.0110 0 10.53 9 0 0 /

33/ 100% of ClO<sub>2</sub> (i.e., 47% of residual) converts to D-Orgs, no sorption.

REACT

58 -59 /

0 0 1 4 0 0 6 9 0 0 /

34/ D2 wash, Norden efficiency 2.4, outlet pulp consistency 9.56%, Cl<sup>-</sup> DR 0.2, DR 0.8,

WASH / no sorption.

59 74 -65 -60 /

2.4 0.0956 1 0 3 6 10 0.2 0.8 /

35/ D2 seal tank overflow (S57), D2 filtrate (S58) recycled back to E2 wash.

SPLIT

60 -61 -62 /

1 0 113.93 /

E-6

36/ D2 filtrate mixes with E1 heat exchanger make-up water, no sorption.

MIXER

61 63 -64 /

0 2 1 /

37/ D2 filtrate is exchanged with live steam before recycled back to E2 tower,

STMIX / no sorption.

64 -49 /

4 0 1 70 4121.7 /

38/ Caustic buffer after D2 tower, exit pulp pH 4, no sorption.

CHARGE

65 66 -67 /

1 0 1 4 /

39/ E1 seal tank overflow (S35), E1 filtrate (S69) recycled for upstream pulp

SPLIT / dilution before E1 stage.

35 -68 -69 /

1 0 13.02 /

40/ E1 filtrate is exchanged with water to reduce the temperature for upstream pulp

STMIX / dilution, no sorption.

68 -70 /

4 0 1 50 4121.7 /

41/ To calculate total active Cl<sub>2</sub> consumption by C- & E-stage organics.

GPMOD

16 -72 /

1 0.33 0.20 -200004 -200005 207211 /

1/ Input pulp stream.

96.77 0.124 24 0 3\*0 0.04 0 0.26 2\*0 0.96 2.67 0 /

2/ WW1, WW2 & WW3 wash water.

243.31 0 15 /

16/ Direct substitution of D/C filtrate for WW1, WW2 & WW3 wash water.

0 0 26.2 /

6/ Chlorine gas to D/C-stage.

0 0 9.5 7\*0 1000 /

7/ Chlorine water to D/C-stage, 3.25% as available chlorine.

0.433 0 14 7\*0 5.8 /

5/ Chlorine dioxide to D/C-stage, 0.67% true ClO<sub>2</sub> (1.75% as available chlorine).

0.088 0 9.5 5\*0 22.93 /

13/ Warm Waikato water to D/C tower for dilution (WW1).

180 0 35 /

19/ Wash water to D/C tower (WW2).

30 0 35 /

23/ E2 filtrate recycled.

15.52 0 70 /

26/ Dilution water after D/C washer (WW3).

13.02 0 41 /

27/ Caustic to E1 tower.

0.404 0 10 8\*0 42.5 57.5 /

31/ Oxygen charge to E1 tower.

0.06 0 10 11\*0 1000 /

29 / Live steam flow to heat pulp before E1 tower.

5.832 0 154.8 0 /

37/ Caustic buffer after E1 tower.

0.058 0 10 8\*0 42.5 57.5 /

38/ Chlorine dioxide to D1 tower.

0.120 0 9.5 5\*0 22.93 /

34/ D1 filtrate out from D1 heat exchanger.

128.64 0 74 /

46/ Caustic flow to E2 tower.

0.107 0 10 8\*0 42.5 57.5 /

49/ D2 filtrate out from D2 heat exchanger.

126 0 69 /

E-8

55/ Chlorine dioxide to D2 tower.

0.053 0 9.5 5\*0 22.93 /

56/ Caustic buffer after E2 tower.

0.030 0 10 8\*0 42.5 57.5 /

73/ E2 filtrate out from E2 heat exchanger.

140 0 70 /

74/ Total hot and cold bore water at average temperature (HBW+CBW).

131.30 0 42 /

66/ Caustic buffer after D2 tower.

0.012 0 10 8\*0 42.5 57.5 /

63/ E1 heat exchanger water make-up to the flow out of D2 seal tank.

6.57 0 65 /

52/ E1 heat exchanger water make-up to the flow out of E2 seal tank.

30.84 0. 65 /

70/ E1 filtrate recycled.

0 0 74 /

72/ Extra chlorine water consumed by organics.

0 0 14 7\*0 0 /

LIQUOR	MT/HR	1
PULP FRACTION		2
TEMP	DEGC.	3
CSTORG	KG/MT	4
ESTORG	KG/MT	5
DSTORG	KG/MT	6
OXIDORG	KG/MT	7
BLIQORG	KG/MT	8
CLO <sub>2</sub>	KG/MT	9
CL <sup>-</sup>	KG/MT	10
ICLA	KG/MT	11
OH <sup>-</sup>	KG/MT	12
NA <sup>+</sup>	KG/MT	13
ICO <sub>3</sub>	KG/MT	14
O <sub>2</sub>	KG/MT	15

1 2 3 4 5 6 7 8 9 11 12 13 14 15 16 17 18 19 20 21 22 23 24

25 26 27 28 29 30 31 32 33 34 35 36 37 38 / 10 41 39 40 CALCULATION ORDER

/

/

**E.2 - No.2 Bleach Plant Simulation (Total Closure Case)**

NO2 BLEACH PLANT SIMULATION 5/12/89 /TOTCLOSE.DAT: CLOSED D/C & E1 CASE

100 200 1 0 10000/LOOPS,MAXERR,IREAD,NFILE,NPRINT  
2 0 0 60 0 0 0/KOP,KPORT,KPWIDE,NRLINE,IBUG,IDCHK,IFPR  
0 0 0/DYNA,MACRO,INCRA,IPLT  
0 0 10000 1 -150 0/KEND,ITSTRT,IAUTO,FACT1,FACT2  
0/NSACC  
.01/DELS  
42 74 27 15/NEB,NSN,NSVS,NEP  
4 4 15 15 1 3 2 0 /II,JJ,KK,LL,ILIQ,ITEM,IPULP  
13 12 0 0 0 10 11 0 0 14/INA,IOH,IDIS,IS2,ISO4,ICL,ICLA,IMG,IK,ICO3  
0 0 0 0 0 0 0 0/ISO3,IHSO3,IS2O3,ICAO,ICACO3,ICAOH2,ICASO4,IINERT  
0 0 0 0 0 0 0/IPR,IKAP, ID1, ID2, ID3, ID4, ID5  
0 0 0 0 15 0 0 0 0 0 0/IAIR,IWV, IN2, ICO2, IO2, ITWB, ITDP, IPHI, IW, IH, IV  
0 0 0 0 0 0 0 0 0 0/IGT,IGPR,INS,INC,INCL,ISO2,ITRS,IHCL,ICO,ICH4  
/  
/  
/

1/ Pulp from N0.5 & 6 HD tank is diluted to 3.45% consistency, sorption in, no sorption out.

MIXER

1 2 16 -3 / STREAM ORDER  
0 3 3 / EQUIPMENT PARAMETERS

2/ 0.67% ClO<sub>2</sub> addition based on AD pulp, sorption.

MIXER

3 5 -4 /  
0 2 0 /

3/ Chlorine gas and chlorine water are mixed, further dilution to 2.84% consistency, no sorption.

MIXER /

4 6 7 72 -8 /  
0 4 1 /

4/ No sorption, existing target pH 1.9, 100% of black liquor & C-Orgs

REACT / convert to Oxidised-Orgs.

8 -9 /

0 0 1 1.9 0 0 7 8 7 4 0 /

5/ 47% ClO<sub>2</sub> convert to C-Orgs, 100% of E-Orgs convert to Oxidised-Orgs.

REACT

9 -10 /

0 0 1 1.9 0 0 4.47 9 7 5 /

6 / 100% ClO<sub>2</sub> (i.e., 53% of the ClO<sub>2</sub> residual) converts to Cl<sup>-</sup>,

REACT / 50% active Cl<sub>2</sub> converts to C-Orgs.

10 -11 /

0 0 1 1.9 0 0 10 9 4.5 11 /

7/ 1.78% pulp degrades to C-Orgs, 100% active Cl<sub>2</sub> (i.e., 50% of Cl<sub>2</sub> residual) converts to Cl<sup>-</sup>,

REACT / heat of reaction 3000kcal/kg pulp.

11 -12 /

3000 0 1 1.9 4.0178 0 10 11 0 0 /

8/ Dilution with warm water, no sorption.

MIXER

12 13 71 -14 /

0 3 1 /

9/ Dilute to 1% consistency with wash water from D/C washer,

DILUTE / excess acidic flow is sewerred, no sorption,

14 21 -18 -15 / no additional liquor make-up if short.

2 0.01 1 1 /

10 / Direct substitution of acid filtrate for brown stock dilution before D/C tower.

SPLIT

15 -16 -71 -17 /

7 3 243.31 180 64.25 /

11/ Norden factor 2, outlet pulp consistency 12.5%, DR 0.46, no sorption,

WASH / specific efficiency factor for temperature & Cl<sup>-</sup> are 6 & 0.2.

18 19 -22 -20 /

2 0.125 1 0 3 6 10 0.2 0.46 /

E-12

12/ D/C wash with E2 filtrate, simulated with 2 WASH blocks, no sorption.

WASH

22 23 -25 -24 /

2 0.125 1 0 3 6 10 0.2 0.46 /

13/ No sorption due to mixing of only the liquid streams.

MIXER

24 20 -21 /

0 2 1 /

14/ Dilution with warm water, caustic to E1 tower, no sorption in, sorption out.

MIXER

25 26 27 70 -28 /

0 4 2 /

15/ Sorption, outlet pulp temperature 75°C, saturated steam pressure 4121.7mmHg.

STMIX

28 29 -30 /

3 0 0 75 4121.7 /

16/ 0.5% of O<sub>2</sub> based on pulp flow is charged, sorption.

CHARGE

30 31 -32 /

5 0 0 15.005 /

17/ E1 tower reaction, 2.45% pulp converts to E-Orgs, exit pulp pH 10.5, sorption.

REACT

32 -33 /

0 0 0 10.5 5.0245 0 0 0 0 0 /

18/ E1 wash with D1 filtrate, Norden factor 2.6, pulp outlet consistency 11%,

WASH / Cl<sup>-</sup> DR 0.8, DR 0.815, sorption.

33 34 -36 -35 /

2.6 0.11 0 0 3 6 10 0.8 0.815 /

19/ Caustic buffer after E1 washer & ClO<sub>2</sub> addition to D1 tower, sorption in, no sorption out.

MIXER

36 37 38 -39 /

0 3 3 /

20/ D1 tower reaction, exit pulp pH 4, 53% of ClO<sub>2</sub> converts to Cl<sup>-</sup>,  
 REACT / 1.11% of pulp degrades to D-Orgs, no sorption.

39 -40 /  
 3000 0 14 6.0111 0 10.53 9 0 0 /

21/ 100% of ClO<sub>2</sub> (i.e.47% of residual ClO<sub>2</sub>) converts to D-Orgs.

REACT  
 40 -41 /  
 0 0 1 4 0 0 6 9 0 0 /

22/ D1 wash with E2 filtrate, Norden factor 2, 11% outlet pulp consistency,  
 WASH / Cl<sup>-</sup> DR 0.2, no sorption in, sorption out.

41 73 -45 -42 /  
 2 0.11 2 0 3 6 10 0.2 0.8 /

25/ Caustic flow to E2 tower, sorption in all streams.

MIXER  
 45 46 -47 /  
 0 2 0 /

23/ D1 seal tank overflow (S40), D1 filtrate (S41).

SPLIT  
 42 -43 -44 /  
 1 0 125 /

24/ D1 filtrate is exchanged with live steam before recycled back to E1 wash, no sorption.

STMIX  
 43 -34 /  
 4 0 1 70 4121.7 /

26/ E2 tower reaction, exit pH 9.8, 1.80% pulp converts to E-Orgs, sorption.

REACT  
 47 -48 /  
 0 0 0 9.8 5.0180 0 0 0 0 0 /

27/ E2 wash, Norden efficiency 2.6, outlet pulp consistency 11%, Cl<sup>-</sup> DR 0.8, DR 0.815,  
 WASH / sorption.

48 49 -54 -50 /  
 2.6 0.11 0 0 3 6 10 0.8 0.815 /

E-14

28/ E2 seal tank overflow (S23) or E2 filtrate.

SPLIT

50 -51 -23 /

1 0 106 /

29/ E2 filtrate mixes with E1 heat exchanger make-up water, no sorption.

MIXER

51 52 -53 /

0 2 1 /

30/ E2 filtrate is exchanged with live steam before recycled back to D1 tower,

STMIX / no sorption.

53 -73 /

4 0 1 71 4121.7 /

31/ Caustic buffer after E2, ClO<sub>2</sub> addition to D2 tower, sorption in, no sorption out.

MIXER

54 55 56 -57 /

0 3 3 /

32/ D2 tower reaction, exit pulp pH 4, 53% of ClO<sub>2</sub> converts to Cl<sup>-</sup>, no sorption,

REACT / heat of reaction 3000kcal/kg pulp, 1.03% pulp degrades to D-Orgs.

57 -58 /

3000 0 1 4 6.0103 0 10.53 9 0 0 /

33/ 100% of ClO<sub>2</sub> (i.e., 47% of residual) converts to D-Orgs.

REACT

58 -59 /

0 0 1 4 0 0 6 9 0 0 /

34/ D2 wash, Norden efficiency 2.4, outlet pulp consistency 9.56%, Cl<sup>-</sup> DR 0.2, DR 0.8,

WASH / no sorption.

59 74 -65 -60 /

2.4 0.0956 1 0 3 6 10 0.2 0.8 /

35/ D2 seal tank overflow (S57), D2 filtrate (S58) recycled back to E2 wash.

SPLIT

60 -61 -62 /

1 0 113.93 /

36/ D2 filtrate mixes with E1 heat exchanger make-up water, no sorption.

MIXER

61 63 -64 /

0 2 1 /

37/ D2 filtrate is exchanged with live steam before recycled back to E2 tower,

STMIX / no sorption.

64 -49 /

4 0 1 70 4121.7 /

38/ Caustic buffer after D2 tower, exit pH 4, no sorption in, sorption out.

CHARGE

65 66 -67 /

1 0 2 4 /

39/ E1 seal tank overflow (S35), E1 filtrate (S69) recycled for upstream pulp

SPLIT / dilution before E1 stage.

35 -68 -69 /

1 0 13.02 /

40/ E1 filtrate is exchanged with water to reduce the temperature for upstream pulp

STMIX / dilution, no sorption.

68 -70 /

4 0 1 50 4121.7 /

41/ To calculate total active Cl<sub>2</sub> consumption by C- & E-stage organics.

GPMOD

16 / (0.33x) + (0.20y) = Z, Z = total Cl<sub>2</sub> conc., x = C-Orgs., y = E-Orgs., the output is sent

1 0.33 0.20 -200004 -200005 104211 / to block 42, stream variable 11.

42/ To calculate total chlorine water consumed by organics i.e., liquor flow.

GPMOD

16 -72 / ZAW = V, A = 1/5.8, W = input stream liquor flow ( i.e., 243.31Mt/Hr ).

2 0.1724 0 -104211 -201601 207201 /

1/ Input pulp stream.

96.77 0.124 24 0 3\*0 0.04 0 0.26 2\*0 0.96 2.67 0 /

2/ WW1, WW2 & WW3 wash water.

0 0 15 /

E-16

16/ Direct substitution of D/C filtrate for WW1, WW2 & WW3 wash water.

243.31 0 28.87 /

6/ Chlorine gas to D/C-stage.

0 0 9.5 7\*0 1000 /

7/ Chlorine water to D/C-stage, 3.25% as available chlorine.

0.433 0 14 7\*0 5.8 /

5/ Chlorine dioxide to D/C-stage, 0.67% true ClO<sub>2</sub> (1.75% as available chlorine).

0.088 0 9.5 5\*0 22.93 /

13/ Warm Waikato water to D/C tower for dilution (WW1).

0 0 35 /

19/ Wash water to D/C tower (WW2).

30 0 35 /

23/ E2 filtrate recycled.

15.52 0 70 /

26/ Dilution water after D/C washer (WW3).

0 0 41 /

27/ Caustic to E1 tower.

0.404 0 10 8\*0 42.5 57.5 /

31/ Oxygen charge to E1 tower.

0.06 0 10 11\*0 1000 /

29 / Live steam flow to heat pulp before E1 tower.

5.832 0 154.8 0 /

37/ Caustic buffer after E1 tower.

0.058 0 10 8\*0 42.5 57.5 /

38/ Chlorine dioxide to D1 tower.

0.120 0 9.5 5\*0 22.93 /

34/ D1 filtrate out from D1 heat exchanger.

128.64 0 74 /

46/ Caustic flow to E2 tower.

0.107 0 10 8\*0 42.5 57.5 /

49/ D2 filtrate out from D2 heat exchanger.

126 0 69 /

55/ Chlorine dioxide to D2 tower.

0.053 0 9.5 5\*0 22.93 /

56/ Caustic buffer after E2 tower.

0.030 0 10 8\*0 42.5 57.5 /

73/ E2 filtrate out from E2 heat exchanger.

140 0 70 /

74/ Total hot and cold bore water at average temperature (HBW+CBW).

131.30 0 42 /

66/ Caustic buffer after D2 tower.

0.012 0 10 8\*0 42.5 57.5 /

63/ E1 heat exchanger water make-up to the flow out of D2 seal tank.

6.57 0 65 /

52/ E1 heat exchanger water make-up to the flow out of E2 seal tank.

30.84 0 65 /

70/ E1 filtrate recycled.

13.02 0 74 /

72/ Extra chlorine water consumed by organics.

0 0 14 7\*0 5.8 /

LIQUOR	MT/HR	1
PULP FRACTION		2
TEMP	DEGC.	3
CSTORG	KG/MT	4
ESTORG	KG/MT	5
DSTORG	KG/MT	6
OXIDORG	KG/MT	7
BLIQORG	KG/MT	8
CLO <sub>2</sub>	KG/MT	9
CL <sup>-</sup>	KG/MT	10

E-18

ICLA	KG/MT	11
OH <sup>-</sup>	KG/MT	12
NA <sup>+</sup>	KG/MT	13
ICO <sub>3</sub>	KG/MT	14
O <sub>2</sub>	KG/MT	15

1 2 3 4 5 6 7 8 9 11 12 13 10 41 42 14 15 16 17 18 39 40 19 20 21 22 23 24

25 26 27 28 29 30 31 32 33 34 35 36 37 38 / CALCULATION ORDER

/

/

### E.3 - No.2 Bleach Plant Expansion

NO2 BLEACH PLANT SIMULATION 20/1/1990 / REVAMPB.DAT  
 200 50 1 0 10000/LOOPS,MAXERR,IREAD,NFILE,NPRINT  
 2 0 0 60 0 0 0/KOP,KPORT,KPWIDE,NRLINE,IBUG,IDCHK,IFPR  
 0 0 0/DYNA,MACRO,INCRA,IPLLOT  
 0 3 10 1 -150 0/KEND,MODZ,ITSTRT,IAUTO,FACT1,FACT2  
 0/NSACC  
 .01/DELS  
 29 54 16 13/NEB,NSN,NSVS,NEP  
 4 4 13 13 1 3 2 0 /II,JJ,KK,LL,ILIQ,ITEM,IPULP  
 11 10 0 0 0 9 0 0 0 12/INA,IOH,IDIS,IS2,ISO4,ICL,ICLA,IMG,IK,ICO3  
 0 0 0 0 0 0 0 0/ISO3,IHSO3,IS2O3,ICAO,ICACO3,ICAOH2,ICASO4,IINERT  
 0 0 0 0 0 0 0/IPR,IKAP,ID1,ID2,ID3,ID4,ID5  
 0 0 0 0 13 0 0 0 0 0 0/IAIR,IWV,IN2,ICO2,IO2,ITWB,ITDP,IPHI,IW,IH,IV  
 0 0 0 0 0 0 0 0 0 0/IGT,IGPR,INS,INC,INCL,ISO2,ITRS,IHCL,ICO,ICH4  
 /  
 /  
 /

1/ BLOCK NUMBER, sorption in, no sorption out, 1% ClO<sub>2</sub> addition to D1 tower.

MIXER

1 2 -3 /STREAM ORDER  
 0 2 3 /EQUIPMENT PARAMETERS

2/ Temperature approach 5°C, overall heat transfer coefficient 423kcal/°C metre square.

HEATD

3 10 -5 -4 /  
 1 5 0 423 /

3/ 100% of BLIQORG converts to OXIDORG, 4% pulp degrades to DSTORG, 47% of ClO<sub>2</sub>

REACT / converts to DSTORG, exit pulp pH 3.5, heat of reaction 3000kcal per kg of pulp.

5 -6 /  
 3000 0 1 3.5 4.04 0 6 7 4.47 8 /

4/ 100% of ClO<sub>2</sub> residual converts to Cl<sup>-</sup>, no sorption.

REACT

6 -7 /  
 0 0 1 3.5 0 0 9 8 0 0 /

E-20

5/ 9% pulp stream consistency , no sorption, no additional liquor makeup if short.

DILUTE

7 8 -9 -10 /

2 0.09 1 1 /

6/ D1 washer, pulp outlet consistency 10%, no sorption in, sorption out, temperature and Cl- DR  
WASH / are 6 & 0.2 respectively, DR of washer 0.58.

9 11 -12 -13 /

2 0.10 2 0 3 6 9 0.2 0.58 /

7/ D1 washer, DR of washer 0.59.

WASH

12 14 -15 -16 /

2 0.10 2 0 3 6 9 0.2 0.59 /

8/ No sorption, mixing of filtrates from two Wash blocks.

MIXER

13 16 -8 /

0 2 1 /

9/ Splitting of pulp stream into two parallel streams.

SPLIT

15 -17 -18 /

7 2 106.81 106.81 /

10/ 1.8% NaOH added to E<sub>0</sub> tower, sorption in, no sorption out.

MIXER

17 19 -20 /

0 2 2 /

11/ No sorption, desired pulp outlet temperature 80°C, saturated steam pressure 4121.7mmHg.

STMIX

20 21 -22 /

3 0 1 80 4121.7 /

12/ 0.5% oxygen charge on pulp, no sorption.

CHARGE

22 23 -24 /

5 0 1 13.005 /

13/ E<sub>O</sub> tower, exit pulp pH 11, 2% pulp converts to ESTORG.

REACT

24 -25 /

0 0 1 11 5.02 0 0 0 0 0 /

14 / E<sub>O</sub> washer, sorption in, sorption out, Norden factor 2.6, pulp outlet consistency 10%,

WASH / temperature and Cl<sup>-</sup> DR are 6 & 0.8, washer DR 0.865.

25 26 -27 -11 /

2.6 0.10 3 0 3 6 9 0.8 0.865 /

15 / 0.7% ClO<sub>2</sub> addition to D2 tower, NaOH added as buffer, sorption in, no sorption out

MIXER

27 28 29 -30 /

0 3 3 /

16/ Pulp outlet temperature 70°C, no sorption, saturated steam pressure 4121.7mm Hg.

STMIX

30 31 -32/

3 0 1 70 4121.7/

17/ D2 tower, 2% pulp degrades to DSTORG, 47% ClO<sub>2</sub> converts DSTORG, exit pulp pH 3.5,

REACT / heat of reaction 3000kcal/kg pulp, no sorption.

32 -33 /

3000 0 1 3.5 4.02 0 4.47 8 0 0 /

18/ D2 tower, 100% of ClO<sub>2</sub> residual converts to Cl<sup>-</sup>, no sorption.

REACT

33 -34 /

0 0 1 3.5 0 0 9 8 0 0 /

19/ D2 washer, no sorption, Norden factor 2.4, pulp outlet consistency 10%, temperature and Cl<sup>-</sup>

WASH / DR are 6 & 0.2, washer DR 0.847.

34 35 -36 -26 /

2.4 0.10 1 0 3 6 9 0.2 0.847 /

20/ 1.8% NaOH addition to E<sub>O</sub> tower, sorption in, no sorption out

MIXER

18 37 -38 /

0 2 2 /

E-22

21/ No sorption, pulp outlet temperature 80°C, saturated steam pressure 4121.7mm Hg.

STMIX

38 39 -40 /

3 0 1 80 4121.7 /

22/ No sorption, 0.5% oxygen charge to pulp.

CHARGE

40 41 -42 /

5 0 1 13.005 /

23/ E<sub>0</sub> tower, 2% pulp degrades to ESTORG, pulp outlet consistency 11%, no sorption.

REACT

42 -43 /

0 0 1 11 5.02 0 0 0 0 0 0 /

24/ E<sub>0</sub> washer, pulp outlet consistency 10%, temperature and Cl<sup>-</sup> DR are 6 & 0.8,

WASH / washer DR 0.865, Norden factor 2.6, sorption in, sorption out.

43 44 -45 -14 /

2.6 0.10 3 0 3 6 9 0.8 0.865 /

25/ 0.7% ClO<sub>2</sub> addition to D2 tower, NaOH added as buffer, sorption in, no sorption out

MIXER

45 46 47 -48 /

0 3 3 /

26/ Pulp outlet temperature 70°C, saturated steam pressure 4121.7mmHg.

STMIX

48 49 -50 /

3 0 1 70 4121.7/

27/ D2 tower, exit pulp pH 3.5, 2% pulp degrades to DSTORG, 47% ClO<sub>2</sub> converts to DSTORG,

REACT/ no sorption, heat of reaction 3000kcal/kg pulp.

50 -51 /

3000 0 1 3.5 4.02 0 4.47 8 0 0 0 /

28/ D2 tower, no sorption, 100% ClO<sub>2</sub> residual converts to Cl<sup>-</sup>.

REACT

51 -52 /

0 0 1 3.5 0 0 9 8 0 0 0 /