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Effluent Recycling in a Kraft Pulp Mill

by

Jason B. Melanson ©

A thesis
submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Masters of Science

in
Chemical Engineering

Department of Chemical and Material Engineering

Edmonton, Alberta

Spring 2000

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The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Effluent Recycling in a Kraft Pulp Mill submitted by Jason Barry Melanson in partial fulfillment of the requirements for the degree of Masters of Science in Chemical Engineering.

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Abstract

Pulp and paper mills around the world have been looking into methods to eliminate effluent discharges from their mills. The driving force into this area of research includes: reduced environmental impact, recovery of valuable process chemicals, recovery of heat, and reduced fresh water treatment costs. The pulp and paper industry has devoted considerable time and effort into the area of research into zero effluent discharge.

System closure at Alberta-Pacific Forest Products Inc. is investigated to determine if the mill effluent could be recycled for use as process water. Lime softening of the secondary treated effluent was examined to determine if the effluent could be returned to the mill as process water.

In this study, a series of jar tests were performed in which lime was added to the mill's secondary treated effluent. The apparatus was designed by Phipps and Bird, and uses six 2-litre square containers so that six experiments can be performed simultaneously. The amount of non-process elements in the system, i.e., elements that do not play a useful role in pulping, was examined to determine if these could be reduced to an acceptable level.

The results indicate that this process could not remove chloride and potassium, and moved the focus of research to another area of study, i.e., progressive system closure.

Progressive system closure involves the internal recycling of mill's streams to gradually reduce the water usage of the mill, and progressively close the water loop. A millwide water balance was performed to help indicate which streams could be used as possible recycle streams. The two most favorable streams for internal recycle were the machine room effluent and the D_n effluent streams.

The machine-room effluent, D_n filtrate, D_o filtrate, and E_{op} filtrate were examined to determine if they could be used to replace fresh water at strategic locations within the mill. The internal white water system of the machine room was examined in detail to determine if individual waste streams from this area could be reused. Recycling the stream leaving the wire pit could save the mill approximately $1,200,000.00 annually.

Acknowledgments

I would like to thank Dr. Philip Mees for his encouragement and support over the duration of this study. His patience and assistance were greatly appreciated.

I would also like to thank Mr. Keith White and Alberta-Pacific Forest Products Inc. for the opportunity, financial support, and area for research. Mr. White provided important feedback and guidance towards the completion of this project. In addition, I would like to thank the operations and technical teams that have helped me throughout this project. Their understanding, and interest in this research were exceptional.

Most of all, I would like to thank my fiancée and daughter for their support and encouragement throughout these two years. I have spent many hours away from them studying and writing this report. They have been very understanding and encouraging through these long times. Their love and belief in me has been greatly needed and cherished.

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Nomenclature

A	pH main effect
a	High level of pH factor
ab	High level of pH and alum interaction terms
AB	Interaction of pH and alum (main effects)
abc	High level of pH, alum, and polymer interaction terms
ABC	Interaction of pH, alum, and polymer (main effects)
ac	High level of pH and polymer interaction terms
AC	Interaction of pH and polymer (main effects)
ADt	Air Dry Tons
AlPac	Alberta-Pacific Forest Products Inc.
B	Alum main effect
b	High level of alum or optical path length
BAT	Best Available Technology
bc	High level of alum and polymer interaction terms
BC	Interaction of alum and polymer (main effects)
BFR	Bleach Filtrate Recycle

BME	Bipolar Membrane Electrodialysis
c	High level of polymer or concentration
C	Polymer main effect
D	ClO_2 bleaching stage
DCS	Distributive Control System
E	Extraction bleaching stage
(1)	Each factor at its low level
ECF	Elemental Chlorine Free
ESP	Electrostatic Precipitator
f	F-distribution variable
k	Number of factors
MS	Mean square
n	Number of replicates or observations
N/S	Not statistically significant
NPE's	Non-Process Elements
NTU	Nephelometric Turbidity Units
ODt	Oven Dry Tons
Paprican	Pulp and Paper Research Institute of Canada
PCB	Polychlorinated Biphenyl
PDR	Precipitator Dust Recovery
ppm	Parts per million
RPM	Revolutions Per Minute
s.e.	Standard error

SRP	Salt Removal Process
SS	Sum of squares
S_{yy}	Total corrected sum of squares
TSS	Total Suspended Solids
US EPA	United States Environmental Protection Agency
V	Variance
$\mathbf{X}$	Matrix of operating variables
x	Operating variable
X	Sample
Y	Predicted value
y	Trials, observations or a vector of observations
Z	Standard normal random variable

Greek

β	Estimated parameter, or vector of estimated parameters
ε	Random error or absorptivity
Σ	Summation
α	Confidence interval
γ	Degrees of freedom
σ	Known standard deviation

Subscripts

$\bullet$	Summation divided by the number of observations

0	Initial
A	pH
AB	Interaction of pH and alum
ABC	Interaction of pH, alum, and polymer
AC	Interaction of pH and polymer
B	Alum
BC	Interaction of alum and polymer
C	Polymer
D	ClO_2 addition
E	Error
n	Open wash
o	Oxygen
p	Peroxide
R	Regression
T	Total

Superscripts

^	Estimate
‘	Transpose
-1	Inverse
‾	Average

Chapter 1.0

Introduction

The pulp and paper industry has devoted considerable time and effort into the research of zero liquid effluent discharge due to reduced environmental impact, recovery of valuable process chemicals, recovery of heat, and reduced fresh water treatment costs. In the past, mills have focused on new technologies and developments to optimize their process, therefore using less water and creating less toxic discharges for the receiving waters. The idea of system closure appears to be the best option to minimize the damage to the environment. This idea is not new; in 1975, a pulp mill in Thunder Bay Ontario attempted to be the first Kraft pulp mill to achieve this goal (Jemaa *et al.*, 1997). After a few years of constant operational problems, the mill shut down. Even after many years of research, there are still numerous problems to overcome.

With the development of newer mills that have the best available technology incorporated into their design, mills can now operate with lower effluent discharge volumes, as well as producing a much cleaner effluent. These improvements in the mill effluent have shifted some research projects into a direction that could be beneficial to these newer mills. The idea that the cleaner and lower volume mill effluent, with some form of treatment, can be economically recycled back into the mill eliminating any liquid effluent discharge to the environment. This treatment process is the main focus of this thesis.

Alberta-Pacific Forest Industries Inc. (AlPac) owns a Kraft mill that was constructed in central Alberta in 1993 with the best available technology incorporated into its design. This Kraft mill discharges low amounts of effluent to the environment. This mill is interested in looking into a new technology to determine if it may be viable to recycle their effluent back into the mill.

The work for this project is intended for a Kraft pulp mill that uses chemicals to break down wood to produce pulp. This work may not apply to other mills such as mechanical pulp mills that use mechanical force to break down the wood to produce pulp.

An overview of the Kraft mill process is given in Chapter 2, which focuses on the process flows, and describes the functions of each of the major areas within the mill. All areas of the mill contribute to the water that is entering the effluent stream and an understanding of where these flows originate is important.

An overview of the literature on system closure is presented in Chapter 3. The different technologies being studied are reviewed with attention focused on the removal of non-process elements and the problems associated with this. Non-process elements are elements that do not play a useful role in pulping and usually affect the Kraft process in a negative way.

The experimental setup for the removal of non-process elements and the methods used for analysis of the samples are discussed in Chapter 4. The experiments involve using jar tests to determine if lime softening of the mill effluent could be used to remove the non-process elements. The apparatus was designed by Phipps and Bird, and uses six 2-litre square containers so that six experiments can be performed simultaneously. The treated samples were then analyzed for non-process elements using an atomic absorption spectrometer, spectrophotometer, and a potentiometric titration device.

Factorial design is also applied in Chapter 4. This statistical approach reduces the number of experiments that need to be performed. The results showed that two non-process elements, chlorides and potassium, are not removed in lime softening of the mill's effluent.

A millwide water balance and effluent characterization are presented in Chapter 5. Volumes and concentrations of non-process elements for some of the major streams were determined. In this chapter, each individual effluent stream is examined to determine if it can be recycled into the mill with or without additional treatment.

Chapter 6 looks at the internal recycling of various process streams. The machine-room effluent, D_n filtrate, D_o filtrate, and E_{op} filtrate were examined to determine if they could be used to replace fresh water at strategic locations within the mill. Several locations for the return of these streams were found, and each was examined to determine if these streams could be recycled. Reasons why one stream is chosen over another are discussed, and an economic analysis of recycling these streams is proposed.

The conclusions of this research are discussed in Chapter 7 with some recommendations for additional research as well as suggestions for the implementation of recycling streams within the mill.

Chapter 2.0

Mill Overview

The pulp and paper industry supplies the world with various types of paper and paper products, each with a unique purpose and application, from printing and writing paper to bathroom tissue. The pulp and paper industry is very important to the Canadian economy. The Canadian Pulp and Paper Association (1997) indicated that the World's total pulp production was 130,986 Ktonnes, of which Canada produced 24,850 Ktonnes. Wood pulps can be produced in different ways; one of these methods is the Kraft process.

This chapter discusses the basic Kraft process and the various processes that occur at Alberta-Pacific Forest Products Inc. Each area is discussed individually to provide a basic understanding of the pulp production process. The areas discussed are: water supply, wood preparation, pulping process, bleaching, pulp finishing, chemical recovery, and effluent treatment.

2.1 Kraft Process

Trees are the main source of fibre for the production of pulp. Wood consists of fibres that are "glued" together by a substance called lignin. In the Kraft process, wood chips are cooked in a vessel with liquor to separate the lignin from these wood fibres. The liberated fibres are first washed and bleached. With some more processing, the fibres are then ready to be used for the production of paper and paper products. The liquor that was used to liberate the fibres contains lignin, some dissolved cellulose, hemicellulose, and used cooking chemicals. This used liquor is burned in a recovery boiler for two purposes: to create steam to power the pulp mill, and to recover the cooking chemicals. These chemicals can be converted into a useful form and re-used in the cooking process. The Kraft process is illustrated in Figure 2.1.

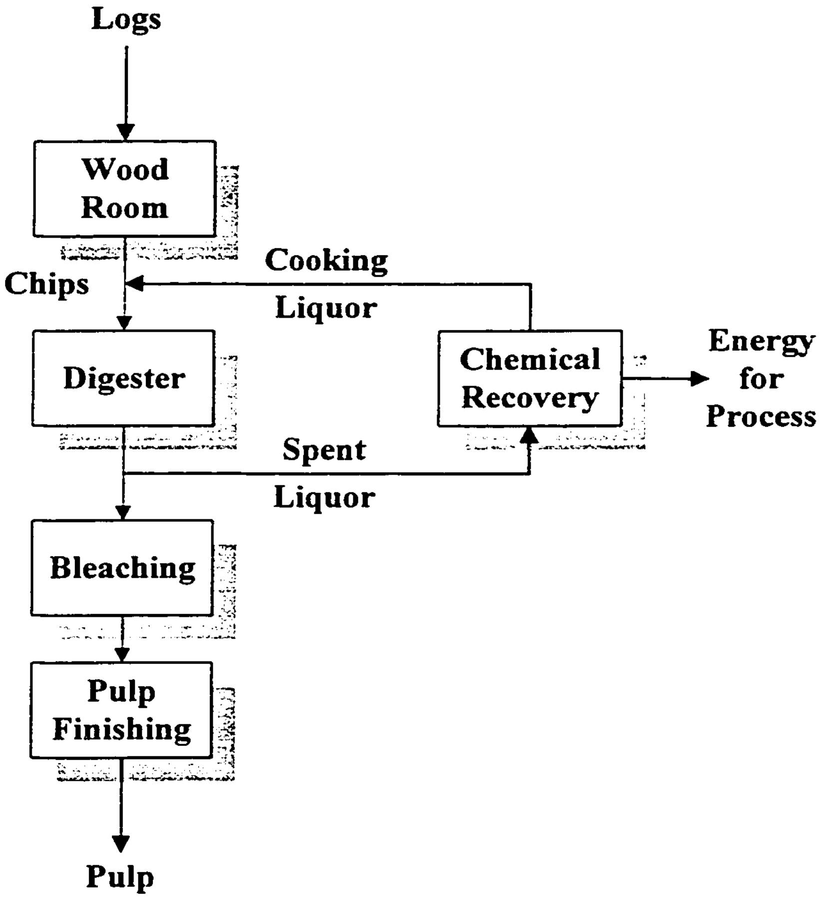


Figure 2.1: Kraft Pulp Process

The process flows at Alberta-Pacific Forest Products Inc. are common to most Kraft mills. The biggest difference here is that this mill is very modern and uses the best available technology at the time it was constructed in 1993.

2.2 Water Supply

The mill receives water from a nearby river. In order for the mill to use this water, it must be treated to reduce the hardness (Mg and Ca) and turbidity. The potable water must be chlorinated to inhibit microbial activity.

The water treatment plant at the mill can treat up to 1350 L/s of water from the river. The turbidity (clearness of the water) of the river can vary from 10 NTU to over 1000 NTU, and the hardness can reach as high as 200 mg/L.

The river water first passes through a screen that removes any debris and fish that may be trapped with the intake of the water. The water then enters a solids contact clarifier that is 61m in diameter and 10 m deep (Figure 2.2). The water is clarified by using a flocculant and coagulant aid that assists in forming larger particles that settle to the bottom of the clarifier. If the hardness is high, lime is added to help remove calcium and magnesium from the water. After treatment, the turbidity is usually under 5 NTU and the hardness is under 80 mg/L. If lime softening is used, the pH may be around 10.

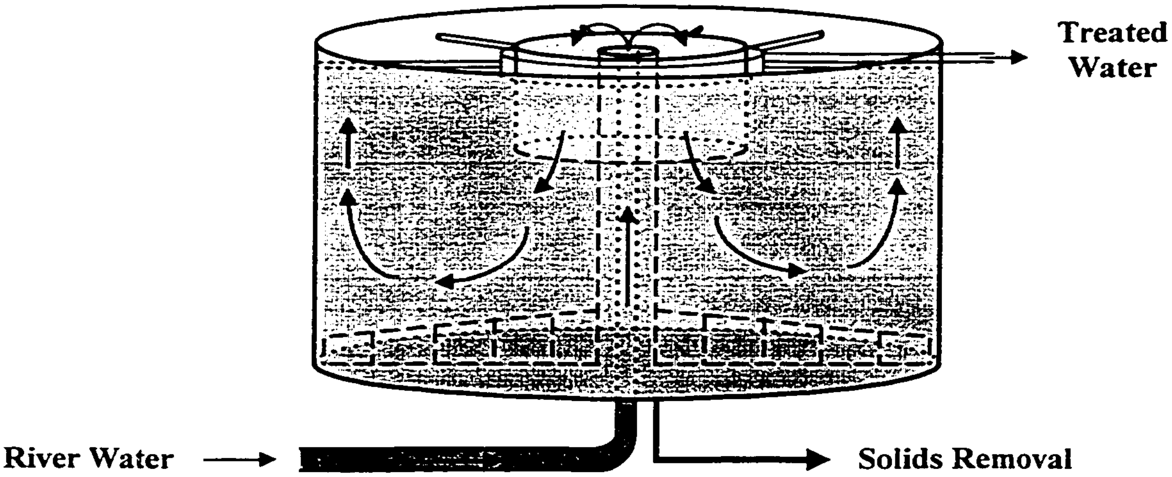


Figure 2.2: Reactor Clarifier

The treated water is sent to a re-carbonation chamber (Figure 2.3) where excess lime is removed or neutralized so it will not precipitate out in the mill's storage tanks and piping. Excess lime may be added to remove magnesium from the system as a hydroxide.

Carbon dioxide is added to the water to form a weak acid that reduces the pH and neutralizes any excess lime that is present. Following this, the treated water is passed through a dual- media filter bed. This removes most of the remaining suspended solids and reduces the turbidity to an acceptable level. The treated water is stored in one of three tanks for: fire, potable, and mill water.

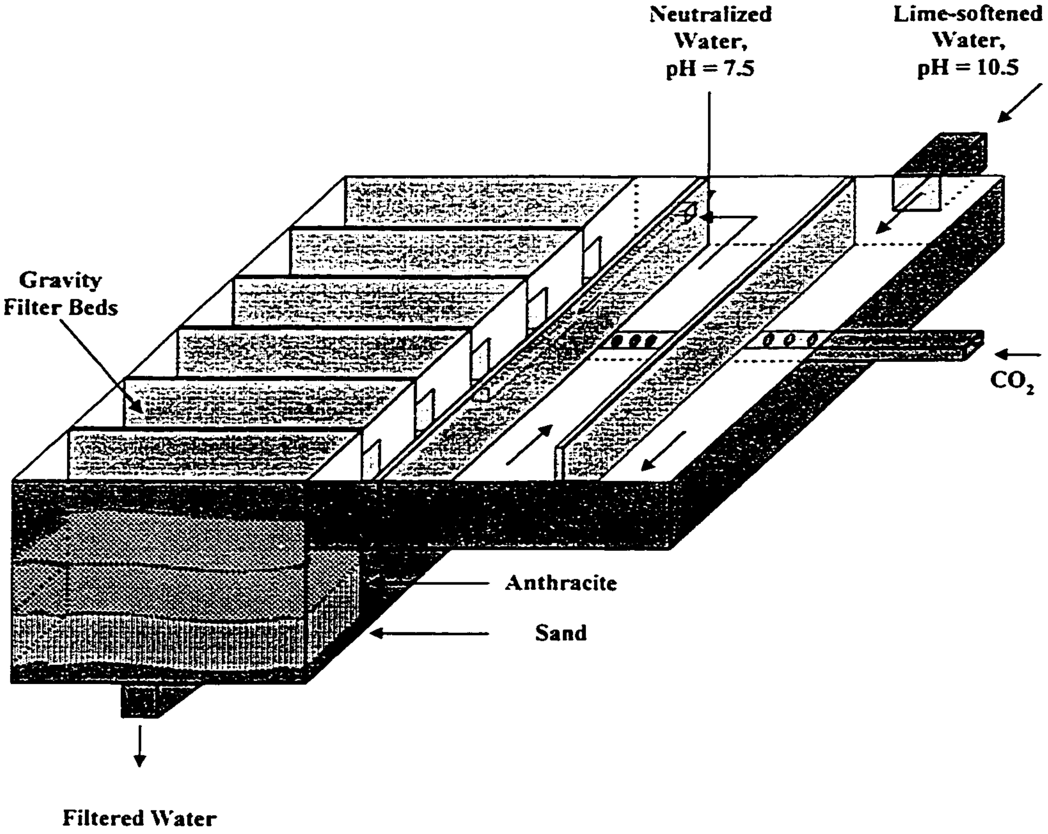


Figure 2.3: Re-Carbonation Chamber and Filter Beds

2.3 Wood Room

The wood room, Figure 2.4, is the area where the trees are stored, debarked, chipped and screened. Trees are harvested and trucked to the mill where they are stored on a log pile in 30-ft. lengths. One of two portal cranes feed the infeed decks where the logs are cut to lengths between 8 - 10 ft. to be fed to the drum debarker, or 15 ft. to be fed to one of four ring debarkers. Logs that are being debarked are washed with warm recycled water from the mill to remove sand, grit, as well as to thaw and soften the bark. The debarked logs are chipped and the chips are stored on one of four hardwood chip piles. The bark from the logs is sent to a hog pile from where it is sent to the power boiler as a fuel source.

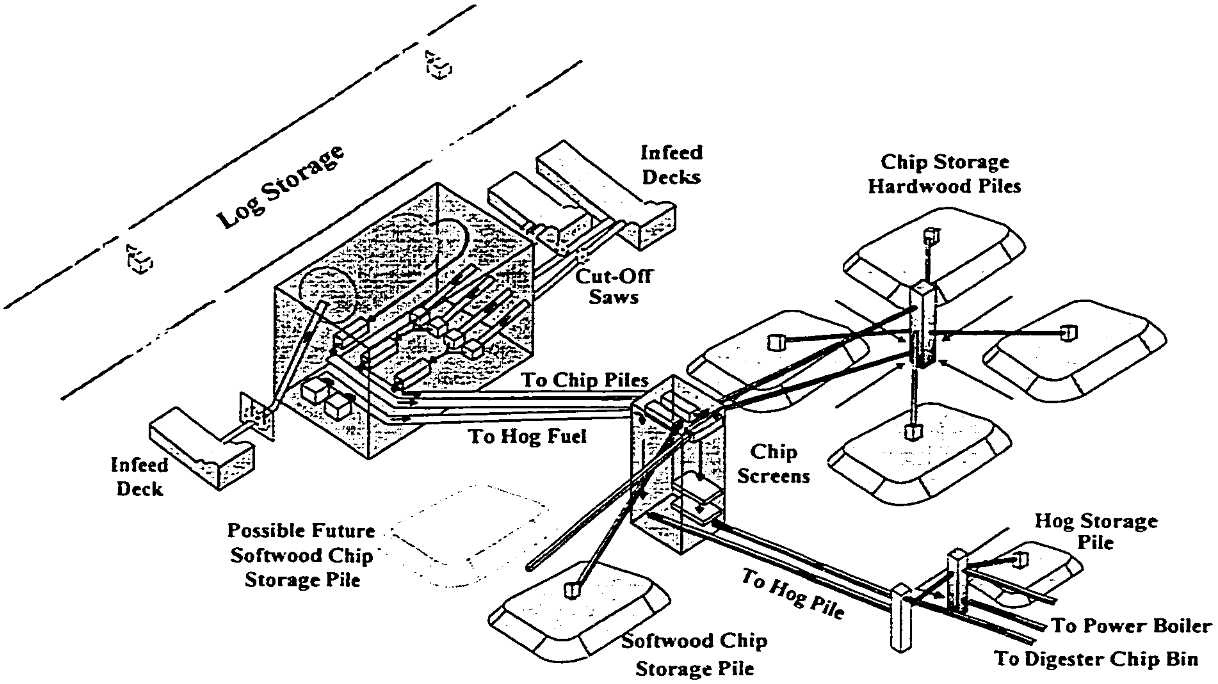


Figure 2.4: Wood Yard (Modified from Alberta-Pacific, 1993)

The chips from the piles are passed through a series of screens. The over-thick chips are removed, and re-sliced while the fines are diverted to the hog pile for fuel, or sent to the digester as a fibre source.

2.4 Pulping Process

The wood chips are transferred to a chip bin from where the chips are fed to the pulping process (Figure 2.5). From the chip bin, the wood chips enter a steaming vessel, where the chips are preheated to allow better penetration of the cooking liquor. From here, chips and liquor (Na_2S and NaOH) enter an impregnation vessel to start the cooking process. The chips then proceed to the digester where they undergo an extensive cooking process to remove most of the lignin. During the digesting process, some of the hemicellulose and cellulose in the wood is also dissolved. The liberated fibres are sent to a 2-stage atmospheric diffusion washer where most of the spent cooking liquor (black liquor) is removed.

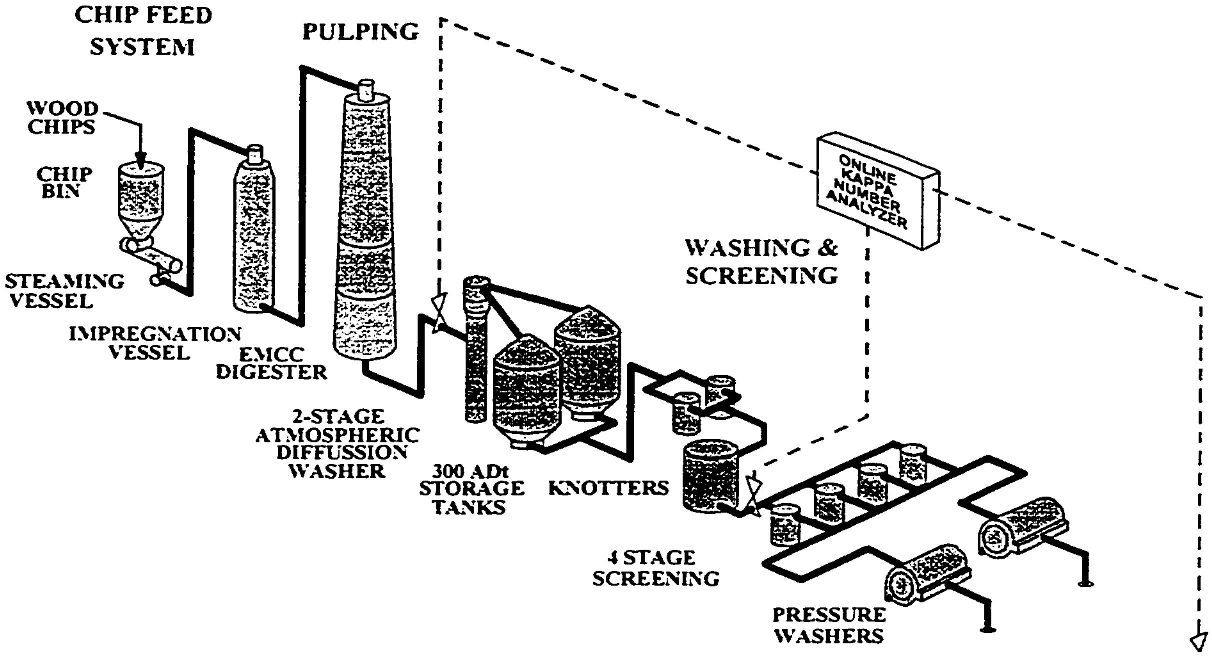


Figure 2.5: Pulping, Washing, and Screening (Modified from Alberta-Pacific, 1993)

This black liquor contains high concentrations of organics and used chemicals, so it is sent to a recovery process where the organics are burned as a fuel source, and the used chemicals are converted to a useful form and returned to the digester as fresh liquor. The pulp fibres are transferred to one of two unscreened high-density storage tanks. From here, they are sent through a screening process where knots and uncooked wood are removed from the pulp stream. The fibres are washed in one of two pressure washers to clean the fibres before entering the oxygen delignification stage (Figure 2.6).

In the oxygen delignification stage, pure oxygen is added to the pulp stream to remove more of the lignin that remains with the fibres. The pulp is then washed, stored in a screened high-density storage tank, and sent to the bleaching stage (Figure 2.7).

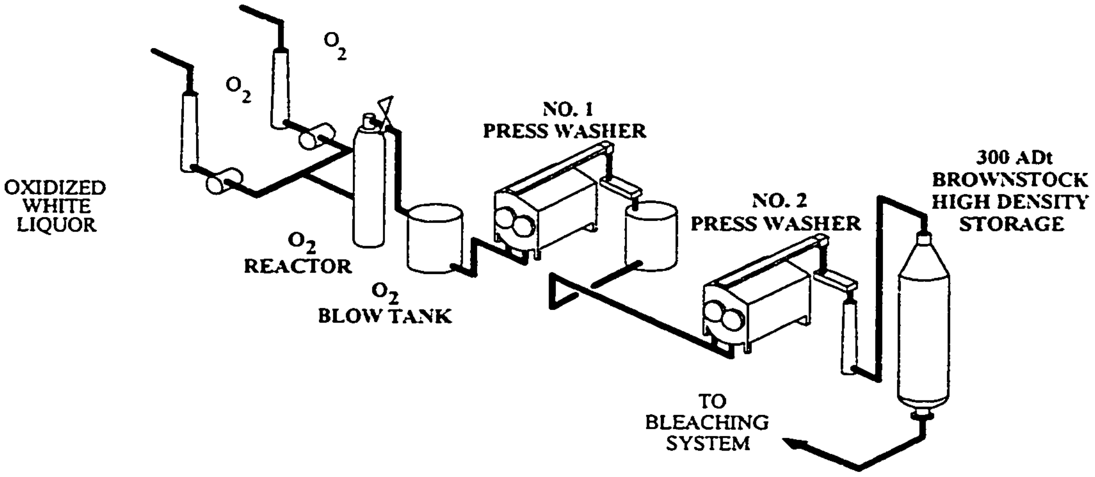


Figure 2.6: Oxygen Delignification and Washing (Modified from Alberta-Pacific, 1993)

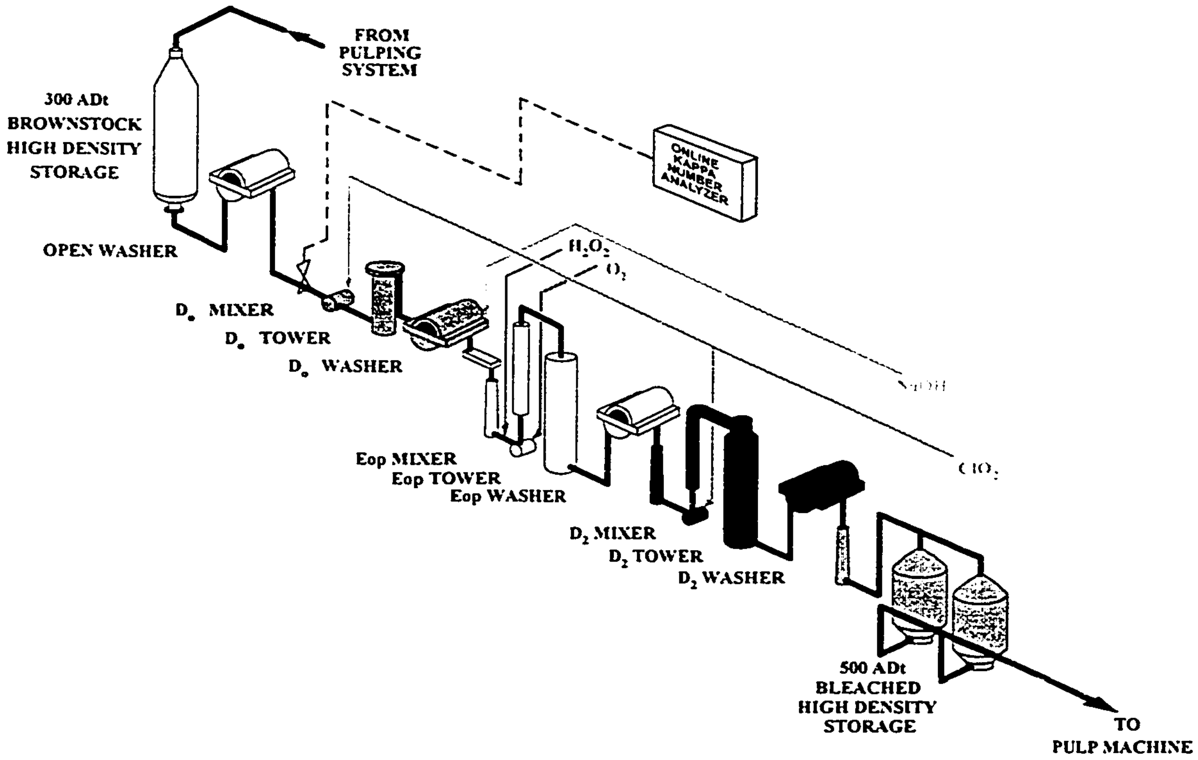


Figure 2.7: Bleaching Area (Modified from Alberta-Pacific, 1993)

2.5 Bleaching

This Kraft mill is an Elemental Chlorine Free (ECF) mill, i.e., it uses chlorine dioxide (ClO_2) for bleaching in a 3-stage (D_o-E_{op}-D_2) bleach plant (Figure 2.7). No Cl_2 is used in the bleaching process.

The pulp leaves the pulping area, and enters a final washing stage to be cleaned before the bleaching process. Each bleaching stage consists of: a mixer where the bleaching chemicals are added to the pulp, a tower where the pulp has time to react with the chemicals, and a washing stage where the spent chemicals are removed from the bleached pulp before proceeding to the next area.

The three stage bleaching process uses a brightening-extraction-brightening sequence. The first is a brightening stage (D_0) in which ClO_2 is added to the pulp. The second uses sodium hydroxide, oxygen, and peroxide (E_{op}) in the extraction process where the lignin fragments from the first stage are removed from the pulp, and the pulp is reactivated for further bleaching in the next ClO_2 stage. The third is a final brightening stage (D_2) that uses ClO_2. Each of these stages uses large amounts of fresh and recycled water to wash the pulp. Most of the filtrate from the D_2 stage is reused in previous washing stages, but the other filtrates are sewered. The pulp is stored in one of two bleached high-density storage tanks before entering the pulp finishing area.

2.6 Pulp Finishing

The bleached pulp needs to be "finished" in such a way that it can be shipped to the customers. To do this, the pulp must be cleaned, de-watered, dried, and packaged.

The pulp leaving the two high-density storage tanks must first be diluted so that the impurities that are in the stream can easily be removed. This section is called the stock preparation area. Water and pulp are mixed together, fed to a blend chest, then passed through a trash screen to remove any of the larger particles. Passing the pulp through a number of centrifugal cleaners and a disc filter removes the smaller impurities. After these cleaning stages, most of the contaminants have been removed from the pulp stream and the final pulp sheet can be formed on the pulp machine.

The next section of the pulp finishing area is the forming section followed by the press section. In the forming area the pulp is spread across a perforated felt to form a pulp sheet from which water is removed by gravity and then suction. The sheet passes through a number of presses where the water is physically forced from the sheet (Figure 2.8). The remainder of the water is removed in a dryer where heat is applied to the pulp mat. The final sheet is cut, wrapped, and stored in a warehouse until it is shipped to the customers. Some of the water used in the pulp finishing area can be recycled within the pulp machine or to the wood room, but a large amount is sewered. Figure 2.9 shows the dryer, cutter, and finishing sections of the machine room.

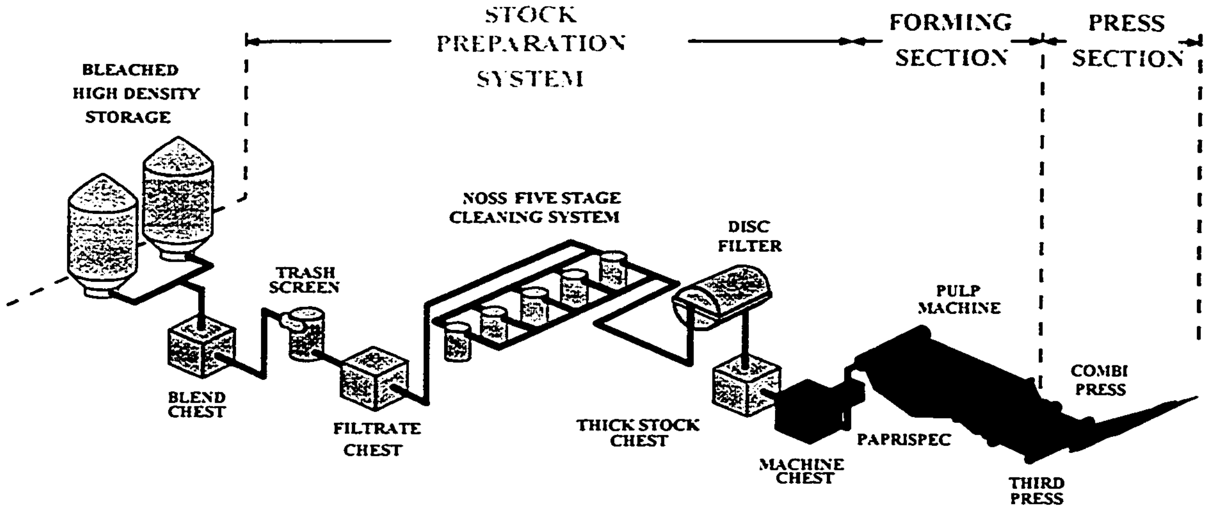


Figure 2.8: Stock Preparation, Forming, and Press Sections (Modified from Alberta-Pacific, 1993)

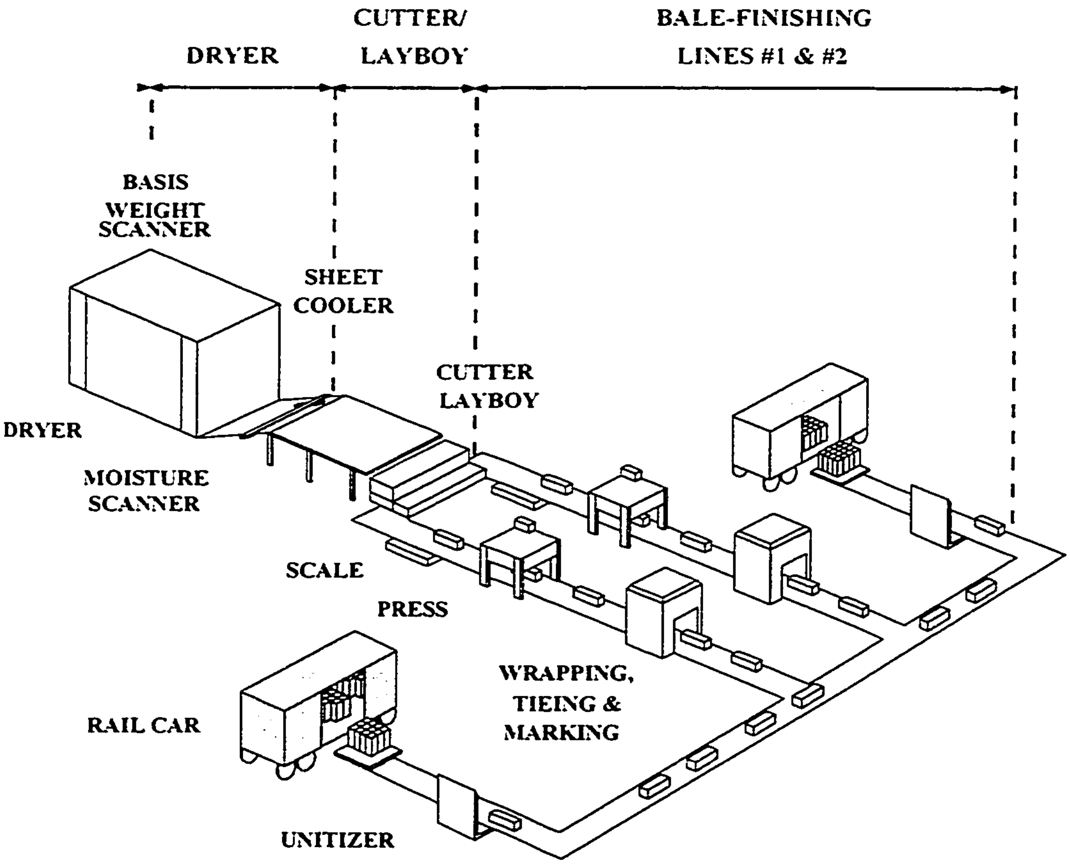


Figure 2.9: Dryer, Cutter, and Finishing Sections (Modified from Alberta-Pacific, 1993)

2.7 Chemical Recovery

The chemical recovery area is an essential integral part of the Kraft process. In this area, the spent cooking chemicals are recovered, and power is generated by the combustion of the black liquor.

The black liquor from the digester contains about 13% solids, and must be concentrated to about 65% solids in order to be burnt in the recovery boiler. To do this, the black liquor is passed through multiple effect evaporators to remove the water from the liquor as shown in Figure 2.10. The concentrated liquor is used as a fuel source in the recovery boiler.

Strong black liquor, mostly Na_2SO_4, is burned in the recovery boiler where steam is produced. This steam is used directly for process use and to power a number of turbo-generators to produce electricity for the mill. A typical composition of black liquor is shown in Table 2.1. In addition, the burnt liquor forms a smelt that contains a high concentration of cooking chemicals that flow from the bottom of the boiler and collected in a smelt-dissolving tank.

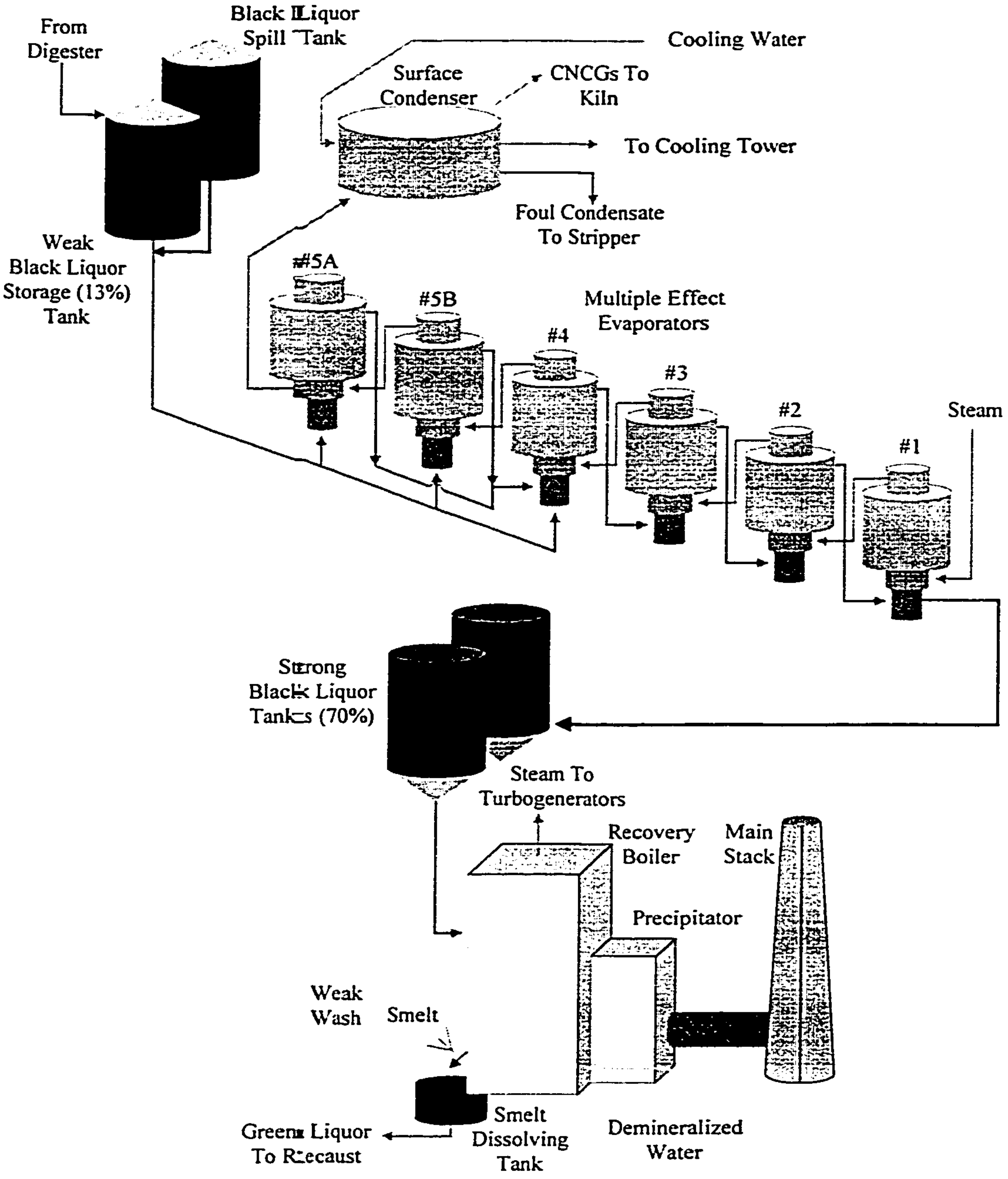


Figure 2.10: Chemical Recovery Area (Modified from Alberta-Pacific, 1993)

	% in Dry Solids
C	38.2
H	3.4
O	31.1
N	0.1
S	5.2
Na	19.8
K	1.9
Cl	0.1
Others (Ca, Si, Fe, Mg, Al, Mn)	0.2

Table 2.1: Typical Composition of Black Liquor (Modified from Adams *et al.*, 1997)

An input/output diagram for black liquor combustion is shown in Figure 2.11.

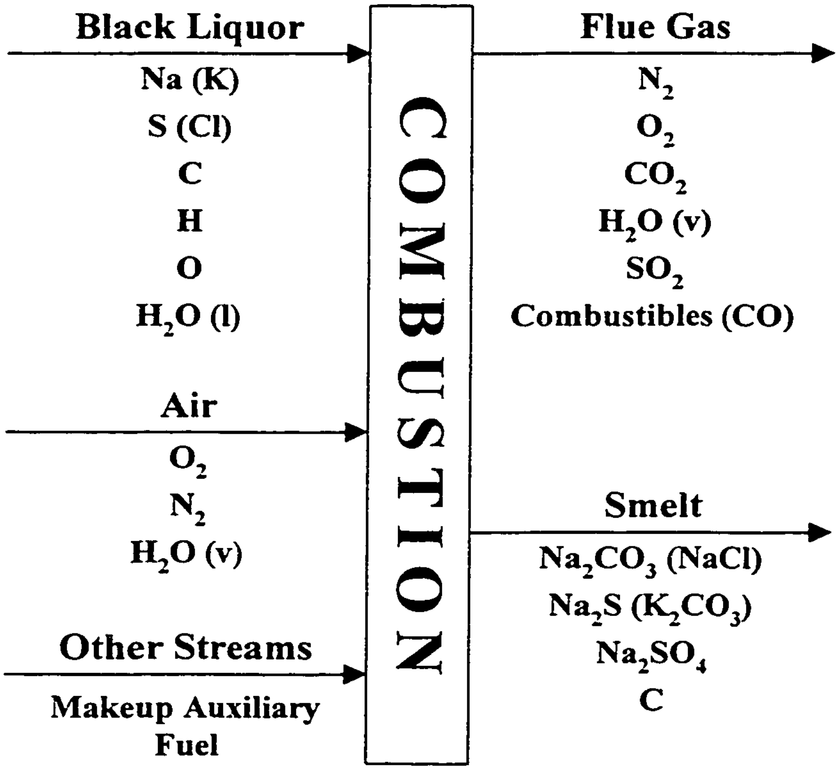


Figure 2.11: Input/output Diagram for Black Liquor Combustion (Modified From Green and Hough, 1992)

The resulting green liquor is transferred to a green liquor clarifier where the insoluble materials settle to the bottom, and the clarified liquor is transferred to a slaker.

In the slaker, lime (CaO) is added to the green liquor (Na_2CO_3 and Na_2S) to convert the spent cooking chemicals to useful cooking chemicals. The solution passes through a number of continuous stirred tank reactors (causticizers) to give the mixture enough time to react. The reactions are shown below.

$$\mathrm{CaO} + \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2} \tag{2.1}$$

$$\mathrm{Ca(OH)_2} + \mathrm{Na_2CO_3} \leftrightarrow \mathrm{2NaOH} + \mathrm{CaCO_3(s)} \tag{2.2}$$

The NaOH produced in this reaction is one of the key components of white liquor. The Na_2S does not react with the lime and passes through the system. The liquor is passed through a pressure filter to remove calcium carbonate ($CaCO_3$) and stored in a white-liquor storage tank for use as fresh cooking liquor in the digester (Figure 2.12).

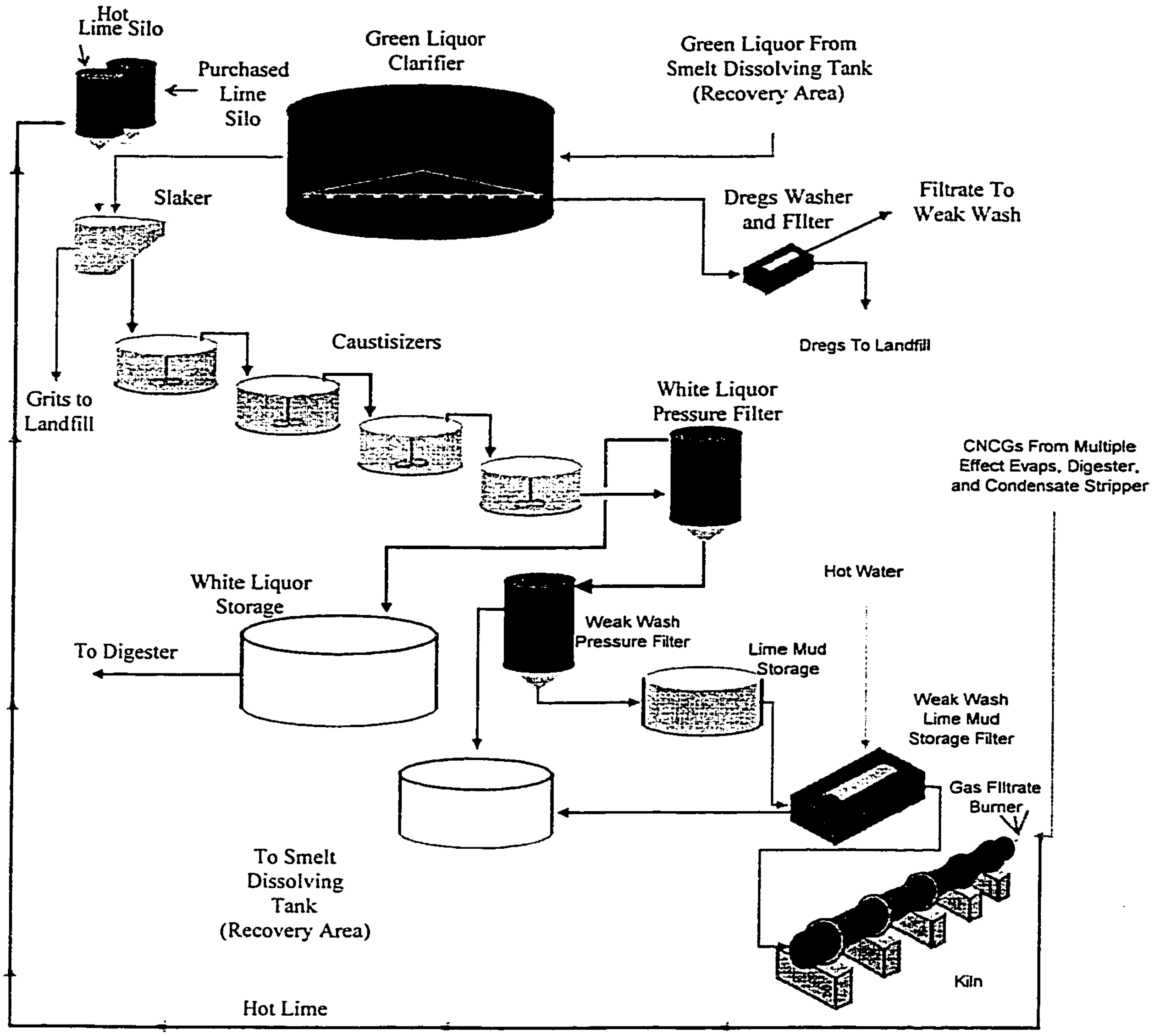


Figure 2.12: Recaust Area (Modified from Alberta-Pacific, 1993)

2.7.1 Cyclic Nature of the Kraft Process

What makes the Kraft process economical is that the cooking chemicals can be recovered and reused in the process. In this manner, the Kraft process can be described as a cyclic process. The above description of the process is illustrated in Figure 2.13. This shows the different cycles of a Kraft recovery process.

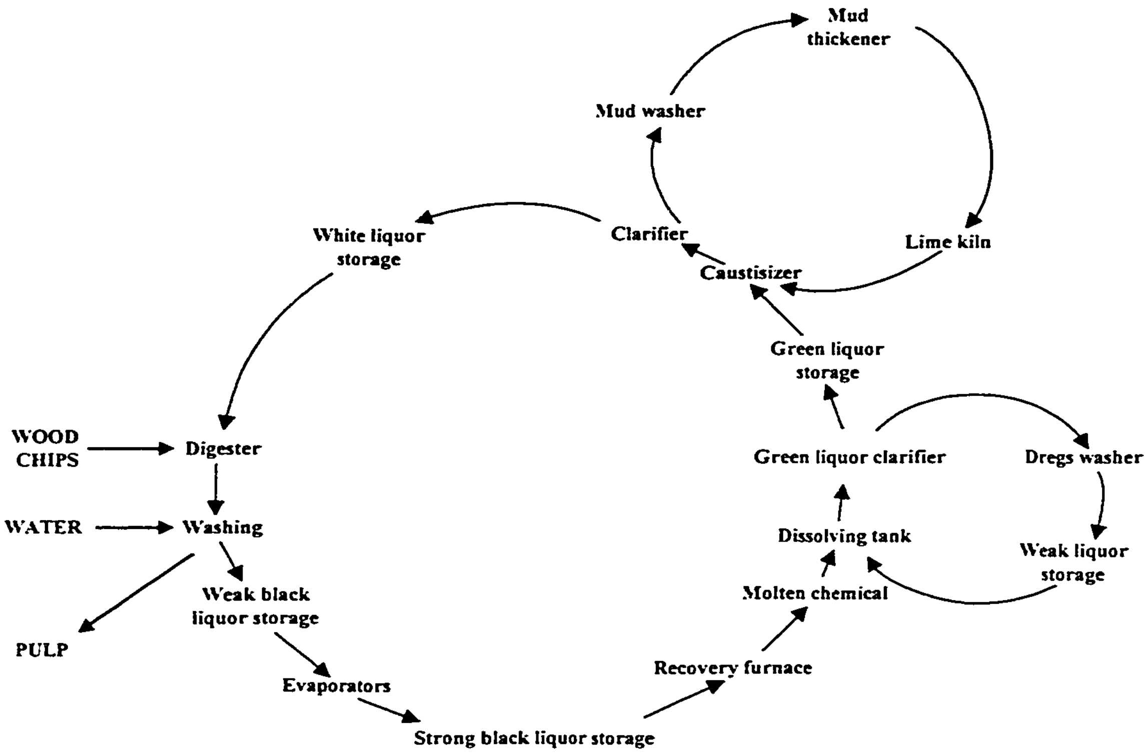


Figure 2.13: Cyclic Nature of the Kraft Recovery Process (Modified from Grace and Malcolm, 1989)

The liquor cycle starts at the point where the wood chips enter the mill and undergo a pulping process to remove the lignin from the wood. The chemicals used to do this are washed from the pulp, concentrated in evaporators to form a strong black liquor, and are then burnt in a recovery furnace. The recovered molten chemicals are sent to a dissolving tank and then a green liquor clarifier. The green liquor gets converted to white liquor to be reused in the digester for cooking the wood chips. This cycle continues on an on-going basis and allows for the reuse of liquor in the system.

The lime cycle starts at the point where lime is used to convert the green liquor to white liquor, where lime (CaO) is added to the caustisizers. Lime mud is removed from the process, washed, thickened, and converted back to lime in the lime kiln. This cycle allows for the reuse of lime in the system.

The additional cycle illustrated in Figure 2.13 is for the dregs removal and washing. This cycle indicates that dregs are removed from the system so that the weak liquor can be returned to the system for reuse in the liquor cycle.

2.8 Effluent Treatment System

All the mill water that may contain compounds that are harmful to the receiving environment is collected and treated together in the mill's effluent treatment system. Figure 2.14 shows a typical effluent treatment facility for a Kraft pulp mill.

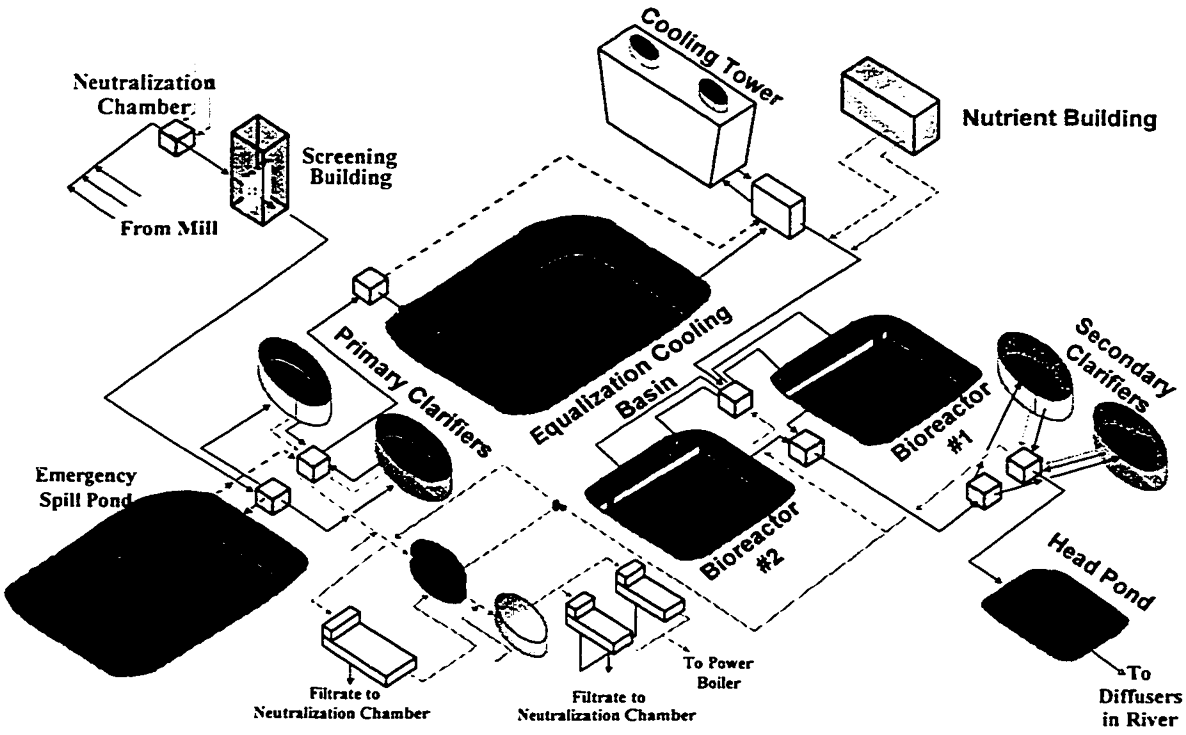


Figure 2.14: Effluent Treatment System (Modified from Alberta-Pacific, 1993)

2.8.1 Effluent Collection and Neutralization

All the process sewers from the mill site are categorized as acid, caustic, or general. These are all collected at a common point called the neutralization chamber where the combined effluent is neutralized using sodium hydroxide or sulfuric acid as shown in Figure 2.15. From here, the effluent flows by gravity through a grizzly screen where large solids are removed.

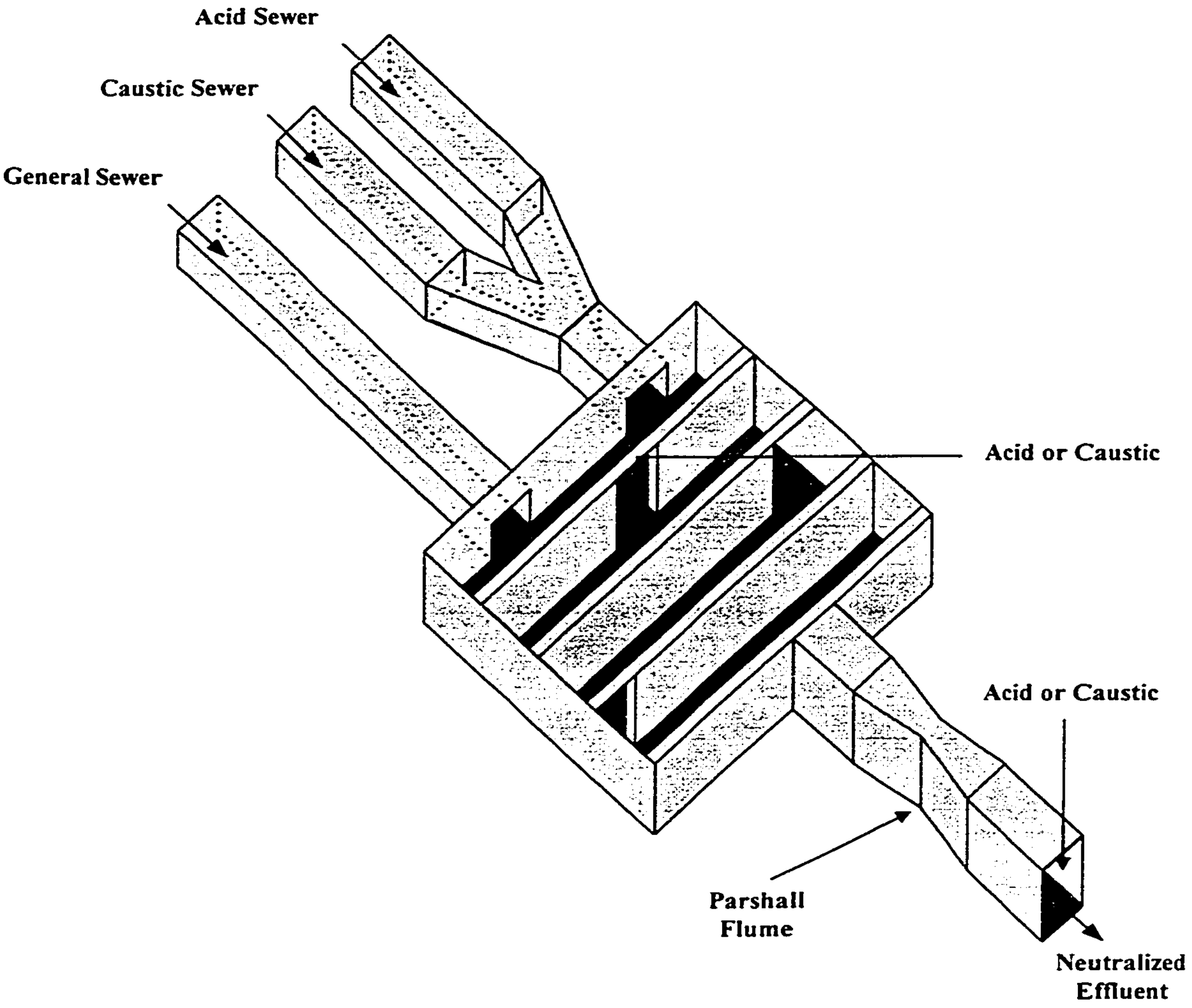


Figure 2.15: Neutralization Chamber

2.8.2 Primary Treatment

The neutralized effluent is split into one of two primary clarifiers that provide a retention time of about 12 hours. Here the suspended solids can be removed by settling to the bottom of the clarifier. The clarified effluent overflows from the top of the clarifier and enters the secondary treatment stage (Figure 2.16).

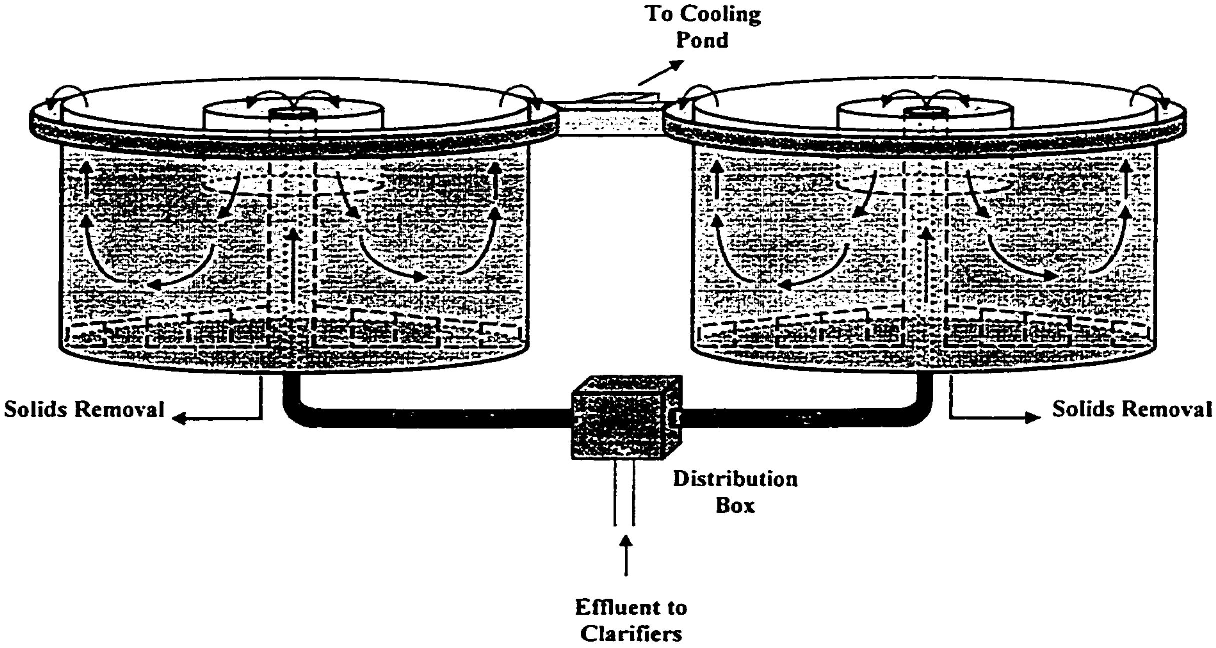


Figure 2.16: Primary Clarifiers

2.8.3 Secondary Treatment

The partially treated water flows into an equalization/cooling basin (Figure 2.17) that has a retention time of 30 hours.

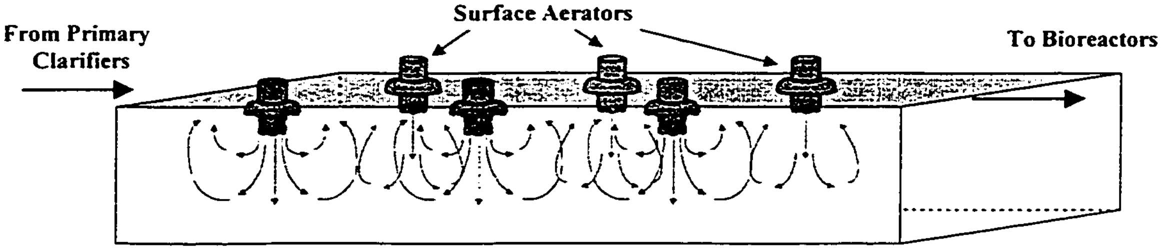


Figure 2.17: Equalization Basin

The purpose of this basin is twofold. First, the effluent must be cooled so that the microbial population in the in the bioreactors will not be harmed as well as ensuring the water discharged to the river is not too warm. Second, the effluent must be equalized or well-mixed so large pockets of contaminants will not be able to travel through the system and upset the secondary treatment stage.

The well-mixed cooled water is now transferred into two bioreactors that have a combined retention time of 38 hours. A bioreactor is an aerated pond that contains microorganisms to break down the contaminants in the effluent. The pond is broken down into 5 cells through which the effluent will cascade from cell 1 to cell 5 as shown in Figure 2.18.

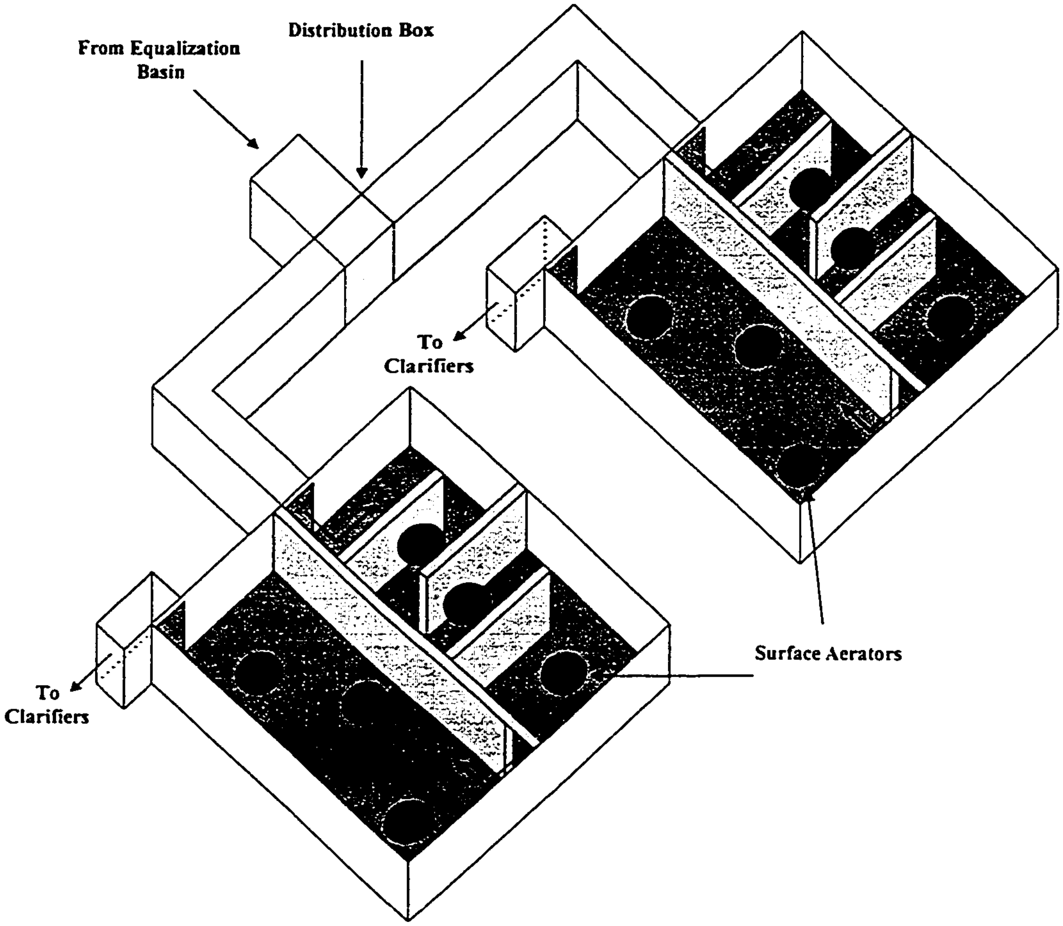


Figure 2.18: Bioreactors

The effluent from the bioreactors contains a settleable sludge that is created by the biological action of the microorganisms. The next step in the effluent treatment system is to clarify this effluent from the bioreactors by two secondary clarifiers (Figure 2.19).

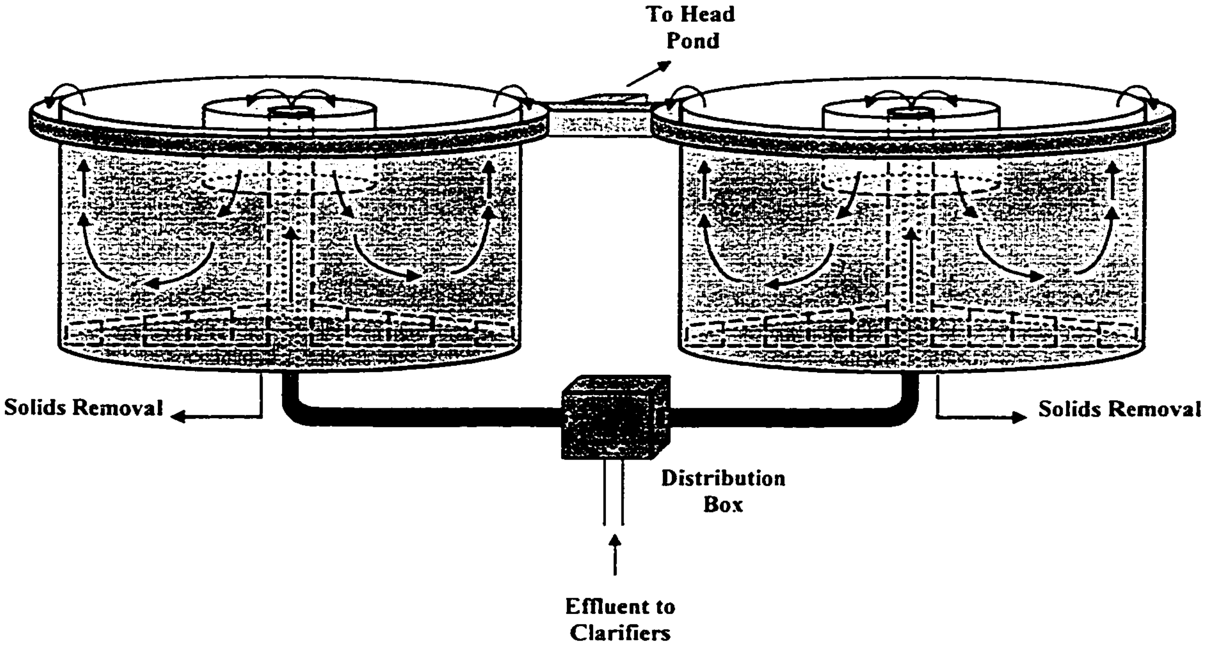


Figure 2.19: Secondary Clarifiers

The effluent quality depends on the effectiveness of the five-hour retention time in the gravity settling secondary clarifiers. Like the primary clarifiers, the settled material can be removed from the bottom of the clarifier, and the clear effluent is removed from the top. Some of the settled material is returned to the bioreactors because it contains a high concentration of microorganisms while the rest is de-watered and burned as a fuel in the power boiler.

To avoid surge feeds to the river, the completely treated effluent is sent to a head pond so that a constant head of water can be maintained to provide a constant flow to the river.

The water flows by gravity to the river where it is discharged through a number of submerged diffusers.

Chapter 3.0

Literature Review

Over the years, the pulp industry has drastically reduced the amount of water that is needed to produce pulp, hence reducing the amount of contaminants released into the environment. Table 3.1 shows the trend to use less water over the past years. Major advances in the industry such as counter-current washing, better washing efficiency, and the recycle of streams within the process have all contributed greatly to the reduction of water use. H.A. Simons (1994) indicate that the newest mills use less than 50 m^3/ADt while current design calls for 30 - 35 m^3/*ADt*. Closed cycle designs would still require some fresh water, about 15 - 20 m^3/*ADt* because of water losses, mostly evaporation. H.A. Simons (1994) also discuss numerous other advances and developments that allowed the industry to use less water.

Year	m^3/ADt
1959	240
1969	156
1975	111
1979	96
1985	79
1988	72

Table 3.1: Average Water Use in the Pulp and Paper Industry
(H.A. Simons, 1994)

In an attempt to reduce the impact of effluents from mills, governments have imposed standards and regulations that industries have to meet in order to keep operating. These government regulations have been getting more stringent, and industries have been forced to invest in new equipment and technologies to meet these limits. This usually involves large capital costs and increased operational cost that must be met by the industry. In some cases the industry cannot afford to make these changes and must be shut down. As a result of this, industries began to look into new areas of research so that they would not be affected by the continuously changing effluent discharge regulations. One of these research areas is zero liquid effluent discharge.

The idea of zero effluent discharge, also known as system closure, has been around for many years. This process would have the mill water completely reused in the process and would not discharge any effluent to the environment. The contaminants from the mill will be removed as solid waste. The idea is simple, but has many problems that have to be overcome before this process can be implemented on a full scale. In the 1970's, Great Lakes Forest Products in Thunder Bay Ontario, attempted the first closed Kraft pulp mill, but was forced to shut down in the early 1980s due to continuous problems that could not be overcome (Jemaa *et al.*, 1997). Jemaa *et al.* (1997) indicate that numerous problems can occur and must be solved before system closure can be implemented in a Kraft pulp mill. Research into these areas is increasing, especially with the introduction of the United States Environmental Protection Agency's (US EPA) new Cluster Rule (Vice *et al.*, 1996).

3.1 Cluster Rule

The cluster rule is a set of regulations based on Best Available Technology (BAT) that the pulp and paper industries in the United States must meet with respect to their effluent discharges and air emissions. This rule was signed in November 1997 and published in April 1998. Vice and Carroll (1998) indicate that many mills in the US will be directly affected by these new rules.

Vice *et al.* (1996; 1998) have followed the progress of the cluster rule, and summarized the key features for bleached paper-grade kraft mill effluent discharge regulations. Some of the rules apply to: bleach plant effluent limitations (dioxin, furan, chlorinated phenols, and chloroforms), final effluent limitations (adsorbable organic halides), best management practices implementation for control of spills, and a voluntary advanced-technology incentives program as an alternative approach to meeting the regulation.

Pulp and paper mills may choose to use the voluntary advanced-technology incentives instead of the rules based on best available technology. Mills can choose to meet one of three tiers:

Tier I: 100% ClO_2 substitution; recycle of fibre-line effluents before the bleaching stages; extended delignification. Mills must comply within 6 years of the publication of the regulations.

Tier II: Includes Tier I with more water conservation and reuse with some bleach-filtrate recycle. Mills must comply within 11 years of publication of the regulations.

Tier III: Includes Tier II with full recycle and reuse of condensates and bleach filtrate recycle. Mills must comply within 16 years of publication of the regulations.

All tiers also include discharge limits that must meet BAT limits for dioxin, furans, chloroforms, and a number of chlorinated phenolics.

These rules directly affect US mills, but may also indirectly affect Canadian mills and other mills around the world. Vice and Carroll (1998) indicate that the cluster rule has been watched closely by Canadian mills as an indication of future environmental control for industry and for possible trade ramifications on Canadian pulp products. There could be market pressures to conform to the same rules that US pulp is produced, and a possible border tax on products entering the US. Customers may demand that the pulp they buy meets or exceeds the standards at which the US pulp was produced, otherwise a tax could be applied to the pulp.

These rules are indications that mills will eventually have to reduce the amount of pollutants being discharged to the environment. The best way to meet these rules and all possible future rules governing effluent discharge limits would be to have zero effluent discharge. This is one of the reasons why more and more research is being done on system closure.

3.2 Non-Process Elements (NPE's)

There are numerous problems that may occur if the mill effluent would be returned into the mill for use as process water. Some of these problems include corrosion, operational, and pulp quality problems. Many non-process elements (NPE's), i.e., elements that do not play a useful role in pulping, contribute to these problems.

NPE's are very important to consider when dealing with system closure. The most important NPE's according to Jemaa *et al.* (1997) are: K, Cl, Ca, Mg, Mn, Ba, Fe, Si, Al, Cu, Ni, Cr, and Zn. These elements enter the pulping process from various locations such as wood chips, process water, and chemicals. Keeping them within the system when it is closed would cause numerous problems. The main sources of these elements, problems associated with them, and their main purge points from the system are summarized in Table 3.2. The information in this table is data from other mills and not necessarily those from Alberta-Pacific Forest Products Inc.

Elements	Main Sources	Potential Problems	Main Purge Points
K	Chips (> 90%)	Boiler plugging, decreases causticizing efficiency, increase heat demand in the lower part of the recovery boiler, and effects black liquor density and viscosity	ESP Catch
Cl	Chips (generally > 50%), Chemicals	Boiler plugging, acts as deadload component, increases energy demands in the recovery boiler and in the lime kiln	ESP Catch
Ca	Chips (>80%)	Forms scales, competes with transition metals for chelants, and affects oxygen delignification	Dregs, pulp
Mn	Chips (>90%)	Forms scales and deposits, lowers product brightness	Dregs
Fe	Chips (>50%), Corrosion of Equipment	Forms scales and deposits, lowers product brightness, hampers lime mud filtration	Dregs
Al	Chips (>50%), Lime	Forms scales and deposits, and competes with transition metals for chelants	Removal of Scales and Deposits
Cu	Chips (>90%)	Decomposes O_2-based bleaching chemicals	Dregs
Co	Chips	Decomposes O_2-based bleaching chemicals	Dregs
Cr	Chemicals	Increases the frequency of ClO_2 generator puffs and affects product brightness	Dregs
P	Chips (>90%)	Decreases the available CaO	Grits
Si	Chips and Lime (>50%)	Forms scales and deposits, causes a decrease in lime porosity	Removal of Scales and Deposits
Mg	Chips (50%)	Disturbs the settling properties of the dregs	Pulp, Dregs, Grits
Ba	Chips	Forms scales and deposits	Removal of Scales and Deposits

Table 3.2: Behaviour of the Non-Process Elements in the Kraft Liquor Cycle (modified from Jemaa *et al.*, 1997)

Alberta-Pacific Forest Products Inc. is an in-land mill. Most of the chlorides introduced into the system would most likely come from the bleaching stages rather than the chips as indicated in Table 3.2.

With current mill operations, NPE's leave the process with wastewater, sludge, electrostatic precipitator dust, and final pulp. If the "water-loop" were closed, one of the purge points for the NPE's would be removed, and an accumulation of these elements would occur. If these elements reach a certain concentration, upsets in mill operations will start to occur. Certain elements (Mg, Al, P) form insoluble complexes and build up in the lime cycle, while other elements (Cl, K, Si, Al) are highly soluble in the liquors, and have a tendency to accumulate in the liquor cycle (Jemaa *et al.*, 1997). The cyclic nature of the Kraft process is described in Chapter 2.

Tran *et al.* (1990) indicate that at high Cl and K levels, the temperature range is lowered in which sticky deposits are formed in the recovery boiler. These deposits accelerate the plugging of the flue gas passages in the boiler and the mill would have to shut down for cleaning after the accumulation reaches a certain level. Elevated levels can also have a negative impact on the efficiency of various mill unit operations. Corrosion rates may increase with the accumulation of NPE's (Sharp, 1996); rates are highly site specific and may increase as the Cl and sulfate concentrations increase. Depending on pH, temperature, dissolved organics, and ionic strength, insoluble compounds such as calcium carbonate ($CaCO_3$), calcium oxalate (CaC_2O_4), calcium sulfate ($CaSO_4$), and barium sulfate ($BaSO_4$) may form and precipitate out of the pulp solution and cause bleaching problems.

Jemaa *et al.* (1997) indicate that scaling in evaporators is caused by the formation of insoluble species containing Ca, Mg, Si, and Al. The low thermal conductivity of scales requires an increase in steam temperature to maintain evaporation capacity. They also indicate that Mg, Fe, Al, P, and Mn in the caustisizing area gradually accumulates until insoluble salts are formed. As the accumulation increases, the ionic strength of the solution increases, and the settling and drainage characteristics of the lime mud are affected. Additional problems caused by the buildup of NPE's (Jemaa *et al.*, 1997) are: Ba combines with sulfate to form deposits when H_2SO_4 is used for pH control, and increased Ca levels harm cellulose during softwood delignifying with O_2. On the positive side, Jemaa *et al.* (1997) indicates that an increase in Mg has a positive effect on bleaching where it: improves brightness, viscosity, and protects pulp from cellulose degradation.

3.3 Current Practices to Remove NPE's

3.3.1 Electrostatic Precipitator (ESP) Dust

After the black liquor is concentrated in the evaporators, it enters the recovery boiler where it is burned as a fuel source as well as a means to recover the spent cooking chemicals (Figure 2.10). The flue gas that exits the recovery boiler passes through an electrostatic precipitator that uses an electric current to separate the dust from the gas. This dust is rich in NPE's, but also in spent cooking chemicals. Normal practice of a mill is to reuse most of this dust to recover the useful chemicals and reduce chemical makeup costs. This is accomplished by mixing the ESP dust into the black liquor to be sent to the recovery boiler. If the NPE's accumulate to high concentrations in the black liquor, the dust is sewered to control the build up of the elements. This practice increases the chemical make-up costs.

Separation in Liquor Clarification

As discussed in chapter 2, after the black liquor is burned in the recovery boiler, inorganic pulping chemicals are recovered as a molten smelt that falls to the bottom of the boiler. The molten smelt is added to water in the smelt dissolving tank (Figure 2.10). The green liquor goes to the green liquor clarifier (Figure 2.12). Here, the undissolved material, called dregs, are settled out of the liquor and landfilled. The dregs usually have a high concentration of carbon, metal carbonates, sulfates, sulfides, hydroxides, and silicates (Biermann, 1996). After the green liquor is clarified it is converted to white liquor to be reused in the digester for cooking of the wood chips.

One of the areas that is often used to separate some of the insoluble NPE's would be through green liquor clarification and the white liquor filters. Gleadow *et al.* (1997) have indicated that green liquor clarification effectively removed Ca, Mg, Mn, and Fe. They also indicated that white liquor filtration removed Ca, Al, and Mg effectively. Noted was the fact that green liquor clarification was probably one of the most important mechanisms for the removal of insoluble NPE's.

3.4 Developing Closed Cycle Technologies

Jemaa *et al.* (1997) indicates that the *Rapson-Reeve Salt Recovery Process (SRP)* was used at Great Lakes Forest Products in Thunder Bay Ontario in the 1970's. This was the first attempt at system closure on a Kraft mill. The SRP process used a two-stage evaporation/crystallization process to recover NaCl (Jemaa *et al.*, 1997). The first stage concentrated the white liquor and then crystallized the Na_2CO_3 and $2Na_2SO_4{\cdot}Na_2CO_3$.

These were removed by clarification and filtration. The second stage involved further concentration of the white liquor and crystallization of NaCl. This was removed by leaching. This process was modified to include another crystallizer to remove KCl from the system. This process was abandoned after the mill ran into a number of major problems, such as the corrosion of the white liquor evaporators.

MacMillan Bloedel also developed a salt removal process in which the ESP dust was leached with SRP process liquor and water (Jemaa *et al.*, 1997). The pH and temperature were controlled to achieve a NaCl/Na_2SO_4 ratio of 3 to 1. This process removed a significant amount of NaCl, but was expensive and difficult to operate.

Thompson *et al.* (1995) developed a new approach for the removal of K and Cl using a three-compartment Bipolar Membrane Electrodialysis (BME) cell (Figure 3.1). This approach is used to separate the NaCl in the ESP dust into NaOH and HCl. They reported that as much as 60% of the Cl was removed without any significant loss of sulfate. The methods and economics of this process were not presented.

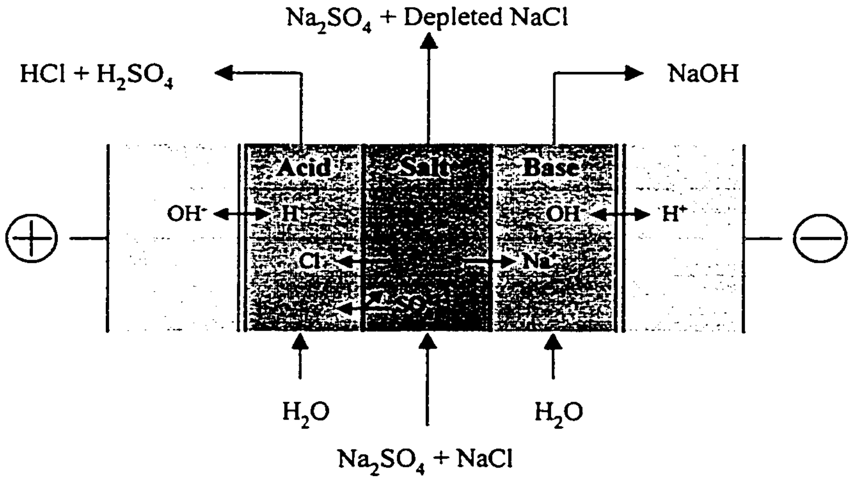


Figure 3.1: Bipolar Membrane Electrodialysis (BME*)* Cell (Modified from Thompson *et al.* 1995)

Jemaa *et al.* (1997) discuss the use of polymers and an aqueous-aqueous separation process in which approximately 60% of the Cl can be removed while recovering approximately 90% of the Na_2SO_4 and Na_2CO_3. This process has only been attempted on a lab scale. Newer technologies involve the use of K selective substrates to remove K from the recovery cycle. K levels in the ESP dust have been reduced by up to 100% (Jemaa *et al.*, 1997) during lab studies.

One of the areas that received great attention has been the development of Champion Corporation's Bleach Filtrate Recycle (BFR). This process includes a chloride removal process as well as a metal removal process that would be used to potentially close up a bleaching line. In the chloride removal process, the ESP dust is dissolved in water and fed to a crystallizer/evaporator unit. The solution is evaporated, increasing the concentration of NaCl while suppressing the solubility of Na_2SO_4. The solution is then passed through a hydro-cyclone and a filter to separate the two salts. The Na_2SO_4 crystals are removed from the drum filter and returned to the black liquor mixing tank. Some of the filtrate from the filter drum is sewered to provide the K and Cl purge. The metal removal process uses two stages of filtration to remove suspended materials followed by two cation exchange units. This arrangement has the potential to allow recycle of the filtrates by removing many of the metal contaminants of the streams. This process was installed at Canton, NC in 1996 (Ferguson, 1996) and is still undergoing trials.

Another technology developed for the removal of K and Cl from ESP dust is by EKA Chemicals. A Precipitator Dust Recovery (PDR) process is used in which the dust is dissolved in hot water and then Na_2SO_4 is crystallized out of the solution. All other chemical species are concentrated in the liquid phase. Here the crystals are separated by a filter drum and dissolved in the black liquor to recover the chemicals. A 90% removal of both K and Cl is achievable (Ferguson and Finchem, 1997). This process is currently being commercialized.

Jemaa *et al.* (1997) discuss the Precipitator Dust Purification (PDP) system developed by Paprican and Prosep Technologies. An aqueous solution of the ESP dust is filtered to remove any suspended solids and then introduced to a fixed resin bed that retains NaCl. It is reported that the Cl removal efficiency is as high as 97% while the recovery of Na_2SO_4 and Na_2CO_3 was as high as 98% (Jemaa *et al.*, 1997). This allows the treated ESP dust to be returned to the kraft recovery cycle.

There are other approaches to system closure. As mentioned above, some research is dedicated to bleach plant effluent recycle, while others concentrate on trying to capture the spent cooking chemicals from the ESP dust while maintaining a purge for K and Cl. Some research institutes, such as Paprican, believe in progressive system closure, with more attention focused on the internal recycling of mill streams.

In the past, mills used mostly fresh water to operate their plants and paid little attention to the internal recycling of streams. H.A. Simons (1994) discusses key areas that newer mills have focused on for water reduction. With wood and chip preparation, water is normally recovered from log cleaning showers and reused, as well as using white water from the pulp machine room for log thawing. The digesting and brown stock systems reuse condensate from relief and flash steam vessels as well as contaminated condensates for water uses in the place of fresh water. The bleach plant reuses some of their filtrates and machine white water as wash water on the bleach washers. The chemical recovery system reuses warm water and stripped condensates in the brown stock area while the machine room reuses much of the white water produced within the machine room.

The focus on some of the research towards system closure is dedicated to the restructuring of older kraft mills to reduce their water consumption. To a large extent, newer mills already have this incorporated into their design. H.A. Simons (1994) indicates that mill effluents at these newer facilities are cleaner and have much lower volumes. In this situation, it may be practical to examine an "end of pipe" treatment strategy to determine if a biologically treated effluent could be recycled back into a newer mill as process water. As well, since the individual waste streams generated within the mill are cleaner, it may be possible to internally recycle these individual streams reducing the flow of total effluent to the environment gradually. Some issues that would have to be addressed are (Dorica *et al.*, 1998): buildup of biological activity in process streams, increased levels of dissolved solids, corrosion, scaling, and increased chemical consumption.

Chapter 4.0

Separation of Non-Process Elements Using Lime Softening

This chapter discusses the proposed system closure process that Alberta-Pacific Forest Products Inc. was interested in studying. Alberta-Pacific wanted to determine if the mill effluent could be recycled as process water using their current raw water treatment equipment and practices. Their current raw water operation is discussed in detail to provide a better understanding of the proposed system closure process. The experimental procedure and setup for the removal of non-process elements and the methods used for the analysis of the samples are also discussed. A factorial design statistical approach was used to analyze the data and the results are discussed.

4.1 The Proposed System Closure Process

Lime softening of the mill effluent was considered as a method toward system closure for a number of reasons. First, the effluent at this mill is very clean compared to older pulp mills because the best available technology was used for development of the mill at the time it was constructed in 1993. Second, if the mill were to accomplish system closure, the raw water clarifier that is currently being used would not be needed for its original purpose. The capital cost of providing technology to achieve system closure could be reduced by using this clarifier. The existing mill process is described in Figure 4.1.

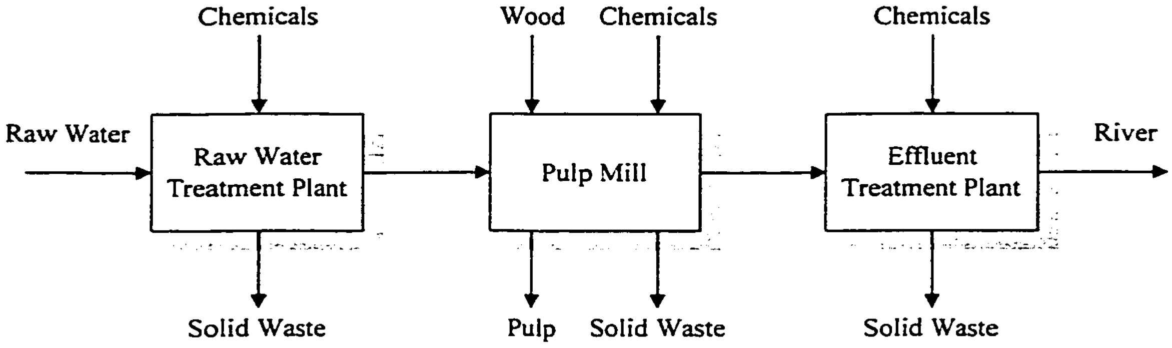


Figure 4.1: Existing Mill Process

As is shown above, mostly wood, treated river water, and chemicals enter the pulping process, and with each of these, a number of non-process elements. With current mill operations, the purge points for these NPE's are through solid wastes produced by the process, the final pulp, and the effluent that leaves the mill.

The idea for system closure at this mill would be to subject the mill effluent to its current raw water treatment as described in chapter 2. A schematic of the hypothetical process is shown in Figure 4.2. The effluent leaving to the river would be recycled, hence removing one of the current purge points for the NPE's. Since an output is removed, an accumulation of these elements would occur if another method to remove these is not found. The NPE's would now only exit the pulping process by means of the final pulp and solid waste streams.

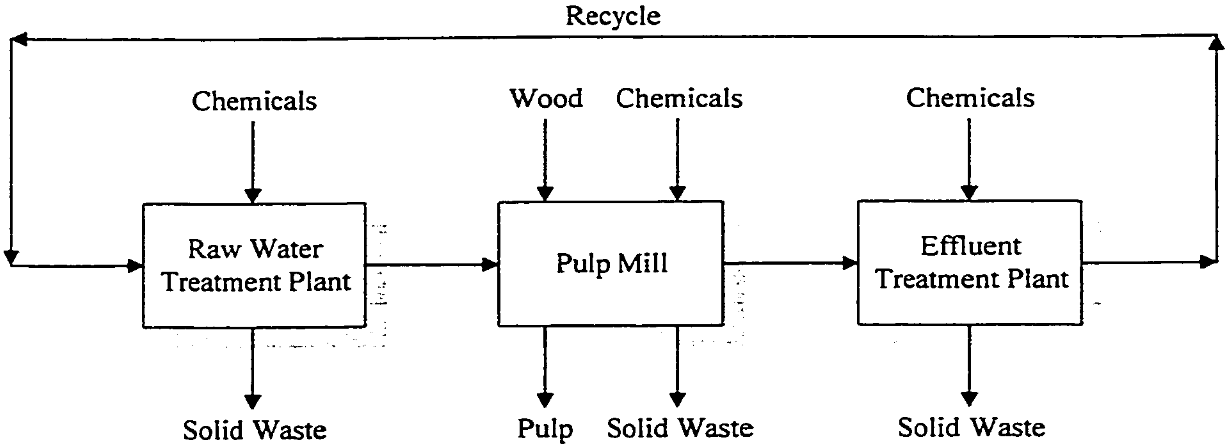


Figure 4.2: Proposed System Closure Process

The proposed system closure process would use the current raw water reactor-clarifier to remove the non-process elements present in the mill effluent. Lime would be added to the effluent to form a hydroxide precipitate (lime softening) using hydrated lime ($Ca(OH)_2$) as the hydroxide source. This is illustrated in Figure 4.3.

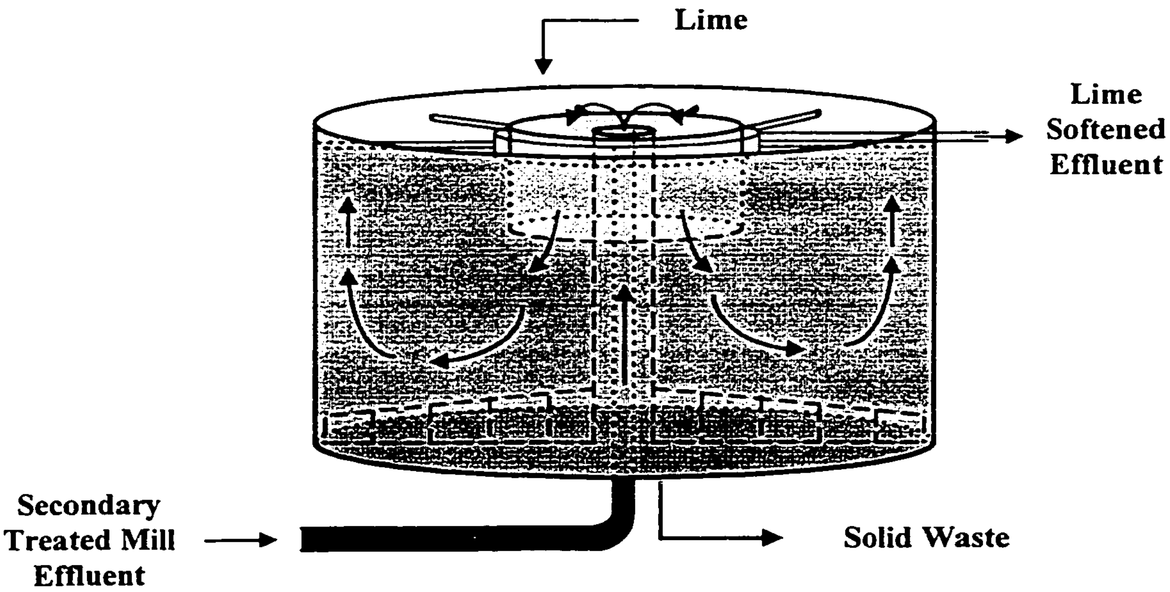


Figure 4.3: Proposed System Closure Process - Lime Softening

Heavy metal precipitates form by the reaction

$$M^{++} + 2OH^{-} \longrightarrow M(OH)_2 \downarrow \tag{4.1}$$

where M^{++} is the metal cation.

Ca and Mg are mostly present as a bicarbonate, so the reactions that would occur are:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O \tag{4.2}$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O \tag{4.3}$$

The precipitates that would form in this process may not be heavy enough to settle out of the solution by themselves, so an alum coagulant and polymer flocculant may have to be added to assist in the settling process. The hydrated metal complex ($M(OH)_2$), $CaCO_3$, and any other heavy materials would precipitate out of the solution and settle to the bottom of the clarifier and form a sludge. The rakes at the bottom of the clarifier would push the NPE (Ca, Mg, Fe, etc.) rich sludge to the center where it is removed from the system to a compression holding tank. The sludge can then be held in this tank for a period such that it settles and compresses, so that the water is removed. The sludge may then be pumped from the bottom of this holding tank to a belt filter press where more water can be removed. The de-watered sludge can then be transported to a landfill for disposal.

As lime is added to the system, the pH (OH^- concentration) increases such that hydroxide precipitates are formed from the NPE's. These precipitates form scale in the mill's process equipment, so the pH would have to be lowered to reduce this scaling. To do this, supernatant from the clarifier would pass through the mill's current re-carbonation chamber where CO_2 is added (Figure 4.4).

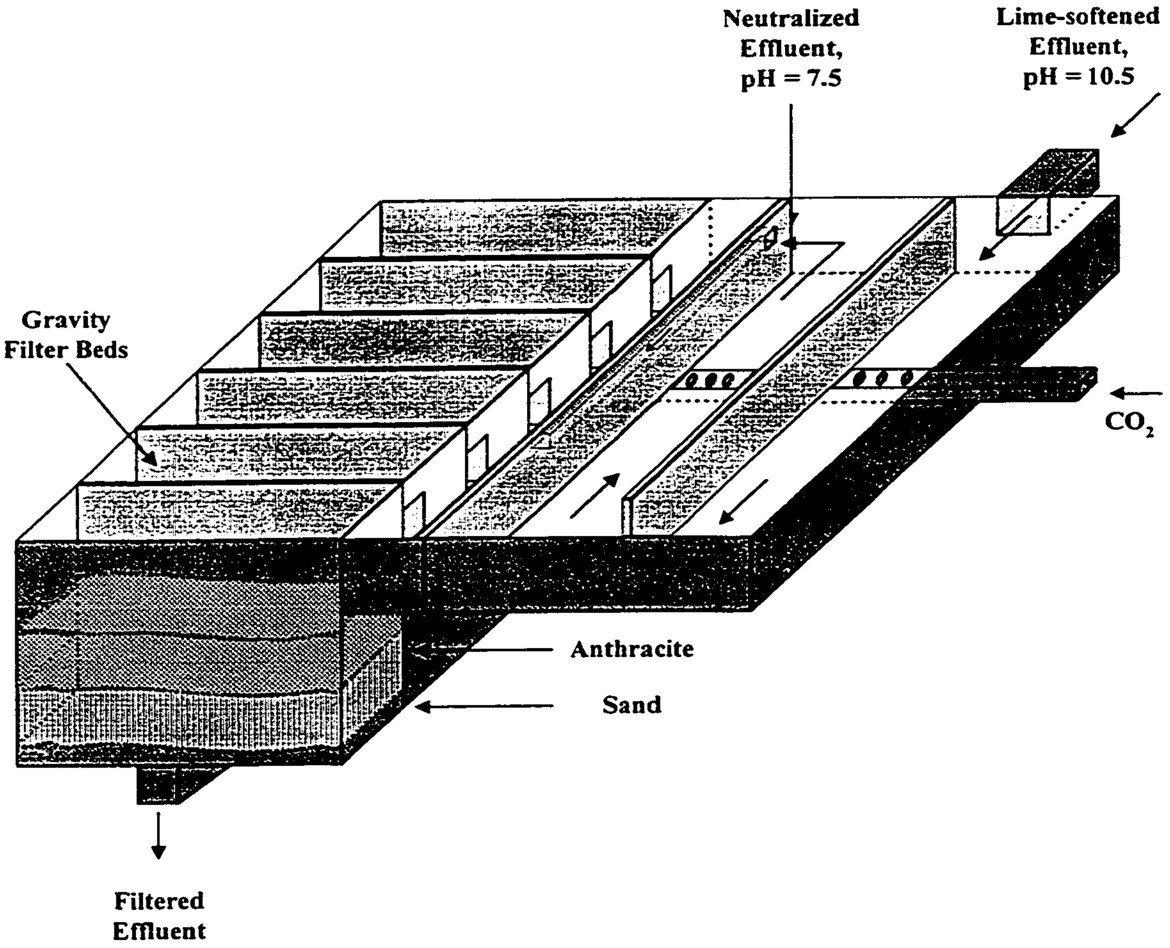


Figure 4.4: Proposed System Closure Process - Re-carbonation and Gravity Filters

For a pH greater than 10.2, a 2-stage re-carbonation system must be used. In this system, CO_2 is added to the re-carbonation chamber by one of two diffusers. The effluent would enter the chamber at a pH greater than 10.2, which would be reduced to approximately

8.5 after the first set of diffusers. This first stage CO_2 addition should neutralize any excess lime by:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O \tag{4.4}$$

The second set of diffusers should reduce the treated effluent to a pH of about 7.5. This should convert caustic and carbonate alkalinity by:

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^- \tag{4.5}$$

$$Mg(OH)_2 + 2CO_2 \longrightarrow Mg^{2+} + 2HCO_3^- \tag{4.6}$$

This lower pH effluent would ensure that the remaining hydroxide precipitates become soluble in the water and not precipitate out in the mill's pipes and equipment. The water would then enter a center pipe where it is fed to the mill's current filter beds.

The dual-media gravity-filtration beds consist of an upper anthracite layer and a lower sand layer. The anthracite used in these filters is relatively coarse and has a depth of approximately 35 cm. The lower sand layer is relatively fine and is about 25 cm in depth. This configuration is used so that the water has to first pass through the coarser material removing any of the larger remaining suspended solids, and then through the finer material to remove the smaller suspended solids. The turbidity of the water leaving each filter bed would be constantly monitored, and when it reaches an unacceptable level (indicating that the filter bed is saturated with suspended solids), the filter can be taken offline and cleaned.

It is not expected that the chlorides and potassium will be removed from the system by this process. Lime softening is used to remove cations, so chlorides, which are anionic, should not be removed. As well, potassium compounds, especially those of hydroxides, are very soluble and will not precipitate out of solution (Kemmer, 1988). This treatment of the mill's secondary effluent may allow the water to be recycled as process water. Experiments were performed to test the feasibility of this proposed process.

4.2 Experimental Procedure

4.2.1 Current Raw Water Treatment Practice

The current raw water treatment process is used to clarify the incoming river water for use as process water in the mill. The river water is usually quite "dirty" and requires chemical and physical treatment in order to make the water acceptable for drinking and the pulping process. Usually, the water contains large amounts of particulate matter (colloids) that have to be removed. The colloids can be either inorganic (clays, silts, etc.) or organic (humic and fulvic acids) and usually have a negative electric charge that repel each other (Kemmer, 1988). The colloids reduce the clarity of the water, increase color, limit the effectiveness of disinfection, provide a possible sink for toxic substances, and cause taste and odor problems.

The most common method to remove colloids is through sedimentation in a clarifier. In order for sedimentation to occur, the colloids need to agglomerate (stick together) to form heavier particles that will sink to the bottom of a clarifier. To do this, chemicals are usually added to coagulate (destabilize the particles) and flocculate (particle-particle contact) the colloidal material.

The electrical repulsion of the colloids makes it very difficult for the colloids to adhere and form larger particle to allow them to be removed from the process. This negative electric charge is neutralized by adding a coagulant to destabilize the particles, allowing them to stop repelling each other. To aid in forming larger particles or flocs, a flocculant aid could be added. At this mill, aluminum sulphate ($Al_2(SO_4)_3$), also called alum, is used as a coagulant while an anionic (negatively charged) polymer is used as a flocculant aid.

The hydrolysis reactions can be indicated by (modified from Kemmer, 1988):

$$Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3(SO_4^{\ 2-}) \tag{4.7}$$

$$Al^{3+} + H_2O \Leftrightarrow Al(OH)^{2+} + H^+ \tag{4.8}$$

$$Al(OH)^{2+} + H_2O \Leftrightarrow Al(OH)_2^{\ +} + H^+ \tag{4.9}$$

Other authors (Benefield *et al.*, 1982) indicate that the alum reacts with the alkalinity in the water. The introduction of alum to the system assists in removing these colloids by three coagulation mechanisms: charge neutralization, adsorption, and sweep flocculation.

Neutralization

The neutralization of colloids takes place by combining any of the cations in equations (4.7) to (4.9) with the colloid. This is illustrated in Figure 4.5.

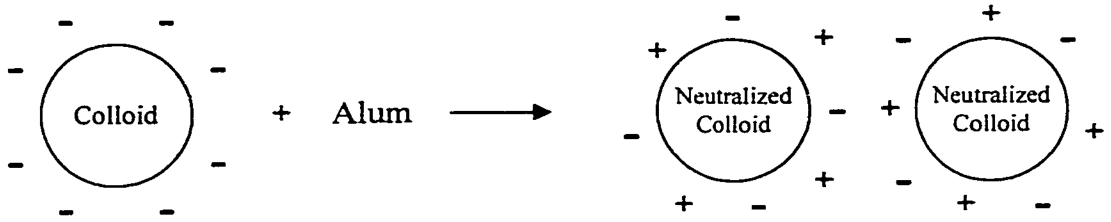


Figure 4.5: Neutralization by Alum Coagulation

This allows the particles to stop repelling each other and have a better chance at colliding and adhering (Kemmer, 1988). These coagulated particles are larger and heavier than the individual colloids and will now settle to the bottom of a clarifier faster than individual colloids would.

Adsorption

The second mechanism of alum coagulation is adsorption. The alum reactions above continue to form $Al(OH)_{3\,(s)}$:

$$Al(OH)_2^+ + H_2O \Leftrightarrow Al(OH)_{3\,(s)} + H^+ \qquad \textbf{(4.10)}$$

Many organics tend to adsorb to the $Al(OH)_{3\,(s)}$ precipitating particle and can be removed in this manner.

Sweep Flocculation

The third mechanism for alum coagulation is sweep flocculation. The solid $Al(OH)_{3\,(s)}$ particle formed with the alum addition process (equation (4.10)) physically entraps colloidal material as it settles out of the solution (Figure 4.6).

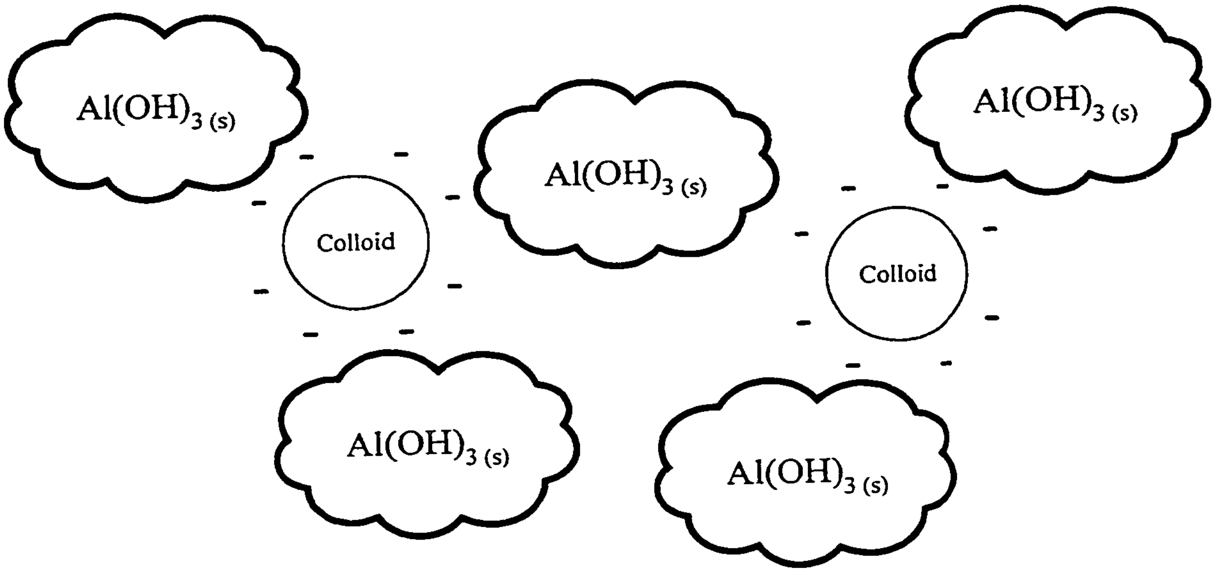


Figure 4.6: Sweep Flocculation

With the addition of an anionic polymer, the particles formed by the addition of alum can be collected and removed at a faster rate. The large molecular weight polymer forms a "net" that physically entraps the coagulated particles and assists in the settling process. This is illustrated in Figure 4.7.

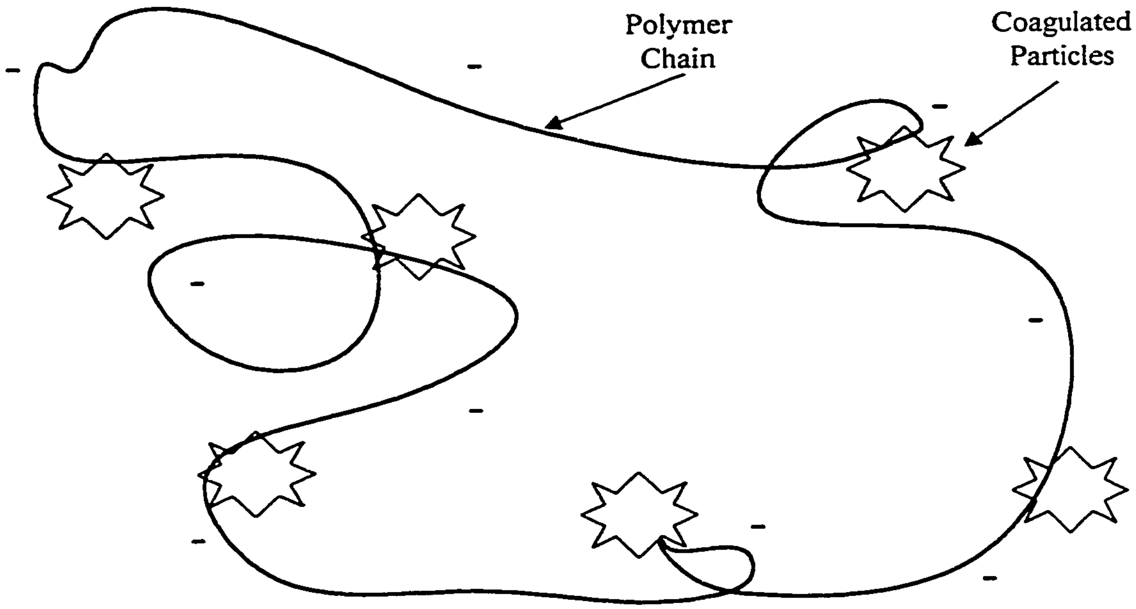


Figure 4.7: Floc Formation with the Addition of an Anionic Polymer

4.2.2 Jar Test Procedure

To simulate the performance of the mill's current reactor-clarifier, the mill effluent was treated in a series of jars using a combination of an alum coagulant, polymer flocculant, and lime softening reagents. The polymer is an anionic, high molecular weight, polyacrylamide blend with a medium charge density. This is provided in powder form and is supplied by Betz-Dearborne. The product name is "aquafloc 468". The hydrated lime ($Ca(OH)_2$) is supplied in powder from and is provided by Continental Lime. The aluminum sulfate ($Al_2(SO_4)_3$) is supplied at 40% strength in liquid form and is supplied by Marsulex.

With agitation, the reagents were added in known amounts to aid in precipitating the ionic species out of the effluent. After a set time, the solution was removed from the agitation and allowed to settle. The supernatant was collected and analyzed for the non-process elements in question. A number of preliminary experiments were conducted to determine if this procedure accurately simulated what was occurring in the reactor-clarifier. The following procedure was used:

- add 2 litres of the water sample into the jar;
- add lime to the water while mixing at 200 rpm until the desired pH is reached;
- add the desired amount of Alum and let mix for 30 seconds;
- slow mixing to 40 rpm and add the desired amount of polymer;
- mix for 1 minute, then slow to 20 rpm;
- mix for 20 minutes and then stop the mixing completely;
- settle for 20 minutes;
- collect the supernatant for analysis.

The mill currently uses this procedure to simulate the reactor-clarifier to determine the dosage of chemicals to add to the river water. The only modification made to this procedure was to add the mill's secondary treated effluent to the jars instead of river water. The reagents were added to the jars in the same order as they were being added to the reactor clarifier.

There are different mixing requirements for rapid mixing and flocculant mixing. The initial mixing at 200 rpm is used to simulate the high speed mixing induced by the turbulence in the pipe that presently feeds the clarifier. This mixing speed allows for good mixing of the water and the reagents. When adding alum to the system, a higher mixing speed is essential for good dispersion and to promote increased frequency of collisions, but with the addition of polymer, too much mixing may shear the polymer-made flocs (Kemmer, 1998). The mixing at 40 rpm simulates the stage at which the water passes through the turbine at the inlet of the clarifier. This allows the polymer to be well mixed in the solution without physically damaging the polymer. In order for the particles to agglomerate, they have to collide. The mixing at 20 rpm stage simulates the mixing that occurs in the reaction zone. The supernatant collected from the jars should be representative of the overflow that enters the re-carbonation chamber.

4.2.3 Experimental Apparatus

The experiments used to simulate the lime softening of the mill effluent were performed using a 7790-400 Phipps and Bird Stirrer equipped with six-two litre Phipps and Bird jars as illustrated in Figure 4.8.

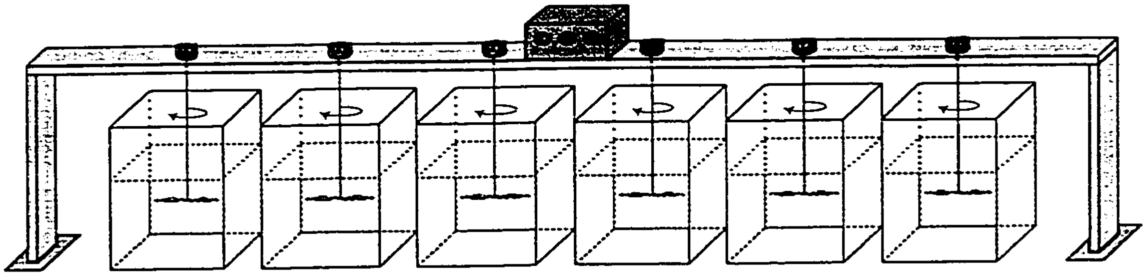


Figure 4.8: Experimental Apparatus

4.2.4 Safety

To avoid injury, the proper use and handling of chemicals must be practiced. In all situations, the proper protection was worn, i.e., safety glasses, rubber gloves, and a lab coat.

4.2.5 Samples

The samples were collected and stored in 1-litre high-density polyethylene containers according to Standard Methods for the Examination of Water and Wastewater (Greenberg *et al.*, 1995). These were cleaned with a metal-free nonionic detergent solution, rinsed with tap water, acid, and then with distilled water. Supernatant was collected in these cleaned containers and preserved to a pH<2 with nitric acid to prevent the metals from being adsorbed and/or precipitation in the sample container.

Sample preparation for analysis followed the standard procedure as outlined in Standard Methods for the Examination of Water and Wastewater (Greenberg *et al.*, 1995).

4.3 Analytical Methods

The non-process elements analyzed in this study are based on a combination of which elements are of a concern in system closure (Table 3.2), and which elements could be analyzed at the mill site. A number of different methods of analysis were available: atomic absorption spectrometry, potentiometric titration, and a spectrophotometer. Sample preparation, operations, and common problems associated with these instruments are well known and can be found in various sources (Christian and O'Reilly, 1986). The elements analyzed for this study were Cu, Mg, Ca, Mn, Fe, K, and Cl.

Atomic absorption spectrometry is one of the most important techniques for the analysis and characterization of the elemental composition of samples. Most of the elements of concern were analyzed by this method, with the exception of chlorides. This method is the simplest and quickest way to analyze most elements. Chlorides are usually analyzed by ion chromatography or potentiometric titration, but a potentiometric titration device was available on site and was used for this analysis. The potentiometry method is discussed in Appendix A.

4.4 Verification of Experimental Procedure

A number of tests were performed to determine whether the jar tests accurately simulate what is occurring in the reactor-clarifier. Over a 6-hour period, jar tests were performed on the influent water to the mill's reactor-clarifier. The procedure used is outlined above in section 4.2.2, with the exception that no lime was added to the samples. This was done because the water being treated in the clarifier was not using lime softening at the time these samples were taken. For comparison purposes, samples of the influent, and the effluent of the reactor-clarifier were also collected and analyzed. Table 4.1 shows the percent removal of the metals from the influent in both the jar tests and the reactor-clarifier. Mg and Cl were not analyzed in this part of the study because it was not know at this time that these elements could be analyzed at Alberta-Pacific.

Time	Fe (%)		Mn (%)		K (%)		Ca (%)		Cu (%)	
	Jar Tests	Clarifier Effluent	Jar Tests	Clarifier Effluent	Jar Tests	Clarifier Effluent	Jar Tests	Clarifier Effluent	Jar Tests	Clarifier Effluent
8:30	99.00	98.92	91.82	86.45	63.13	63.32	8.72	0.24	85.25	98.20
11:00	99.34	98.82	93.89	87.10	63.23	62.22	13.14	-4.40	44.95	70.64
12:00	99.29	98.83	92.78	86.53	61.30	62.34	21.01	1.85	77.27	72.73
14:00	99.79	99.53	98.07	96.30	78.47	77.61	41.53	40.14	93.90	95.61

Table 4.1: Percent removal of metals from influent

The percent removal of the metals from the jar tests appears to indicate that the jar tests do simulate what is occurring in the reactor-clarifier accept for Ca and Cu. The percent difference in readings was lower than 2% for both Fe and K, and 8% for Mn. The readings for Cu were very low and outside the range of accuracy for the atomic adsorption spectrometer. This does not obey Beer's law and cause high error in the readings (Appendix A), therefore the analysis for Cu has been omitted for the remainder of this study. The readings for calcium were erratic due to the exclusion of an ionization suppressant (Appendix A). A potassium suppressant was used for the reading of Ca for the remainder of this study.

4.5 Lime Softening of the Mill Effluent

The mill effluent was treated using the procedure outlined in section 4.2.2. A number of trials were performed to determine the effects of varying the dosages of the reagents. It appeared that a large amount of sampling would have to be done in order to get an indication of which effects each reagent has on the process, so a statistical approach to testing was used.

4.5.1 Factorial Design of Experiments

One method of performing experiments would be to vary all the possible parameters and attain results for all these trials. This would be very time consuming and extremely inefficient. Factorial design of experiments is a method that can be used to drastically reduce the amount of sampling that has to be performed to get the same information from all the possible combinations of experiments. This method is *not* used to provide an exact model of the process, but rather as a *screening* process to determine which operating variables have the strongest influence on the response. Montgomery and

Runger (1994) describe the power of this approach and some of its drawbacks.

In factorial design experimentation, trials are usually performed at all combinations of factor levels, so when several factors are of interest in an experiment, this approach should be used. In this set of experiments, two levels and three factors are of interest. This is generally called a 2^3 factorial design.

4.5.2 The 2^3 Factorial Design

The purpose of factorial design is to be able to represent all areas of interest with a minimum amount of experimentation. Therefore, two operating limits, high and low, were used to analyze all possible combinations of each operating variable (x_i). The three factors used in this experiment were polymer dosage, alum dosage, and pH (lime addition). In order to get the information required from these, a total of 2^3 = 8 experiments had to be performed. Table 4.2 shows the design used for this project.

y_i	x_1 (pH)	x_2 (Alum, ppm)	x_3 (Polymer, ppm)
y_1	10.3	40	0.1
y_2	10.3	120	0.1
y_3	10.3	40	0.3
y_4	10.3	120	0.3
y_5	11.0	40	0.1
y_6	11.0	120	0.1
y_7	11.0	40	0.3
y_8	11.0	120	0.3

Table 4.2: Factorial Design Setup

Here, the y_i values are the trial numbers (1 to 8), and the other values are the high and low level combinations. Note that all possible combinations ($2^3 = 8$) of the factors are used for these trials. The values for alum and polymer dosages were based on mill operator experience, and the pH value was determined by solubility versus pH diagrams shown in Figure 4.9 (Broughton, 1999).

Figure 4.9 shows a pH versus solubility curve that can be created for hydroxide precipitation of various metals that provide a graphical representation of the solubility of each element at different pH's. The lower the solubility, the greater the amount that can be removed, i.e., the lower solubility limit indicates the concentration that is soluble in water, so the less that is soluble, the more can be removed by precipitation. The lower pH limit of 10.3 was used because the majority of metals approach their lower solubility limits at this pH and would precipitate out of the solution. The upper limit of pH 11 was used because this appears to be the pH at which some of the hydroxides start become soluble (Broughton, 1999).

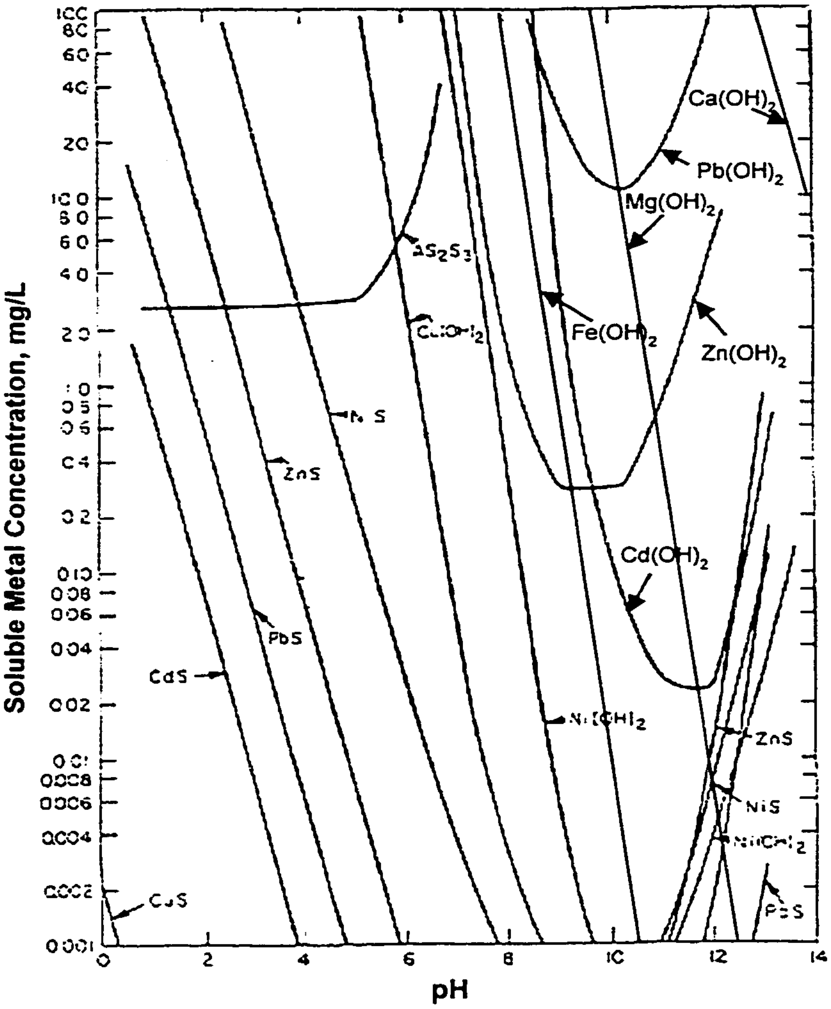


Figure 4.9: Solubility vs pH Diagram (Modified from Broughton, 1999)

The results of these experiments along with a replicate are shown in Table 4.3 and Table 4.4. The replicate is another sample of the mill effluent that was taken several weeks later.

y_i	Turbidity (NTU)		Apparent Color		Mg (mg/L)		Ca (mg/L)	
	1	2	1	2	1	2	1	2
Raw	10.4	8.6	397	252	18.22	15.19	124.8	112.7
y_1	53	28	407	263	14.57	14.30	52.5	62.5
y_2	21	2.1	283	104	13.90	13.82	56.0	58.6
y_3	66	28	513	230	13.98	14.18	58.0	59.0
y_4	20	2.1	263	106	13.04	13.65	56.1	55.2
y_5	6.3	6.1	139	106	5.34	7.97	39.4	56.0
y_6	4.9	1.8	114	113	1.58	11.82	54.8	68.4
y_7	4.7	4	136	76	5.34	3.34	48.6	75.7
y_8	5.8	2.4	124	86	2.22	8.74	50.3	81.2

Table 4.3: Results of the 2^3 Factorial Design

y_i	Mn (mg/L)		Fe (mg/L)		K (mg/L)		Cl (mg/L)	
	1	2	1	2	1	2	1	2
Raw	0.1002	0.2579	0.1524	0.0813	45.93	26.65	148.8	117.5
y_1	0.0069	0.0566	0.0525	0.1072	46.09	26.66	147.9	116.0
y_2	0.0056	0.0329	0.0394	0.0222	45.55	26.33	147.2	115.6
y_3	0.0064	0.0494	0.0471	0.0808	46.06	26.52	148.3	116.5
y_4	0.0068	0.0356	0.0273	0.0451	45.56	26.80	146.6	115.6
y_5	0.0032	0.0137	0.0252	0.0301	45.98	26.54	147.8	115.9
y_6	0.0049	0.0205	0.0160	0.0167	46.35	26.37	146.8	115.3
y_7	0.0032	0.0039	0.0329	0.0000	46.45	26.56	147.6	115.2
y_8	0.0016	0.0110	0.0274	0.0082	45.70	26.21	146.8	114.8

Table 4.4: Results of the 2^3 Factorial Design

Note that the "Raw" value in these tables represent the concentration of the untreated mill effluent.

Turbidity and color are not considered non-process elements, but are "operator" variables. These values give an indication of how "clean" treated water samples are, and provide an indication to the performance of the coagulation and flocculation process. Turbidity is essentially the "dirtiness" of the water that is caused by colloidal matter.

Apparent color includes color due to substances in the solution as well as that due to suspended solids. Apparent color was analyzed because it is easily determined and provides Alberta-Pacific Forest Products Inc. with more data than what is required for this project.

The linear model that will be used to describe the response (y_i) of pH (x_1), alum dosage (x_2), and polymer (x_3) is:

$$Y=\beta_0+\beta_1x_1+\beta_2x_2+\beta_3x_3+\beta_{12}x_1x_2+\beta_{13}x_1x_3+\beta_{23}x_2x_3+\beta_{123}x_1x_2x_3+\varepsilon \qquad \textbf{(4.11)}$$

where Y - predicted value
x_i - operating variables
β_j - estimated parameters
ε - random error

β_0 is the grand average of all the readings, β_1 is the estimated parameter for pH, β_2 for alum, and β_3 for polymer. β_{12}, β_{13}, β_{23}, and β_{123} are all interaction parameters that provide information on any possible interactions between operating variables.

In equation (4.11), the units of the regression coefficients (β_j) with the exception of β_o are (units of y) / (units of x_i), so the magnitude of the regression coefficients are dependent on the units of x_i. These units are not the same for each x_i, therefore working with dimensionless regression coefficients can make it easier to compare the relative importance of each variable. If, for example, $|\beta_1| > |\beta_2|$, then it can be concluded that x_1 produces a larger effect than does x_2. For example, if equation (4.11) were used to describe the amount of Ca that was removed in a system, then the units for β_o would be

%Ca, β_1 would be $\frac{\%Ca}{pH}$, β_2 would be $\frac{\%Ca}{ppm\ alum}$, etc. An orthogonal factorial design can be set up so that the variables are all +1 and –1. The following equation can be used to put the factors into dimensionless form:

$$x_i = \frac{(\text{Value of Operating Variable}) - \frac{1}{2}(\text{Upper Limit} + \text{Lower Limit})}{\frac{1}{2}(\text{Upper Limit} - \text{Lower Limit})} \qquad \textbf{(4.12)}$$

Table 4.2 can now be rewritten as:

y_i	x_1 (pH)	x_2 (Alum, ppm)	x_3 (Polymer, ppm)
y_1	-1	-1	-1
y_2	-1	1	-1
y_3	-1	-1	1
y_4	-1	1	1
y_5	1	-1	-1
y_6	1	1	-1
y_7	1	-1	1
y_8	1	1	1

Table 4.5: Factorial Design Setup (Dimensionless Factors)

The idea of factorial design can be represented graphically as shown in Figure 4.10.

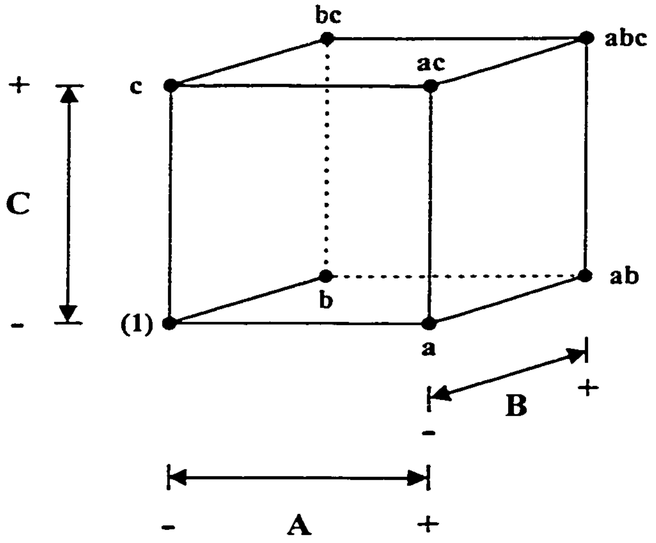


Figure 4.10: The 2^3 Factorial Design (Modified from Montgomery and Runger, 1994)

The eight combinations used in this set of experiments are represented by the corners of a cube as shown above, with the space between these points representing all possible combinations. Figure 4.10 represents the main effect of pH by "A", alum by "B", polymer by "C", and the high level at which each factor is represented by the corresponding lower case letter. For example, (1) indicates that each factor is at its low level, and “a” represents pH (A) at its high dosage with alum (B) and polymer (C) at its low values. The “bc” term represents alum and polymer at their high dosages while pH is at its low value. The other terms are represented in a similar way. The low and high values are shown in Table 4.2 while the combinations are shown in Table 4.6.

	Factor		
	pH	Alum	Polymer
(1)	low	low	low
b	low	high	low
c	low	low	high
bc	low	high	high
a	high	low	low
ab	high	high	low
ac	high	low	high
abc	high	high	high

Table 4.6: Treatment Combinations

The main effects of each factor can be easily estimated. The main effect of pH is determined by simply averaging the four treatment combinations at the high level pH, and subtracting the average of the four treatment combinations of the low level. This can be represented by the planes of a cube as shown in Figure 4.11. Note that the high levels are indicated by dark circles at the corners of the cube, while the low levels are indicated by the light circles.

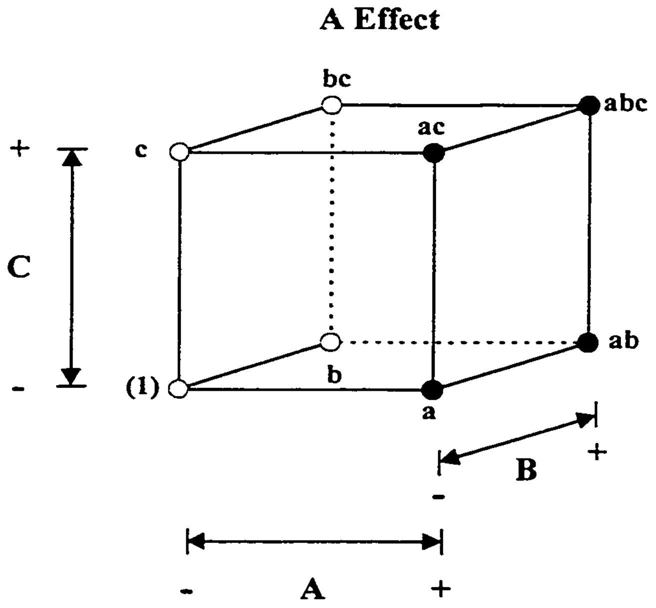
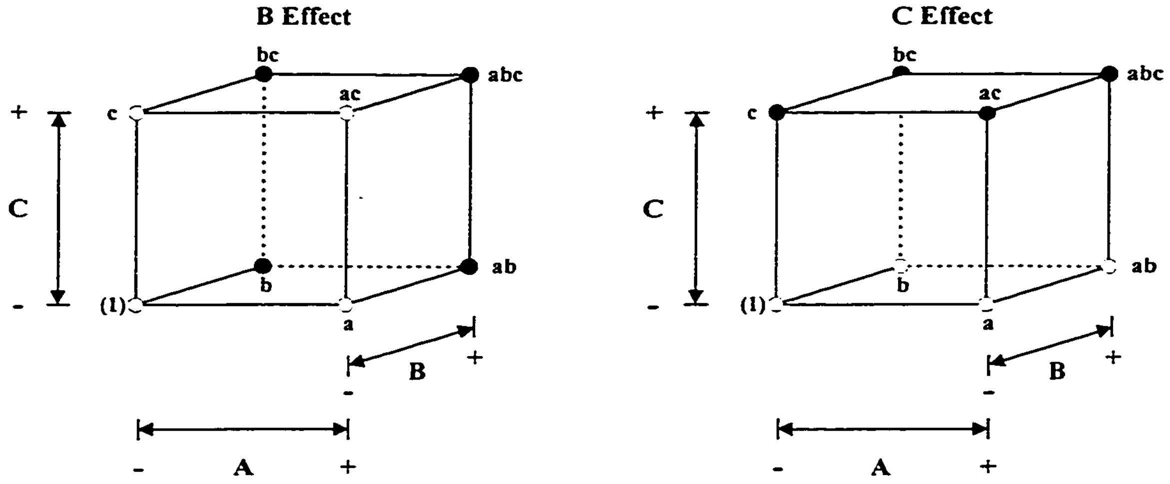


Figure 4.11: High and Low Levels of pH (A) Represented by the Planes of a Cube (Modified from Montgomery and Runger, 1994)

The other high and low levels of B and C can be represented in a similar fashion (Figure 4.12).


B Effect

C Effect

Figure 4.12: High and Low Levels of Alum (B) and Polymer (C) (Modified from Montgomery and Runger, 1994)

The main effects can be determined by:

$$A = \frac{a + ab + ac + abc}{4} - \frac{(1) + b + c + bc}{4} \tag{4.13}$$

$$B = \frac{b + ab + bc + abc}{4} - \frac{(1) + a + c + ac}{4} \tag{4.14}$$

$$C = \frac{c + ac + bc + abc}{4} - \frac{(1) + a + b + ab}{4} \tag{4.15}$$

The two factor interactions for pH and alum can be calculated by taking the difference of the average of the "A" effects at the two levels of "B". This can be represented graphically as shown in Figure 4.13.

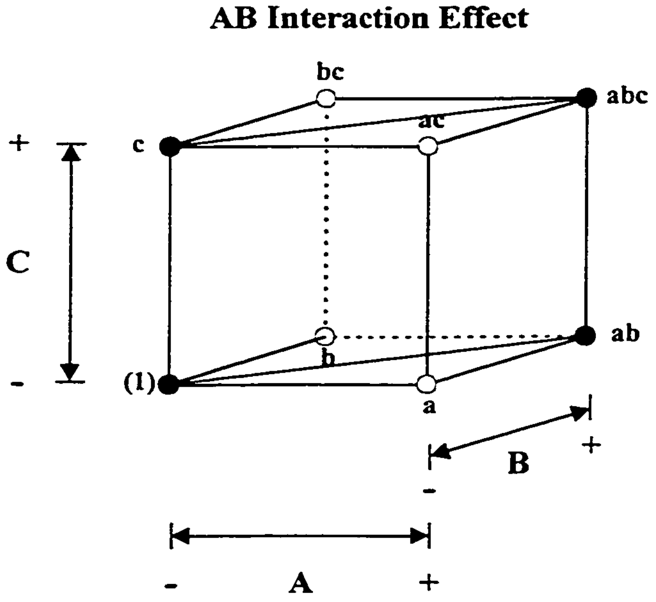


Figure 4.13: Two Factor Interaction Between pH (A) and Alum (B) (Modified from Montgomery and Runger, 1994)

The other interaction terms can be represented in a similar manner (Figure 4.14).

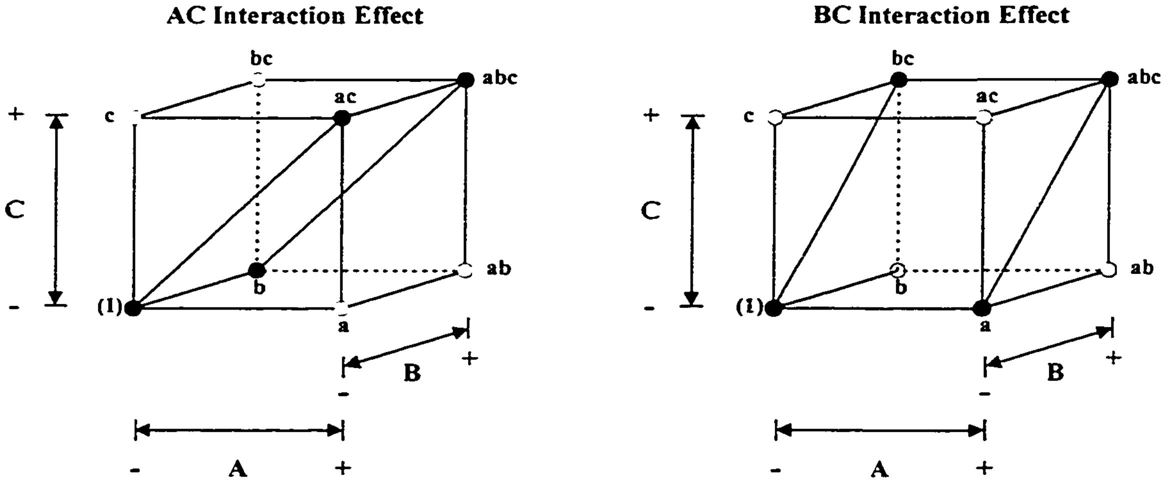


Figure 4.14: Two Factor Interactions – AC and BC (Modified from Montgomery and Runger, 1994)

The two-factor interaction terms can be calculated by:

$$AB = \frac{(1) + c + abc + ab}{4} - \frac{ac + a + bc + b}{4} \quad \textbf{(4.16)}$$

$$AC = \frac{(1) + b + ac + abc}{4} - \frac{a + ab + c + bc}{4} \quad \textbf{(4.17)}$$

$$BC = \frac{(1) + a + bc + abc}{4} - \frac{b + ab + c + ac}{4} \quad \textbf{(4.18)}$$

Finally, the ABC interaction is the average difference of the AB interaction at the different levels of C (Figure 4.15).

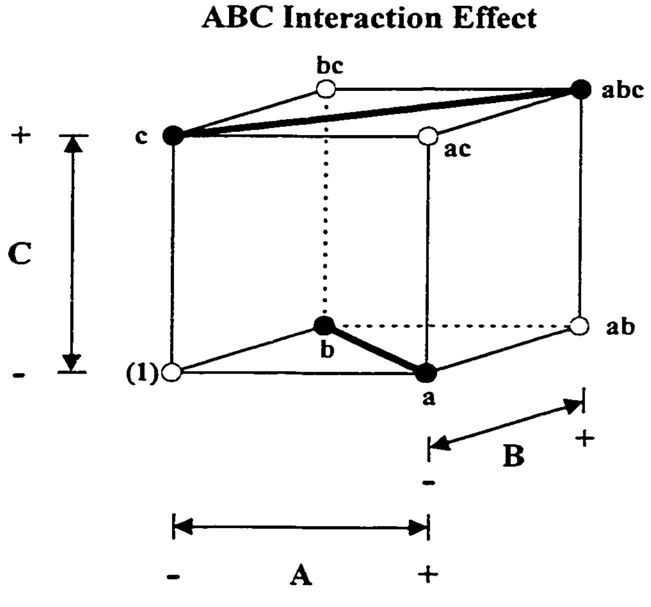


Figure 4.15: Three-Factor Interaction ABC (Modified from Montgomery and Runger, 1994)

This gives:

$$ABC = \frac{abc + c + b + a}{4} - \frac{bc + ac + ab + (1)}{4} \qquad \textbf{(4.19)}$$

The result of the factorial design provides parameters that could help determine what effects each factor has on each response. An equation would result and fit the form of equation (4.11). By convention, the estimated parameters (β_j) are defined as one half of the main effects of equations (4.13)- (4.19).

Two sets of experiments were performed to give replicates of the data (Appendix B). Table 4.7 shows the values of the regression coefficients for all the elements of these two sets of experiments. Recall that β_0 is the grand average of all the readings, and that the other β_j readings are half the main effects.

Weight	Component							
	Turbidity	Color	Mg	Ca	Mn	Fe	K	Cl
β_0	16	191	9.86	58.27	0.0164	0.036	36.23	131.5
β_1	-12	-80	-4.07	1.03	-0.0086	-0.017	0.04	-0.2
β_2	-9	-42	-0.01	1.79	-0.0015	-0.011	-0.13	-0.4
β_3	1	0	-0.55	2.25	-0.0016	-0.003	0.00	-0.1
β_{12}	8	40	0.31	2.57	0.0033	0.008	0.01	0.0
β_{13}	-1	-7	-0.33	2.40	-0.0012	0.000	-0.04	-0.1
β_{23}	-1	-5	0.12	-1.61	0.0005	0.004	-0.04	-0.1
β_{123}	1	7	0.16	-0.95	-0.0009	-0.001	-0.12	0.1

Table 4.7: β_j Values for Equation (4.11)

Recall that the estimated parameters (weights) are: β_1 for pH, β_2 for alum, and β_3 for polymer. Turbidity and color are not considered part of the NPE's that are attempted to be removed, but are measurements of how well the effluent is treated. These parameters are easily determined, and are used routinely by mill operators to determine the performance of the treatment systems.

The values from Table 4.7 can now be substituted into equation (4.11). For example, the model for Mg is:

$$Mg = 9.86 - 4.07x_1 - 0.01x_2 - 0.55x_3 + 0.31x_1x_2 - 0.33x_1x_3 + 0.12x_2x_3 + 0.16x_1x_2x_3 \qquad \mathbf{(4.20)}$$

Where x_1, x_2, and x_3 are the normalized values for pH, alum, and polymer additions respectively. A positive value for β_j indicates an increase in Y (magnesium), while a negative value indicates a decrease in Y.

This equation can be read as: for every unit of pH increase Mg decreases by 4.07 units, for every unit of alum increase Mg decreases by 0.01 units, and so on. The effect of Mg that appears most important from this model is from pH.

It should be noted that the same results could have been achieved by using a linear least squares regression analysis (Appendix B). This least squares regression form is:

$$\mathbf{y} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon} \qquad \mathbf{(4.21)}$$

Where

$$y = \begin{bmatrix} y1 \\ y2 \\ \vdots \\ yn \end{bmatrix} \qquad X = \begin{bmatrix} 1 & x_{11} & x_{12} & \cdots & x_{1k} \\ 1 & x_{21} & x_{22} & \cdots & x_{2k} \\ \vdots & \vdots & \vdots & & \vdots \\ 1 & x_{n1} & x_{n2} & \cdots & x_{nk} \end{bmatrix} \qquad \beta = \begin{bmatrix} \beta_0 \\ \beta_1 \\ \vdots \\ \beta_k \end{bmatrix} \qquad \varepsilon = \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_n \end{bmatrix} \tag{4.22}$$

The least squares estimate of β is:

$$\hat{\beta} = (X'X)^{-1} X'y \tag{4.23}$$

The value of β_j is half the main effect because it is based on a 2 unit change from –1 to +1, while the regression coefficient is based on the measure of 1 unit change in x_l from the mean of Y.

4.5.3 Statistical Analysis

The Analysis of Variance

The analysis of variance is a statistical technique that can be used to test for the significance of the model (Montgomery and Runger, 1994). This equation representing the analysis of variance is given by:

$$\sum_{i=1}^{n} (y_i - \bar{y})^2 = \sum_{i=1}^{n} (\hat{y}_i - \bar{y})^2 + \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \tag{4.24}$$

where y_i - observation
$\bar{y}$ - observation average
$\hat{y}_i$ - predicted value
n - number of replicates in a set

This can also be represented as:

$$S_{yy} = SS_R + SS_E \tag{4.25}$$

where $S_{yy} = \sum_{i=1}^{n} (y_i - \bar{y})^2$

$SS_R = \sum_{i=1}^{n} (\hat{y}_i - \bar{y})^2$

$SS_E = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2$

Here SS_E represents the error sum of squares with (n-2) degrees of freedom, SS_R represents the regression sum of squares with 1 degree of freedom, and S_{yy} represents the total corrected sum of squares with (n-1) degrees of freedom. Another term used in the analysis of variance is the mean sum of squares (MS_R and MS_E) which is just the sum of squares divided by the corresponding degrees of freedom.

The results from the analysis of variance follow an F-distribution. We would reject our values if $f_o < f_{\alpha,\gamma 1,\gamma 2}$, where α represents the confidence interval, and γ_i represents the degrees of freedom. Values for $f_{\alpha,\gamma 1,\gamma 2}$ can be found in F-distribution tables in many statistics books (Montgomery and Runger, 1994). The f_o value can be calculated from the mean square of the effect divided by the mean square of the error:

$$f_o = \frac{MS_{effect}}{MS_E} \tag{4.26}$$

For a 95% confidence interval, $\alpha = 0.05$, γ_1 represents the degrees of freedom in the numerator of equation (4.26), and γ_2 represents the degrees of freedom in the denominator. For all the values here, $\gamma_1 = 1$ and $\gamma_2 = 8$, so $f_{0.05,1,8} = 5.32$.

An analysis of variance table for a 2^3 factorial design is show in Table 4.8.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F_o
A	SS_A	$a-1$	MS_A	$\frac{MS_A}{MS_E}$
B	SS_B	$b-1$	MS_B	$\frac{MS_B}{MS_E}$
C	SS_C	$c-1$	MS_C	$\frac{MS_C}{MS_E}$
AB	SS_{AB}	$(a-1)(b-1)$	MS_{AB}	$\frac{MS_{AB}}{MS_E}$
AC	SS_{AC}	$(a-1)(c-1)$	MS_{AC}	$\frac{MS_{AC}}{MS_E}$
BC	SS_{BC}	$(b-1)(c-1)$	MS_{BC}	$\frac{MS_{BC}}{MS_E}$
ABC	SS_{ABC}	$(a-1)(b-1)(c-1)$	MS_{ABC}	$\frac{MS_{ABC}}{MS_E}$
$Error$	SS_E	$abc(n-1)$	MS_E	
$Total$	SS_T	$abcn-1$		

Table 4.8: Analysis of Variance Table for a 2^3 Factorial Design (Modified from Montgomery and Runger, 1994)

This method is one way to be able to determine the adequacy of the individual parameters. An example of an analysis of variance table for one of the elements is shown in Appendix B, and the results are shown in Table 4.9.

Source of Variation	f_o							
	Turbidity	Color	Mg	Ca	Mn	K	Fe	Cl
A	12.26	9.93	26.69	0.12	3.01	0.00	11.30	0.00
B	6.68	2.80	0.00	0.36	0.09	0.00	4.84	0.01
C	0.03	0.00	0.49	0.57	0.11	0.00	0.26	0.00
AB	5.52	2.48	0.16	0.74	0.43	0.00	2.87	0.00
AC	0.07	0.07	0.18	0.65	0.06	0.00	0.00	0.00
BC	0.03	0.03	0.02	0.29	0.01	0.00	0.74	0.00
ABC	0.13	0.07	0.04	0.10	0.03	0.00	0.05	0.00

Table 4.9: Adequacy of Parameters – Analysis of Variance

These values can be compared to $f_{\alpha,\gamma 1,\gamma 2}$ of 3.46, 5.32, and 11.26 for 90%, 95%, and 99% confidence intervals respectively. If the values in Table 4.9 are greater than 5.32 for a 95% confidence interval, then these values would be accepted (statistically significant), otherwise, they would be rejected (not statistically significant). As an example, equation (4.20) worked out for Mg shows that only the main effect "A" (value for β_1) is statistically significant, i.e., only effect "A" has any real significance on removing Mg from the mill effluent. The statistically significant values for β_j at a 95% confidence interval using the analysis of variance approach are shown in Table 4.10.

Weight	Component							
	Turbidity	Color	Mg	Ca	Mn	Fe	K	Cl
β_0	16	191	9.86	58.27	0.0164	0.036	36.23	131.5
β_1	-12	-80	-4.07	N/S	N/S	-0.017	N/S	N/S
β_2	-9	N/S	N/S	N/S	N/S	N/S	N/S	N/S
β_3	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
β_{12}	8	N/S	N/S	N/S	N/S	N/S	N/S	N/S
β_{13}	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
β_{23}	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
β_{123}	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S

Table 4.10: β_j Values at a 95% Confidence Interval Using Analysis of Variance

The "N/S" values indicate that the values are not statistically significant at a 95% confidence interval.

Standard Error

Montgomery and Runger (1994) indicate that there are other methods to determine the significance of individual effects. One of these methods is called the Standard Error. The standard error is essentially the standard deviation of a sampling distribution. If the distribution had a known standard deviation, the standard error would be:

$$s.e.\left(\overline{X}\right) = \frac{\sigma}{\sqrt{n}} \tag{4.28}$$

where s.e. - standard error
σ - known standard deviation
n - replicates
$\overline{X}$ - sample mean (point estimator)

For a certain confidence interval:

$$\overline{X} \pm Z_{\alpha/2} \frac{\sigma}{\sqrt{n}} \qquad \textbf{(4.29)}$$

To find the standard error for each effect, an estimate of the variance at the ith run can be determined by:

$$s_i^2 = \frac{1}{n-1} \sum_{j=1}^{n} \left(y_{ij} - \bar{y}_{i\bullet} \right)^2 \quad \mathrm{i} = 1,2,\ldots,2^k \qquad \textbf{(4.30)}$$

Where

k = represents the number of factors in the experiment.

$\bar{y}_{i\bullet} = \dfrac{\sum_{j=1}^{n} y_{ij}}{n}$

All the $2^3 = 8$ variance estimates can be combined to give an overall variance estimate

$$s^2 = \frac{1}{2^k (n-1)} \sum_{i=1}^{2^k} \sum_{j=1}^{n} \left(y_{ij} - \bar{y}_{i\bullet} \right)^2 \qquad \textbf{(4.31)}$$

This is also the mean square error (MS_E) from the analysis of variance procedure.

Therefore, each effect has a variance

$$V(Effect) = V\left[\frac{Contrast}{n2^{k-1}}\right] = \frac{V(Contrast)}{\left(n2^{k-1}\right)^2} \qquad \textbf{(4.32)}$$

The contrast here is the sum of the numerator term for *each* equation (4.13) - (4.19). For example, the contrast for effect "A" is:

$$\text{Contrast A} = [\text{a} + \text{ab} + \text{ac} + \text{abc} - (1) - \text{b} - \text{c} - \text{bc}] \qquad \textbf{(4.33)}$$

where

$$\text{V(Contrast)} = \text{n}2^{\text{k}}\sigma^2 \qquad \textbf{(4.34)}$$

because each contrast has a total of n observations, and is a linear combination of the 2^k treatments. Substituting this into equation (4.32):

$$V(Effect) = \frac{n2^k\sigma^2}{\left(n2^{k-1}\right)^2} = \frac{\sigma^2}{n2^{k-2}} \qquad \textbf{(4.35)}$$

Replacing σ^2 by its estimate s^2 from equation (4.31):

$$s.e.(Effect) = \sqrt{\frac{s^2}{n2^{k-2}}} \quad \textbf{(4.36)}$$

From equation (4.29):

$$Effect \pm Z_{\alpha/2} * s.e.(Effect) \quad \textbf{(4.37)}$$

For 90%, 95%, and 99% confidence intervals, $Z_{\alpha/2}$ values are 1.65, 1.96, and 2.58 respectively. These values are compared in Table 4.11.

	Standard Error	Half Confidence Interval		
		90%	95%	99%
Turbidity	6.58	10.85	12.89	16.97
Color	50.57	83.44	99.11	130.46
Mg	1.57	2.60	3.09	4.06
Ca	5.95	9.82	11.67	15.36
Mn	0.01	0.02	0.02	0.03
K	6.88	11.36	13.49	17.76
Fe	0.01	0.02	0.02	0.03
Cl	11.23	18.53	22.01	28.97

Table 4.11: Confidence Intervals

The values for the effects are listed in Table 4.7. As an example, consider the fitted model for Mg given by equation (4.20):

$$Mg = 9.86 - 4.07x_1 - 0.01x_2 - 0.55x_3 + 0.31x_1x_2 - 0.33x_1x_3 + 0.12x_2x_3 + 0.16x_1x_2x_3$$

The 95% confidence interval gives *Effect* ± *3.09*. From examining the above equation, none of the effects for Mg are statistically significant, except for the effect by "A" pH because the values for the other effects are less than 3.09. This gives the same results as the analysis of variance.

The statistically significant values for β_j at a 95% confidence interval using the standard error approach is summarized in Table 4.12.

Weight	Component							
	Turbidity	Color	Mg	Ca	Mn	Fe	K	Cl
β_0	16	191	9.86	58.27	0.0164	0.036	36.23	131.5
β_1	-12	-80	-4.07	N/S	-0.0086	-0.017	N/S	N/S
β_2	-9	N/S	N/S	N/S	N/S	-0.011	N/S	N/S
β_3	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
β_{12}	8	N/S	N/S	N/S	N/S	N/S	N/S	N/S
β_{13}	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
β_{23}	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S
β_{123}	N/S	N/S	N/S	N/S	N/S	N/S	N/S	N/S

Table 4.12: β_j Values at a 95% Confidence Interval Using Standard Error Analysis

The N/S values in the above table indicate that they are not statistically significant at a 95% confidence interval.

Certain assumptions are used when a least squares analysis is performed. Appendix B provides information on these assumptions, and some of the techniques that can be used to verify these. Wadsworth (1990) indicates that these assumptions are not necessary when the regression is used to simply examine the relationship between Y and X and to develop a regression model.

4.6 Repeatability

To ensure that the jar tests performed were repeatable, a sample of the mill effluent was treated 5 times in the exact same manner. The pH was raised to 10.3, 80 ml of alum was added, and 2 ml of polymer was added for each of the 5 samples. The samples were treated as described in section 4.2.2. The results are shown in Table 4.13 and Table 4.14.

Sample	Turbidity		Mg		Ca		Mn	
	(NTU)	% Diff.	(mg/L)	% Diff.	(mg/L)	% Diff.	(mg/L)	% Diff.
1	3.6	2.17	16.76	0.05	86.4	0.35	0.0421	1.48
2	3.6	2.17	16.73	0.13	86.3	0.23	0.0415	2.88
3	3.8	3.26	16.77	0.11	86.1	0.00	0.0456	6.84
4	3.9	5.98	16.81	0.35	85.7	0.46	0.0443	3.80
5	3.5	4.89	16.69	0.37	86.0	0.12	0.0400	6.28
Average	3.7		16.75		86.1		0.0427	
Std. Dev.	0.2		0.04		0.3		0.0022	

Table 4.13: Repeatability Experiments

Sample	Fe		K		Cl	
	(mg/L)	% Diff.	(mg/L)	% Diff.	(mg/L)	% Diff.
1	0.0396	14.06	16.76	0.05	137.7	0.10
2	0.0521	13.06	16.73	0.13	137.4	0.12
3	0.0483	4.82	16.77	0.11	137.4	0.09
4	0.0445	3.43	16.81	0.35	137.6	0.04
5	0.0459	0.39	16.69	0.37	137.7	0.07
Average	0.0461		16.75		137.6	
Std. Dev.	0.0046		0.04		0.1	

Table 4.14: Repeatability Experiments

The precision and accuracy of each of these elements was determined and is recorded in Appendix A. Mg, Ca, K, and Cl all have less than a 1% difference while Fe is as high as 14% and Mn as high as 7%. These numbers are still within the precision determined in Appendix A. Iron has the highest relative error because the transmittance was low (Appendix A). These results indicate that the experiments are reproducible.

4.7 Interpretation of Results

In Table 4.3 and Table 4.4, the levels of turbidity, color, Mg, Ca, Mn, Fe, Cl, and K are reported for varying amounts of lime, alum, and polymer. Table 4.7 shows the effect of each of these parameters and provides a quantitative value of the effect of lime, alum, and polymer dosage on each non-process element. Table 4.10 and Table 4.12 indicate the statistically significant values.

The turbidity of a system provides an indication of the effectiveness of the sedimentation (coagulation and flocculation) process. As indicated in Table 4.10 and Table 4.12, the statistically significant effects on turbidity are from lime addition, alum dosage, and the lime-alum interaction. Substituting the values from Table 4.7 into equation (4.11), and removing the statistically insignificant values (at 95% confidence), the model for turbidity is:

$$turbidity = 16 - 12x_1 - 9x_2 + 8x_1x_2 \tag{4.38}$$

These results indicate that lime and alum alone decrease the turbidity (indicated by the –12 and –9 values for β). The effect of the combined use of alum and lime is less than the sum of the individual applications (+8 value of β). This indicates that the addition of lime and alum overall decreases turbidity. As discussed in section 4.2.1, it was expected that alum would reduce the turbidity of the sample by destabilizing the colloidal particles in the system. The alum reactions that take place in a high pH environment are similar to those represented by equations (4.7) to (4.10):

$$Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{\ 2-} \tag{4.39}$$

$$Al^{3+} + OH^- \Leftrightarrow Al(OH)^{2+} \tag{4.40}$$

$$Al(OH)^{2+} + OH^- \Leftrightarrow Al(OH)_2^{\ +} \tag{4.41}$$

$$Al(OH)_2^{\ +} + OH^- \Leftrightarrow Al(OH)_{3\ (s)} \tag{4.42}$$

$$Al(OH)_{3(s)} + OH^- \Leftrightarrow Al(OH)_4^{\ -} \tag{4.43}$$

As the reactions take place, Al^{3+} is being formed and consumed. At higher pH, more OH^- ions are consumed by the Al^{3+}, forming the hydroxide compounds indicated in the above equations. In certain pH ranges, $Al(OH)_{3\ (s)}$ is formed and precipitates out of the solution. As this solid particle falls through the solution, it physically enmeshes and captures the colloidal particles to remove these at the same time. If the pH is increased, then $Al(OH)_4^-$ is formed which re-dissolves floc. In the pH range of this set of experiments (pH of 10.3 to 11.0), the majority of the alum most likely forms $Al(OH)_4^-$ and prevent effective coagulation with alum. Most likely there is little $Al(OH)_{3\ (s)}$ present in the system to assist in the precipitation of the colloids.

Depending on the composition of the water, lime could also reduce the turbidity. If the turbidity consists mostly of negatively charged silica colloids, then the silica adsorbs to the $Mg(OH)_2$ that was formed (equation (4.3)) in the lime softening process (Kemmer, 1988). To some extent, silica would also adsorb to iron hydroxide as well. In addition, the precipitation of $CaCO_3$ and the hydroxide precipitates may physically entrap the colloids as they settle out of the solution.

The interaction of lime and alum, however, increases the turbidity. This may be explained by looking at the reactions that occur in this process. The alum ($Al_2(SO_4)_3$) reaction in the process is represented by equation (4.39). When lime ($Ca(OH)_2$) is added to the system, there is an introduction of hydroxyl ions (OH^-). These may react with the Al in the system as shown in equations (4.40) to (4.43). This appears to reduce the effectiveness of the alum to destabilize any of the colloids in the system (Figure 4.5). At this high pH, mostly $Al(OH)_4^-$ is present. This would re-dissolve the floc, breaking apart the coagulated particle. Hence, it appears that alum and lime are consuming each other and lowering the performance of both reagents in the system.

The anionic polymer has little effect on the removal of turbidity from the system. Polymer alone does not decrease turbidity because the colloids and polymer are both negatively charged and repel each other instead of attaching together. The polymer and lime interaction may not affect the process due to the high concentrations of hydroxyl ions in the system. The anionic polymer chain and the hydroxyl ions are most likely repelling each other and not allowing the formation of polymer-made flocs. The alum-polymer interaction should affect the turbidity removal, but does not appear as significant from the factorial design. This could be due to the design of experiments used in this study. The system has a large amount of hydroxyl ions present even at the low level of lime addition because the study was performed at pH between 10.3 and 11.0. The essential role of a flocculant is to create a larger and faster settling particles (flocs) so that they will be removed from the system at a faster rate. This allows a smaller clarifier to be designed to remove the same amount of particles than from a larger system that is not using a flocculant aid. This essentially lowers the capital cost of installing a larger settling unit.

The interaction of lime-alum-polymer does not appear to have any significant effect on the turbidity removal. The reasons listed above explain why this may be so.

The color in a system is another indication of how well a sedimentation process is performing. Factorial design results indicate that removal of color from the system is affected by lime only (at a 90% confidence level). Substituting the values from Table 4.7 into equation (4.11), the model for color is:

$$color = 191 - 80x_1 \tag{4.44}$$

At pH>7, the removal of color occurs by the adsorption of humic substances (organic materials that include most of the naturally occurring dissolved organic matter in water) on $Al(OH)_{3\,(s)}$ precipitates (Kemmer, 1988). $Al(OH)_{3\,(s)}$ is formed according to equation (4.42). As well, since lime ($Ca(OH)_2$) is added to the system, and not all of this is dissolved in the process, it is possible that humic substances are adsorbed to this surface as well. As indicated for turbidity, the formation of $CaCO_3$ in the system may physically entrap the color substances, hence removing these with the calcium carbonate precipitate. As indicated before, lime and alum consume each other, leading to a possible interaction term and a reduction of the cumulative effect. The conditions for polymer effects are the same as noted above for turbidity.

Lime addition had the most effect on Mg, Mn, and Fe removal. According to equations (4.1) and (4.3), hydroxide precipitation is supposed to assist in removing these elements from a water stream by forming a hydroxide precipitate that can be removed from the solution. Alum addition would not help in hydroxide precipitation, and in fact would actually harm it according to equations (4.40) to (4.43) by removing some of the hydroxyl ions from the system. Alum addition would also add another NPE (aluminum) to the system if it were not removed in the precipitation process. The polymer likely did not assist in forming flocs in the high-pH system. The hydroxide compounds formed in the process would most likely carry a negative charge (Benefield *et al.*, 1982), so the anionic polymer should not assist in agglomerating the particles.

The results from the factorial design analysis indicate that all combinations of chemicals remove the same amount of Ca from the system. One of the main purposes of lime softening is to remove calcium as shown in equation (4.2), and examining the results in Table 4.3, calcium is definitely removed from the system (up to 68%). Substituting the values from Table 4.7 into equation (4.11), the model for Ca is:

$$Ca = 58.27 \qquad \textbf{(4.45)}$$

This linear equation indicates that lime, alum, and polymer do not play an important role in the removal of calcium within the factor range of this set of experiments. Other experiments at different factor levels would have to be performed to provide an indication on what happens outside the range of this set of experiments.

Based on the linear model given by equation (4.11), it appears that there is no dependence of the removal of chloride and potassium on lime addition, alum dosage, and polymer dosage. The results are tabulated in Table 4.7. Chlorides are completely soluble and do not form a hydroxide precipitate. As is shown in equation (4.1) to equation (4.3), hydroxide precipitation only works on cations, and since chlorides are anionic, hydroxide precipitates do not form. Most chloride compounds are very soluble, except those of Ag^+ and Hg^+ (Kemmer, 1988). Most forms of potassium compounds are very soluble, especially those of hydroxides, and do not form a precipitate, hence are not removed from the process (Kemmer, 1988).

From the results obtained using factorial design of experiments, it is clear that lime softening of the mill effluent assists in removing some of the NPE's, however, potassium and chloride are not removed in this process. Therefore, another method to remove K and Cl is needed before effluent recycle as a means of system closure is feasible.

If the chemicals were added in a different sequence, then there may have been a better removal of some of the elements. The addition of alum prior to lime would provide the alum time to react with and destabilize the colloids. The lime could then be added to remove the cations by hydroxide precipitation. This may reduce the effect of lime and alum consuming each other. This was not attempted because potassium and chlorides would still not be removed.

One option suggested by Alberta-Pacific was to find a way to concentrate the Cl and K rich streams of the mill and to examine the possibility of using deep well injection as a method to dispose of this stream. This may enable the rest of the streams to be treated by lime softening and returned to the mill. The stream that would contain most of the chlorides leaving this mill would be from the first bleaching stage (D_0 stage). It may be possible to segregate this stream from the rest to allow for a better opportunity for system closure. Deep well disposal is discussed in Appendix C and should only be considered if the treated wastewater does not comply with surface water discharge limits. The conclusion from this study is that deep well injection would not be a desired method for attaining system closure.

4.8 Conclusion

The proposed system closure process suggested by Alberta-Pacific Forest Products Inc. was studied. Lime softening of the mill effluent was simulated by performing a number of jar tests to determine if non-process elements would be removed by this method. The experiments were performed based on a factorial design in which a minimal amount of experiments was performed to represent all areas of interest.

The amount of turbidity, apparent color, as well as the concentrations of Mg, Ca, Mn, Fe, K, and Cl were measured. The results from the factorial design provided a quantitative measure of how effective each of lime addition, polymer concentration, and alum concentration were on the removal of NPE's from the system. These results indicated that lime, alum, and the lime-alum interaction had the most effect on the removal of turbidity, while only lime affected the removal of color. Lime addition had the most effect on the removal of Mg, Mn, and Fe, while the results indicate that all combinations of chemicals remove the same amount of Ca. Chlorides and potassium were not removed with any of the chemicals added to the process.

Lime softening of the mill effluent removed some of the NPE's, but in order for this method to be used as a means of system closure, another method to deal with the removal of Cl and K must be found.

Chapter 5.0

Mill Wide Water Balance and Effluent Characterization

As discussed in chapter 4, it was determined that lime softening of the mill effluent alone would not be sufficient to allow the wastewater to be recycled back into the mill. A method of removing the chlorides and potassium must be found in order for this wastewater to be reused. In this chapter, a mill wide water balance is performed to provide information on where the wastewater is being generated, and how much is being generated at each location. Also, the major contributing streams are analyzed for non-process elements. One reason for doing this is that it may be possible to segregate one stream from the rest if this stream contained most of the chlorides and potassium. It may be possible to treat this steam individually by some other method. In addition, a water balance may also identify streams that could be used for internal recycling that could help reduce the amount of fresh water that the mill currently uses.

5.1 Water Balance

Appendix D shows all the information that was gathered for the mill water balance. It was determined that the bleach plant, wood room, and the machine room were the largest constant contributors of mill effluent. With the aid of the mill's instrumentation and storage database, an online water balance of these major contributing streams was performed. The code for this program is also found in Appendix D.

The mill effluent is divided into three main streams: acid, caustic, and general sewers. The wood room adds to the acid sewer, the bleach plant adds to the acid and caustic sewers, and the machine room adds to the general sewer. The wood room effluent is not acidic, but enters the acid sewer line right before the neutralization chamber. A general flow sheet of the mill process is shown in Figure 5.1.

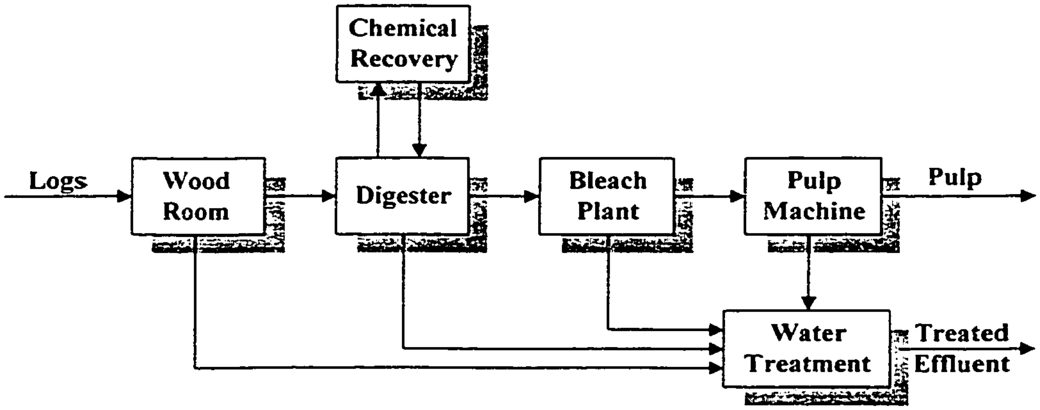


Figure 5.1: Simplified General Mill Process Flow Sheet

All the areas of the mill use water; some use fresh water while others use recycled water. The wood room receives recycled white water from the pulp machine for washing and debarking of the logs. A flow sheet of the wood room water use is shown in Figure 5.2, and a summary of the average flows is shown in Table 5.1. These numbers do not vary considerably when the mill is operating at steady-state.

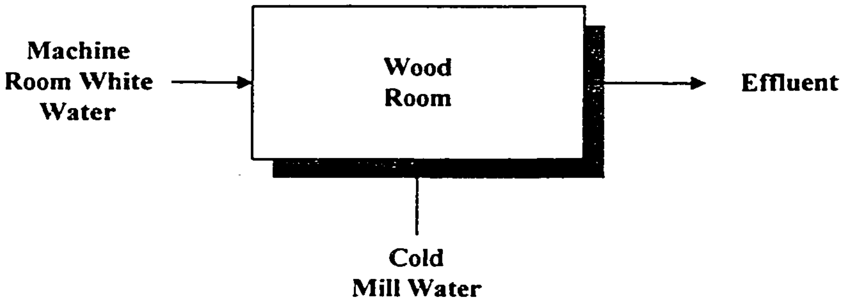


Figure 5.2: Simplified Wood Room Effluent Generation Flow Sheet

Stream	Inputs (L/s)	Outputs (L/s)
White Water	80	
Cold Water	30	
Effluent to Sewer		***110***

Table 5.1: Wood Room Water Balance for July 1997

The bleach plant uses a variety of fresh and recycled water streams from the mill. An overview of the flows is shown in Figure 5.3.

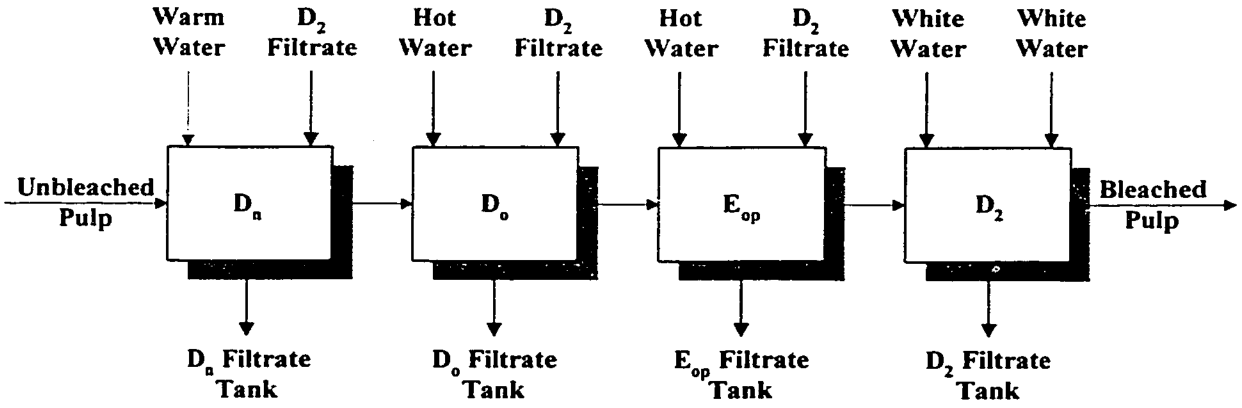


Figure 5.3: Simplified Bleach Plant Flow Sheet

The purpose of each of the bleaching stages is to brighten and clean the pulp. Each of the bleach washers takes pulp slurry and forms a mat on a filter medium to remove contaminants. The pulp mat is washed with water and then proceeds to the next bleach stage. This pulp is filtered and contains a lower amount of water than the pulp mat that entered the washer. The used wash water and some of the water that came in with the pulp slurry is sent to the corresponding filtrate tanks for each individual washer. The filtrates from these stages can either be used in other areas of the mill, or sent to sewer. Each individual filtrate tank is set up so that hot water can be input to the tank if this filtrate is to be used for any other purpose as well as to ensure that the level does not get too low.

In order to determine an overall effluent flow from the bleach plant, a water balance for each stage had to be performed individually. The D_n stage of the bleach plant was initially designed to be the first bleaching stage of a four-stage bleach plant. With process modifications, the mill now only uses three stages for bleaching, therefore, this stage is now used for an open wash. Warm water, recycled D_2 filtrate, and water that comes in with the pulp make up the bulk of the water that enters this stage. Some of the D_n filtrate is reused for diluting the pulp that enters the D_n washer, some water leaves with the pulp to keep the consistency to required levels, and the rest exits to the caustic sewer. The hot water is mainly used for level control of the filtrate tank and is not often used. A simplified schematic of these flows is shown in Figure 5.4 and the average flows for this area are shown in Table 5.2.

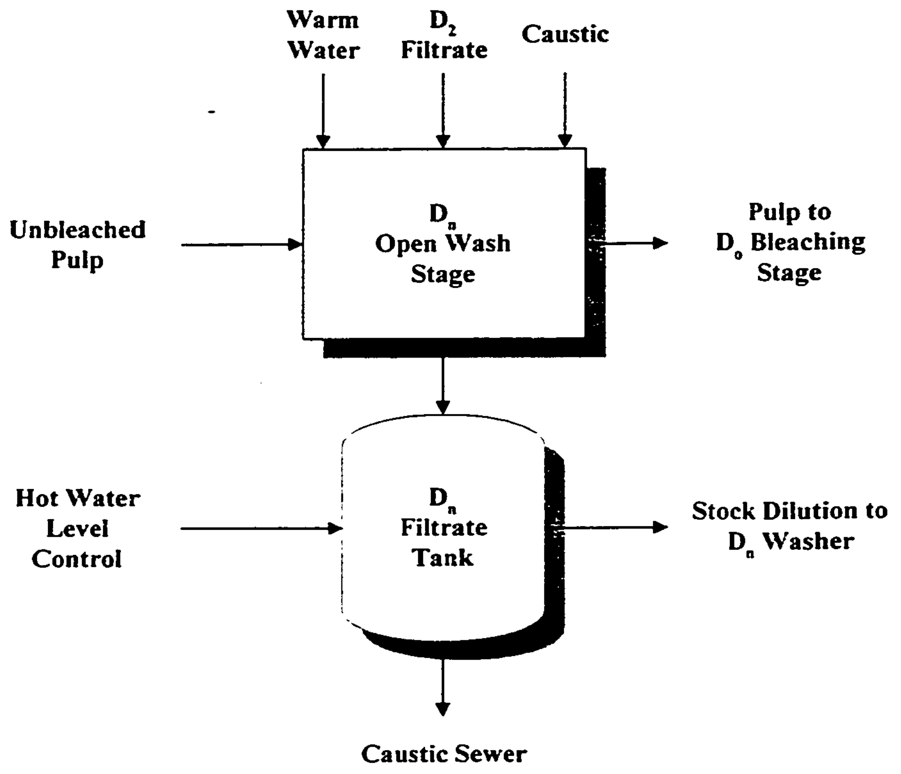


Figure 5.4: Simplified D_n Stage Flow Sheet

Stream	Inputs (L/s)	Outputs (L/s)
Warm Wash Water	56	
D_2 Wash Water	55	
Caustic Addition	2	
Water With Pulp	522	134
Level Control	-	
Filtrate to D_n Washer		359
Effluent to Sewer		***142***

Table 5.2: D_n Stage Water Balance for July 1997

The washed pulp from the D_n area now enters the first ClO_2 (D_o) bleaching stage. The D_o bleach stage receives water from the pulp, hot water, and recycled D_2 filtrate. The hot water entering the filtrate tank is used for level control. The water that leaves this area is located in the pulp leaving for the E_{op} stage, dilution to the D_o tower, and the rest exits to the acid sewer. Figure 5.5 shows a schematic of the process, and Table 5.3 gives a summary of the flows.

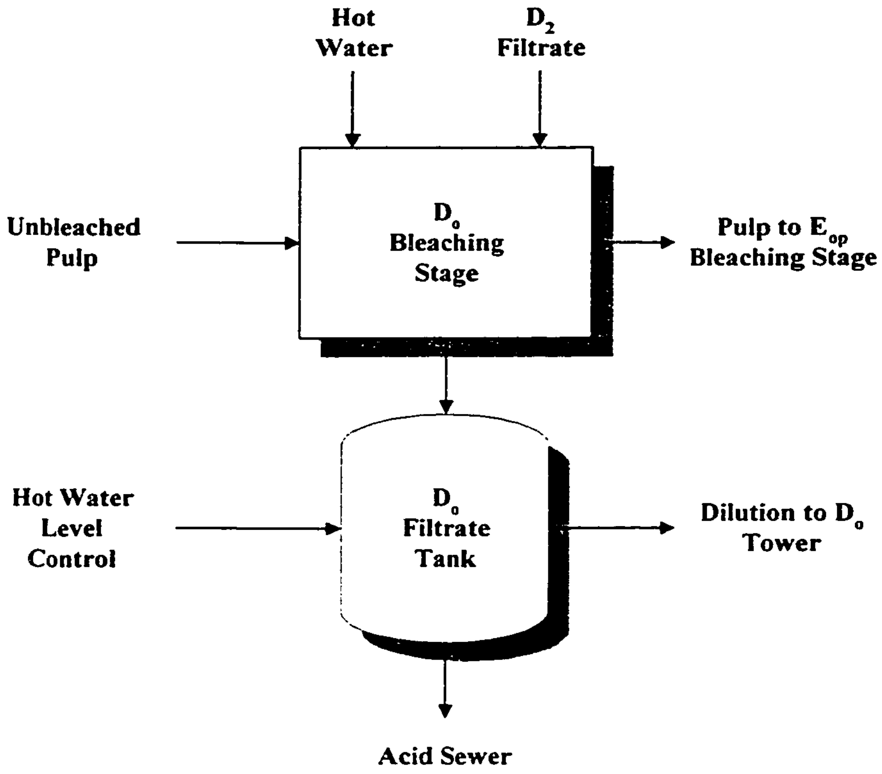


Figure 5.5: Simplified D_0 Stage Flow Sheet

Stream	Inputs (L/s)	Outputs (L/s)
Hot Wash Water	56	
D_2 Wash Water	47	
Water in Pulp	674	108
Level Control	-	
D_0 Bleach Tower		408
Effluent to Sewer		***260***

Table 5.3: D_0 Stage Water Balance for July 1997

The bleached pulp now enters the E_{op} (extraction with oxygen and peroxide brightening) stage for extraction with sodium hydroxide. This bleaching stage washes the pulp with hot water and recycled D_2 filtrate. Water also enters this stage with the pulp and hot water for level control of the E_{op} filtrate tank. Some of the filtrate is used in the D_o repulper, dilution for the E_{op} bleaching tower, as well as for use in the pulp machine room for addition to the couch pit. The remaining water from the filtrate tank that is not reused is disposed of to the caustic sewer. A schematic showing a simplified flow of these streams is shown in Figure 5.6. Table 5.4 gives a summary of the flows in this area of the bleach plant.

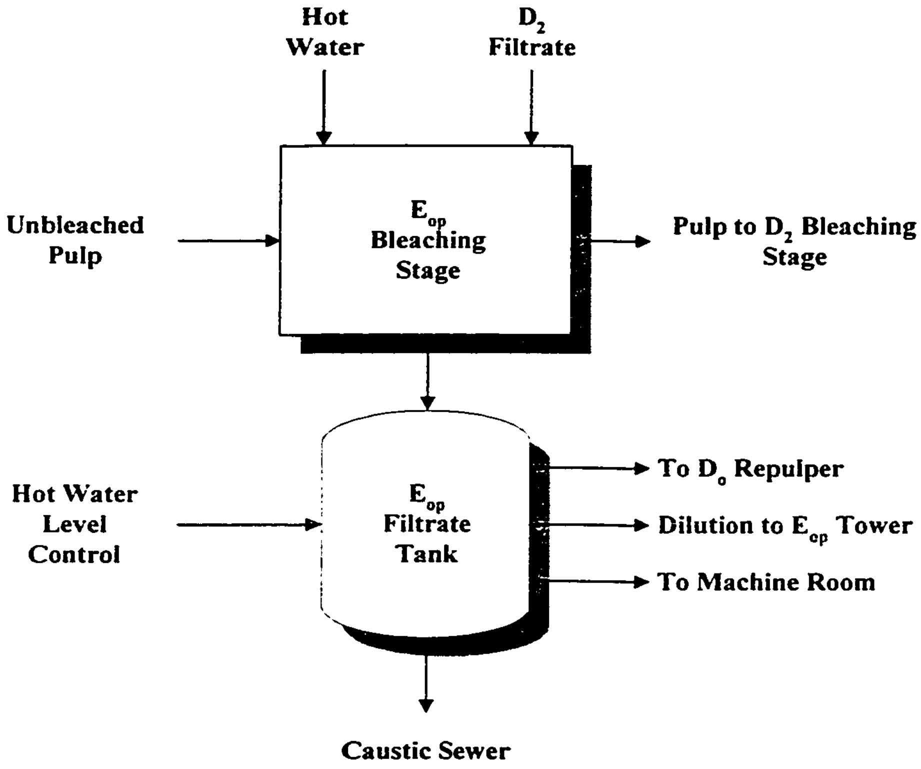


Figure 5.6: Simplified E_{op} Stage Flow Sheet

The pulp leaves the E_{op} stage and enters the final bleaching stage; the D_2 area. This stage uses recycled white water from the bleach plant to wash the pulp and uses hot water for level control of the filtrate tank. This stage is the final bleaching stage and has the cleanest pulp, therefore, the filtrate from this stage will be the cleanest filtrate. The

Stream	Inputs (L/s)	Outputs (L/s)
Hot Wash Water	58	
D_2 Wash Water	56	
Water in Pulp	476	122
Level Control	-	
Eop Bleach Tower		337
D_o Repulper		4
Effluent to Sewer		***128***

Table 5.4: E_{op} Stage Water Balance for July 1997

filtrate leaves this area to be recycled to a number of places: as dilution water to the D_2 bleach tower, to the E_{op} and D_n repulpers, and to the 3 previous washing stages. Figure 5.7 shows a simplified flow sheet of this process, and Table 5.5 gives the results of the water balance in this area.

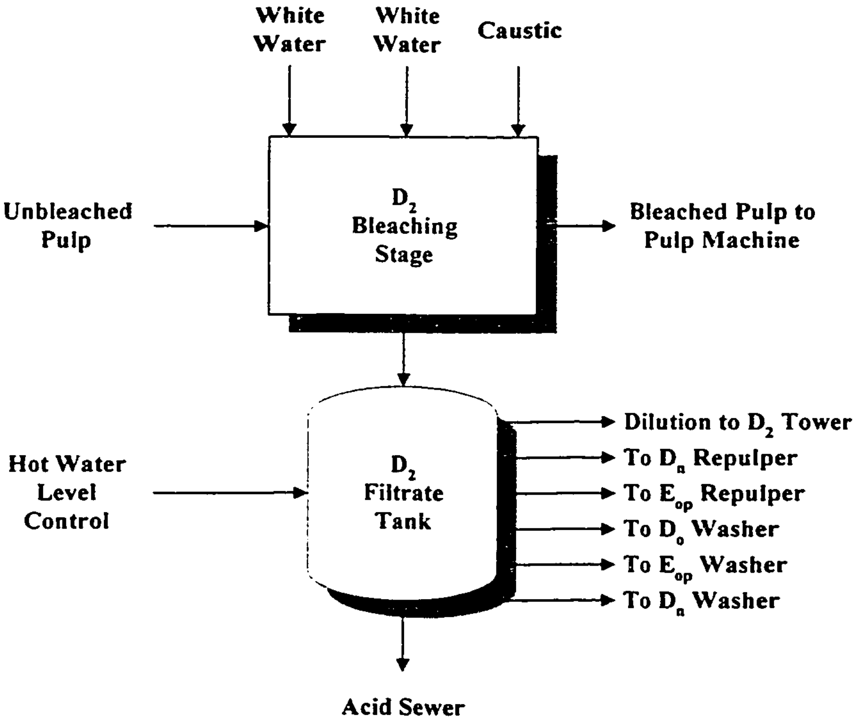


Figure 5.7: Simplified D_2 Stage Flow Sheet

Stream	Inputs (L/s)	Outputs (L/s)
White Water	53	
White Water	52	
Water in Pulp	449	144
Level Control	28	
D_2 Bleach Tower		272
Washers		158
Repulper		7
Effluent to Sewer		***0***

Table 5.5: D_2 Stage Water Balance for July 1997

The other areas that contribute to the overall effluent from the mill were determined and are tabulated in Appendix D. Table 5.6 summarizes the results.

Location	Flows (L/s)
Total Acid Sewer	383
Total Caustic Sewer	283
Total General Sewer	102
Others	253
Total	***1,021***

Table 5.6: Total Water Balance

During July 1997, the average water intake to the mill was 1026 L/s.

Input – Output =1026 L/s – 1021 L/s = 5 L/s

This indicates that 5 L/s of water cannot be accounted for, and that the overall water balance on the mill appears to be excellent. A number of streams cannot be accounted for because they only contribute to the effluent stream at undetermined intervals for an unknown period, but in the overall averaged flow leaving the mill, they do not represent a major portion.

5.2 Effluent Characterization

An effluent sampling and characterization project was undertaken to determine the amount of non-process elements that were entering the effluent from each major stream, most importantly Cl and K. This involved sampling the machine room, wood room, and bleach plant effluent streams. A total of four composite samples (taken over an 8-hour period) were analyzed for Cl, K, Mg, and Mn. The Cl and K were analyzed because these are the NPE's that cannot be removed by lime softening of the mill effluent and Mg and Mn were analyzed to provide Alberta-Pacific with additional information to the amount of NPE's in the effluent. The main idea to this sampling and analysis is to determine if the Cl and K rich streams could be segregated form the combined stream and treated separately. These results are found in Table 5.7 to Table 5.10.

Area	K (ppm)					Standard Deviation
	Sample 1	Sample 2	Sample 3	Sample 4	Average	
Wood Room	10.49	7.84	7.94	6.78	8.26	1.58
D_n Filtrate	49.77	65.83	65.10	66.32	61.75	8.01
D_o Filtrate	22.71	29.19	27.80	23.97	25.92	3.07
E_{op} Filtrate	6.04	8.64	7.99	5.30	6.99	1.58
D_2 Filtrate	3.25	4.96	4.67	6.01	4.72	1.14
Machine Room	10.65	16.02	4.61	4.07	8.84	5.64

Table 5.7: Potassium Concentrations in the Effluent Streams

Area	Cl					Standard Deviation
	Sample 1	Sample 2	Sample 3	Sample 4	Average	
Wood Room	40.58	27.68	25.36	29.77	30.85	6.74
D_n Filtrate	4.82	7.31	5.67	5.84	5.91	1.03
D_o Filtrate	336.12	281.16	284.38	314.28	303.98	26.10
E_{op} Filtrate	114.19	117.14	98.69	79.09	102.28	17.45
D_2 Filtrate	87.79	132.09	85.70	152.11	114.42	33.00
Machine Room	138.08	3.54	31.30	53.87	56.70	58.03

Table 5.8: Chloride Concentrations in the Effluent Streams

Area	Mg (ppm)					Standard Deviation
	Sample 1	Sample 2	Sample 3	Sample 4	Average	
Wood Room	9.29	12.15	11.99	11.86	11.32	1.36
D_n Filtrate	14.08	15.41	16.50	16.93	15.73	1.27
D_o Filtrate	26.94	33.27	31.11	30.78	30.53	2.63
E_{op} Filtrate	3.98	3.57	3.62	4.22	3.85	0.31
D_2 Filtrate	12.86	20.21	18.32	19.44	17.71	3.32
Machine Room	10.51	12.96	12.71	13.52	12.42	1.32

Table 5.9: Magnesium Concentrations in the Effluent Streams

Area	Mn					Standard Deviation
	Sample 1	Sample 2	Sample 3	Sample 4	Average	
Wood Room	0.1787	0.0973	0.1374	0.1111	0.1311	0.0358
D_n Filtrate	0.1968	0.1918	0.1736	0.1667	0.1822	0.0144
D_o Filtrate	0.5821	0.6627	0.5274	0.5178	0.5725	0.0665
E_{op} Filtrate	0.0280	0.0148	0.0218	0.0217	0.0216	0.0054
D_2 Filtrate	0.0756	0.1341	0.1122	0.1223	0.1110	0.0253
Machine Room	0.0372	0.0754	0.0424	0.0522	0.0518	0.0169

Table 5.10: Manganese Concentrations in the Effluent Streams

At the time that sample 1 and sample 2 were taken, the mill was bypassing some effluent from other areas of the mill and dumping it into the machine-room effluent channel. This is shown by the K and Cl concentrations in Table 5.7 and Table 5.8 for the machine-room effluent concentrations. A higher concentration of K for these two samples was expected, as this other stream that was added to the machine room effluent is expected to have higher concentrations of this element. The lower amount of Cl for sample 2 may be from an upset in mill operations at the time these samples were taken. This additional stream most likely contained a lower Cl content because the brown stock area did not pass through a bleaching stage yet.

The higher standard deviation indicated in Table 5.8 for chloride concentrations in the D_o, E_{op}, D_2, and machine-room effluent is mainly due to the different amounts of ClO_2 used for bleaching requirements. Some pulp requires more bleaching while others require less, therefore, the amount of Cl introduced to the system would vary.

To check if these results were typical, they were compared to another mill that is located within the same geographical area as this mill, and pulps the same type of wood. Alberta-Pacific Forest Products Inc. uses a three-stage bleach plant (D_o-E_{op}-D_2) while the mill compared to uses a five-stage bleach plant ($C_{D(30\%\ sub.)}E_{op}DED$) with 30% ClO_2 substitution in the first bleaching stage. This means that the first bleaching stage should have a much higher concentration of Cl in the effluent. For comparison purposes, the mill that is being compared to is "Mill B. Mill B only gives results of a combined acid and caustic sewer. These results can be found in Table 5.11.

	Cl (ppm)		K (ppm)		Mg (ppm)		Mn (ppm)	
	AlPac	Mill B	AlPac	Mill B	AlPac	Mill B	AlPac	Mill B
Acid Sewer	262	750	26	41	30	30	0.6	0.5
Caustic Sewer	54	350	34	4.6	10	6.8	0.1	0.1

Table 5.11: Comparison of NPE's in Acid and Caustic Sewers

For AlPac, the caustic sewer consists of the D_n and E_{op} streams combined, while the acid sewer consists of only the D_o stream. The D_2 stream does not enter the acid-sewer as most of this water is reused within the mill; therefore, this stream is not involved in these comparisons.

As expected, the Cl concentrations in the acid sewer are higher for Mill B. The K concentration in the caustic sewer for AlPac is a bit higher than Mill B. This is probably because AlPac has two different streams added to the caustic sewers (D_n and E_{op}) while Mill B probably only adds the E_{op} stages to theirs. If only AlPac's E_{op} stage was compared to the caustic sewer from Mill B, then the results for K concentration compare better.

Other areas of the mill contribute to the effluent collection system as well. When the mill is running at steady state, small amounts of water leave the mill at locations other than the ones listed above. For example, water such as that used for cleaning, seals on pumps and mixers, general sewage, storm water, and various others also contribute to the effluent in smaller amounts. If there is an upset within the mill, spill control systems collect any upset materials into a number of sumps that can be pumped back into the process or sewered.

5.3 Conclusion

A water balance for the major streams leaving the mill was performed. The effluent flow leaving these areas and entering the mill sewers was calculated. The results indicate that the majority of the consistent flows are from:

- Wood room – 110 L/s
- Bleach Plant
    - D_n Stage – 142 L/s
    - D_0 Stage – 260 L/s
    - E_{op} Stage – 128 L/s

The wood room, bleach plant, and machine room effluent streams were sampled and analyzed for Cl, K, Mg, and Mn. The highest concentration of chlorides, magnesium, and manganese was found in the D_0 effluent stream, while the highest concentration of potassium was found in the D_n stream.

Chapter 6.0

Effluent Recycling

This chapter discusses some of the issues around recycling various streams at Alberta-Pacific Forest Products Inc. First, some basic water recycling guidelines are discussed that others have used when determining how to approach water recycling. Next, some of the areas that are available for water recycling at Alberta-Pacific are examined as well as the amount of fresh water used in these areas. Most of the areas that discharge water to the effluent treatment system are examined in detail to determine if this water can be used for recycling purposes in other areas of the mill. Different ideas, process problems, effects on equipment, economic evaluations, and areas where water can be recycled are also studied. In summary, a suggested order in which streams should be considered for recycle is discussed along with how much of the mill's fresh water intake could possibly be reduced.

6.1 Water Recycling Guidelines

A guide on the water use reduction in the pulp and paper industry has been put together (H.A. Simons, 1994) to assist mills in reducing the amount of water that is used in pulping processes. Some basic ideas suggested in this guide are to recycle the water as close to the source as possible to save on pumping and piping costs, and to use the lowest quality water available to do the job to free up cleaner water to be used elsewhere. Recycling water could provide an opportunity to save on fresh water, fibre, heat, and chemicals. H.A. Simons (1994) also suggest that replacing fresh water streams in a mill with recycled water is the best place to start on a recycling project because some mills may "feel" that they require fresh water when in reality a recycled stream would be fine. Before a mill uses fresh water, it should be convinced that its requirements are supported by technical information. Sometimes, the recycled water may need to be polished before being used in certain areas of the mill. The type of contaminant in the recycled water would indicate what type of treatment might be required. The recycled water should replace higher quality water so that this higher quality water could be used elsewhere.

The mixture of recycled waters must be compatible with the equipment and the process, so the technical specifications of the equipment need to be examined. Most times the manufacturer will provide the minimum water quality standards for the equipment. H.A. Simons (1994) also state that many mills may use water that is nearby rather than pipe in lower quality water, therefore not taking advantage of optimal recycling opportunities. They also indicate some problems that could be associated with recycling: drainage of the pulp mat could be affected with an increase in fine fibre content in the water, increase in temperature could increase the slime content, and increased dissolved solids may increase scaling, corrosion, as well as affect the pulp quality. Many considerations must be examined before water can be recycled within a mill.

The more pulp moves through the process, the cleaner it gets, hence, the cleaner the water leaving each area is that is in contact with the pulp; dirtier water is produced in the digester area, while cleaner water is produced in the pulp machine area. This is important to consider. To use dirty recycled water from the beginning of the process to an area downstream in the process that is cleaner would just be contaminating that area. It is preferred to use recycled water from the downstream areas (e.g. pulp finishing area) to the upstream areas (e.g. bleach plant).

In all recycle considerations, any upset conditions (such as start-up or shut-downs of the mill) must be taken into consideration. Any lines that would be recycled within the mill should also have another source of water to rely on in case the recycled water is not available. In these cases, the piping could be set up so that the mill could still use fresh water if required.

6.2 Destinations for Recycled Water

An area in the mill has to be chosen to accept recycle streams. H.A. Simons (1994) indicate that white water can often be used for cleaning showers, stock dilutions, and chemical dilutions. Other processes from the mill produce water that is contaminated but may still be clean enough to reuse in other areas of the mill. Replacing a fresh water stream in the mill with a recycled water stream is the best place to begin instead of trying to replace an already existing recycled stream. Figure 6.1 shows AlPac's fresh water usage for 1998.

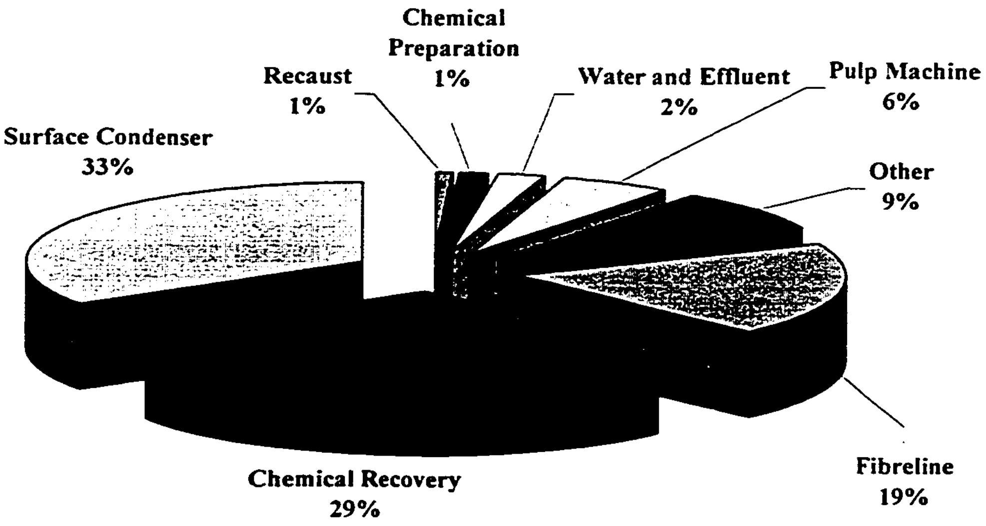


Figure 6.1: 1998 Average of Fresh Water Usage in the Mill

The "Other" category includes water used in the cooling towers, turbines, neutralization chamber, and a few other areas. Most of the areas that use fresh water in the wood room, fibreline, and pulp machine area are listed in Table 6.1.

Area	Water Type	Use
Wood Room	White, cold	Clean and debark logs, air conditioning
Brownstock		
• Number 2 Press	Hot, warm, combined condensate	Displacement wash in the presses
• Number 2 Press Dilution Conveyor	Warm, hot	Dilution water to lower consistency of stock
• Number 2 Press Standpipe	Hot	Dilution to keep pulp from compacting at bottom of standpipe
• Number 1 Press Filtrate Tank	Hot, number 2 press filtrate	Level control
• Number 2 Press Filtrate Tank	Warm	Level control
• Drainer Screens Rejects	Warm, brownstock washer filtrate	Wash water to wash rejects to sewer
• Brownstock Washers Filtrate Chest	Hot	Level control, increase temperature of filtrate
• Brownstock Washers Standpipes	Hot	Dilution water
• Brownstock Washers	Contaminated Condensate Hot	Wash water to clean wire in washers
• 300 Tonne High-Density Storage Tanks	Hot	Assist in draining tower and for dilution
Bleach Plant		
• Filtrate Tanks	Hot	Level control
• D_n Washer	Hot, warm, D_2 filtrate	Wash water
• D_o Washer	Hot, D_2 filtrate	Wash water
• E_{op} Washer	Hot, D_2 filtrate	Wash water
• D_2 Washer	White, hot, warm	Wash water
Pulp Machine		
• White Water Surge Tank	Hot, warm	Level control
• Cleaners	Cold	Assist in draining rejects
• Vacuum Pumps	Cold	Seal water
• Pressate Collection Tank	Hot	Level control

Table 6.1: Types of Water used in Various Mill Areas

6.3 Determination of Fresh Water Use

If recycled water is to replace fresh water, an indication to the quantity of recycled water required needs to be determined. This section discusses the most probable areas that could use recycled water that currently use fresh water. Each of these areas was examined for the amount of fresh water that is currently used to provide an indication to the quantity of recycled water that would be required. The methods used to determine these flows, as well as the quantity of fresh water used in each area are discussed below.

6.3.1 Bleach Plant Filtrate Tanks

Each of the filtrate tanks in the bleach plant were monitored over one year to determine how much hot water they normally use. There are no flow indicators located on any of these hot water lines, so the values were determined by searching the mill's historical data-base and recording how often the control valves on the hot water lines were open. The results are shown in Figure 6.2 and indicate that the hot water used for level control for the D_2 filtrate tank was used for a total of 249 hours over a one-year period. The amount of hot water used in the other tanks is negligible. An illustration of the D_2 area is shown in Figure 6.3. These results do not give an indication to the amount of hot water that is being used in these tanks, but provides an indication to which tanks should be investigated further.

The D_2 filtrate tank is operated on a level control, using hot water as make-up water when the level gets too low. The filtrate from this tank is used for wash water in other areas of the bleach plant. If the required amount of D_2 filtrate cannot be supplied by the filtrate in the tank, hot water is added to help meet this loading. Hot water is used instead of cold water to maintain the temperature of the filtrate at about 70 °C.

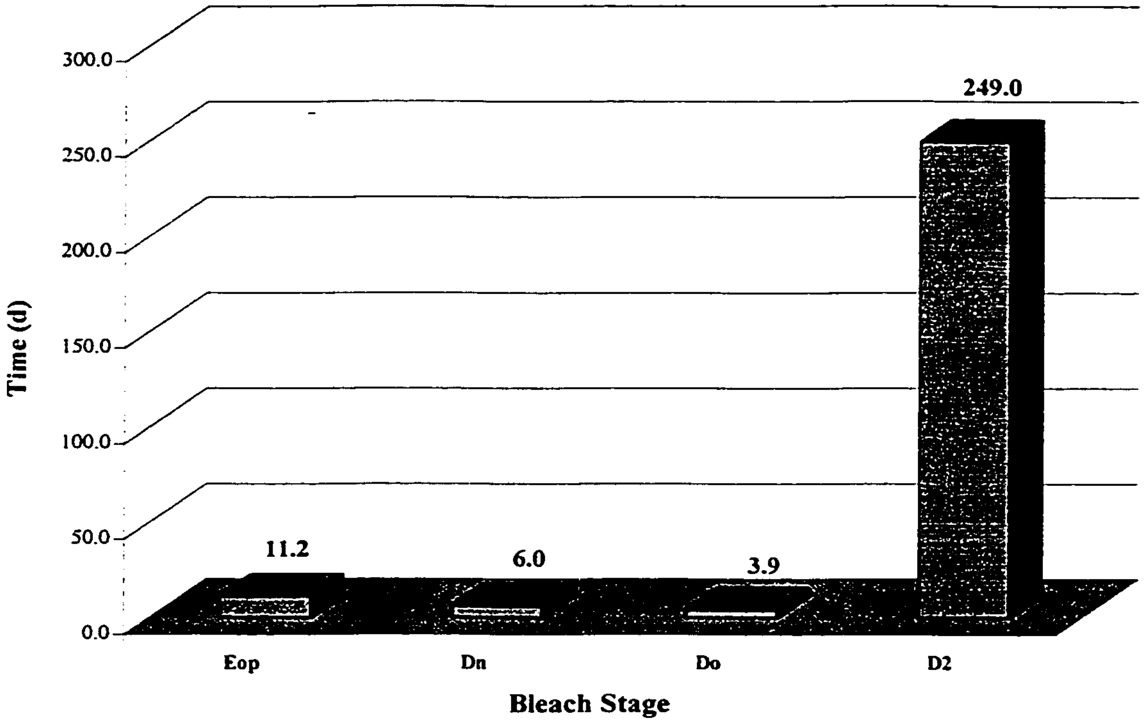


Figure 6.2: Filtrate Tank Hot Water Make-up (1998 Data)

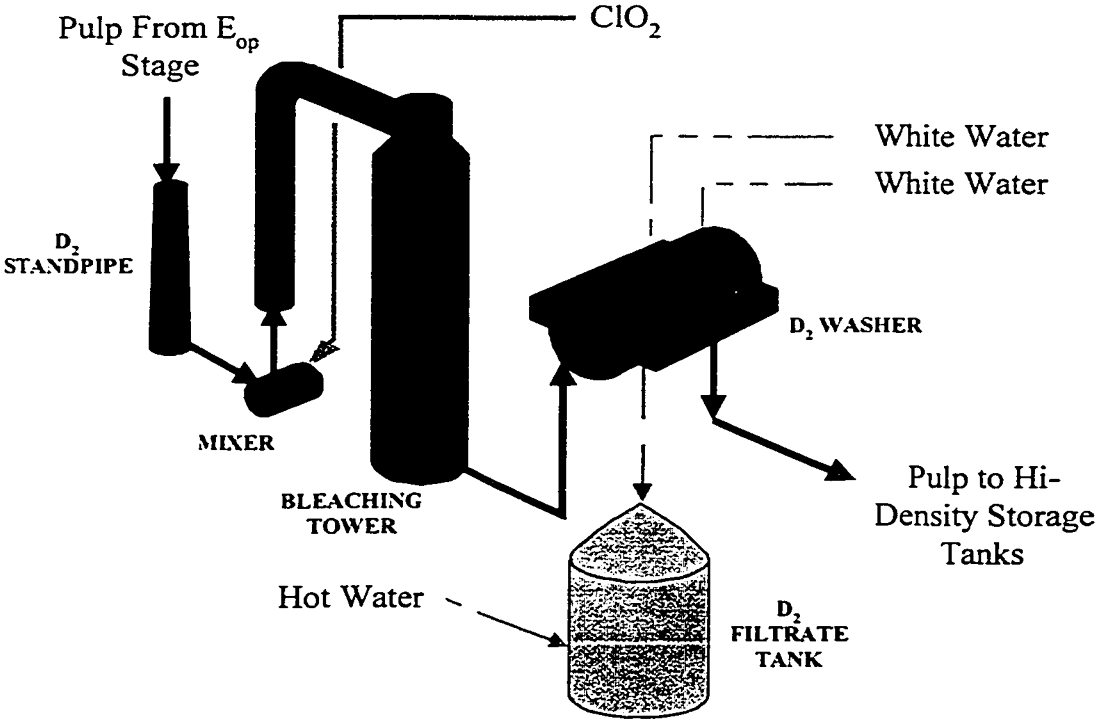


Figure 6.3: D$_2$ Bleaching Stage (Alberta-Pacific Forest Products Inc., 1993)

The amount of hot water used for level control was determined to see if an effluent stream would be able to supply this flow. Initially, the mill's design specifications for the valve on the hot water line were used to see if a flow could be determined. The specification is supplied by the mill's design sheet and is data that is used for specific applications and for specific areas within the mill. This indicates a valve % opening and a corresponding flow rate. A polynomial was fitted to these data (Appendix D). From here, a flow rate was inferred, but appeared high. The results indicated that the average flow of hot water used in the filtrate tank was 50 L/s.

To check these numbers, a "bucket and stop-watch" method was used to determine how much hot water was being supplied to the filtrate tank (Appendix D). The level in the filtrate tank was recorded as the valve % opening was varied. Knowing this and the dimensions of the filtrate tank, enough information was provided to develop a curve and fit a quadratic equation to the points. The flow rate of the hot water entering the tank was inferred by the % opening of the control valve. These numbers did not compare very well to the numbers determined by the valve specifications, but this method appeared to be the best for determining the flow rate of the hot water. Figure 6.4 indicates the average amount of hot water use that was calculated using the "bucket and stopwatch" calibration for each month in 1998. These values do not take into account any upsets or down time that may have occurred during this time.

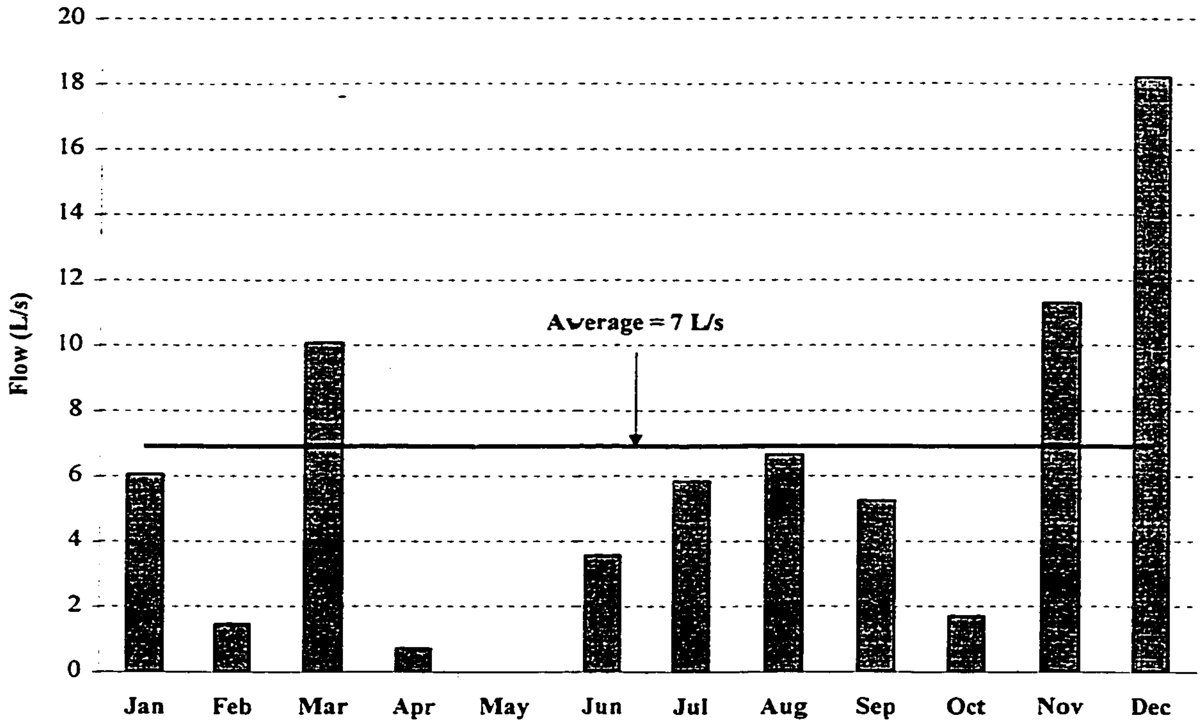


Figure 6.4: Average Amount of Hot Water Used for Level Control in the D_2 Filtrate Tank for 1998

These flow rates are relatively low. The average hot water usage in the D_2 filtrate tank over 1998 was approximately 7 L/s. At some points in 1998, the flow rate used for level control did reach over 200 L/s, but this was very rare, and only lasted for a short time. The flow rates for the month of December are shown in Figure 6.5 to show the fluctuations that can occur.

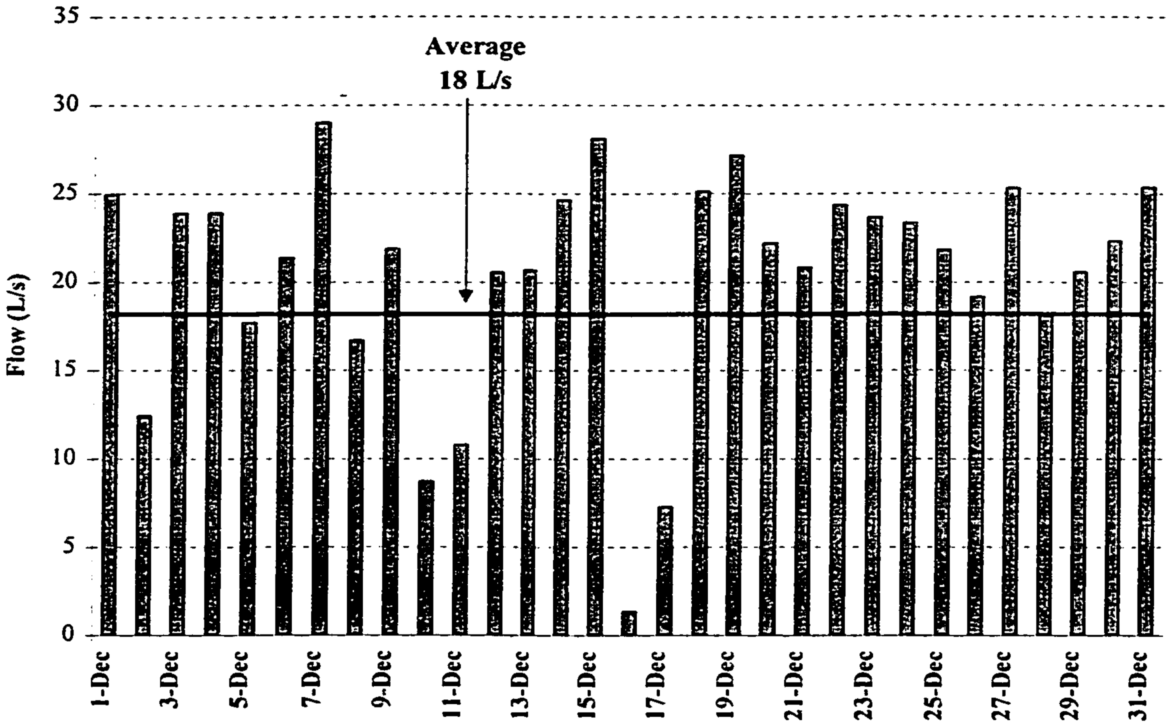


Figure 6.5: Average Daily Amount of Hot Water Used for Level Control in the D_2 Filtrate Tank for December, 1998

6.3.2 D_n Washer

All of the bleach plant washers have the capability of using fresh water, or combinations of other recycled water. As discussed in Chapter 5, normal operations have the D_n washer using large amounts of fresh warm water as well as recycled D_2 filtrate. The original configuration of the mill had this stage as the first bleaching stage, but this has been modified to be an open wash. The filtrate from this stage is used for dilution of the pulp entering the D_n area, and the rest goes to sewer. Figure 6.6 illustrates this process.

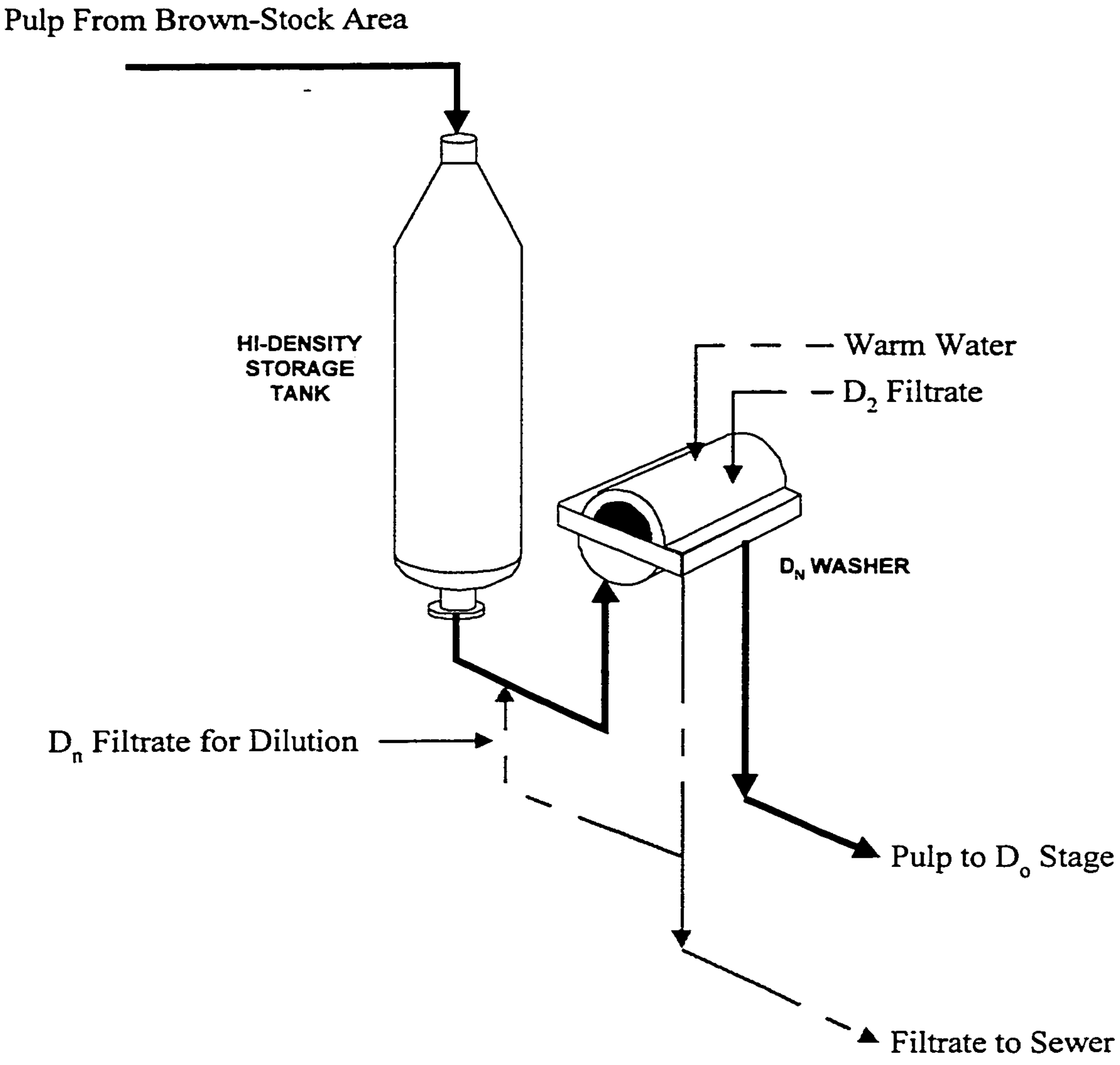


Figure 6.6: D_n Washing Stage (Alberta-Pacific Forest Products Inc., 1993)

Figure 6.7 shows the amount of warm water that was used on the D_n washer for 1998, while Figure 6.8 shows the amount of water used for December 1998. On average, approximately 50 L/s warm fresh water was used on the D_n washer.

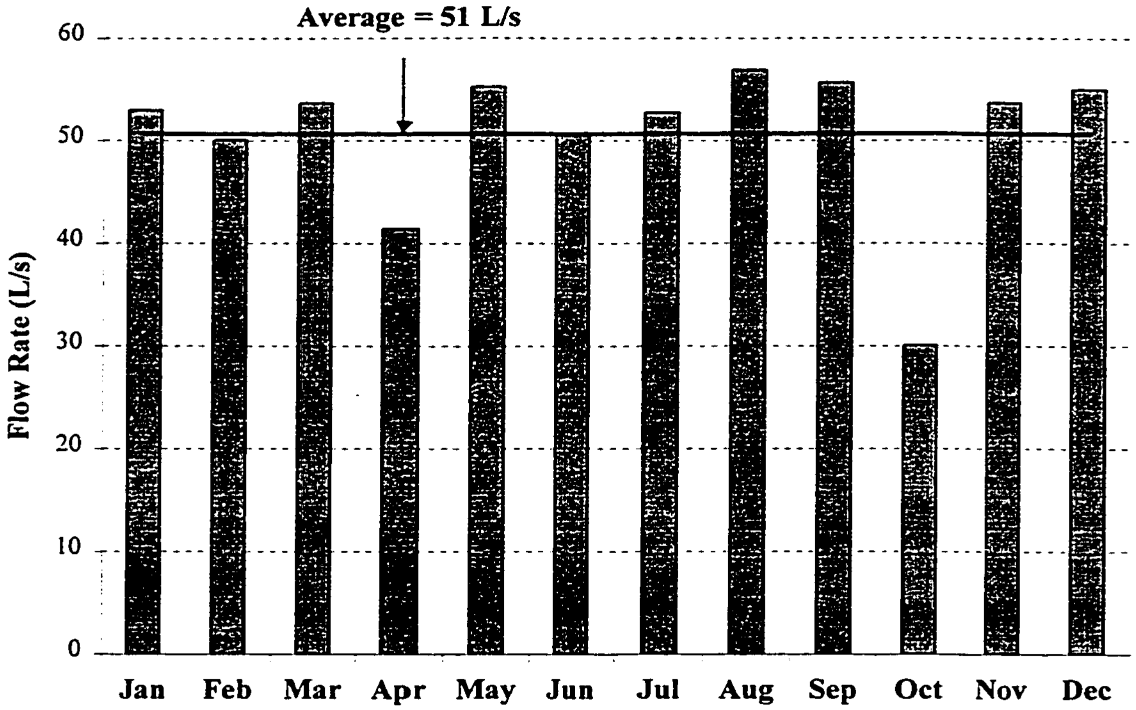


Figure 6.7: Average Amount of Warm Water Used for Washing on the D_n Washer for 1998

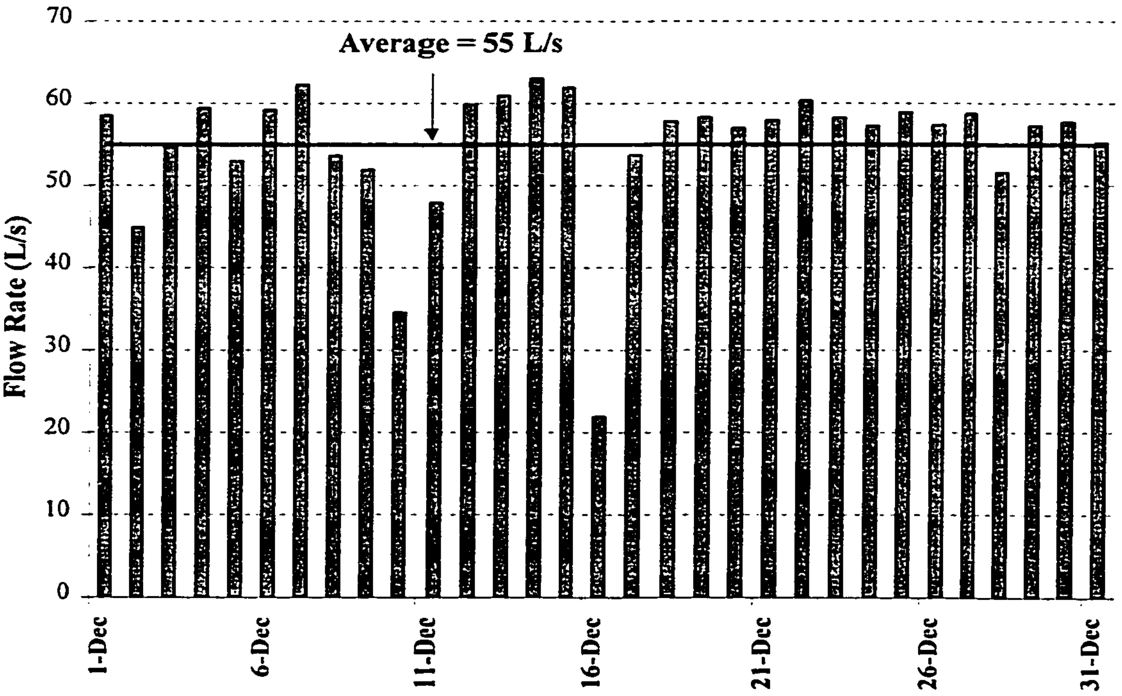


Figure 6.8: Average Daily Amount of Warm Water Used on the D_n Washer for December 1998

6.3.3 D_o Washer

As discussed in Chapter 5, the D_o washer in the bleach plant usually washes the pulp mat with hot fresh water and recycled D_2 filtrate. The filtrate from this stage is used for dilution of the pulp entering the D_o area while the rest goes to sewer. In 1998, the average amount of hot water used in this area was approximately 50 L/s, as shown in Figure 6.9.

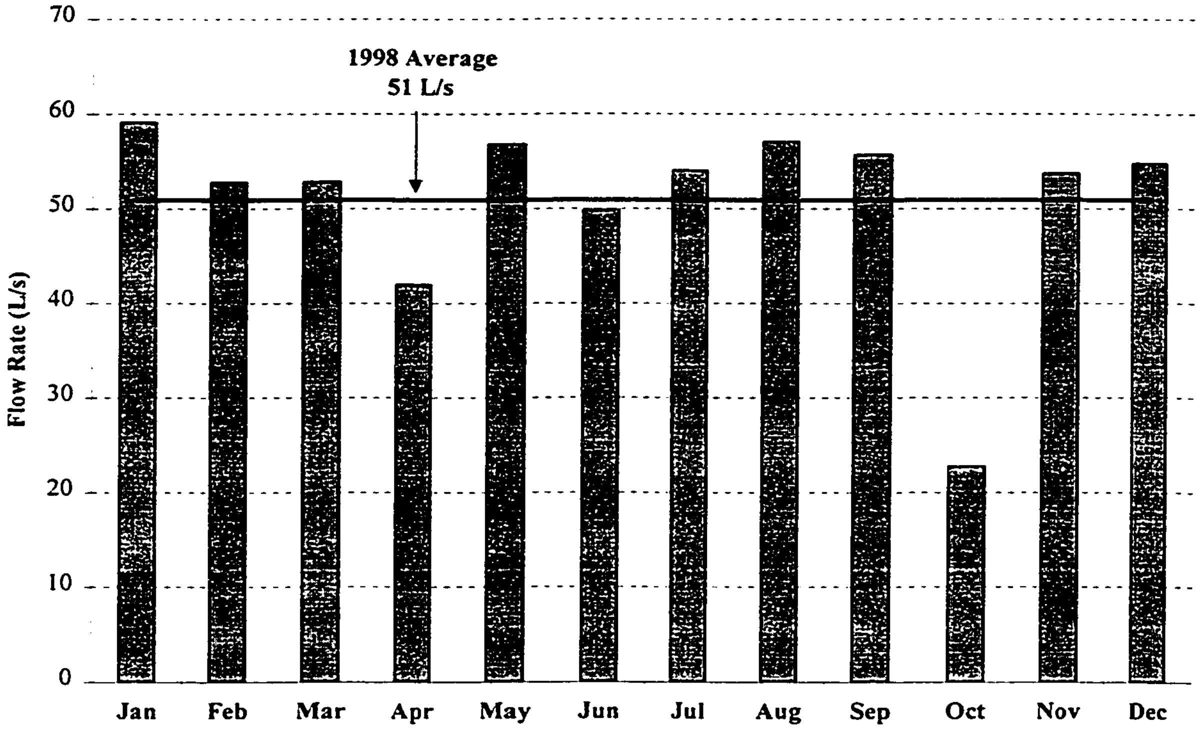


Figure 6.9: Average Amount of Hot Water Used for Washing on the D_o Washer for 1998

6.3.4 E_{op} Washer

The E_{op} washer in the bleach plant uses fresh hot water and recycled D_2 filtrate to wash the pulp. As discussed in Chapter 5, the filtrate from this stage is used for dilution in the D_o repulper, dilution of the pulp entering the E_{op} stage, and sometimes as wash water to the wood room. The rest of the filtrate that is not used in these areas is sent to the sewer. Figure 6.10 shows that the average amount of hot water used on the E_{op} washer in 1998 was approximately 50 L/s.

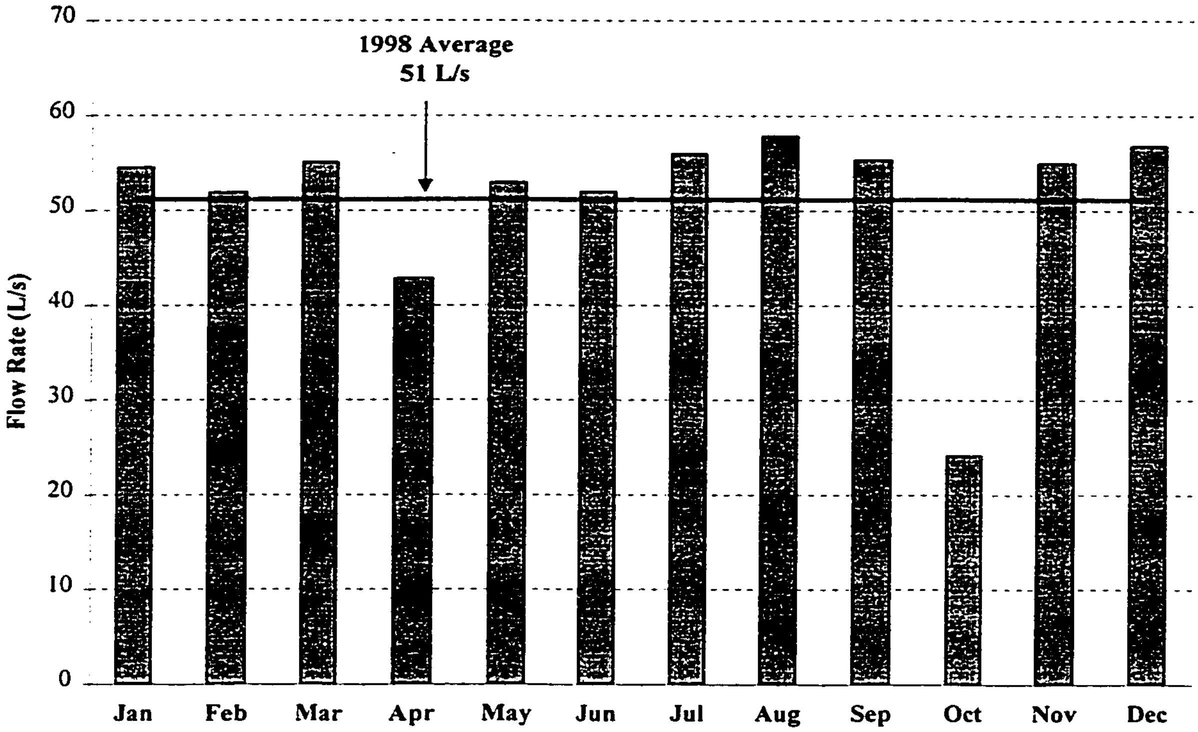


Figure 6.10: Average Amount of Hot Water Used for Washing on the E_{op} Washer for 1998

Each of the washers use approximately the same amount of fresh water because the washers are designed the same and are controlled to use the same amount of water in each stage.

6.3.5 Dilution Conveyor

There are two inputs of fresh water to the dilution conveyor; a hot water dilution line, and a warm water dilution line. Figure 6.11 illustrates this process.

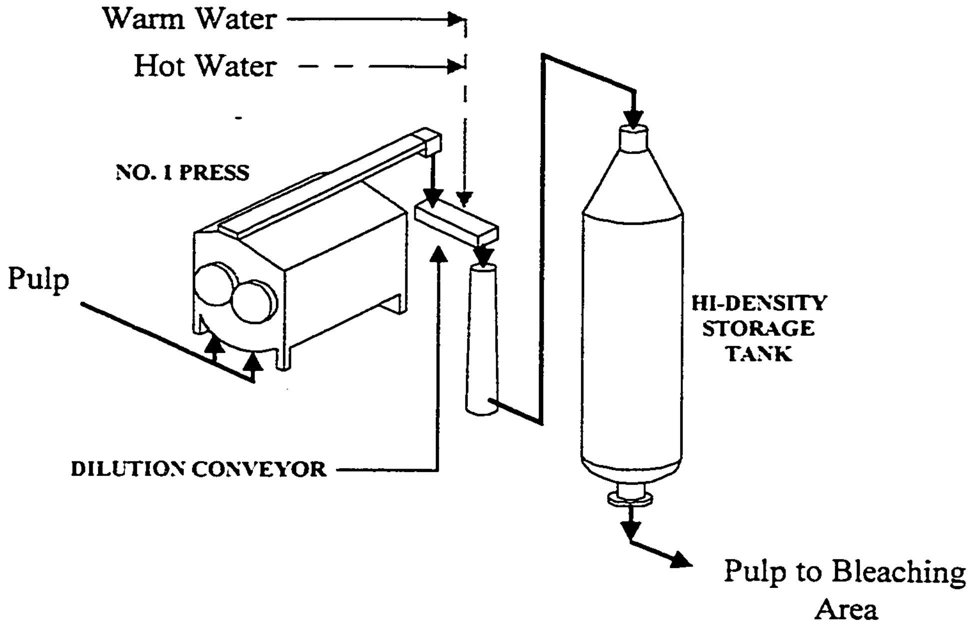


Figure 6.11: Fresh Water Addition to the Dilution Conveyor (Alberta-Pacific Forest Products Inc., 1993)

Figure 6.12 indicates that approximately 74 L/s of fresh water was used in this area for 1998. Figure 6.13 shows the flows for December 1998 to show the variations that may occur.

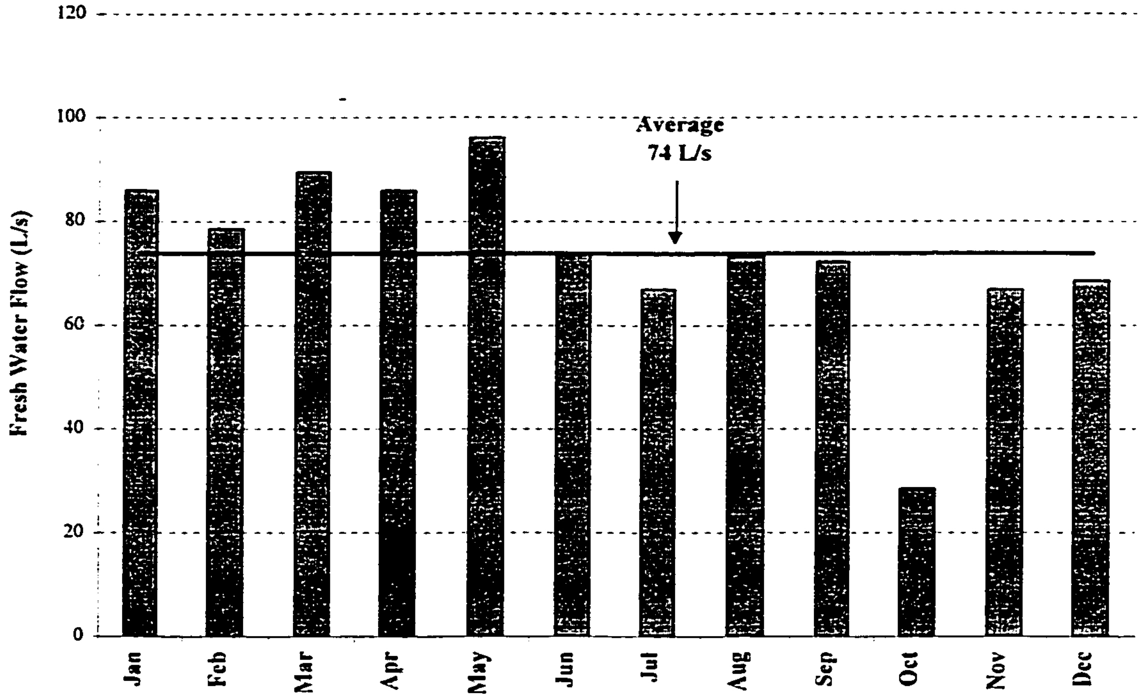


Figure 6.12: Average Amount of Warm and Hot Water Used on Number 2 Dilution Conveyor for 1998

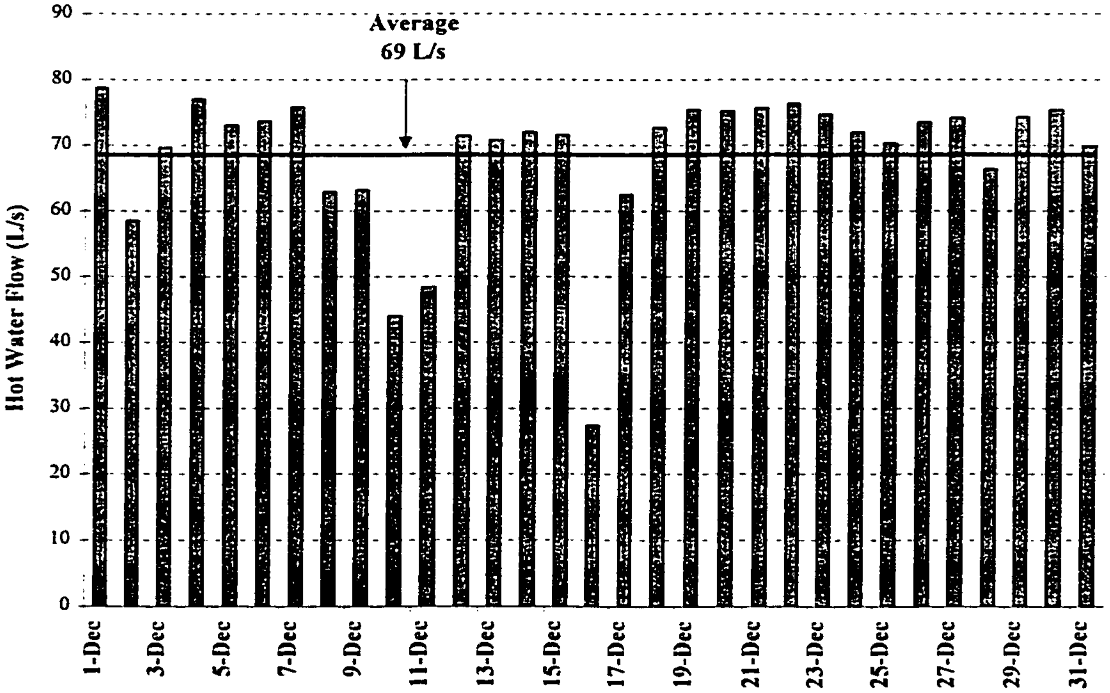


Figure 6.13: Average Daily Amount of Warm and Hot Water Used on the Number 2 Dilution Conveyor for December 1998

6.3.6 300-Tonne Screened High-Density Storage Tank

Another area that uses fresh water is the 300 tonne high-density storage tank that is located at the end of the brown stock area. This tank is used to store the screened pulp from the brown stock area until it is used in the bleach plant. An illustration of the tank is shown in Figure 6.14.

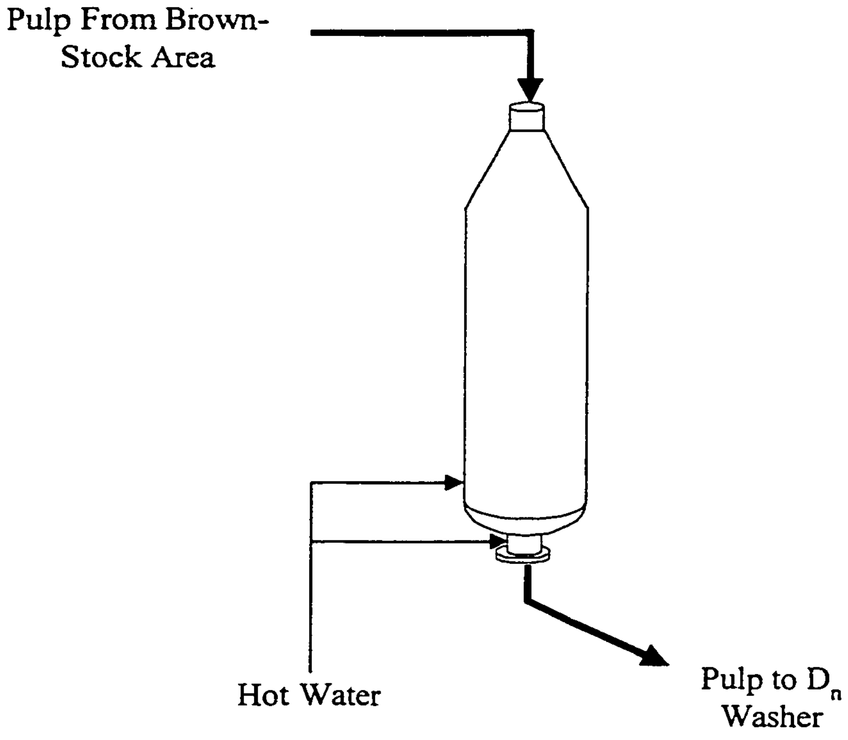


Figure 6.14: 300 Tonne High-Density Storage Tank (Alberta-Pacific Forest Products Inc., 1993)

The hot water in the upper section of the High-Density tank is used to slightly dilute the pulp stream to assist in "pushing" the pulp out of the tank. The water added at the bottom of the tank is used for dilution purposes. This flow is on consistency control, which means that in order for the pulp to be able to be pumped to the D_n washer, it must first be diluted.

The amount of water used in the upper section of the storage tank is controlled by a flow controller, and is easily measured. The hot water entering the bottom had to be inferred by performing a water balance around the tank (Appendix D). The total flow of hot water added to both these areas on the high-density storage tank for 1998 was 14 L/s and is shown in Figure 6.15. Figure 6.16 shows the flow fluctuations for the month of December 1998.

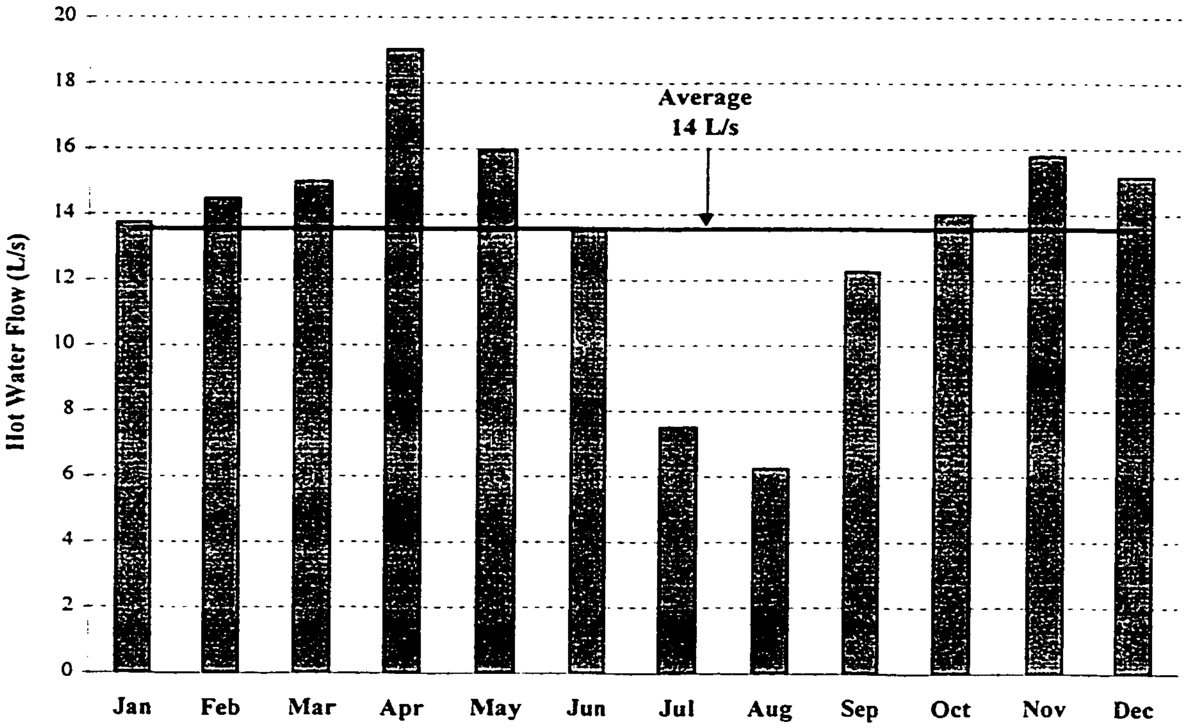


Figure 6.15: Average Amount of Hot Water Added to the Screened High-Density Storage Tank for 1998

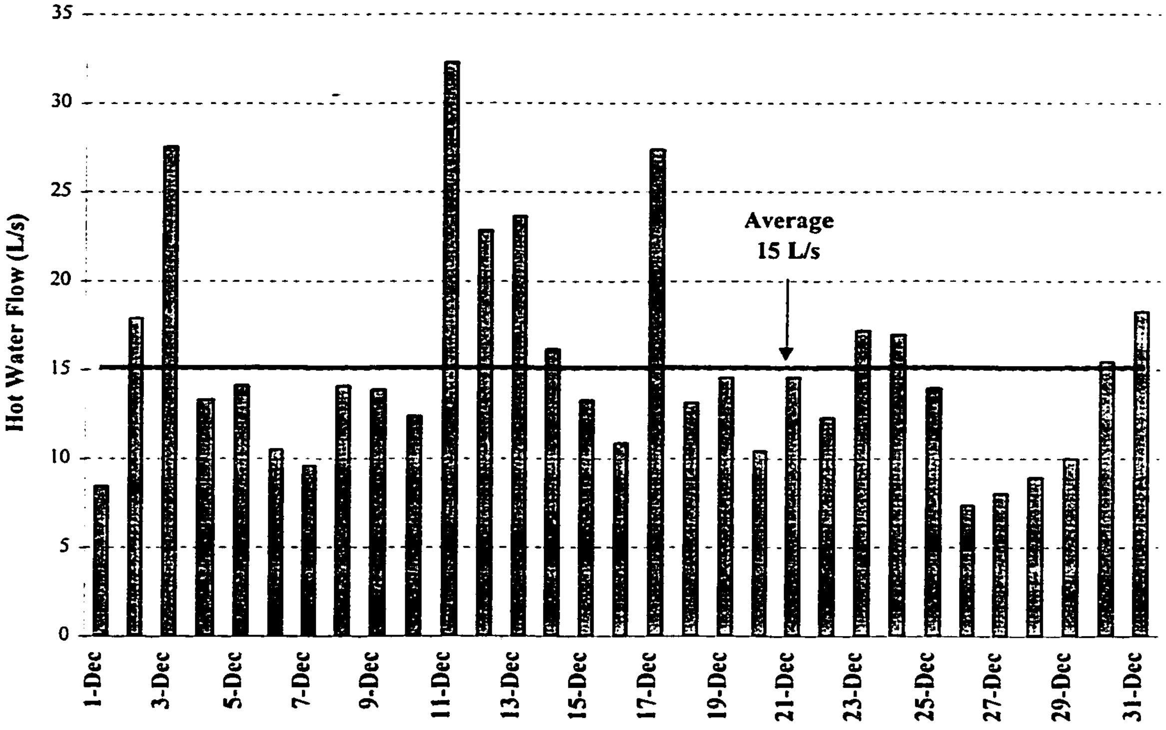


Figure 6.16: Average Daily Amount of Hot Water Added to the Screened High-Density Storage Tanks for December 1998

The fresh water flows determined in this section are summarized in Table 6.2.

Area	Amount of Fresh Water (L/s)
D_2 Filtrate Tank	7
D_n Washer	51
D_o Washer	51
E_{op} Washer	51
Dilution Conveyor	74
High Density Storage Tank	14

Table 6.2: Summary of Fresh Water Usage

6.4 Machine-Room Effluent Recycle

Some of the possible areas that can use recycled water were determined in section 6.3, and the initial characterization of the major effluent streams was determined in Chapter 5. The machine room effluent appears to be the best candidate for recycle to the mill for a variety of reasons. The recovery of the fibre in this stream may provide immediate cost savings to the mill. Also, the machine room effluent makes up about 10% of the total flow leaving the mill. If this were recycled, the cost of producing fresh mill water would be reduced by approximately 10%. There would also be an environmental benefit with a reduced effluent volume being discharged to the environment. This reduced volume has been a major focus for most pulp and paper mills throughout North America since the introduction of the Cluster Rule as discussed in Chapter 3.

There may be some drawbacks to recycling the machine room effluent into the process. Some points of discharge from the machine-room are purge points for contaminants that may be harmful to the process if allowed back in. The machine-room goes through a rigorous process to remove pitch, a contaminant introduced during the pulping process, from the pulp before forming the final pulp sheets. If the pitch re-entered the process, it would accumulate in the system and create poor pulp quality. Also, the machine room effluent provides a purge point for fines from the system. If the fines content of the pulp stream accumulates within the system, the wire on the machine may become plugged, and prevent proper drainage of water from the sheet. This leads to operational problems within the machine-room, and the sheet forming process may fail and have to be shut down for cleaning.

6.4.1 Machine Room Effluent Flow Rate Characterization

To determine if the machine-room effluent stream is a possible candidate for recycle, a flow characterization of this stream was performed. The online water balance program (Appendix D) that was implemented for this project determined the flow rates. The daily and monthly averaged flow rates from November 1 1998 to January 17 1999 were determined and are shown in Figure 6.17. These time frames were chosen because the water balance was only implemented on November 1, 1998.

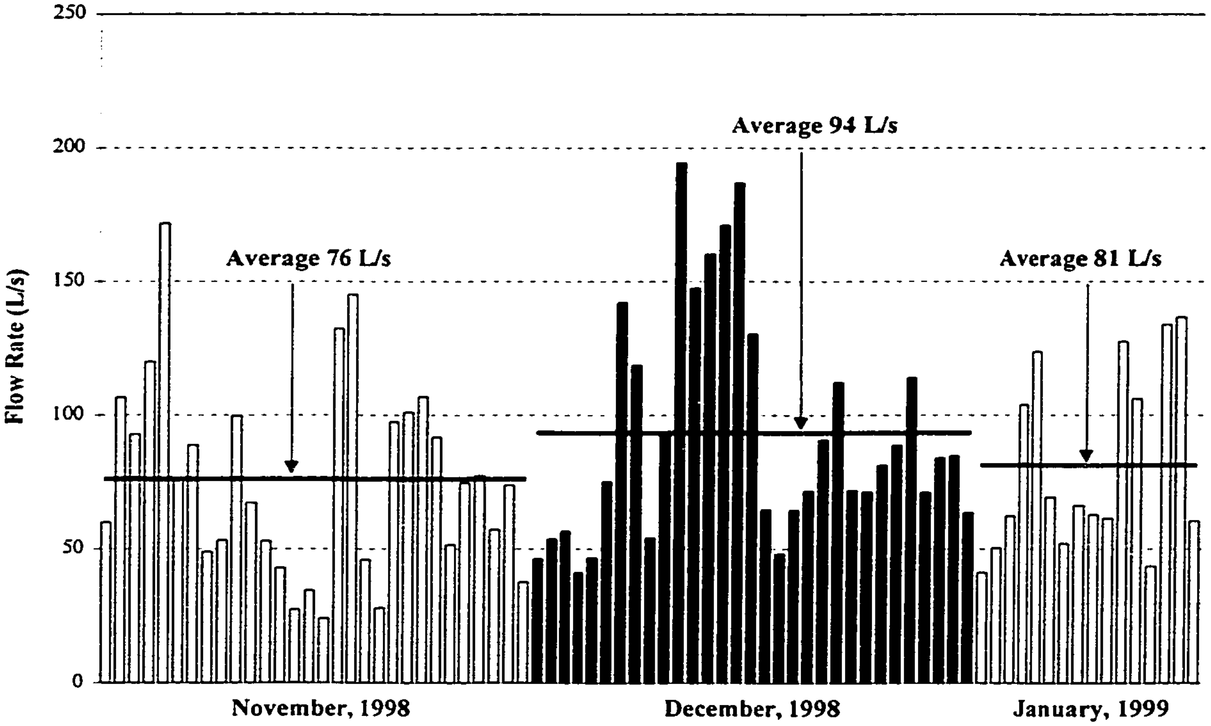


Figure 6.17: Machine Room Average Effluent Flows (November 01, 1998 - January 17, 1999)

The flow rates of this effluent stream appear to fluctuate significantly from day-to-day. For a stream to be recycled there should be a consistent flow that the mill could rely on. Factors that could cause the fluctuations in effluent flow could be: process upsets, operation variability, or poor design in operating equipment.

6.4.2 Sources of Machine Room Effluent

The majority of the fluctuating flow rates of this effluent stream were caused from tanks overflowing to the sewer. Most of the storage equipment used on the mill site has overflow weirs as a means to displace water if the tanks become too full. Some tanks overflow to sewer. Table 6.3 shows the vessels in the machine room, and indicates the destination of the overflow when the level of the vessel reaches over 100%. For example, this table shows that the white water silo would overflow to the machine white water chest while the surge tank overflows to the sewer.

Machine White Water Chest	Fibre Recovery Chest	Sewer
White Water Silo	Blend Chest	Surge Tank
Flat Box Seal Pit	Thick Stock Chest	Filtrate Chest
	Machine Chest	Machine White Water Chest
		Pressate Collection Tank
		Pressate White Water Collection Tank
		Couch Pit
		Hot Water Tank
		Broke Tank
		Fibre Recovery Chest
		Dry End Pit

Table 6.3: Overflow Destination of Machine Room Area Equipment

Other sources of water also enter the sewer system. Rejects from the centrifugal cleaners, seal water used for packing in pumps and agitators, wire pit, fresh water that is used for cleaning purposes, and any tanks that are being drained by opening the drain valve on the bottom of the tank. In particular, the vacuum pump seal tank and wire pit are constantly draining to sewer. The seal tank water contains chemicals that are used in cleaning the equipment and returning this to the process would be undesirable. Currently, some of this water is being returned to the D_2 bleaching stage but will soon be completely sent to sewer because of the problems associated with the chemicals. Fortunately, the rejects from the centrifugal cleaners enter the effluent stream by means of one line and can be separated from the rest of the effluent leaving the machine room. This would mean that if the machine-room effluent were recycled, most of the pitch could still be removed from the system.

Figure 6.18 indicates which tanks were overflowing to the sewers, as well as the amount of time they overflowed from November 5 1998 to January 17 1999. This was determined by analyzing each tank, and recording the amount of time that the level exceeded 100%. Note that these numbers do not give an indication of how much flow is being discharged from the tanks, but only the amount of time each tank is overflowing.

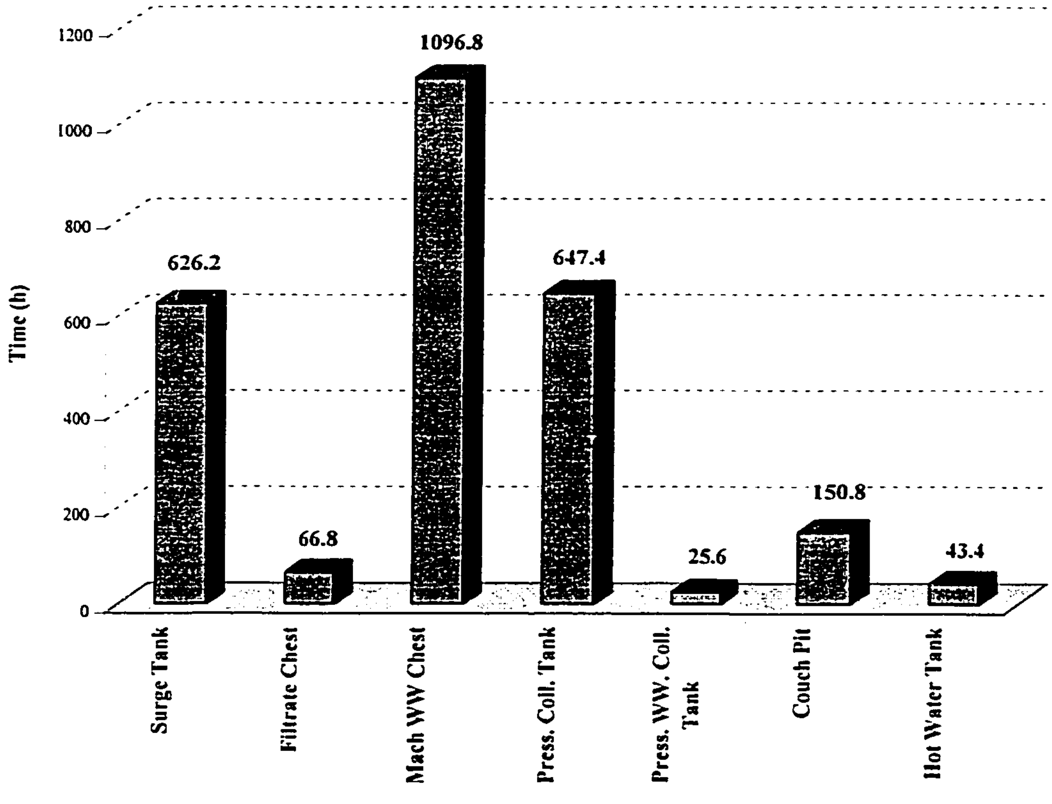


Figure 6.18: Machine Room Equipment Overflow Distribution (November 5, 1998 - January 17, 1999)

From Figure 6.18, it is shown that the majority of the overflows in the system occur within the surge tank, machine white water chest, and pressate collection tanks.

6.4.3 Quantification of Machine-Room Effluent

In order to quantify the amount of water leaving the machine-room area, a detailed study was performed on the white water system. All the streams that combine to give the total machine-room effluent were analyzed. The methods used can be found in Appendix D. The fine content of fibres, i.e., any fibre less than 0.2 mm in length, of each stream contributing to the effluent system was determined. A stream high in fine content is not suitable for recycling within the mill, so this information provides some guidance on which streams can be recycled. Figure 6.19 shows the fine content distribution within the machine-room area.

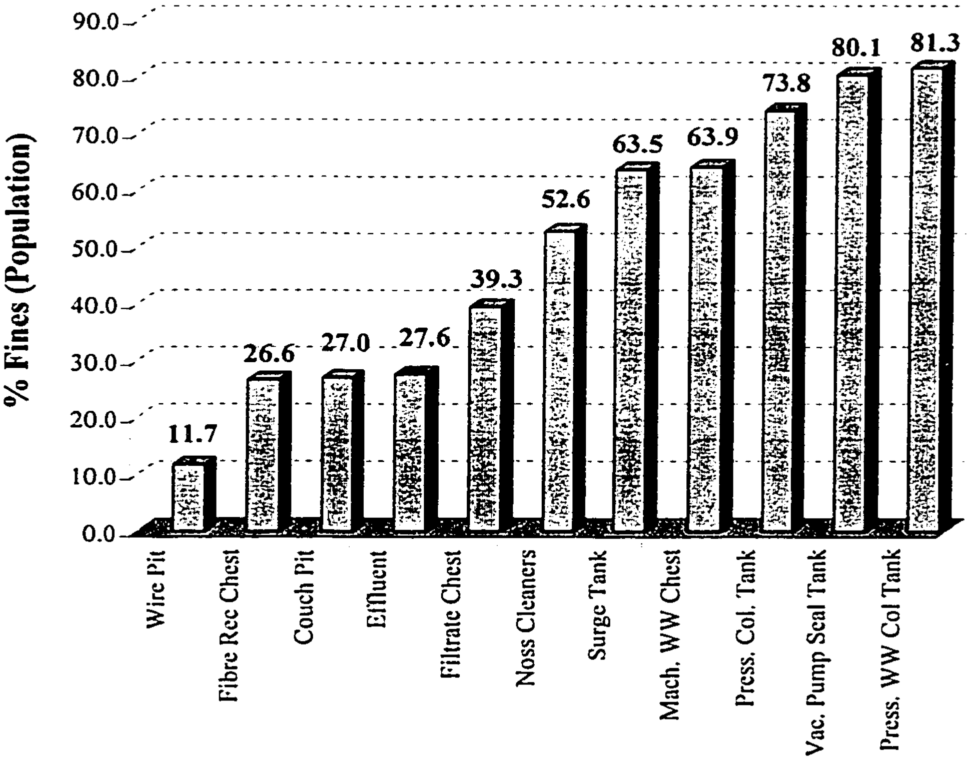


Figure 6.19: Percent Fines by Population in Machine Room Area

In addition, the total suspended solids (TSS) was calculated to determine how much fibre was present in the streams. This is shown in Figure 6.20. As well, the flow of these streams was quantified to determine how much could be recycled. Figure 6.21 shows the tanks that were overflowing and streams contributing to the effluent system over a three-month period as well as the corresponding flow rates. Figure 6.22 shows the distribution of fibres that are exiting the machine room with the effluent. The procedures used to determine the flow and fibre content of these streams are shown in Appendix A and Appendix D.

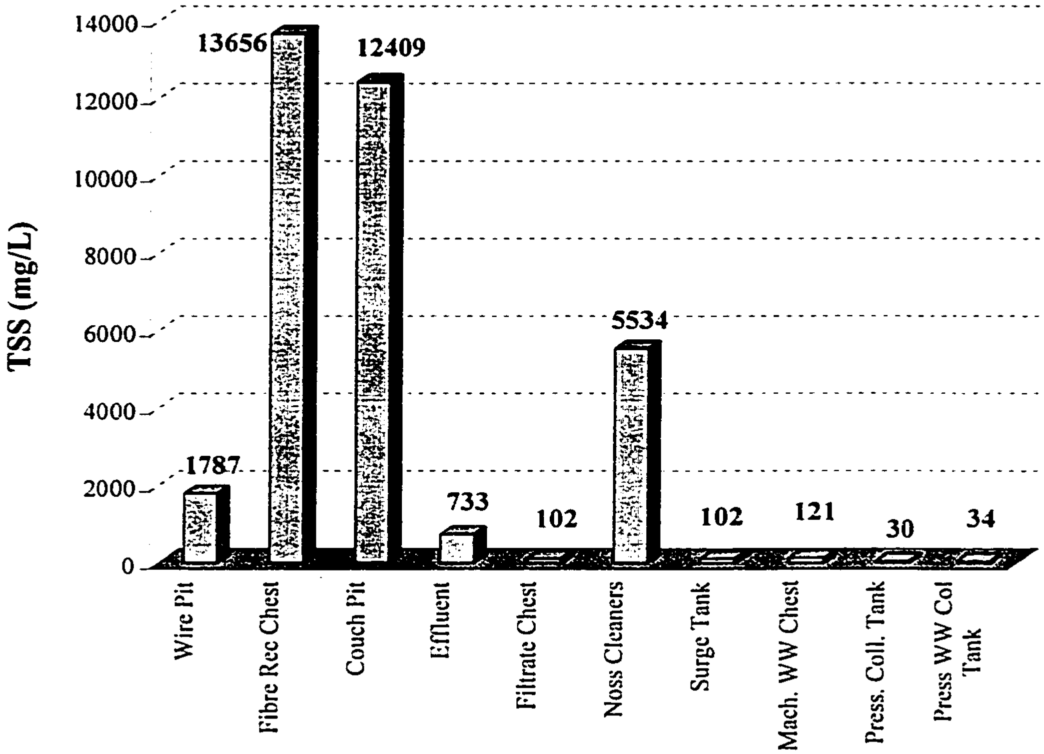


Figure 6.20: Total Suspended Solids (TSS) Distribution in Machine Room Area

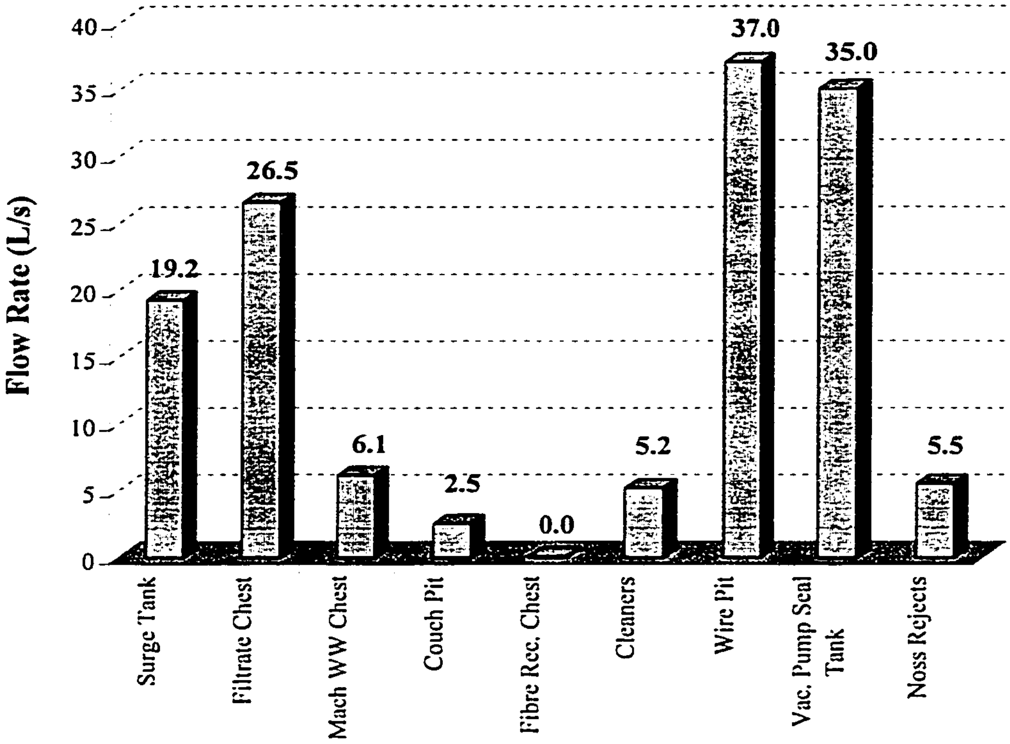


Figure 6.21: Flow Distribution in Machine Room Area

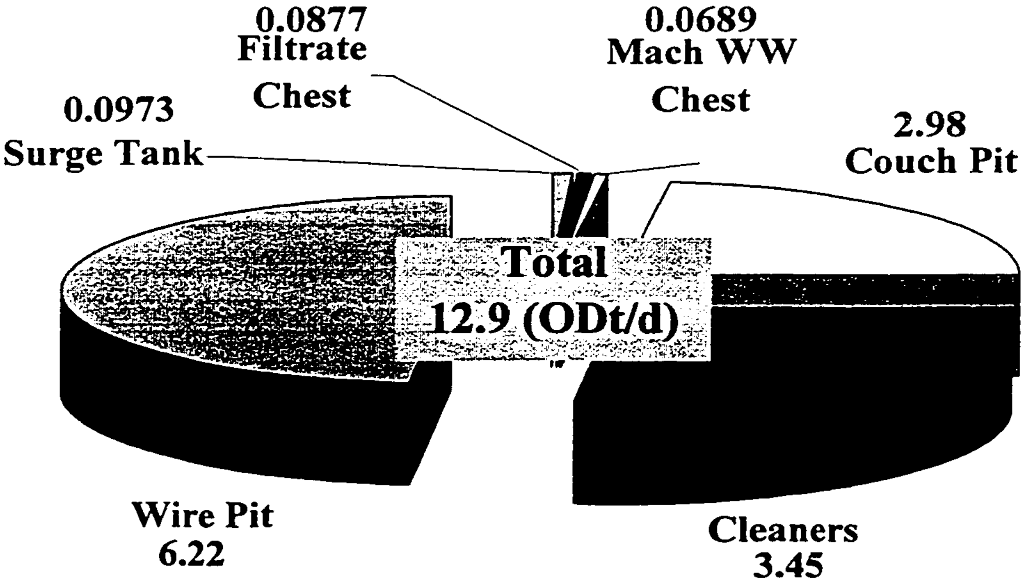


Figure 6.22: Average TSS (ODt/d) in Effluent From Machine Room Area

One interesting result was attained when these effluent lines were traced and analyzed. The wire pit stream has a significant amount of "good" fibres present that are constantly discharged to sewer. This is a discharge of approximately 6.22 oven dry tonnes of fibre per day.

6.4.4 Machine Room Effluent Recycle Considerations

In this section, several considerations are discussed on how to recycle machine-room effluent to other areas of the mill. Three recycle strategies, process problems associated with these, as well as equipment considerations are also discussed.

Section 6.3 described the areas that are available for replacing fresh water with the machine room effluent; any one of these areas can be considered for a recycle candidate. Besides fresh water, the effluent from the machine room should be the cleanest effluent from within the mill. Any recycle destination for this water would be receiving cleaner water than from anywhere else in the pulping process. There are some considerations that should be examined because of the origin of some of this water from the machine room.

The recycled water should be compatible with the area it is being used. Most of this recycled water would be white water, and this is already used in the washing stages of the bleach plant. The machine room effluent would not be desired in the brown stock area because this stream has higher concentrations of Cl and K than fresh water (Appendix C). If these elements were returned into the brownstock area of the mill, they would be collected in the liquor cycle and make it to the recovery boiler, therefore increasing the Cl and K loading. The bleach plant filtrates and the dilution water for press number 2 dilution conveyor do not enter the liquor loop, hence would not cause these problems.

As discussed in Chapter 5, white water is used fully on the D_2 stage, and could be used on other washing stages if there was enough available. From the information in Figure 6.17, there is approximately 80 L/s of machine room effluent available for recycle; a lot less than the fresh water streams identified in section 6.3. Figure 6.21 shows the flows of individual streams that could be recycled.

Recycle Strategies

Three ideas were considered for possible recycle of machine-room effluent: complete effluent recycle, reviewing the current white water control strategy, and recycling individual streams within the process.

The first idea involved the recycle of the complete effluent stream. A problem with this idea is that the contaminants in this stream would accumulate in the pulping process if returned as recycle water. The mill normally sewers about 80 L/s from the machine room. For example, if 51 L/s of white water were to be used as warm water on the D_n washer, this would reduce the amount of white water leaving the mill by approximately 51 L/s. The reduced flow of effluent (approximately 30 L/s) leaving the machine room would cause an accumulation of contaminants present within the white water. The effluent stream provides a purge of contaminants from the process, so if this stream was reduced by 51 L/s, then an accumulation of approximately 64 % of the contaminants in the system could result. If 74 L/s were to be reused on the number 2 press dilution conveyor, a 93% accumulation of contaminants would occur. Tests on the effect of returning white water into the system would also have to be performed. A more detailed water analysis would also have to be done in order to determine what would be accumulating in the system, as well as to help in determining possible process problems. To help minimize the accumulation, the rejects from the centrifugal cleaners could bypass this stream and be sent to the sewer. As well, to ensure that a consistent flow rate is maintained, a storage tank with sufficient holding capacity could be installed.

An examination of the filtrates leaving the bleach plant was performed to see if the fines in the system could be purged if the recycled stream was placed here. The washers in the bleach plant are designed to hold all fibre back, and only allow the filtrate to pass through the washer felts; however, some fibres do pass through. Table 6.4 and Table 6.5 indicates the amount of fibre that is present in the filtrate from the various bleaching stages.

	D_n			D_o		
	Fibre Loss (mg/L)	Flow (L/s)	Fibre loss (t/d)	Fibre Loss (mg/L)	Flow (L/s)	Fibre Loss (t/d)
24-Jun-98 (HW)	70	152	0.919	37	138	0.441
26-Jun-98 (HW)	42	149	0.541	23	131	0.260
30-Jun-98 (SW)	21	120	0.218	19	37	0.060
1-Jul-98 (SW)	21	127	0.230	34	80	0.236
1-Jul-98 (SW)	5	127	0.055	23	80	0.160
2-Jul-98 (SW)	31	131	0.351	20	102	0.176
3-Jul-98 (SW)	25	132	0.285	30	81	0.210
20-nov-98 (HW)	38	140	0.464	30	167	0.436

HW indicates hardwood pulping
SW indicates softwood pulping

Table 6.4: Fibre Loss From D_n and D_o Bleaching Stages

	E_{op}			D_2		
	Fibre Loss (mg/L)	Flow (L/s)	Fibre Loss (t/d)	Fibre Loss (mg/L)	Flow (L/s)	Fibre Loss (t/d)
24-Jun-98 (HW)	91	106	0.833	39	0	0.000
26-Jun-98 (HW)	45	111	0.432	30	0	0.000
30-Jun-98 (SW)	28	82	0.198	12	0	0.000
1-Jul-98 (SW)	29	81	0.203	37	0	0.000
1-Jul-98 (SW)	21	81	0.147	43	0	0.000
2-Jul-98 (SW)	31	88	0.237	27	0	0.000
3-Jul-98 (SW)	21	67	0.122	25	0	0.000
20-nov-98 (HW)	52	140	0.629	45	0	0.000

HW indicates hardwood pulping
SW indicates softwood pulping

Table 6.5: Fibre Loss From E_{op} and D_2 Bleaching Stages

The fibre loss in the first column indicates what is passed through the washer felt while the fibre loss in the third column is the amount of fibres being discharged to the sewer. Note that the D_2 area does not have any fibres discharged to the sewer because there is no filtrate entering the sewer.

The fibre loss values indicate that there may be some form of a purge within the bleach plant system to remove the fines. If the effluent stream were to be recycled to this area, it may be better to send the white water to the number 2 press dilution conveyor or the D_n washer instead of the other washers in the bleach plant. The contaminants would stand a better chance at being removed earlier on in the bleaching area. If the fines are not removed here, then some other separation method may have to be considered to remove these from the system.

This idea was rejected due to the possibility of unknown impurities entering this stream from various sources. The introduction of these impurities to the pulping process may have negative impacts on pulp production.

The second idea considered would be to analyze the various sources of the machine-room effluent and determine if it is possible to decrease the amount of white water that discharges to the sewer, i.e., review the control strategy of the white water system. This could be accomplished by pumping more of the white water to the surge tank, and from here to the area requiring the recycled stream. Ideally, the only flows entering the sewer should be from the centrifugal rejects. Figure 6.23 shows a flow diagram of the current white water system.

The purpose of the surge tank is to collect surges from within the machine room so that this water can be reused. If the amount of white water entering the machine white water chest were greater than the flow leaving, then the excess amount would be returned to the surge tank to be redistributed within the white water system. If the flow leaving the surge tank were to increase to accommodate the additional recycle stream, the white water distribution within the machine room should be able to change to accommodate this extra load by not allowing the tanks within the system to overflow to the sewer. The machine white water chest and the filtrate chest can pump access water to the surge tank instead of overflowing to the sewer. The amount of white water being added to the pressate collection tank from the surge tank could be monitored to provide just enough flow to prevent the collection tank from overflowing.

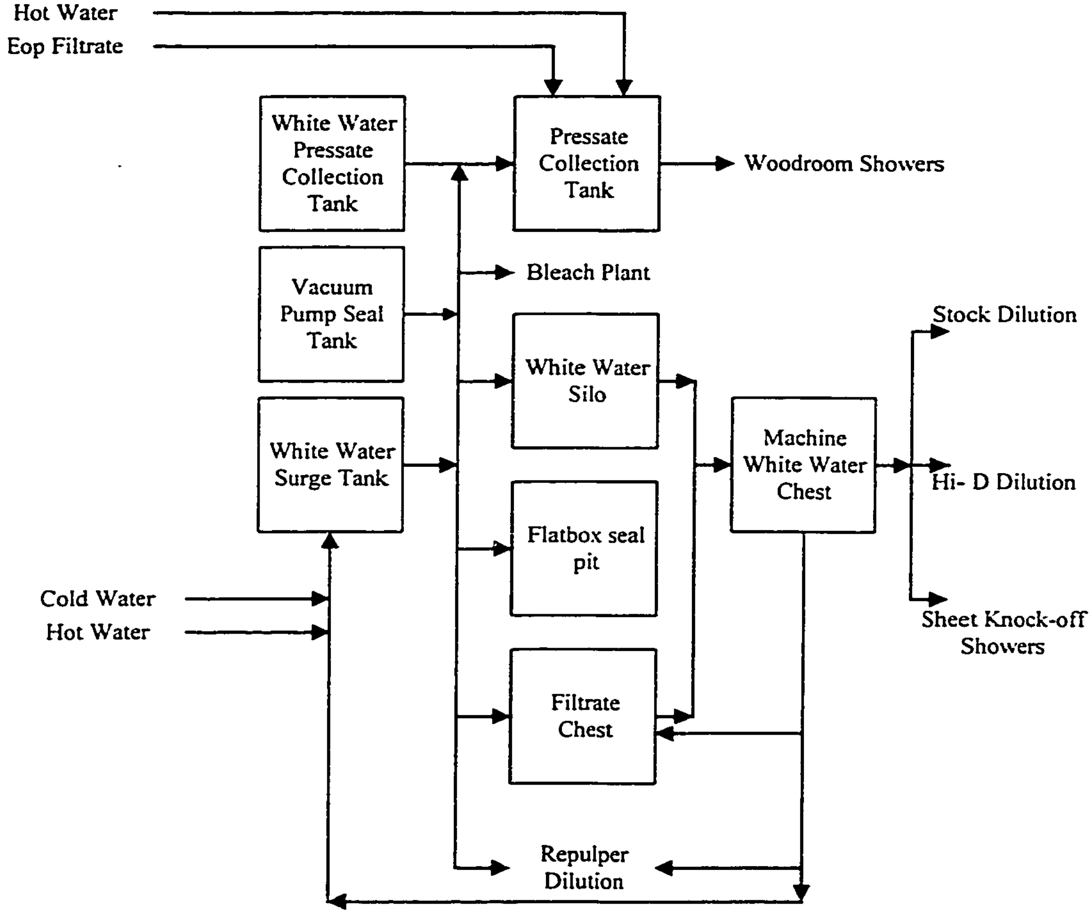


Figure 6.23: White Water Flows

The third idea considered is to recycle individual streams from the white water system back into the process. From Figure 6.19, the areas that should be considered as recycle streams back to the process are: the wire pit, fibre recovery chest, couch pit, and filtrate chest. The other areas contain too many fines and would not be as desirable. One possibility to overcome the problems with fines in these other streams would be to add a white water filter to assist in removing the fines. A cost analysis of this was not performed, but should be done to determine if this would be a feasible option. Other processes such as flotation should also be considered.

Process Problems

Water from the pressate collection tank comes from the suction boxes located at the end of the forming section of the machine. The suction applied in this area not only drains the water from the pulp, but may also remove felt fibres from the felt that carries the pulp mat. These felt fibres might cause problems if recycled back into the process because they are plastic, and adding this to the pulp would cause major problems. Having individual plastic fibres enter the pulp stream may not be that harmful as these would blend in with the pulp, but if the water from the pressate collection tank were to be recycled, a buildup of these plastic fibres would cause them to agglomerate and pass larger plastic particles into the pulp. These larger particles would be very noticeable in the final product and cause quality problems. Some way of removing these felt fibres would have to be examined if this stream were recycled. The addition of a white water filter, as mentioned above, may be a possible solution.

The wire pit is an area that is used to collect the water from the wire of the pulp machine. The initial design placed this water in the couch pit, but is now diverted to sewer. The couch pit supplies water to the showers on the pulp machine. When the wire pit water is added to the couch pit, the showers become plugged because of the higher consistency (higher concentration of fibres). If the wire pit water were returned to the process, possibly into the bleached hi-density storage tanks, then these fibres could be recovered and sold as a final product. It can be seen in Figure 6.19 that the fine content of this stream is small, so an accumulation of fines in the process should not occur.

Process problems would need to be examined with the build-up of NPE's and compounds within the system if any recycle consideration were to be used. The main problems associated with Ca, Ba, SO_4, and CO_3 is that they form insoluble compounds and may precipitate out and cause problems. Calcium carbonate ($CaCO_3$), calcium oxalate (CaC_2O_4), calcium sulphate ($CaSO_4$), and barium sulfate ($BaSO_4$) are the precipitates that may form. Other factors that affect precipitation are: pH, ionic strength, temperature, and dissolved organics (Jemma *et al.*, 1997). Scaling within mills is highly site specific, and very little information can be found on the levels that the NPE's can accumulate without causing problems. Some of the contaminants in the white water are listed in Table 6.6.

	SO_4 (ppm)	**Cl (ppm)**	**Ba (ppm)**	**Ca (ppm)**
White Water	193	26.1	0.20	45.2
Fresh Water	205	1.6	0.06	36.9

Table 6.6: Composition of white and fresh water

A more complete analysis of white water is shown in Appendix B. An analysis for CO_3 was not performed for these samples.

The precipitates are mainly a concern if the accumulation builds up in the bleaching stages. Most compounds remain soluble in acidic environments (D_n, D_o, and D_2) , but will form precipitates in caustic (E_{op}) environments. If these contaminants accumulate in the caustic stage they will precipitate out of the solution and cause scaling of the equipment. From the results in Table 6.6, it appears that the white water is very low in Ca, Ba, and SO_4 concentrations and the accumulation of these contaminants should not pose a significant problem, but precipitation problems should still be addressed.

Other process problems that need to be considered are those associated with the accumulation of chlorides. The problems associated with increased chloride levels in a kraft mill are an increased rate of plugging of the flue gas passages in the recovery boiler, as well as an increased rate of corrosion. For the destinations listed in section 6.3, the white water would not enter the liquor-loop, hence the plugging of the recovery boiler will not be affected. The rate of corrosion of carbon steels increases slightly with increasing levels of chlorides. Research into these areas (Sharp, 1996) have determined that corrosion rate is generally site specific, and depends on many factors. Stainless steels withstand corrosion better than carbon steels in high chloride environments. AlPac uses carbon steel, specific stainless steels, and titanium depending on the process stream in contact with these metals.

Another process consideration to examine would be the pH of the white water. White water has a pH of approximately 5. If the stream were to be recycled to the bleach plant, acid is usually added to the D_n, D_o, and D_2 stages while caustic is added to the E_{op} area.

If the white water were to be recycled to an acidic area, this could be beneficial by reducing the amount of acid required in the area. If the white water were recycled to the E_{op} area, then additional caustic would have to be added to increase the pH to the desired value resulting in an increased caustic cost.

The approach to use when recycling water within a mill would be to recycle the water gradually and find a recycle amount that the mill can operate at with minimal process upsets and minimal pulp quality deterioration.

Equipment

The metallurgy of the bleaching washers is the same throughout the bleach plant. Currently most of the water that is added to the D_2 washing stage is white water. The addition of white water on the D_n washer to replace the fresh warm wash water or to replace the hot water make-up in the D_2 filtrate tank should not harm the process from a metallurgical point of view.

All the equipment and piping that the recycled stream would pass through would have to be investigated to determine if there would be any negative effects. The equipment investigated is discussed below. As well, an analysis of the streams that are used in the bleaching area was performed by Paprican, and can be found in Appendix B.

The 300-ton screened high-density storage tower is illustrated in Figure 6.11 and Figure 6.14, and is one area that white water could be used if it were to be recycled within the mill. The manufacturer supplied specifications for the storage tower. The interior of the high-density storage tank is made of tile. A vinyl ester resin is used to bind the tiles together. This material can handle a pH range of 3.5 to 11.5 up to a temperature of 65 °C. The bottom third of the tower is shaped like a bowl and has a brick membrane lining that allows basically any temperature and even lower pH ranges. The outer frame of the tank is supported with a concrete shell.

The specifications above are general guidelines provided from the manufacturer of the tower. The design of the 300-tonne high-density tower allows a maximum temperature gradient across the tower of 90 °C. If the difference in temperature of the internal process stream, and the external ambient air were to exceed this 90 °C temperature gradient, the tile and concrete shell could crack and damage the structure. An additional insulation layer on the tower could help in preventing this damage. Currently, the internal stream operates at about 60 °C. This is controlled by the hot (80 °C), and warm water (50 °C) that is currently added to the dilution conveyor from the number 2 press.

The white water is approximately 70 °C, so recycling this stream to the number 2 press dilution conveyor may cause a problem. A temperature transmitter should be placed on this line to ensure proper temperature control is provided. One possibility would be to replace the amount of hot water added to the dilution conveyor instead of both hot and warm.

Other equipment includes the dilution conveyor, fabricated from type 316L stainless steel, and the high-density standpipe, that has all wetted parts fabricated from type 316L stainless steel. Also, the high-density pump is fabricated from type 317L stainless steel and the piping within the area is fabricated from type 316L or 317L stainless steel.

Type 317L stainless steel withstands corrosion better than type 316L stainless steel. The major concerns with these types of materials involve changes in pH, oxidant (ClO_2), and temperature (Clarke, 1996). As long as the temperature is maintained at current operating conditions, there should be no problem with the metallurgy.

6.4.5 White Water Recycle Economic Evaluation

There are a number of economic advantages to recycling the machine-room effluent. First, the fibre content of the white water could be recovered. This may show an immediate cost savings of recovering fully bleached fibres. A sample of the effluent stream was collected and analyzed for suspended solids in which this value was assumed to be all fibres. Approximately 12.9 tonnes per day of fibres (Figure 6.22) is being discharged to the effluent treatment system from this area. Currently, pulp is sold for about $500.00 a tonne, so a potential saving of approximately $6,500.00 per day ($2.3 million per year based on a 350 day operating year) could be realized. If the wire pit stream were recycled, approximately 6.22 ODt/d of fibre could be recovered. This would amount to approximately $1.2 million a year.

Second, fresh water use would be reduced, and the savings would reflect on the cost of treated water. It costs approximately \$0.04 per m^3 water (provided by the mill) to pump the water from the river and treat it so that it is acceptable to the mill. A savings of about 80 L/s of fresh water would be realized if all of the machine-room effluent were recycled. This is approximately \$97,000 a year in raw water treatment costs, an 8% reduction in fresh water intake currently used at the mill. In addition, this effluent is hot (> 70 °C), so energy savings could also be considered. It costs about \$0.02 per m^3 water (provided by the mill) to heat the river water up to this temperature. This would amount to approximately \$48,000 energy savings per year.

Third, the slightly acidic nature of the stream would reduce the amount of acid that is added to these washing stages. Acid is added in the standpipes before the bleaching towers of the D_o, D_2, and D_n stages. Since white water is slightly acidic (pH ~5), adding this water to an acidic washing stage (D_o, D_2 or D_n), may decrease acid addition costs. If white water would be added to the E_{op} washer, then there would be an extra cost associated with the additional caustic required to raise the pH. An economic analysis was not performed on the acid savings.

Fourth, there would be an overall effluent treatment savings/cost. This area of economic analysis would require additional research. The effluent loading to the treatment plant would be reduced, but does not necessarily indicate that there would be a reduced cost associated with this. The effluent treatment plant does not require any addition of chemicals or nutrients to keep the plant operating, so decreasing the flow through the plant would not decrease the amount it would cost to operate. It may actually increase the cost because fibre helps in the settling of the sludge from the effluent treatment plant. If this fibre were removed, then the sludge would be more difficult to press, therefore, an additional operating cost would be realized. The major advantage of the reduced effluent loading would be an efficiency issue. The smaller the flow rate, the longer the effluent has in the treatment plant, therefore, a more efficient treatment of the effluent may occur.

Different capital and operating costs would be dependent on recycle location. The installation of piping, valves, and additional pumps may be required. As well, a filter to remove the fine fibres and the dirt may have to be installed before the white water could be recycled within the mill.

6.5 D_n Filtrate Recycle

6.5.1 D_n Filtrate Flow Rate Characterization

Except for the D_n filtrate used to dilute the stock to the D_n washer, the rest of the effluent is discharged to the sewer (Figure 6.6). Figure 6.24 shows the average daily and monthly D_n filtrate flow rates that are discharged to the sewer.

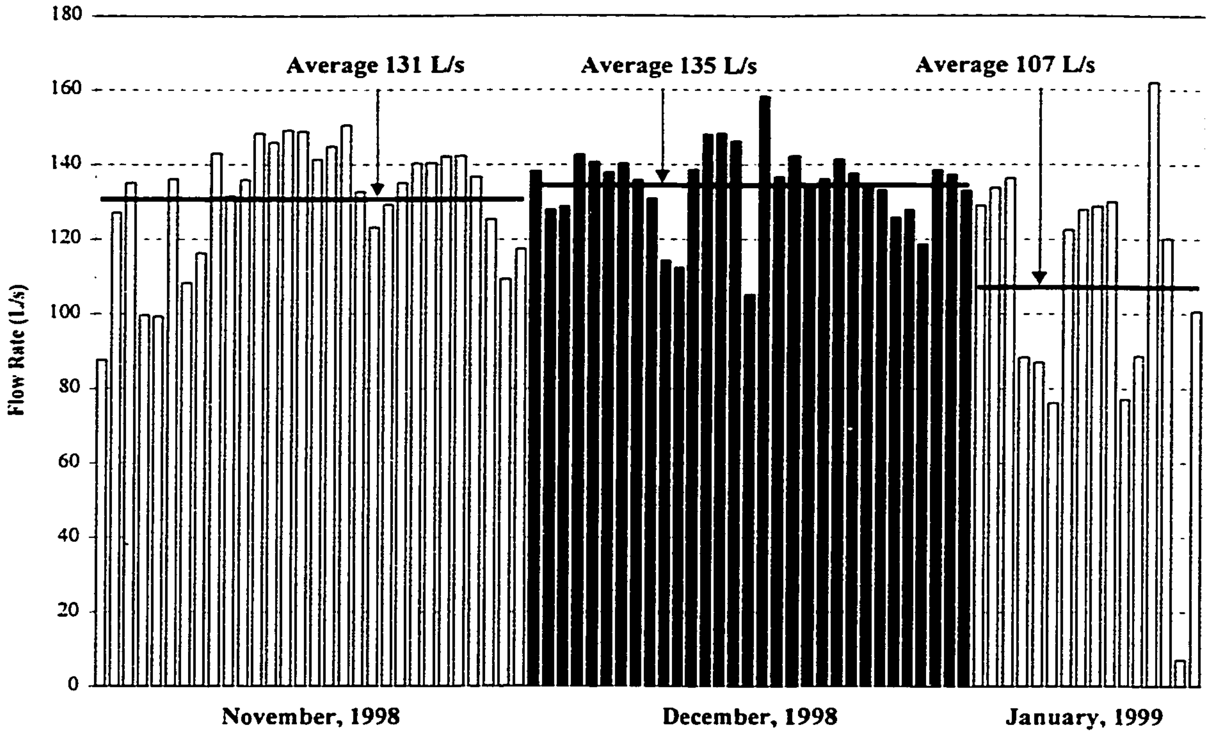


Figure 6.24: D_n Average Effluent Flows (November 01, 1998 - January 17, 1999)

6.5.2 D_n Filtrate Destination

As mentioned earlier, it would be preferred to use the D_n filtrate in an area before the D_n washing stage (counter-current washing). Likely areas to consider would be to replace the fresh water that is currently used on the Number 2 Press Dilution Conveyor and the hot water that is being used in the screened high-density storage tank as discussed in section 6.3. It would not be recommended to use this filtrate on any following bleaching stages or in the machine room because this would be washing a clean pulp with dirtier water and contaminate the pulp.

This recycle strategy is proposed because the D_n filtrate is currently used to dilute the pulp coming into the D_n washer (Figure 6.6). Diluting this pulp further upstream with this filtrate should not cause any process problems provided that the buildup of NPE's does not reach unacceptable limits.

6.5.3 D_n Filtrate Recycle Considerations

The recycled water used here would not enter the liquor loop, so the higher concentrations of K and Cl in the recycled water would not cause a problem in the recovery area. Also, the filtrate from the D_n washing stage is acidic. Acid is added to the pulp stream before the D_n washer to allow better washing of the fibres. If this stream were to be recycled into the process, a possible reduction in acid could occur, saving on chemical cost. One thing that should be examined is the carry-over of contaminants from the D_n filtrate as these could cause a problem in the bleaching stages. Some of the contaminants in the D_n filtrate are shown in Table 6.7.

	SO_4 (ppm)	**Cl (ppm)**	**Ba (ppm)**	**Ca (ppm)**
D_n Filtrate	415	10.9	0.30	50.7
Fresh Water	205	1.6	0.06	36.9

Table 6.7: Composition of D_n Filtrate and Fresh Water

The considerations listed above for white water recycling are the same considerations for here. Using D_n filtrate in these areas instead of white water may be beneficial. First, the fibre content of this stream is very small. No pre-treatment of this stream should be necessary to recycle this filtrate. If white water were used, the fines would accumulate in the system because the D_n filtrate does not have a large amount of fines. Second, the D_n filtrate could be used counter-currently here, but could not be used to replace wash water on any of the other bleach stage washers. This would contaminate the pulp. As mentioned above, white water could be used on the dilution conveyor or in the screened hi-density storage tank as well. Using D_n filtrate instead would allow the cleaner white water to be used elsewhere. This could increase the possibility for more water to be recycled within the mill by utilizing recycle water appropriately.

There is approximately 120 L/s of D_n filtrate being discharged to the sewer, 74 L/s of fresh water added to the dilution conveyor, and 14 L/s to the high-density storage tank. If all the fresh water were replaced with filtrate (approximately 70%), then about a 70% accumulation of NPE's could occur. Some of the accumulated NPE's could be removed elsewhere in the system, but without installing something specific to remove these, most of the NPE's would most likely remain in the system.

As stated in section 6.4, it is very hard to determine a level of NPE's that are acceptable in a process. In recycling the D_n filtrate, the recycle flow should gradually increase until a flow was attained that would not cause any significant process problems. The benefit with this form of recycle is that the D_n – open wash stage filtrate is still very clean, and using this to wash the pulp counter-currently would make very efficient use of available wash water.

Metallurgical Considerations

The equipment investigated is the same as investigated in section 6.4.4 with some different considerations that should be taken into account.

300 Ton Screened High-Density Storage Tank

The D_n filtrate is approximately 60 °C, so recycling this stream to the number 2 press dilution conveyor should provide the same temperature control that is currently used. A temperature transmitter should be placed on this line to ensure proper temperature control is provided.

Other Equipment

The major concerns with these types of materials (316 and 317 stainless steels) involve changes in pH, oxidant (ClO_2), and temperature (Clarke, 1999). The D_n filtrate has approximately the same temperature and pH as is currently used in the area. Since the D_n stage is an open wash, there is no residual ClO_2 with the filtrate. As far as the metallurgy is concerned, there should not be a problem with recycling the D_n filtrate.

6.5.4 D_n Filtrate Recycle Economic Evaluation

The savings of approximately 88 L/s of fresh water would reduce the amount of fresh water coming in from the river. Based on \$0.04 / m^3, this would indicate a savings of about \$110,000 per year. As well, about 45 L/s of this water is hot, so an additional savings of \$27,000 per year (based on \$0.02 / m^3 to heat the water) would be realized.

The capital cost of installing the equipment needed to supply this D_n filtrate line is shown in Table 6.8.

Equipment	Amount	Price	Unit	Total
Piping (317 SS or FRP)	60 feet	$ 50.00	foot	$ 3,000.00
90 degree elbows	4	$ 125.00	each	$ 500.00
Gate Valve	1	$ 3,000.00	each	$ 3,000.00
Check Valve	1	$ 3,000.00	each	$ 3,000.00
Flanges		$ 1,000.00	total	$ 1,000.00

Table 6.8: Capital Costs for D_n Filtrate Recycle

There is already a pump installed (currently not used) to supply the required flow. Table 6.9 shows the cost breakdown for this unit.

Investment	Cost
Capital	$10,500
Installation	$10,500
Contingency	$9,000
Total	$30,000

Table 6.9: Cost Breakdown

Note that capital costs are based on prices supplied at the mill site, and installation and contingency costs are based on those supplied from the maintenance operators at the mill.

This amounts to possible savings of $140,000 per year with a total known cost of about $30,000.

The operating costs associated with recycling D_n filtrate are currently not known. There would also be acid savings since the stream is slightly acidic and there may also be an effluent treatment savings/cost as indicated in the machine-room effluent economic evaluation. The operation strategy of recycling this stream would be the same as that for the D_2 filtrate recycle. The D_n filtrate chest would hold the filtrate, and if additional flow were required, hot water would be added to the tank.

The recycling of about 88 L/s would reduce the total amount of water coming into the mill by approximately 8.5%. More samples would have to be analyzed of the D_n filtrate in order to ensure that the NPE accumulation would not affect the process.

6.6 D_0 Effluent Recycle

6.6.1 D_0 Filtrate Flow Rate Characterization

The amount of D_0 effluent available for recycle is shown in Figure 6.25. This figure shows the average daily and monthly filtrate that was discharged from the D_0 bleach stage to sewer from November 1998 to January 1999.

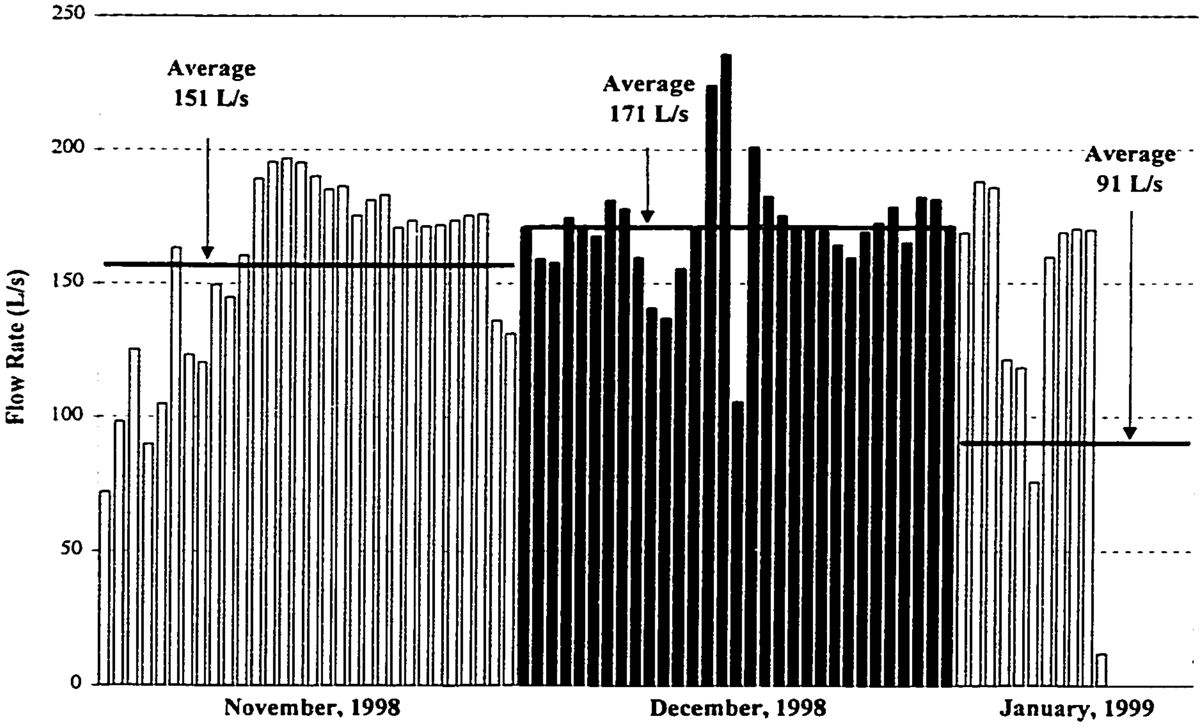


Figure 6.25: D_0 Average Effluent Flows (November 01, 1998 - January 17, 1999)

6.6.2 D_o Filtrate Destination

The D_o effluent was considered as a recycle option in the same manner that the D_n filtrate was. The D_o effluent could be considered for recycle back onto the dilution conveyors, and for dilution water for the pulp leaving the 300 tonne high-density storage tank. In addition, this stream could also be used to replace the fresh warm water used on the D_n open wash stage.

6.6.3 D_o Filtrate Recycle Considerations

The recycle of approximately 75 L/s of D_o filtrate to the Number 2 Press Dilution Conveyor, would mean that approximately 50% of the 150 L/s D_n filtrate flow would not be discharged to the sewer. The process concerns dealing with the accumulation of the components present in the D_o filtrate would have to be addressed. Some of the contaminants in the D_o filtrate are shown in Table 6.10.

	SO_4 (ppm)	**Cl (ppm)**	**Ba (ppm)**	**Ca (ppm)**
D_o Filtrate	622	254.0	0.49	265.0
Fresh Water	205	1.6	0.06	36.9

Table 6.10: Composition of D_o Filtrate and Fresh Water

The contaminants of this stream are much higher than those of the white water or D_n filtrate streams and would most likely cause heavy scaling if recycled back into the system.

Metallurgical Considerations

The same considerations must be taken into account as for the D_n effluent recycle. The main concern here from a metallurgical point of view is the residual amount of ClO_2 that could be present in the filtrate. The D_n open wash stage does not use ClO_2 while the D_o bleaching stage does. If there is any residual ClO_2 present in the filtrate, and this is recycled to the dilution conveyor, the materials of construction (316 and 317 stainless steel) would not be able to withstand this residual. ClO_2 would corrode the material and shorten the life of the equipment. Figure 6.26 shows the ClO_2 residual from June to December 1998 in the D_o vat (the area of the D_o drum washer that holds the pulp mixture before it is washed on the washer).

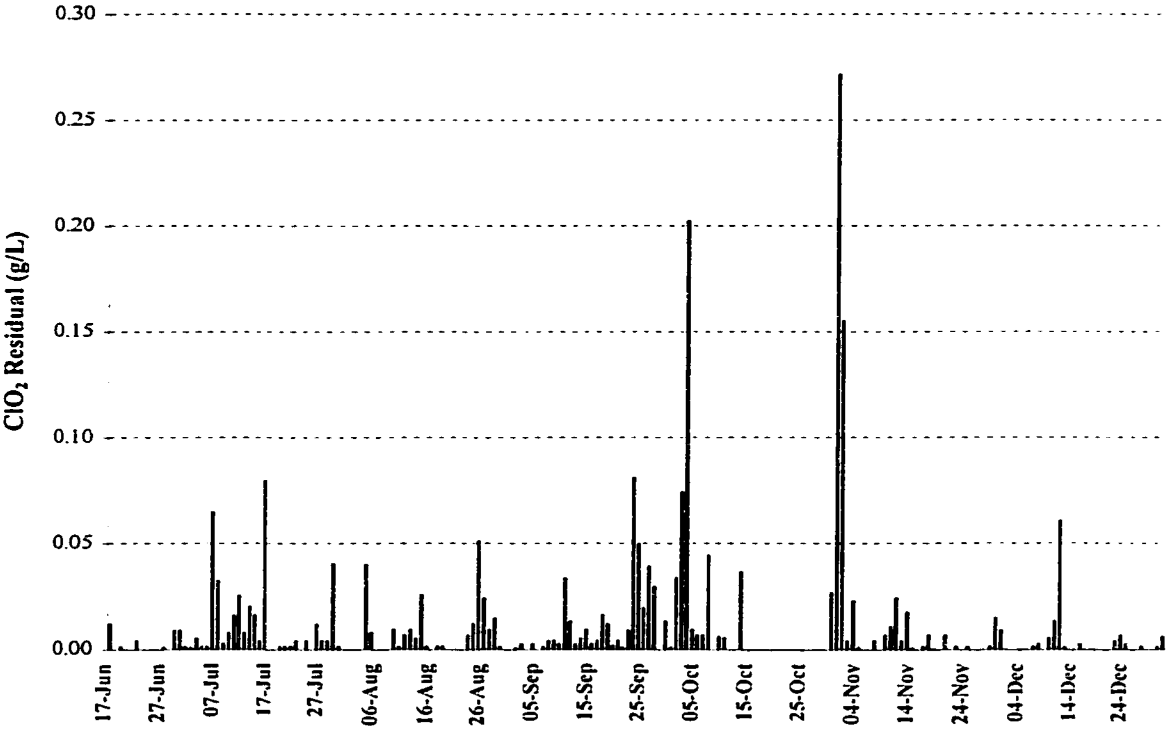


Figure 6.26: Chlorine Dioxide Residual in the D_o Washer Vat

Figure 6.26 shows that the residual ClO_2 is not constant. During normal operation of the mill, the residual is kept to a minimum, however it is not always zero. This residual will affect the life of the equipment. More research would have to be performed to determine how long it would take until the materials that could corrode would have to be replaced.

From the above information, it appears that there would be numerous problems that would have to be addressed in order for D_o filtrate stream to be used. The D_n filtrate appears to be much cleaner than the D_o filtrate and therefore a better recycle candidate. There would be less accumulation of the NPE's in the system, hence less of a chance for problems with this accumulation to occur. Most likely an additional treatment stage would have to be used to treat the D_o filtrate before being reused within the mill.

An economic evaluation was not performed on for the D_o filtrate recycle because it does not appear to be a feasible recycle strategy.

6.7 E_{op} Filtrate Recycle

6.7.1 E_{op} Filtrate Flow Rate Characterization

The online water balance was used to monitor the flow of E_{op} filtrate being discharged to the sewer from November 1998 to January 1999. The average daily and monthly flows are shown in Figure 6.27.

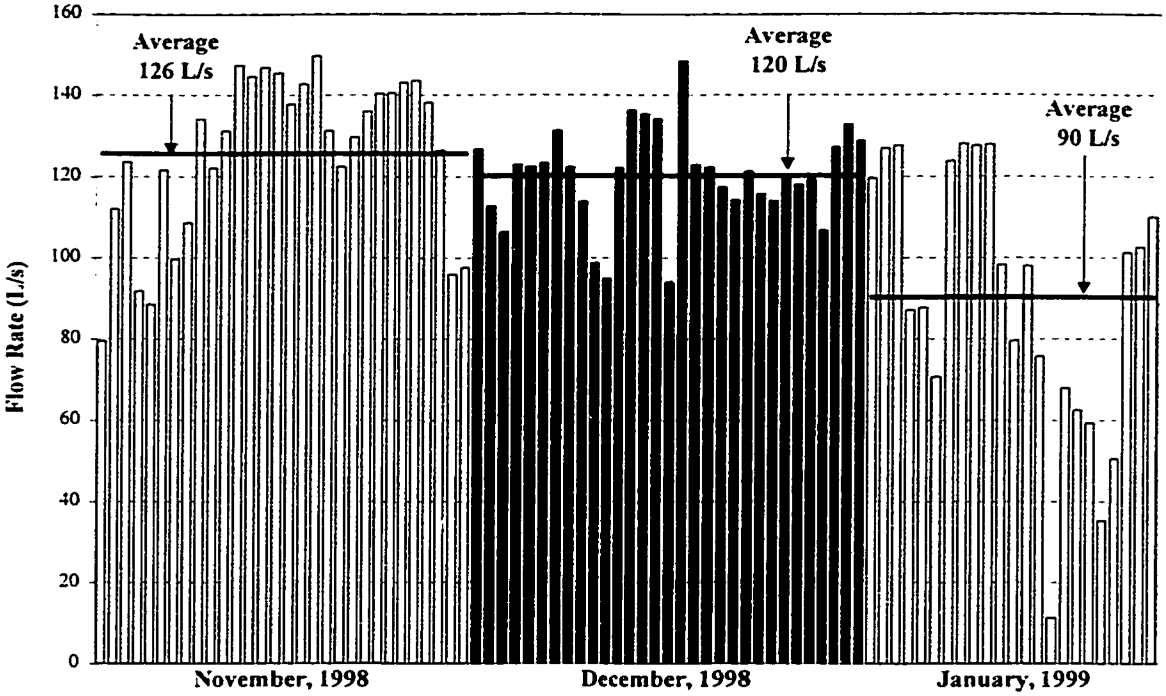


Figure 6.27: E_{op} Average Effluent Flows (November 01, 1998 - January 17, 1999)

6.7.2 E_{op} Filtrate Destination

The destination considered for E_{op} filtrate recycle is to replace the white water going to the wood room with E_{op} filtrate. This would allow the white water to be used elsewhere in the mill.

The wood-room can use different types of water for the de-barking, thawing, and rinsing of the logs. White water from the pressate collection tank is currently used for this process, but the system is currently set up so that E_{op} filtrate could also be used. Figure 6.28 shows the amount of water that the wood-room used from November 1998 to January 1999, while Figure 6.29 indicates the flows for December 1998. This is a substantial flow that is used on a regular basis.

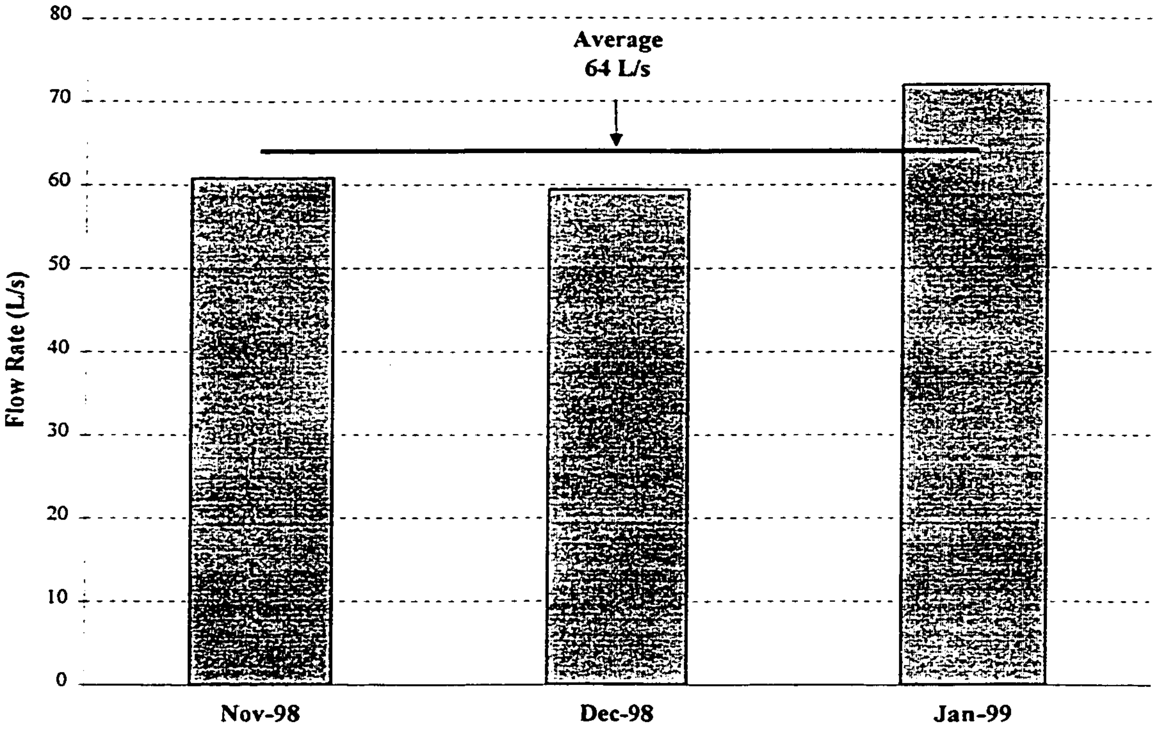


Figure 6.28: Water Flow Rate to the Wood-Room (November 1998 to January 1999)

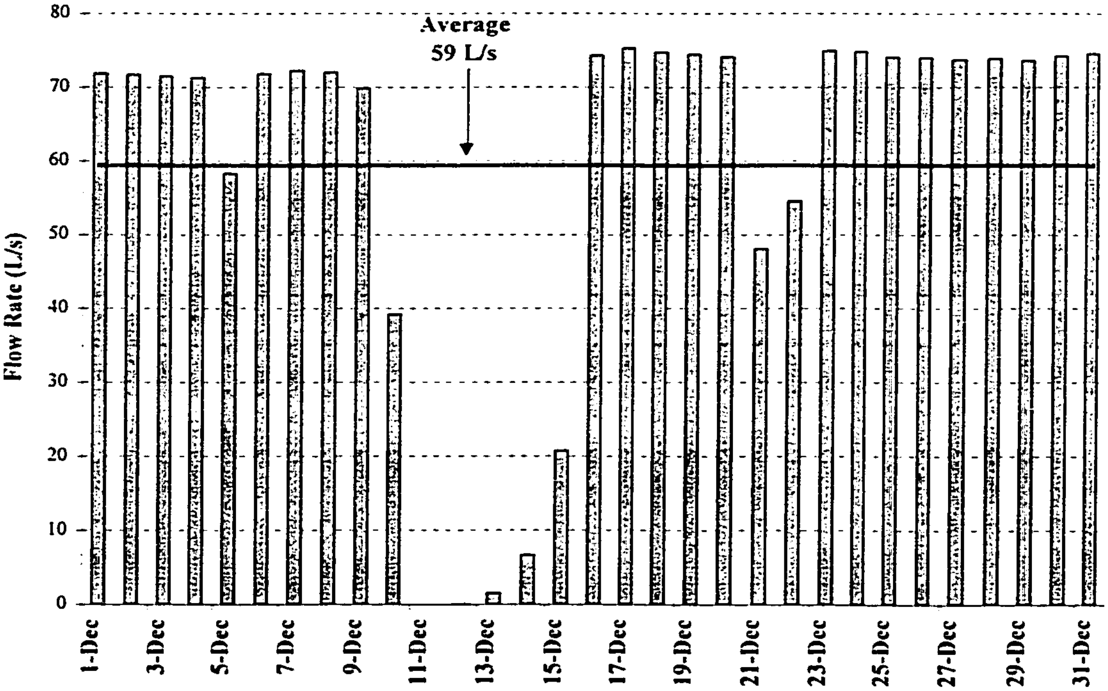


Figure 6.29: Water Flow Rate to the Wood-Room (December 1998)

If there is not enough white water available to be pumped to the wood-room, then water is supplied by the E_{op} filtrate to make up for this. The filtrate from the E_{op} area is supplied to the pressate collection tank in the machine-room and from here to the wood-room. There is no flow indicator on the E_{op} line to the pressate collection tank, but there is a control valve. The control valve can be monitored for the amount of time it was open over a certain period to indicate how often E_{op} filtrate was used in the wood-room. This is shown in Figure 6.30 for 1998. The amount of time that E_{op} filtrate was used as make-up water to the wood-room is shown in Figure 6.31 for November 1998.

Since most of the E_{op} filtrate is sewered, recycling this stream into the wood-room would benefit the mill. First, the white water could be used elsewhere in the mill with the potential of recovering the fibre content in the stream. Second, the E_{op} filtrate is not desired for use in other areas of the mill. The pulp that enters the E_{op} stage is acidic, and contains many dissolved metals. Once the pH is increased in the E_{op} stage, the metals precipitate out of the pulp and form deposits on the surfaces of the operating equipment. Sending these precipitated deposits to other parts of the mill would only cause them to re-dissolve in acidic streams, or precipitate out and scale other areas of the mill. The wood-room can use the E_{op} filtrate with no operational or process problems. This is simply replacing one recycled stream with another of worse quality.

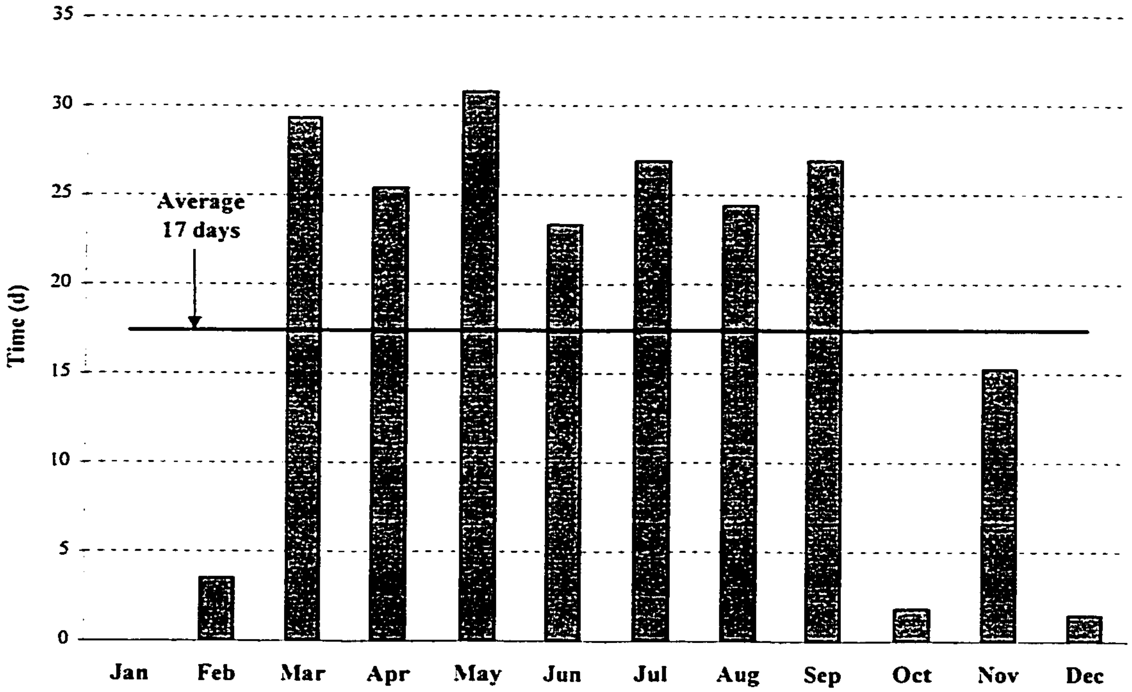


Figure 6.30: Time E_{op} Filtrate was Used for Make-up Water to the Wood-Room in 1998

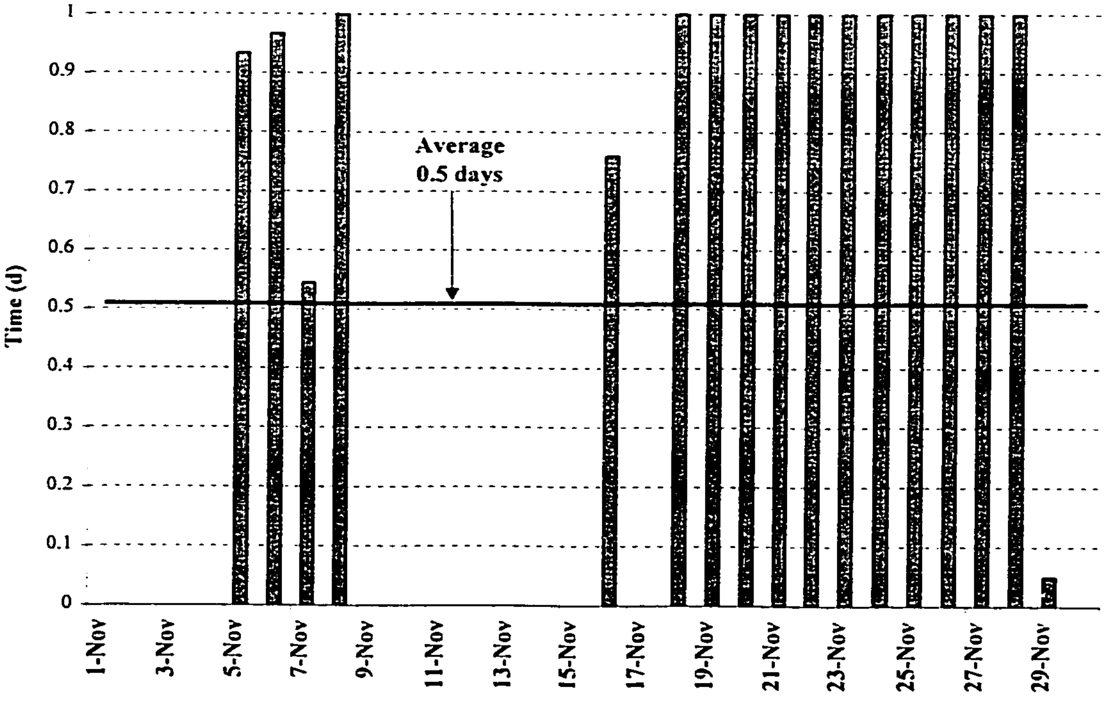


Figure 6.31: Time E_{op} Filtrate was Used for Make-Up Water to the Wood-Room in November 1998

From Figure 6.28, it is shown that the average flow of white water supplied to the wood-room is 64 L/s, but usually runs between 70 and 80 L/s. The E_{op} filtrate leaving the bleaching stage is usually over 100 L/s and should be able to provide enough water to meet these demands. If it cannot, make-up water by means of fresh water or white water could be used to meet the requirements of the wood-room. The use of E_{op} filtrate in the wood-room would free up about 64 L/s of white water to be used elsewhere in the process.

6.7.3 E_{op} Filtrate Recycle Considerations

If the E_{op} filtrate were to replace the white water that is currently used, a number of issues would have to be considered. The white water currently used is from the pressate collection tank. The water that enters this tank is from the suction of the water off the pulp machine felt, therefore, may contain tiny pieces of felt with the water. These felt pieces may cause quality problems if they remain attached to the pulp, so a method of removing these particles before recycling this water elsewhere in the mill may have to be found. A detailed analysis of this water stream would have to be performed to determine what contaminants are present as well as to determine if these would be harmful to the process if recycled into the mill. After the contaminants are determined, it may be possible to determine a feasible separation process to remove the contaminants so that this water could be reused within the mill. A filter used to separate these felt particles may be one option.

6.7.4 E_{op} Filtrate Recycle Economic Evaluation

Most of the equipment is already provided to make this recycle option possible. A filter to remove the felt particles would be an additional cost and would need further investigation.

Recycling the E_{op} filtrate:

- $68,000 per year (fresh water costs)
- $34,000 per year (hot water costs)

- Possible savings of approximately $100,000 per year

- Operating costs and a filter cost are not yet known.

The recycling of E_{op} filtrate to the wood-room could reduce the amount of fresh water used by the mill by about 5%.

6.8 Conclusion

The possibility of recycling various streams within the mill appears promising. White water could be used almost anywhere within the bleach plant because of the low concentrations of non-process elements. It must be determined if the fines in the white water have to be removed before recycling and then options to do this should be examined. The effect of other impurities would have to be examined in greater detail to determine if it is feasible to reuse this water. There could be savings if the fibres could be recovered and sold as pulp, as well as a saving with the reduced amount of fresh water used in the process. Costs associated with the recycle of white water would be capital costs, installation, and possible process changes.

If streams were to be recycled, a gradual flow of the recycled stream should be added to the recycle destination. This should increase until the mill was satisfied that the recycled stream was not harming the process.

The order in which the recycling of streams should be considered is:

- recycle the wire pit effluent to the bleached hi-density storage tank – a potential reduction of 3.7% fresh water use,
- replace fresh hot water into the D_2 filtrate tank with white water – a potential reduction of approximately 0.7% fresh water use,
- replace fresh hot water into 300-tonne screened high-density storage tank with D_n filtrate – approximately 1.4% reduction in fresh water consumption,
- replace fresh hot and warm water added to the dilution conveyor of number 2 press with D_n filtrate – 7.4% possible reduction in fresh water,
- replace fresh water added to the D_n washer with white water – about a 5% reduction in fresh water,
- replace fresh water added to the other bleach plant washers with white water.

In all recycle considerations, any upset conditions (such as start-up or shut-downs of the mill) must be taken into consideration. Any lines that would be recycled back within the mill should also have another source of water to rely on in case the recycled water is not available. In these cases, the piping could be set up so that the mill could still use fresh water if required.

Chapter 7

Conclusions and Recommendations

Lime softening of a Kraft pulp mill effluent was examined to determine if this would enable the mill effluent to be recycled as process water. A 2^3 factorial design of experiments was used to help determine if lime softening of the effluent would reduce the amount of non-process elements to an acceptable level within the system. Tests were performed using a series of jar tests on the mill effluent that indicated the concentrations of many non-process elements were reduced, with the exception of chloride and potassium. The rate of corrosion would increase with an increased amount of chlorides in the system. As well, the plugging of the recovery boiler would increase with an increase in concentration of both potassium and chlorides within the system. Therefore, lime softening alone of the complete effluent stream leaving the mill would not be adequate for returning this water back into the system.

The results from this study indicated that many of the non-process elements were reduced in concentration from the addition of lime to the effluent. If an additional treatment stage were implemented to reduce the chloride and potassium concentration of this stream, then lime softening may be one method to use as a step towards system closure. If the recycle of the effluent were to be attempted, a small amount of treated effluent should be recycled to the mill at a time. This would allow the system to reach steady state and determine if there were any negative effects caused by the recycle.

In addition to lime softening of the mill effluent, a progressive system closure approach was examined. Here, a number of individual streams within the mill were examined to determine if they could be recycled to gradually reduce the amount of effluent leaving the mill. A millwide water balance was performed that provided information on which streams could be examined for recycle. The machine-room effluent, wood-room, and bleach plant streams were examined. The most promising stream for recycle, the wire pit discharge, is an individual stream from within the machine-room area. This stream appears most favorable due to the high amount of fibres that can be recovered along with reducing the amount of effluent being discharged from the mill. It is suggested to recycle this stream to the bleached hi-density storage tank. This would recover approximately 6 ODt of fibre per day, and amount to a saving of approximately $1.2 million a year.

The main problem with recycling any of the streams within the machine-room area would be the accumulation of fine fibres within the pulping process. This would be undesirable due to operational problems that would occur. A method to remove these fines from the system should be examined. A white water filter or flotation should be methods to consider.

The D_n filtrate leaving the bleach plant area appeared to be another good candidate for recycle. If this stream were to be recycled to the number 2 press dilution conveyor, the amount of fresh water entering the mill as well as the amount of effluent leaving the mill could be reduced by approximately 70 L/s. No additional pre-treatment of this stream should be required. If this stream were to be recycled, the recycle flow should gradually increase until a flow was attained that would not cause any significant process problems.

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Appendix A

Analysis Methods

A.1 Atomic Absorption Spectrometry

A.1.1 Procedure and Theory

Atomic absorption spectrometry is one of the most important techniques for the analysis and characterization of the elemental composition of samples, and is used frequently in the analytical industry. Figure A.1 shows a block diagram of an atomic absorption spectrometer.

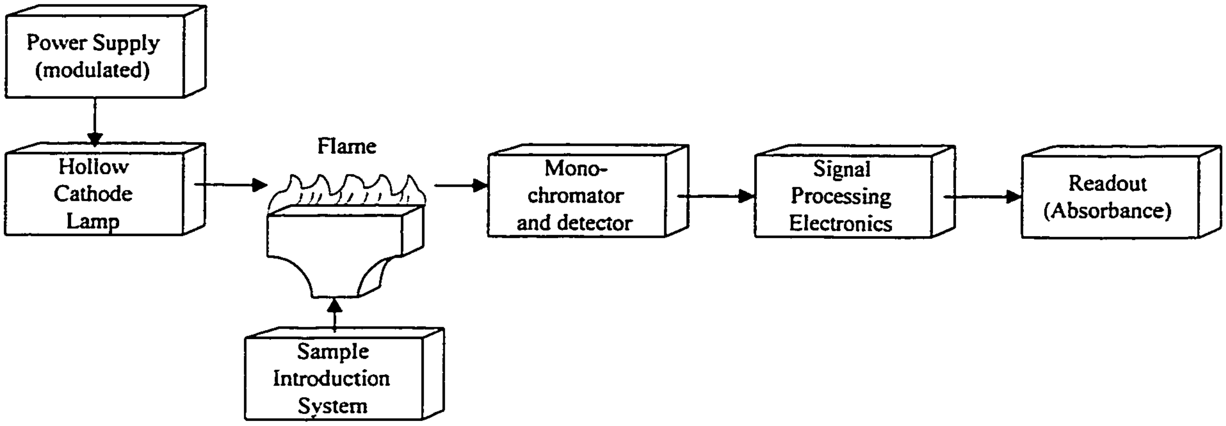

Figure A.1: Block Diagram of an Atomic Absorption Spectrometer (Modified From Christian and O'Reilly, 1986)

Calibration of the Atomic Absorption Spectrometer

The calibration curve for this instrument is obtained by using known amounts of a certified standard and aspirating it through the spectrometer as well as a blank. The amount absorbed by these solutions are recorded and plotted against the known concentrations of the certified standards.

An example of the concentration versus absorbance data for Calcium is shown in Table A.1 and Figure A.2.

Calcium (ppm)	10	30	50	100
Absorption *	0.092	0.268	0.422	0.744

* indicates the average of three readings

Table A.1: Atomic absorption spectrometer calibration data

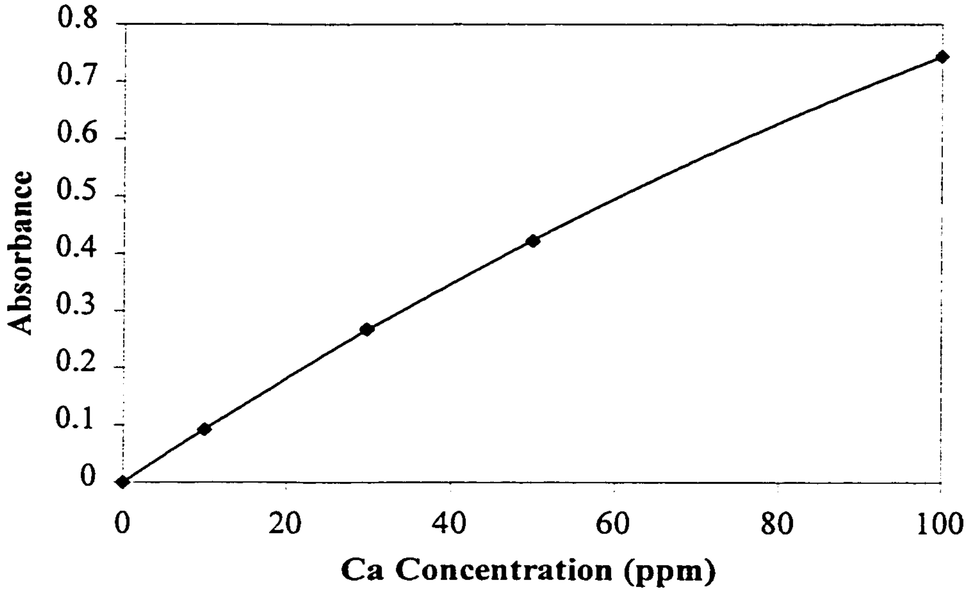

Figure A.2: Calibration Curve for Calcium

The atomic absorption spectrometer automatically produces a graph similar Figure A.2. When a sample is aspirated into the spectrometer, an absorbance reading is determined. This absorbance is calculated into a concentration using the previously constructed concentration curve.

The theory of atomic absorption spectrometry is governed by Beer's law (Christian and O'Reilly, 1986):

$$\log\left(\frac{I_0}{I_T}\right) = A \qquad \text{[A-1]}$$

Where I_0 – incident intensity
I_T – transmitted intensity
A - εbc (absorbance)
ε - absorptivity (L/mole-cm)
b - optical path length (cm)
c - concentration (mole/L)

If the transmittance $\left(\frac{I_T}{I_0}\right)$ is too high or too low, the relationship between transmittance and concentration becomes non-linear and the error in concentration increases. Beer's law would no longer apply as shown in Figure A.3.

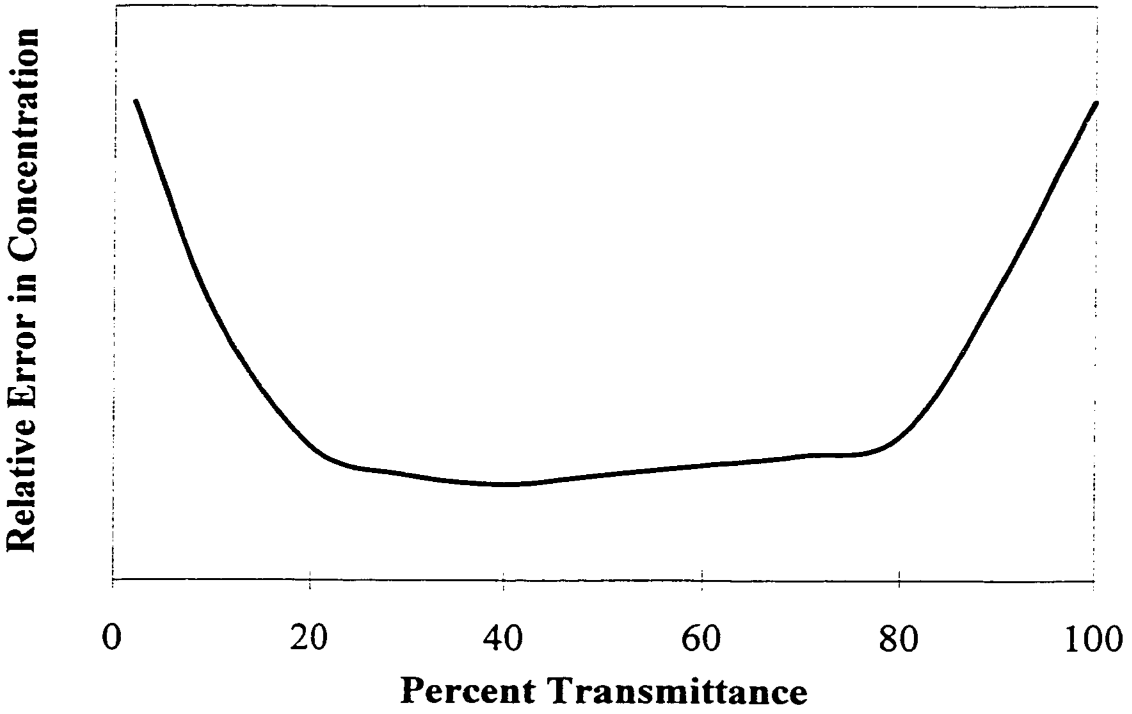

Figure A.3: Importance of Beer's Law (Modified From Christian and O'Reilly, 1986)

Therefore, in order for Beer's law to be valid, the transmittance range should be between 20% and 60%.

A.1.2 Accuracy and Precision

Accuracy

To determine the accuracy of the atomic absorption spectrometer, a certified check sample was purchased. This sample has a known value that was determined from six independent laboratories, as well as an acceptable performance limit. This sample was analyzed using the atomic spectrometer and the results are tabulated in Table A.2.

	Mg (mg/L)	Ca (mg/L)	Mn (mg/L)	Fe (mg/L)	K (mg/L)
Check Sample	35.9	43.9	0.230	0.216	22.1
Certified Value	35.2	42.0	0.235	0.206	20.2
P.A.L. *	29.9-40.5	35.7-48.3	.193-.277	.169-.243	17.2-23.2

*P.A.L. – Performance Acceptance Limits

Table A.2: Accuracy Determination of the Atomic Spectrometer

As shown above, the check sample analyzed by the atomic spectrometer agreed well with the certified value and was well within the performance acceptance limits. These results indicate that the accuracy of the spectrometer is very good. Please note that 1 mg/L = 1 ppm and these are used interchangeably in this report.

Some elements, such as calcium, can have ionization interference. When calcium is vaporized in the flame, it can exist in several forms such as CaOH, Ca^0, and Ca^+. In atomic adsorption, free neutral atoms are desired. Addition of an excess amount of an easily ionized element enhances the neutral-atom emission of Ca by forcing the equilibrium back towards the neutral atom. This increases the accuracy of the reading by "freeing" up more Ca in the sample.

Precision

To establish precision in the preparation procedure and in the readings from the spectrometer, a series of tests were performed. A number of samples were prepared and the concentration reading from the spectrometer was recorded. A second set of the same samples was prepared again and the concentrations were determined from the spectrometer. The differences in these readings were determined for precision in preparation procedure. Other tests were performed with similar results to establish the precision of the spectrophotometer. The results from the tests are shown in Table A.3 and Table A.4. Note that the % Differences are the differences between the sample reading and the sample average.

	Mg (mg/L)				Ca (mg/L)				K (mg/L)			
Sample	(1)	(2)	% Diff.	Std. Dev	(1)	(2)	% Diff.	Std. Dev	(1)	(2)	% Diff.	Std. Dev.
1	14.48	14.65	0.58	0.12	52.4	52.6	0.24	0.2	46.44	45.74	0.76	0.49
2	13.97	13.98	0.04	0.01	58.1	57.9	0.22	0.2	46.80	45.32	1.60	1.04
3	5.33	5.34	0.09	0.01	39.4	39.5	0.16	0.1	45.82	46.15	0.37	0.24
4	5.34	5.34	0.00	0.00	49.0	48.1	0.90	0.6	46.69	46.21	0.52	0.34

Table A.3: Precision Determination Data

	Fe (mg/L)				Mn (mg/L)			
Sample	(1)	(2)	% Diff.	Std. Dev.	(1)	(2)	% Diff.	Std. Dev.
1	0.0503	0.0547	4.19	0.0031	0.0060	0.0077	12.41	0.0012
2	0.0531	0.0410	12.86	0.0086	0.0059	0.0069	7.81	0.0007
3	0.0306	0.0197	21.67	0.0077	0.0047	0.0016	49.21	0.0022
4	0.0248	0.0410	24.62	0.0115	0.0026	0.0038	18.75	0.0008

Table A.4: Precision Determination Data

Two different mill effluent samples were determined for chlorides. Each sample was titrated 3 different times. The results are shown in Table A.5:

Sample	Trial 1		Trial 2		Trial 3		Std. Dev.
	(mg/L)	% Diff.	(mg/L)	% Diff.	(mg/L)	% Diff.	
1	147.2	0.05	147.1	0.11	147.5	0.16	0.21
2	147.8	0.09	148.1	0.11	147.9	0.02	0.15

Table A.5: Precision Determination Data

For Mg, Ca, K, and Cl, the precision is very good. The samples all appeared to agree under a 1% difference (except for one K sample). For Fe and Mn, the results were not so good. This is most likely due to the low concentrations. These low values have a low absorbance and do not obey Beer's law as shown in Figure A.3. The amount of error at these low absorbance areas is greatly increased.

The method used for this study is method 3111 B and 3111 D found in the Standard Methods for the Examination of Water and Wastewater (1995).

A.1.3 Operating Parameters and Materials

The operating conditions for atomic absorption spectrometry are indicated in Table A.6.

	Ionization Suppressant	Wave Length (nm)	Flame	Slit Width (nm)
Iron	No	248.3	Air-Acetylene	0.2
Magnesium	No	285.2	Nitrous-Oxide	0.5
Manganese	No	279.5	Nitrous-Oxide	0.2
Potassium	Cesium Chloride	769.9	Air-Acetylene	1.0
Calcium	Potassium Nitrate	422.7	Air-Acetylene	0.5

Table A.6: Operating Conditions

All samples used to create the calibration curve were Fisher Scientific certified standards: Mn number CSM81-500, K number CSP351-500, Ca number CSC191-500, Fe number CSI124-500, and Mg number CSM51-500 were used. The cesium chloride and potassium nitrate ionization suppressants are Fisher Scientific certified standard number

C-24 and P263-100 respectively. A 20,000 mg/L cesium chloride solution and 5000 mg/L potassium nitrate solution were prepared and used to saturate the samples to 1000 mg/L with the suppressant. The certified samples used as check samples were Priority PollutnT Trace Metals catalog number 531 and Cations catalog number 530.

A.2 Potentiometric Titration

A.2.1 Procedure and Theory

The analysis of chlorides was performed using a potentiometric titration method found in the Standard Methods for the Examination of Water and Wastewater (1995), method number 4500-Cl^-. The application of this method involves the use of an electrochemical cell that has a reference electrode and an indicator electrode. The reference electrode maintains a constant potential while the indicator electrode responds to the sample composition. The potentiometric device used at AlPac for this research used a silver nitrate solution, a silver/silver chloride reference electrode, and a glass indicator electrode. The change in potential between the two electrodes is measured by an electronic voltmeter during the titration. An endpoint is reached when the greatest change in voltage has occurred for a small and constant increment of silver nitrate as shown in Figure A.4..

For this method, 100 ml of the sample was used. The sample must be slightly acidic because the hydroxyl group (OH^-) may be mistaken as a chloride (Cl^-) so the sample was raised to a pH between 4.5 and 6.0.

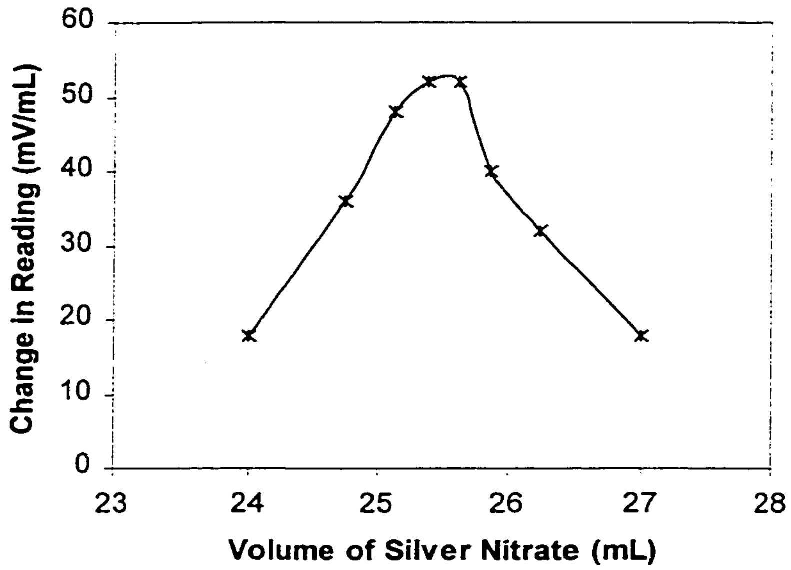

Figure A.4: Example of potentiometric titration curve (end point is 25.5 mL)

The amount of chloride in the sample is determined by:

$$\frac{\text{mg Cl}^-}{L} = \frac{(\text{mL AgNO}_3 - \text{mL blank}) * \text{Normality of AgNO}_3 * 35.450}{\text{mL sample}}$$

A.2.2 Accuracy and Precision

Accuracy

To determine the accuracy of the Potentiometric Auto-Titrator, two separate samples of NaCl were dried and weighed out to give ***1.000 g/L*** of NaCl as follows,

(1) 0.4997 g of NaCl was dissolved in 500 ml demineralized water.

(2) 0.4997 g of NaCl was dissolved in 500 ml demineralized water.

Following the chloride procedure, 25 ml of each of these samples was added to 75 ml demineralized water (total of 100 ml) and then titrated to the end point.

Results (corrected for mass variance):

(1) .9869
(2) .9929

This gives a reading of NaCl in the solution. The differences of these are:

$$(1)\ \frac{1.0000-.9869}{.9869}*100\%=1.33\%$$

$$(2)\ \frac{1.0000-.9929}{.9929}*100\%=0.72\%$$

This indicates that NaCl is accurate up to 1.33%.

Precision

Two different mill effluent samples were determined for chlorides. Each sample was titrated 3 different times. The results are:

	Chlorides (mg/L)			
	Reading			Standard Deviation
	(1)	(2)	(3)	
Sample 1	147.2	147.1	147.5	0.18
Sample 2	147.8	148.1	147.9	0.15

Table A.7: Chloride Precision

The silver nitrate solution used for this analysis was a Fisher Scientific certified standard number SS72-4. The precision of the potentiometric titration analyzer appears to be excellent.

A.3 Kajaani FS-200 Fibre Length Analyzer

To determine the amount of fines present in the mill samples, a Kajaani FS-200 fibre length analyzer was used. This device measures the fibre length by an optical technique using polarized light. This is based upon the birefringence of the wood species (Bentley *et al.,* 1994). The FS-200 has a measurement range of 0 to 7.2 mm that is divided into 144 intervals (0.05 mm in length). When a sample is passed through the analyzer, the number of fibres in each classification is counted and the fibre length averages are calculated. The number of fines present in the sample is determined by any fibre that is less than 0.2 mm in length. The accuracy and precision were not determined for this device.

A.4 Turbidity

Turbidity is measured by the intensity of light that is scattered by the sample. The higher the intensity of scattered light, the higher the turbidity. Turbidity is measured laboratory device that has a light source for illuminating the sample and photoelectric detectors with a readout device to indicate the intensity of light scattered at 90 degrees to the incident light path. The units of turbidity are measured in "NTU" or Nephelometric Turbidity Units. The method used for this study is method 2130 B found in the Standard Methods for the Examination of Water and Wastewater (1995).

A.5 Apparent Color

Apparent color includes color due to substances in solution as well as color due to suspended matter. Apparent color is determined on the original sample without centrifugation or filtration. The method used for this study is method 2120 C found in the Standard Methods for the Examination of Water and Wastewater (1995). This method is slightly modified to exclude the filtering or centrifugation of the sample.

A.6 Total Suspended Solids

Total suspended solids (TSS) were analyzed by method 2540 D in the Standard Methods for the Examination of Water and Wastewater (1995). This method measures the amount of solids that is collected on a filter paper. A well-mixed sample is filtered through a weighed filter and dried at 103 to 105 degrees Celsius.

Appendix B

Historical Data, Sample Results, and Analytical Analysis

B.1 Historical Data

The initial part of the research for this project involved determining what the input to the reactor clarifier was, as well as determining what the output from the mill was. A historical compilation of the river water was collected and is shown in Table B.1 and Table B.2.

Influent Heavy Metals (ppm)							
Time	**Al**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Zn**
1984 - 1993	0	0.008	0.008	0	0.142	0.022	0.023
1991 - 1993	1.48	0	0.006	1.74	0.05	0	0.02
1991 - 92	0.12	0	0.005	0.12	0	0	0.01
1992 - 93	0.04	0	0	0.12	0	0	0
1993 - 94	0.16	0	0.005	0.111	0.004	0	0.317
1994 -95	0.04	0.005	0.0015	0.195	0.0065	0	0.0265

Table B.1: Historical Data for River Water

Influent Heavy Metals (ppm)					
Time	Cl	Mg	Ca	K	Ba
1984 - 1993	1.5	8	31.9	1	0
1991 - 1993	7.83	12.6	48	1.53	0.09
1991 - 92	11				
1992 - 93	9.5				
1993 - 94	3.78				
1994 -95	3.65				

Table B.2: Historical Data for River Water

A historical compilation of the metals and ions in the mill effluent is tabulated in Table B.3 and Table B.4.

Effluent Yearly Average of Heavy Metals (mg/L)							
Time	**Al**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Zn**
1993	0.932	0.002	0.006	0.224	0.061	0.003	0.089
1994	0.790	0.003	0.009	0.222	0.065	0.003	0.086
1995	1.142	0.000	0.003	0.361	0.140	0.002	0.062
1996	1.074	0.000	0.001	0.418	0.092	0.001	0.063
1997	0.548	0.013	0.000	0.151	0.178	0.000	0.067

Table B.3: Historical Data for Mill Effluent Metal Concentration

Effluent Yearly Average of Heavy Metals (mg/L)					
Time	Cl	Mg	Ca	K	Ba
1993	87.8	13.15	86.97	7.81	
1994	115.5	14.06	106.42	28.56	
1995	128.4	12.09	111.32	35.59	
1996	120.4	12.53	75.97	38.57	
	133.2	11.71	84.76	41.58	

Table B.4: Historical Data for Mill Effluent Metal and Ion Concentration

From the values in the first two tables, it can be determined what levels of metals and ions the reactor clarifier usually treats. This provides and idea of what quality of water can be treated on a regular basis. This provided some guidance to what the effluent quality should be if it were to be treated in the reactor clarifier.

B.2 Factorial Design Results

B.2.1 Raw Data

Sample	Alum (ppm)	Polymer (ppm)	pH (before)	pH (after)
1	40	0.1	10.33	10.21
2	120	0.1	10.30	10.14
3	40	0.3	10.33	10.15
4	120	0.3	10.34	10.19
5	40	0.1	10.97	10.82
6	120	0.1	10.96	10.75
7	40	0.3	10.98	10.81
8	120	0.3	10.98	10.82
Raw	0	0	8.28	8.28

Table B.5: Results of the 2^3 Factorial Design – September 1998

Table B.5 shows the amount of alum and polymer that was added to each sample, as well as the pH that the samples were brought to. Note that the "pH before" column indicates the level that the pH was brought to initially, and the "pH after" column indicates the pH value of the solution after the precipitation occurred. This value is important because if the value dropped low enough, the metals may have become soluble in the solution and not have precipitated out. The "raw" value in these tables show the analytical values for the untreated mill effluent that was used to perform these tests. These raw values are the basis that the other samples are compared.

To ensure precision of the analytical results, a number of duplicates of the same sample were analyzed. The duplicated samples do not appear to deviate significantly. The accuracy of these results were determined by analyzing a known check sample that has a certified value and a performance acceptance limit. This is used to ensure that the readings obtained were accurate. All of the check samples agreed well with the certified values. The results for September 1998 are shown in Table B.6 to Table B.8 while the results for March 1999 are shown in Table B.9 to Table B.11.

Sample	Turbidity (NTU)	Apparent Color	Al (mg/L)	Mg (mg/L) (1)	Mg (mg/L) (2)	Mg (mg/L) Average
1	53	407	2.3	14.48	14.65	14.57
2	21	283	5.9	13.90		13.90
3	66	513	2.2	13.97	13.98	13.98
4	20	263	6.4	13.04		13.04
5	6.3	139	2.3	5.33	5.34	5.34
6	4.9	114	4.6	1.58		1.58
7	4.7	136	2.1	5.34	5.34	5.34
8	5.8	124	4.6	2.22		2.22
Raw	10.4	397	0.22	18.22		18.22
Check Sample				35.86		
Certified Value of Check Sample				35.20		
Performance Acceptance Limits of Certified Check Sample				29.9 - 40.5		

Table B.6: Results of the 2^3 Factorial Design – September 1998

Sample	Ca (mg/L) (1)	Ca (mg/L) (2)	Ca (mg/L) Average	Mn (mg/L) (1)	Mn (mg/L) (2)	Mn (mg/L) Average	Fe (mg/L) (1)	Fe (mg/L) (2)	Fe (mg/L) Average
1	52.4	52.6	52.5	0.0060	0.0077	0.0069	0.0503	0.0547	0.0525
2	56.0		56.0	0.0056		0.0056	0.0394		0.0394
3	58.1	57.9	58.0	0.0059	0.0069	0.0064	0.0531	0.0410	0.0471
4	56.1		56.1	0.0068		0.0068	0.0273		0.0273
5	39.4	39.5	39.4	0.0047	0.0016	0.0032	0.0306	0.0197	0.0252
6	54.8		54.8	0.0049		0.0049	0.0160		0.0160
7	49.0	48.1	48.6	0.0026	0.0038	0.0032	0.0248	0.0410	0.0329
8	50.3		50.3	0.0016		0.0016	0.0274		0.0274
Raw	124.8		124.8	0.1002		0.1002	0.1524		0.1524
Check Sample	43.9			0.2304			0.2163		
Cert. Value	42.0			0.2350			0.2060		
Perform. Limits	35.7 - 48.3			.193 - .277			.169 - .243		

Table B.7: Results of the 2^3 Factorial Design – September 1998

Sample	K (mg/L)			Cl (mg/L)			
	(1)	(2)	Average	(1)	(2)	(3)	Average
1	46.44	45.74	46.09	147.9			147.9
2	45.55		45.55	147.2	147.1	147.5	147.3
3	46.80	45.32	46.06	148.3			148.3
4	45.56		45.56	146.6			146.6
5	45.82	46.15	45.98	147.8	148.1	147.9	147.9
6	46.35		46.35	146.8			146.8
7	46.69	46.21	46.45	147.6			147.6
8	45.70		45.70	146.8			146.8
Raw	45.93		45.93	148.8			148.8
Check Sample	22.11						
Cert. Value	20.20						
Perform. Limits	17.2 - 23.2						

Table B.8: Results of the 2^3 Factorial Design – September 1998

Sample	Alum (ppm)	Polymer (ppm)	pH (before)
1	40	0.1	10.26
2	120	0.1	10.28
3	40	0.3	10.27
4	120	0.3	10.28
5	40	0.1	11.08
6	120	0.1	11.12
7	40	0.3	11.10
8	120	0.3	11.09
Raw	0	0	7.85

Table B.9: Results of the 2^3 Factorial Design – March 1999

Sample	Turbidity (NTU)	Apparent Color	Mg (mg/L)	Ca (mg/L)
1	28	263	14.30	62.5
2	2.1	104	13.82	58.6
3	28	230	14.18	59.0
4	2.1	106	13.65	55.2
5	6.1	106	7.97	56.0
6	1.8	113	11.82	68.4
7	4	76	3.34	75.7
8	2.4	86	8.74	81.2
Raw	8.6	252	15.19	112.7
Check Sample			36.88	43.2
Cert. Value			35.20	42.0
Perform. Limits			29.9-40.5	35.7-48.3

Table B.10: Results of the 2^3 Factorial Design – March 1999

Sample	Mn (mg/L)	Fe (mg/L)	K (mg/L)	Cl (mg/L)
1	0.0566	0.1072	26.66	116.0
2	0.0329	0.0222	26.33	115.6
3	0.0494	0.0808	26.52	116.5
4	0.0356	0.0451	26.80	115.6
5	0.0137	0.0301	26.54	115.9
6	0.0205	0.0167	26.37	115.3
7	0.0039	0.0000	26.56	115.2
8	0.0110	0.0082	26.21	114.8
Raw	0.2579	0.0813	26.65	117.5
Check Sample	0.2340	0.2006	18.66	
Cert. Value	0.2350	0.2060	20.20	
Perform. Limits	.193-.277	.169-.243	17.2-23.2	

Table B.11: Results of the 2^3 Factorial Design – March 1999

The data attained by combining these two sets of experiments are shown in Table B.12 and Table B.13:

y_i	Turbidity (NTU)		Apparent Color		Mg (mg/L)		Ca (mg/L)	
	1	2	1	2	1	2	1	2
y_1	53	28	407	263	14.57	14.30	52.5	62.5
y_2	21	2.1	283	104	13.90	13.82	56.0	58.6
y_3	66	28	513	230	13.98	14.18	58.0	59.0
y_4	20	2.1	263	106	13.04	13.65	56.1	55.2
y_5	6.3	6.1	139	106	5.34	7.97	39.4	56.0
y_6	4.9	1.8	114	113	1.58	11.82	54.8	68.4
y_7	4.7	4	136	76	5.34	3.34	48.6	75.7
y_8	5.8	2.4	124	86	2.22	8.74	50.3	81.2
Raw	10.4	8.6	397.0	252.0	18.22	15.19	124.8	112.7

Table B.12: Combined Results of the 2^3 Factorial Design

y_i	Mn (mg/L)		Fe (mg/L)		K (mg/L)		Cl (mg/L)	
	1	2	1	2	1	2	1	2
y_1	0.0069	0.0566	0.0525	0.1072	46.09	26.66	147.9	116.0
y_2	0.0056	0.0329	0.0394	0.0222	45.55	26.33	147.2	115.6
y_3	0.0064	0.0494	0.0471	0.0808	46.06	26.52	148.3	116.5
y_4	0.0068	0.0356	0.0273	0.0451	45.56	26.80	146.6	115.6
y_5	0.0032	0.0137	0.0252	0.0301	45.98	26.54	147.8	115.9
y_6	0.0049	0.0205	0.0160	0.0167	46.35	26.37	146.8	115.3
y_7	0.0032	0.0039	0.0329	0.0000	46.45	26.56	147.6	115.2
y_8	0.0016	0.0110	0.0274	0.0082	45.70	26.21	146.8	114.8
Raw	0.1002	0.2579	0.1524	0.0813	45.93	26.65	148.8	117.5

Table B.13: Combined Results of the 2^3 Factorial Design

B.2.2 Statistical Analysis

B.2.2.1 Least Squares

Using Mg as an example, the least squares linear regression can be performed:

$$\mathbf{y} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon}$$

where

$$y=\begin{bmatrix} y1 \\ y2 \\ \vdots \\ yn \end{bmatrix} \qquad X=\begin{bmatrix} 1 & x_{11} & x_{12} & \cdots & x_{1k} \\ 1 & x_{21} & x_{22} & \cdots & x_{2k} \\ \vdots & \vdots & \vdots & & \vdots \\ 1 & x_{n1} & x_{n2} & \cdots & x_{nk} \end{bmatrix} \qquad \beta=\begin{bmatrix} \beta_0 \\ \beta_1 \\ \vdots \\ \beta_k \end{bmatrix} \qquad \varepsilon=\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_n \end{bmatrix}$$

The least squares estimate of β is:

$$\hat{\beta}=(X'X)^{-1}X'y$$

$$X=\begin{bmatrix} 1 & -1 & -1 & 1 & -1 & 1 & 1 & -1 \\ 1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 \\ 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 \\ 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\ 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix} \qquad y=\begin{bmatrix} 14.43 \\ 6.65 \\ 13.86 \\ 6.70 \\ 14.08 \\ 4.34 \\ 13.35 \\ 5.48 \end{bmatrix}$$

$$X'X=\begin{bmatrix} 8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 8 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 8 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 8 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 8 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 8 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 8 \end{bmatrix}$$

$$\hat{\beta}=\begin{bmatrix} 9.86 \\ -4.07 \\ -0.02 \\ 0.31 \\ -0.55 \\ -0.33 \\ 0.12 \\ 0.16 \end{bmatrix}$$

The combined results from Table B.5 to Table B.11 are used to determine the effects of pH, alum, and polymer on the mill effluent. Statistical analysis was performed on each of the elements above to determine the confidence of the results.

B.2.2.2 Analysis of Variance

The analysis of variance was performed for each parameter in the 2^3 factorial design. The analysis of variance results for turbidity are indicated in Table B.14. The other parameters have results that were obtained in a similar manner to these.

Turbidity

Analysis of Variance of the Parameters

Source of Variation	Effects	Sum of Squares	d.o.f.	Mean Square	fo
A	-23.025	2120.6025	1	2120.6025	12.26
B	-17.000	1156.0000	1	1156.0000	6.68
C	1.225	6.0025	1	6.0025	0.03
AB	15.450	954.8100	1	954.8100	5.52
AC	-1.775	12.6025	1	12.6025	0.07
BC	-1.100	4.8400	1	4.8400	0.03
ABC	2.400	23.0400	1	23.0400	0.13
Error		1384.1600	8	173.0200	
Total		5662.0575	15	377.4705	

Table B.14: Analysis of Variance

B.2.2.3 Residual Analysis

McLean (1990) indicates that residuals from a fitted model can provide all information necessary to assess the adequacy of the model. The residuals should match the behavior for the random error term (ε) of equation (4.11). Four assumptions that are used for a least squares analysis are:

1. the variance of the operating variables are exactly known,
2. the form of the model is correct,
3. the random error term has constant variance, and
4. the random error for one data point does not have a systematic association with another.

Mclean (1990) also indicates that it is not required to have a normal probability density function of the random error term.

To check the assumptions used in a least squares analysis, a number of plots should be performed. The first should be a plot of the residual versus the fitted response values which would provide an indication to such things as outliers and changing variances. A plot of the residual versus run order can provide information on if there are any time trends. The residual versus each factor (x_i) can indicate if there is any model form deficiencies. The independence of the data can be verified by plotting a residual (e_u) versus the previous residual (e_{u-1}).

B.3 Analysis of Mill Streams and Wood Chips

To determine what the effects would be if various streams were to be recycled within the mill, a detailed analysis of the streams was required. This is shown in Table B.15. The analysis of the wood chips was also performed and is recorded in Table B.16. This was done to provide an indication to the various sources of non-process elements that enter into the mill system.

Analysis (mg/L)	D_n Filtrate	D_o Filtrate	E_{op} Filtrate	D_2 Filtrate	Hot Water	(replicate) Hot Water	Warm Water	Machine White Water
Total organic carbon	170	335	265	104	4.7		3.7	39
Total dissolved solids	908	1760/1760	1640	1130	144		160	432
Total chloride, Cl	10.9	254	90.4	72.8	1.7		1.5	26.1
Sulfate, SO_4	415	622	297	386	68.2		341	193
Aluminum, Al	0.08	0.47	<0.05	0.16	<0.05	<0.05	<0.05	0.08
Arsenic, As	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Barium, Ba	0.3	0.49	0.19	0.33	0.06	0.06	0.06	0.2
Cadmium, Cd	<0.005	0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Calcium, Ca	50.7	265	17.5	73.8	37.9	36.8	36.1	45.2
Chromium, Cr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cobalt, Co	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Copper, Cu	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Iron, Fe	<0.01	0.5	<0.01	0.1	<0.01	<0.01	<0.01	0.1
Lead, Pb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Lithium, Li	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Magnesium, Mg	10.2	26.9	1.7	15.5	10.3	9.88	9.72	11.7
Manganese, Mn	0.1	0.55	<0.01	0.1	<0.01	<0.01	<0.01	0.04
Molybdenum, Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Nickel, Ni	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
Phosphorus, P	3.1	3.4	<0.1	0.9	<0.1	<0.1	<0.1	0.2
Potassium, K	41	22.2	6	3.2	1.4	1.4	1.2	1.7
Silicon, Si	3.5	7.6	2.9	3.7	1.3	1.3	1.3	3.9
Sodium, Na	215	180	587	202	7.39	7.05	7.13	72.3
Titanium, Ti	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Vanadium, Va	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zinc, Zn	0.06	0.5	<0.01	0.06	<0.01	<0.01	<0.01	0.02

Table B.15: Analysis of Internal Streams (Paprican, October 20, 1997)

Analysis of Wood Chips (mg/kg or ppm)		
	Alberta-Pacific *	Mill C **
Wood Species	Aspen	Aspen
Total Sulphur (S)	29	55.5
Chloride (Cl)	13	5.84
Aluminum (Al)	6	3
Calcium (Ca)	1280	1105
Chromium (Cr)	0.2	ND
Iron (Fe)	8.7	ND
Lead (Pb)	ND	ND
Magnesium (Mg)	190	125
Manganese (Mn)	3.5	2.9
Phosphorous (P)	78	65.3
Potassium (K)	680	517
Silica (Si)	18	<10
Sodium (Na)	2.2	ND
Zinc (Zn)	11	12.3
Copper (Cu)	Not Analyzed	ND
Nickel (Ni)	Not Analyzed	ND
Cadmium (Cd)	Not Analyzed	ND
Barium (Ba)	Not Analyzed	8.9
Cobalt (Co)	Not Analyzed	ND
Vanadium (V)	Not Analyzed	ND
Platinum (Pt)	Not Analyzed	ND
Lithium (Li)	Not Analyzed	ND
Molybdenum (Mo)	Not Analyzed	ND
Arsenic (As)	Not Analyzed	ND
Titanium (Ti)	Not Analyzed	ND
Strontium (Sr)	Not Analyzed	ND
DCM Extractives (%)	Not Analyzed	1.87***

* Alberta-Pacific samples were whole Aspen logs sent to PAPRICAN November, 1998.

** Mill C is screened aspen wood chips used at another mill in Alberta.

*** DCM extractives performed on chips that were sitting around for 3 months. The value determined on frozen chips was 2.50 %

ND = Not detected

Table B.16: Wood Chip Analysis

Appendix C

Deep Well Disposal

One idea proposed to achieve a recycle of the mill effluent as process water is to determine which streams contain the problematic components (K and Cl) and remove them. If the majority of these components are present in only one stream, this could be removed and the bulk of the effluent could be used as recycle water and returned to the mill. The stream that is rich in K and Cl must be disposed, and one option available is deep-well injection of this waste stream.

Deep Well Disposal

One option available for the disposal of wastes is by deep well injection. This subsurface treatment of wastewater involves the drilling of a deep hole into the earth and disposing of the water in a manner that there would be minimal environmental impact. The well would have to be drilled in a geological zone that would meet requirements dictated by the government. The injection well would have to be drilled into a zone that could accept the waste volumes, as well as ensuring that the waste would not seep into fresh water systems. Figure C.1 shows a schematic of an industrial waste injection well.

The Energy Resources Conservation Board (1994) gives detailed information on deep well injection such as, cementing and casing requirements, approval for injection, logging requirements, and other tests and submission requirements. Summaries of wastes that are acceptable for deep well disposal as well as guidelines for this option are presented below.

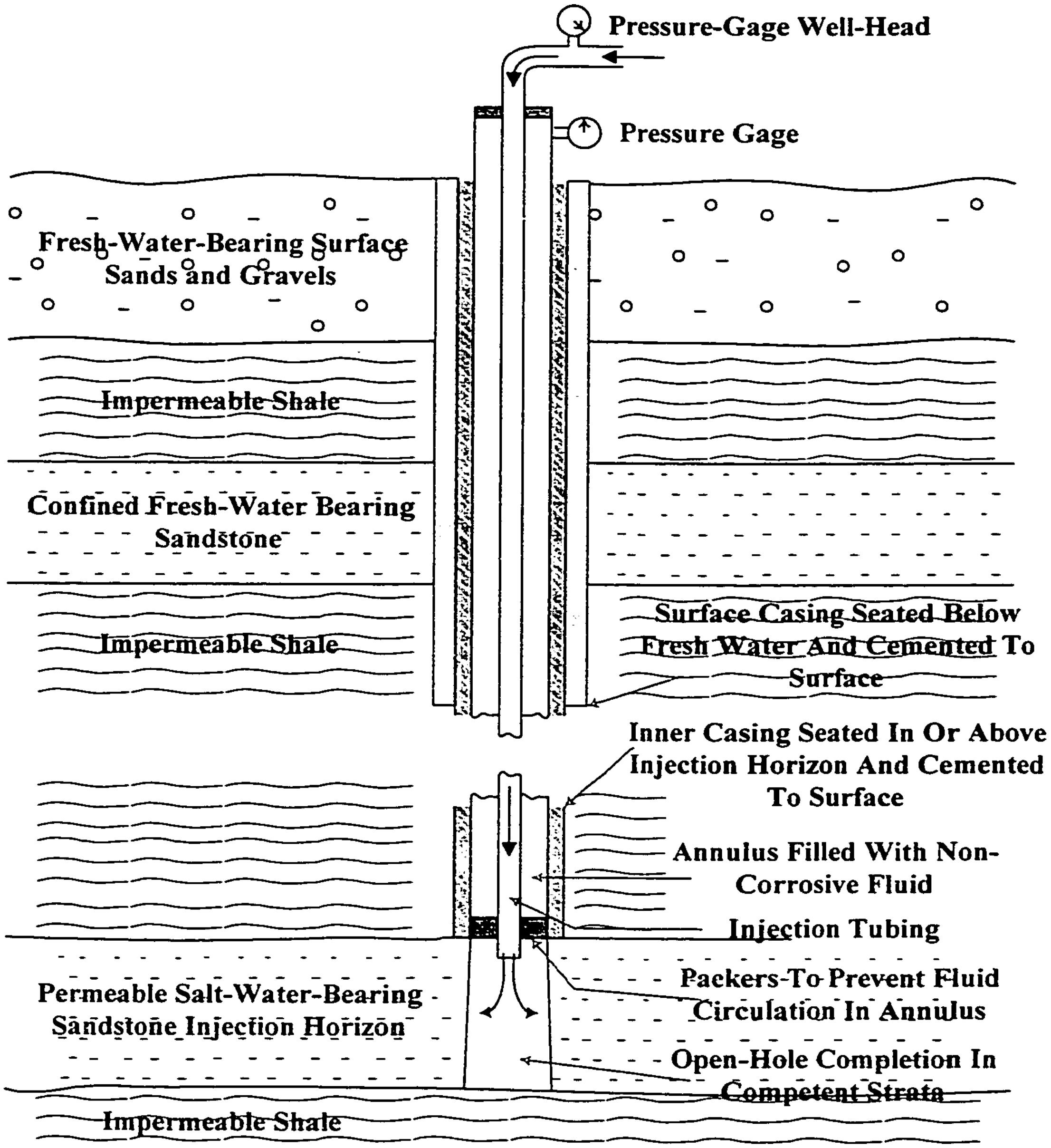

Figure C.1: Schematic Diagram of an Industrial Waste Injection Well Completed in Competent Sandstone (modified from Warner and Lehr, 1981)

Deep-well disposal is proposed to be a safe and viable disposal option for wells that are properly constructed, operated, and monitored. Prior to using deep-well disposal, waste minimization must be implemented, and whenever possible, resource conservation should be pursued. For monitoring and surveillance of operations of these wells, they should be classified and designed based on the fluid being injected. In most cases, the fluids should not be diluted, and for industrial waste wells, it is expected that they will be designed and operated using sound waste management practices and principles of waste minimization.

The issues that are focused on by regulatory activities are: ensuring well-bore integrity and formation suitability for the initial and ongoing confinement of the waste, the suitability of the waste stream, manifesting and reporting of disposed wastes, as well as ensuring that these principles have been followed. It is the primary responsibility of the waste generator to ensure that these principles are followed as well as to ensure that each stream is properly identified, characterized, handled, treated, and disposed.

A wastewater acceptable for deep well disposal in the province of Alberta should have a pH between 4.5 and 12.5 because of potential well-bore integrity problems due to corrosion. The deep-well disposed wastewater must not comply with surface water discharge limits; it is preferred to treat the water and return it to the surface because these treatment technologies are standard and well established. The waste must contain a non-halogenated organic fraction less than 10 wt. %, otherwise incineration would be a better option. The water should have a total combined concentration less than 1000 mg/kg of one or more halogenated organic compounds, and have a concentration of less than 50 mg/kg polychlorinated biphenyl (PCB).

The approach of using deep-well disposal in this manner could allow the mill to achieve drastic water use reductions, and make the mill one of few Kraft mills that use very little fresh water. The idea of zero effluent discharge, however, requires that no effluent be released by the pulp mill, either to surface waters or subsurface locations. For this mill to meet the requirements for this idea, deep-well disposal would not be an option. This pulp mill currently meets surface discharge limits with the present treatment system installed. If these limits were to change in the future, deep-well disposal may be an option to be considered.

Appendix D

Water Balance Calculations

D.1 Acid, Caustic, and General Effluent Flow Calculations

The drains entering each of the sewer lines below were determined by using the mills process and control diagrams to trace the lines leaving each area and dumping into the sewers. In a lot of places, no instrumentation was available to determine the flows, so mill operators provided the missing information. In the cases where instrumentation was available, a month when the mill was running steady (July 1997) was chosen and averaged values were used. Below is a summary of all the places that were looked into to determine what flows were entering each sewer line.

D.1.1 Acid Sewer

- Boiler Acid Wash
    - Rarely used, only for shutdowns
    - Approximately 0 times per year
    - 0 L/s
- Caustisizing
    - Pressure Filter Acid Wash
    - Approximately 2-3 times per year
    - 0 L/s

    - Dregs and Mud Filter Acid Wash
    - Approximately 2-3 times per year
    - 0 L/s
- Demineralized Water
    - 4 Cation Ion Exchange Columns
    - Regenerated each day
    - 1100 L of acid each per regeneration
    - 4400 L/day

    - 3 Anion Ion Exchange Columns
    - Regenerated each day
    - 8100 L of caustic each per regeneration
    - 24,300 L/day

    - 1 Mixed Ion Exchange Column
    - Regenerated once every 4 days

	- 175 L of acid and 1500 L of caustic - 12, 981 L/day
▪ Chemical Preparation	- Salt-cake Slurry Dissolving Tank - Open to sewer for 3840 minutes a month. - Average flow 43.47 L/min - Average monthly flow-rate 0.06 L/s.
▪ Sulfamic mixing tank	- 0 L/s
▪ Digester	- Acid sewers leaving here are for drainage only - No constant or monthly flows - 0 L/s
▪ Impregnation Vessel	- Acid sewers leaving here are for drainage only - No constant or monthly flows - 0 L/s
▪ Acid Cleaning Tank	- Never been used - 0 L/s
▪ NCG	- Foul Condensate Tank - No consistent flows - During July 1997, may have been draining for maximum of 1 hour - 0 L/s
▪ Stripper Feed Tank	- Overflows into sewer - No overflow for July 1997 - 0 L/s
▪ D_2 Bleaching Stage	- Filtrate tank drains to acid sewer - Mass balance performed on this stage - 33.11 L/s for July 1997
▪ D_o Bleaching Stage	- Filtrate tank drains to acid sewer - Mass balance performed on this stage - 239.40 L/s for July 1997
▪ Wood Room	- Mass balance performed with operators - Water drains into the acid sewer line directly before the neutralization basin - 110 L/s

Total Flow to Acid Sewers: 383 L/s

D.1.2 Caustic Sewer

▪ Chemical Preparation	- 0 L/s (operator information)
▪ Chip Bin Vent	- 1 L/s (operator information)
▪ Moisture Separator	- 1.3 L/s intermittent for 5-minutes per hour - 0.10 L/s
▪ D_n Bleaching Stage	- Mass balance performed on this stage - 146.82 L/s
▪ E_{op} Bleaching Stage	- Mass balance performed on this stage - 135.08 L/s

Total Flow to Caustic Sewer: 283 L/s

D.1.3 General Sewer

Note: Most flows to the general sewer are from the overflows from the sumps in each area of the mill. No instrumentation was available for the overflow rates, and in most cases a piece of pulp added to the overflow (or inflows to the sump) in the floor trenches and timed to get a flow. The dimensions of the trenches were easy to determine.

▪ Brownstock sump	- Operator pumped the water from the sump into a storage tank. After the sump was drained to a certain level, the pumping was stopped and the water allowed to raise in the sump. This was timed. Knowing the dimensions of the sump and the increase in level, the overflow rate was determined. - 33 L/s
▪ Evaporator Sump	- Floated a piece of pulp and timed how long it took to travel a length of trench. - 13 L/s
▪ Turbogenerator Sump	- Floated a piece of pulp - 1.6 L/s

▪ Bleach Plant Sump	- Floated a piece of pulp - 14.8 L/s
▪ Power Boiler Sump 1	- Floated a piece of pulp - 8.3 L/s
▪ Power Boiler Sump 2	- Floated a piece of pulp - 4.9 L/s
▪ Machine Room	- Mass balance was performed - 26 L/s

Total General Sewer: 101.6 L/s

D.1.4 Other Sources of Water Loss

▪ Cooling Towers	- 3 cells at 50 L/s evaporation loss per cell - Mass balance around cooling tower - 150 L/s
▪ Machine Room	- Evaporation losses (operator and instrumentation data) - 10 L/s
▪ Potable Water Usage	- Operator data and design flows - 37 L/s
▪ Mill Services	- Operator data and design flows - 56 L/s

Total Extra Water Loss: 253 L/s

D.1.5 Overall Mill Water Balance

Total Input (Water Treatment Plant)	***1026 L/s***
Total Output (All sewers and other losses)	***1021 L/s***
Difference	***5 L/s***

Please note that a lot of the information attained for this water balance is based on a few assumptions:

- Operators information is what is actually happening in the mill
- Instrumentation data is reliable
- Flows determined for the sumps indicate what is always overflowing to the sewer

This information is based on numerous assumptions. There are many sources of error possible in these calculations.

D.2 Bleach Plant Filtrate Tank Hot Water Flow Calculation

D.2.1 Method 1: Manufacturer Valve Specifications

The valve specifications supplied by the manufacturer were first used to calculate the amount of hot water that was being used in the bleach plant filtrate tanks for level control. The valve specifications provided a % opening of the control valve along with a corresponding flow rate. These values are shown in Table D.1.

% Open	Flow (L/s)
0	0
37	75
58	150

Table D.1: Valve Specifications

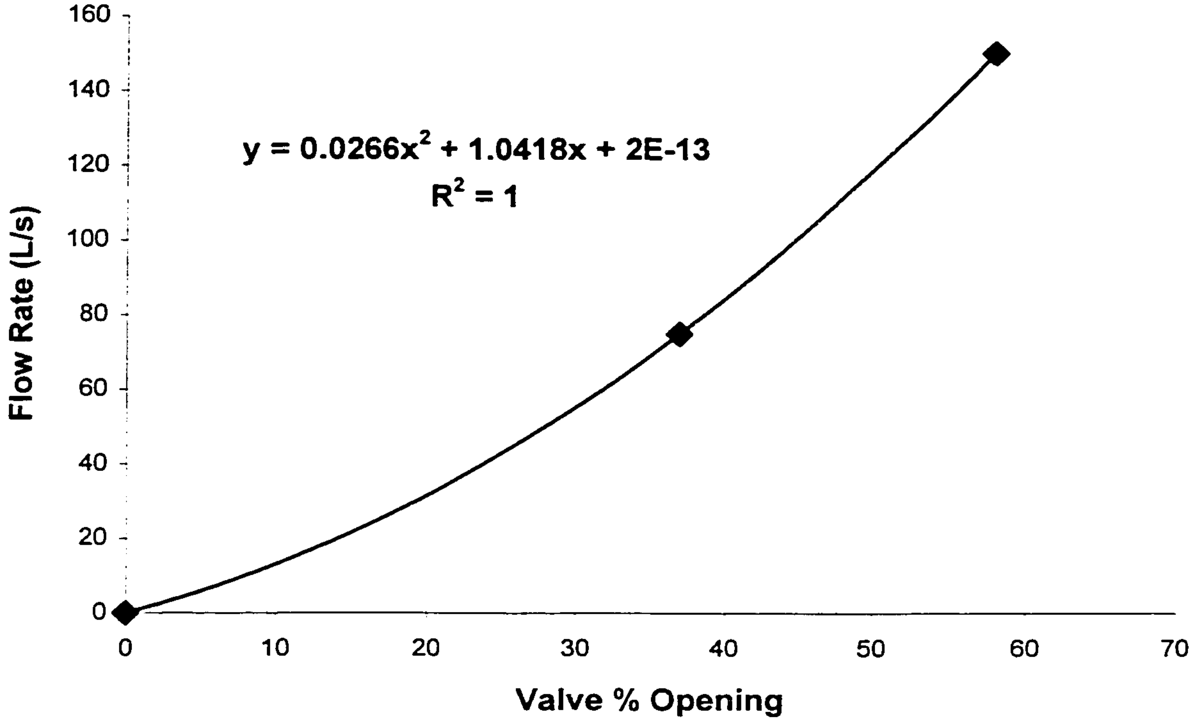

Figure D.1: Valve Specification Flow Rate versus % Open Curve

A quadratic was fitted to the data points in Table D.1 resulting in Figure D.1. The equation could then be used to determine a flow rate through the valve knowing the % open. The % opening of the valve was determined by accessing the historical database. The results showed average flows of approximately 50 L/s for December 1998. These values appeared high, so a water balance was performed to check these numbers.

D.2.2 Method 2: Water Balance

As part of the on-line water balance that was performed for this project, a balance was performed around the D_2 area. All areas except the hot water intake to the filtrate tank is known. The D_2 filtrate rarely overflows to sewer, so this value can be taken as zero. The consistencies of the pulp are determined from transmitters or by lab data and may not be that accurate. As a result, the average flow of hot water in to the filtrate tank was approximately 70 L/s with this calculation. This result does not compare well with the valve specification calculation, and appears very high. As a third approach, a "bucket and stopwatch" method was used.

D.2.3 Method 3: Bucket and Stopwatch Method

This method involved using the distributive control system (DCS) at the mill. The valve supplying the hot water to the filtrate tank was varied, and the time to change the level in the tank was recorded. Knowing the dimensions of the filtrate tank, the flow rate can be calculated for each % change in level. The results are recorded in Table D.2 to Table D.4. The tests were performed 3 times to ensure accurate data was produced.

% open	Flow (L/s)
100	323.8
75	189.9
65	174.6
50	101.6
40	67.6
35	37.6
25	10.3

Table D.2: Bucket and Stopwatch Data – Trial 1 (February 1 1999)

% open	Flow (L/s)
100	320.5
75	204.4
65	161.5
50	100.8
40	62.8
35	44.5
25	9.5

Table D.3: Bucket and Stopwatch Method – Trial 2
(February 1 1999)

% open	Flow (L/s)
100	323.8
77	201.6
50	90.0
40	56.0
35	42.3
30	27.2
25	12.9

Table D.4: Bucket and Stopwatch Method – Trial 3
(February 2 1999)

From these values, a graph was produced and a quadratic curve was fit to the points, shown in Figure D.2. From this it is possible to determine the flow rate by the % opening of the valve supplying the hot water to the filtrate tank.

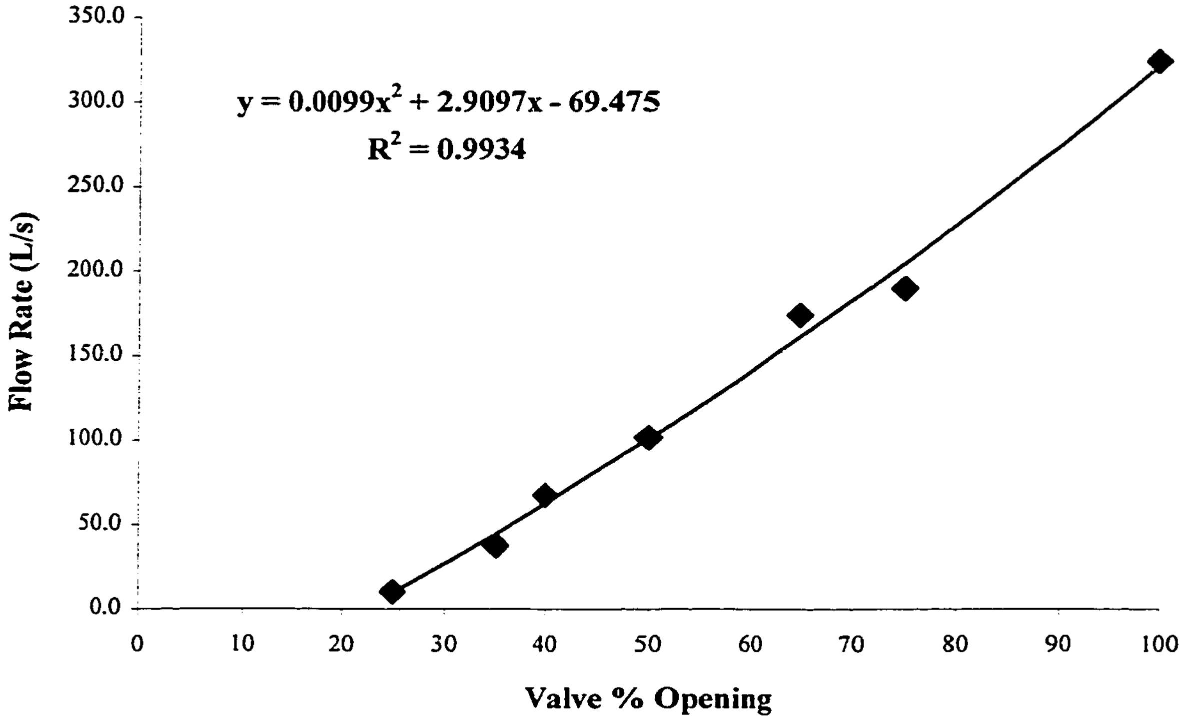

Figure D.2: Bucket and Stopwatch Method – Flow Rate versus Valve % Opening

Note that in Figure D.2 that the readings for the % opening of the valve only go to 25% open. The reason for this is that below this point, the amount of water entering the filtrate tank is so small that it is very hard to determine the change in level of water in the tank. For this reason, a linear relationship was extended from 25% open to 5% open. Below this, it was assumed that the valve was completely closed.

From Figure D.2, the values for a given % opening of the valve were determined, and are shown in Table D.5.

% open	Flow (L/s)
100	323.2
77	202.3
50	89.8
40	56.2
35	41.0
30	26.9
25	13.9
20	9.7
15	6.5
10	3.2
5	0.0

Table D.5: Bucket and Stopwatch Method – Analysis

The bucket and stopwatch method was the one used to determine the amount of hot water entering the filtrate tank.

D.3 Hot Water Added to the High-Density Storage Tank

There are no flow transmitters on the hot water line entering the unscreened high-density storage tank. The amount of water added to this point had to be determined from a water balance around this area. A schematic of this balance is shown in Figure D.3.

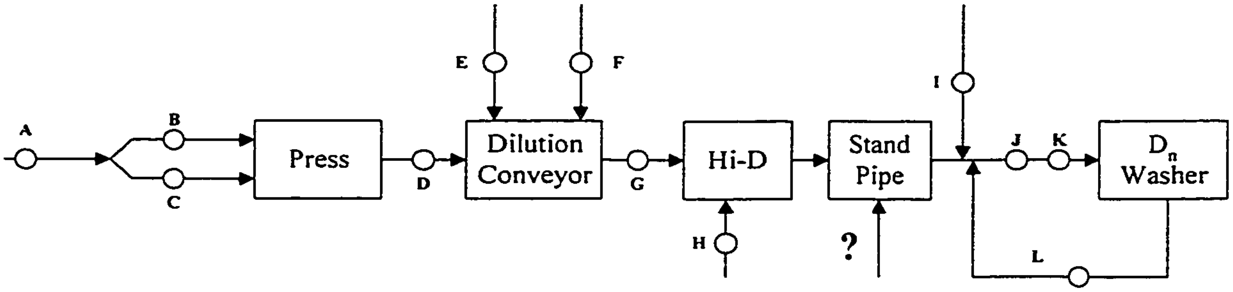

Figure D.3: Water Balance Flow Sheet

A – consistency transmitter (%)
B – stock feed transmitter (L/s)

C – stock feed transmitter (L/s)
D – consistency transmitter (%)
E – warm water flow transmitter (L/s)
F – hot water flow transmitter (L/s)
G – consistency transmitter (%)
H – hot water flow transmitter (L/s)
I – sulfuric acid flow transmitter (L/min)
J – stock feed transmitter (L/s)
K – consistency transmitter (%)
L – D_n filtrate flow transmitter (L/s)

Knowing these values, a series of mass balances can be performed to get the amount of hot water that is added to the standpipe from the 300-tonne high-density storage tank.

$$\text{Consistency} = \frac{\text{mass of fibre}}{(\text{mass of fibre})(\text{mass of water})} * 100\%$$

and at all the consistency values used in this area, 1 L pulp = 1 kg pulp.

Referring to Figure D.3:

1. ***Mass of fibre into press:***

$$(\mathrm{C} + \mathrm{B}) * \frac{A}{100} = \mathbf{M\ (kg)} \tag{D.1}$$

2. ***Mass of fibre out of press:***

$$J * \frac{K}{100} = \mathbf{N\ (kg)} \tag{D.2}$$

3. ***Water out of press:***

$$\frac{N - \frac{N * D}{100}}{\frac{D}{100}} = \mathbf{P\ (L/s)} \tag{D.3}$$

4. ***Flow out of press:***

$$P + N = \mathbf{Q}\ \text{(L/s)} \qquad \textbf{(D.4)}$$

5. ***Total water into Hi-D:***

$$P + E + F = \mathbf{R}\ \text{(L/s)} \qquad \textbf{(D.5)}$$

6. ***Flow to Hi-D:***

$$N + E + F = \mathbf{S}\ \text{(L/s)} \qquad \textbf{(D.6)}$$

7. ***Fibre out of Hi-D:***

$$\frac{J * K}{100} = \mathbf{T}\ \text{(kg)} \qquad \textbf{(D.7)}$$

8. ***Water into Hi-D and standpipe area (except hot water into standpipe):***

$$\frac{\left[T - \dfrac{T * K}{100}\right]}{\dfrac{K}{100}} = \mathbf{U}\ \text{(L/s)} \qquad \textbf{(D.8)}$$

9. ***Hot water added for dilution:***

$$U - L - \frac{I}{60} - R = \mathbf{?}\ \text{(L/s)} \qquad \textbf{(D.9)}$$

From part 9 above, the amount of hot water added to the standpipe was determined.

D.4 Overflow Calculations from Tanks in Machine Room

The quantity of water overflowing from the tanks in the machine room was estimated based on the size of the tank, the level of the tank, and the amount of effluent leaving the machine room. The volume of each of the tanks is given below in Table D.6.

Tank	Volume (m^3)
White Water Surge Tank	1203
Filtrate Chest	182
Machine White Water Chest	154
Pressate Collection Tank	2.5
Hot Water Tank	11.8
Pressate White Water Collection Tank	3.5
Couch Pit	52
Broke Storage Tank	1203
Fibre Recovery Chest	33
Dry End Pit	120

Table D.6: Volumes of Tanks

Over a period of 2 weeks (June 1999), when the mill was operating at steady state, the flows contributing to the effluent system were analyzed. The flow results are tabulated in Table D.7.

Area	Day 1 (L/s)	Day 2 (L/s)
Floor Drains	1	1
Wire Pit	33	43
Noss Rejects	5	5
Vac. Pump Seal Tank	36	33
Press Roll Cool. Tank	2	2
Average Total	80 L/s	

Table D.7: Flows From Machine Room

These flows indicate constant flows that are leaving the machine room area. These flows are assumed constant at any one given time when the mill is running at steady state.

Knowing the total amount of effluent flow leaving the machine room (mass balance), and subtracting the constant flow of 80 L/s (determined above), the total flow contributed by the tanks overflowing to sewer can be estimated by:

$$\text{Total effluent flow} - 80\text{ L/s} = \text{Flow contributed to overflowing tanks} \qquad \textbf{(D.10)}$$

For example, if the total flow leaving the machine room area was 100 L/s, then the flow contributed to the tanks overflowing would be 20 L/s.

Knowing the volumes of each of the tanks, and when each tank was overflowing (i.e., when the level was over 100%), it is assumed that the amount of flow overflowing from each tank is proportional to the volume of the tank. For example, if the machine white water chest (volume = 154 m^3) and the filtrate chest (volume = 182 m^3) were the only 2 tanks overflowing at the time, then out of the 20 L/s flow contributed to the tanks overflowing,

$\frac{154}{154+182} * 20L/s = 9.17L/s$ from the machine white water chest, and

$\frac{182}{154+182} * 20L/s = 10.83L/s$ from the filtrate chest.

The fine content of the effluent streams were analyzed on a KAAJANI FS-200 instrument.

D.5 Computer Code For Online Water Balance

This code was written using a “Report Definition Editor (RDE)” software package that was available at the mill site.

```
;       Change what consistency tags we use during softwood and hardwood
;       41yp338 is for hardwood
;       41yp338b is for softwood
;       NOTE:  The transmitters are innacurate for SOFTWOOD runs.
;              Only use this information for HARDWOOD runs

10      ;Report No.      17:995
20      ;Title           Mill Wide Effluent Calculations
30      ;Owner           Environmental Manager
40      ;Created         10-JUL-98
50      ;By              Jason Melanson
60      ;Revised
70      ;By
80      ;Issue schedule
90      ;Revised
100     ;By
110     ;Changes
120     ;Revised
130     ;By
140     ;Changes

160     ;Description: Mill Wide Effluent Calculations
170

;+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
;                          Bleach Plant Effluent Calculations
;+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;
;                        D2 Bleaching Stage
;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;


250     format  (f10.2) ;Formats the size of the outputs
260     tbas    1       ;Sets the base time at 1 minute
270     tlen    30      ;Sets the length of the reading

280     tstart  1       ;Takes the reading starting at the input time

290     let     V1=41fc352  av    ;D2 Lower Shower Flow Rate
300     let     V2=41fc344  av    ;D2 Upper Shower Flow Rate
305     let     V3=41lc336-op-ctl  av    ;Hot Water Level Control Valve
310     let     V4=41fc330  av    ;D2 Filtrate Tank to D2 Tower
320     let     V5=41fc337  av    ;10% Caustic to D2 Tower
330     let     V6=41fc333  av    ;Pulp Flow to D2 Washer
```

```
340     let     V7=41yp338 av    ;Pulp Consistency to D2 Washer
350     let     V8=41fc139  av    ;D2 Filtrate to Eop Washer
360     let     V9=41fc140  av    ;D2 Filtrate to Eop Repulper
370     let     V10=41fc054  av   ;D2 Filtrate to Do Washer
380     let     V11=41fc231  av   ;D2 Filtrate to Dn Repulper
382     let     V12=41fc230  av   ;D2 Filtrate to Dn Upper Wash

;       This Calculation Determines the Flow of Water Leaving the
;       D2 Area with the Pulp
390     cal     V13=('V6'*('V7'/100)/0.100)-('V6'*('V7'/100))

;       Calc performs the amount of water that enters the D2 Washer
;       with the Pulp
400     cal     V14='V6'*(1-'V7'/100)

;       Calculates the amount of hot water flowing through the valve
;       (May not be that accurate)
410     cal     V15=0.0266*('V3'*'V3')+(1.0418*'V3')

;       Calculates the Valid Inputs of Water into the D2 Area
420     cal     V16='V1'+'V2'+'V14'+'V15'

;       Calculates the Valid Outputs of Water from the D2 Area
430     cal     V17=('V4'-'V5')+'V11'+'V9'+'V10'+'V8'+'V12'+'V13'

;       Calculates the Amount of Effluent going into the Acid
;       Sewer (Input-Output)
440     cal     V18=('V16'-'V17')

441     ;Make sure the flow into the sewer is not negative

445     if      ('V18'<0)
446     cal     V99=0
447     else
448     cal     V99='V18'
449     endif

449     cal     V18='V99''>D2eff';449    hdbupdate d2eff,'V18'

450     rval    A1='V16'        ;Inputs to the D2 Area
460     rval    A2='V17'        ;Outputs from the D2 Area
470     rval    A3='V99'        ;Effluent Flow to Acid Sewer
480     rtime   tim             ;Time the reading was taken

481     rval    A4='V1'
482     rval    A5='V2'
483     rval    A6='V14'
491     cal     V20='V4'-'V5'
484     rval    A7='V20'
485     rval    A8='V11'
486     rval    A9='V9'
487     rval    A10='V10'
488     rval    A11='V8'
489     rval    A12='V12'
490     rval    A13='V13'
491     rval    A14='V15'
```

```
;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;
;                         Eop Bleaching Stage                      ;
;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;

565     format   (f10.2)
570     let     V20=41fc138 av  ;Lower Eop Shower Flow Rate
580     let     V21=41fc139 av  ;Upper Eop Shower Flow Rate
590     let     V22=41fc057 av  ;Eop Filtrate to Do Repulper
600     let     V23=41fc126 av  ;Dilution Water to Eop Tower
630     let     V24=41FC128 av  ;Pulp Flow Rate to Washers
640     let     V25=41YP172 av ;Pulp Consistency to Washers
645     let     V26=41lc130-op-ctl av  ;Valve pos for hot water lvl ctrl
647     let     V27=59lc453-op-ctl av  ;Valve pos for filt to mach. room

649     rval    U28='V27'
651     rval    Z20='V20'
652     rval    Z21='V21'
653     rval    Z22='V22'
654     rval    Z23='V23'

;       This Calculation Determines the Flow of Water Leaving the
;       Eop Area with the Pulp
650     cal     V28=('V24'*('V25'/100)/0.124)-('V24'*('V25'/100))
655     rval    Z24='V28'

;       Calc performs the amount of water that enters the Eop Washer
;       with the Pulp
660     cal     V29='V24'*(1-'V25'/100)
661     rval    Z25='V29'

;       Calculates the amount of hot water used for level control
;       (May not be that accurate)
;665    cal     V30=(0.0322*'V26'*'V26')+(1.21*'V26')
;666    rval    Z26='V30'

;       Calculates the amount of Eop filtrate going to the machine room
;       (May not be that accurate)

668     seldef  '41245M' > 0
668     let     V7=59lc453-op-ctl av,s
668     cal     V31=(0.0096*'V7'*'V7')+(1.11*'V7')-2.3588
format (I3)
669     if      ('41245m'=0)
669     cal     V31=0
669     endif

        format (f10.2)
671     rval    Z27='V31'

;       Calculates the Valid Inputs of Water into the Eop Area
680     cal     V32='V20'+'V21'+'V29'    ; +'V30'
```

```
;        Calculates the Valid Outputs of Water from the Eop Area
690      cal     V33='V22'+'V28'+'V23'+'V31'

;        Calculates the Amount of Effluent going into the Caustic
;        Sewer (Input-Output)
700      cal     V34=('V32'-'V33')

701      ;Make sure the flow into the sewer is not negative

705      if      ('V34'<0)
706      cal     V1=0
707      else
708      cal     V1='V34'
709      endif

449      cal     V18='V1''>eopeff'
;700     hdbupdate eopeff,'V34'

710      rval    Z4='V32'          ;Inputs to the Eop Area
720      rval    Z5='V33'          ;Outputs from the Eop Area
730      rval    Z6='V1'          ;Effluent Flow to Caustic Sewer


;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;
;                        Dn Bleaching Stage                         ;
;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;

870      format  (f10.2)
880      let     V35=41fc229 av  ;Lower Dn Shower Flow Rate
890      let     V36=41fc230 av  ;Upper Dn Shower Flow Rate
920      let     V37=41fc227 av  ;Caustic flow rate
930      let     V38=41FC224 av  ;Dilution Water to Dn Washer
940      let     V39=41FC223 av  ;Pulp Flow Rate to Washers
950      let     V40=41NC225 av  ;Pulp Consistency to Washers
900      let     V41=41lc239-op-ctl av  ;Contrl valve opening for hot
water

;        This Calculation Determines the Flow of Water Leaving the
;        Dn Area with the Pulp
960      cal     V42=('V39'*('V40'/100)/0.118)-('V39'*('V40'/100))

;        Calc performs the amount of water that enters the Dn Washer
;        with the Pulp
970      cal     V43='V39'*(1-'V40'/100)

;        Calculates the amount of hot water used for level control
;        (may not be that accurate)
;980     cal     V44=(0.0349*'V41'*'V41')+(0.5619*'V41')

;        Calculates the Valid Inputs of Water into the Dn Area
990      cal     V45='V35'+'V36'+'V43'      ; +'V44'

;        Calculates the Valid Outputs of Water from the Dn Area
1000     cal     V46='V42'+'V38'-'V37'/60

;        Calculates the Amount of Effluent going into the Caustic
;        Sewer (Input-Output)
```

```
1010     cal      V47=('V45'-'V46')


705      if       ('V47'<0)
706      cal      V1=0
707      else
708      cal      V1='V47'
709      endif

449      cal      V18='V1''>Dneff'
;1010    hdbupdate dneff,'V47'

1020     rval     Z7='V45'          ;Inputs to the Dn Area
1030     rval     Z8='V46'          ;Outputs from the Dn Area
1040     rval     Z9='V1'           ;Effluent Flow to Caustic Sewer
1041     rval     B1='V35'
1042     rval     B2='V36'
;1043    rval     B3='V44'
1044     rval     B4='V43'
1045     rval     B5='V42'
1046     cal      V20='V38'-'V37'/60
1047     rval     B6='V20'

;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;
;                       Do Bleaching Stage                        ;
;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;

870      format   (f10.2)
880      let      V48=41fc054 av   ;Do Lower Shower Flow Rate
890      let      V49=41fc053 av   ;Do Upper Shower Flow Rate
900      let      V50=41ft306 av   ;Flow of pulp to ClO2 mixer
910      let      V51=41nt307 av   ;Consis. of pulp to ClO2 mixer
930      let      V52=41yp043 av   ;Consis. of pulp to Do Washer

931      rval     Z30='V48'
932      rval     Z31='V49'
;933     rval     Z40='V51'
;934     rval     Z41='V50'

;        Determines if the fibre salvage tank is adding to the flow into
;        the Do Washer.

001      let      V1=41fc503 av   ;Flow of fibre
002      let      V2=41nc506 av   ;Consis of fibre flow
003      let      V3=41hs516 av   ;Valve to Do Tower

;        Note that WinMops shows that the valve is only open if all the
;        other valves are closed around this area.

004      if       ('V3'>0)
;        assume the flow is all water (Consis < 1.0 mostly)
005      cal      V4='V1'
006      else
007      cal      V4=0
008      endif

;        This Calculation Determines the Flow of Water Leaving the
```

```
;       Do UPFLOW tower with the Pulp

;       This value was used because cons. meters are unreliable
;960    cal     V53=('V50'*(9.97/100)/(2.40/100))-
('V50'*(9.97/100))+'V4'

960     cal     V53=('V50'*('V51'/100)/('V52'/100))-
('V50'*('V51'/100))+'V4'
961     rval    Z33='V53'
;962    rval    Z98='V50'
;963    rval    Z97='V52'

;       Calc performs the flow of fibre that enters the Do Washer
970     cal     V54=2.40/100*'V53'/(1-2.40/100)

;       Calculates the amount of water leaving the Do Area
980     cal     V55='V54'*(1-0.133)/0.133
;       0.133 is cons. of pulp leaving Do Washer
981     rval    Z34='V55'

;       Calculates the amount of  hot water used for level control
;982    let     V56=41lc045-op-ctl av  ;Cntrl vlv % open
;985    cal     V57=(0.0322*'V56'*'V56')+(1.21*'V56')
;986    rval    Z35='V57'

;       Calculates the Valid Inputs of Water into the Dn Area
990     cal     V58='V48'+'V49'+'V53'     ;+'V57'

;       Calculates the Valid Outputs of Water from the Eop Area
;       Note that there is some flow going to lime slurry tank, but that
;       just comes back and enters the sewer line.
995     let     V25=41fc042 av  ;Dilution water from Do filt to tower
1000    cal     V59='V55'+'V25'
1001    rval    Z36='V25'

;       Calculates the Amount of Effluent going into the Acid
;       Sewer (Input-Output)
1010    cal     V98=('V58'-'V59')

705     if      ('V98'<0)
706     cal     V1=0
707     else
708     cal     V1='V98'
709     endif


449     cal     V18='V1''>Doeff'
;1010   hdbupdate doeff,'V98'

1020    rval    Z10='V58'        ;Inputs to the Eop Area
1030    rval    Z11='V59'        ;Outputs from the Eop Area
1040    rval    Z12='V1'        ;Effluent Flow to Acid Sewer

1050    let     V1=41fc010      ;ClO2 Addition
;1051   rval    Z43='V1'
```

```
;+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
;                          Machine Room Effluent Calculations
;+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

02      tbas    1       ;Sets the base time at 1 minute
03      tlen    240     ;Sets the length of the reading

04      tstart  1       ;Takes the reading starting at the input time

10      let V1=59nc035 av       ;Hi-D Consis. (%BD)
20      let V2=59nc045 av       ;Hi-D Consis.
30      let V3=59fc039 av       ;Flow Rate from Hi-D (L/s)
40      let V4=59fc049 av       ;Flow Rate from Hi-D
50      let V5=41yp333 av       ;Flow into Hi-D (ADt/d)
60      let V6=59adl561avg av   ;Consis. of final pulp (%AD)
70      let V7=59FT011 av       ;White Water to Bleach Plant (L/s)
80      let V8=59ft830 av       ;Mill Water Into Machine Room (L/s)
90      let V9=59ft835 av       ;Hot Water Into Machine Room (L/s)
100     let V10=pr59drying av   ;Evaporation Losses of Steam (kg/h)
110     let V12=23ft438 av      ;White Water to Wood Room (L/s)
115     let V13=pr59deprod-cv-cal av ;Pulp Production Rate (ADt/d)

;       Calculate the flow of water into the Hi-D's with the pulp

120     cal V14='V5'/24/3600*1000
130     cal V15='V14'*0.1
140     cal V16='V14'-'V15'

151     if      (('V3'==0) & ('V4'==0))
152     cal     V17=0
153     else

154     cal     V17=('V16'-0.10*'V16')/0.10        ;0.10 is Consis. of
pulp into Hi-D's
155     endif

;       Calculate the amount of water leaving with the final product

160     cal V18='V6'*0.9/100             ;Consis of pulp converted to %BD
170     cal V19='V13'/24/3600*1000*(1-'V18')  ;Water leaving in pukp
(L/s)

;       Convert Steam evap from kg/h to L/s

175     cal V23='V10'/3600

;       Calculate the valid inputs

180     cal V20='V17'+'V8'+'V9'

;       Calculate the valid outputs

190     cal V21='V19'+'V7'+'V23'+'V12'
```

```
;       Calculate the effluent flow (input - output)

200     cal V22=('V20'-'V21')

705     if      ('V22'<0)
706     cal     V1=0
707     else
708     cal     V1='V22'
709     endif

449     cal     V18='V1''>macheff'
;200    hdbupdate macheff,'V22'

210     rval M1='V17'
220     rval M2='V8'
230     rval M3='V9'
240     rval M4='V19'
250     rval M5='V7'
260     rval M6='V23'
270     rval M7='V12'
280     rval M8='V1'
290     rval M9='V10'
291
;+++++++++++++++++++++++++++++++++

02      tbas    1
03      tlen    30

04      tstart  1

;       Woodroom Flow

01      cal     V64=('V12'+30)'>woodeff' ; 30 L/s is cold water to
wodroom (approx)
;01     hdbupdate woodeff,'V64'
02      rval    W1='V64'

;       Sumps (Except Clearwater Sump Overflow)

01      cal     V65=80          ; Done by co-op students Aug 1997
02      rval    S1='V65'

;+++++++++++++++++++++++++++++++++

;       Total Effluent Calculation

;       Acid
01      cal V66='V99'+'V98'+'V64'

;       Caustic
02      cal V67='V34'+'V47'

;       General
03      cal V68='V22'+'V65'

;       Total
04      cal V69=('V66'+'V67'+'V68')'>neueff'
```

```
;04     hdbupdate neueff,'V69'

05      rval T1='V66'
06      rval T2='V67'
07      rval T3='V68'
08      rval T4='V69'
09
;++++++++++++++++++++++++++++++++

;       Other inputs and outputs of water to the mill

01      tbas    1       ;Sets the base time at 1 minute
02      tlen    60      ;Sets the length of the reading
03      tstart  61

04      let     V70=16fc101 av  ; Raw water flow to the mill
05      rval    T10='Z70'

10      let     V71=77ft089 av  ; Water to cooling tower
12      let     V72=77ft094 av  ; Cooling water recirc flow
14      let     V73=77fc093 av  ; Cooling water to dump condenser
16      let     V74=78fc354 av  ; Cooling water to surface condenser
17      cal     V77='V72'+'V73'+'V74'

445     if      ('V77'<1)
446     cal     V75=0
447     else
448     cal     V75='V71'-'V77'
449     endif

20      rval    T15='V75'       ; Cooling tower evap losses

30      rval    T20='V23'       ; Evap losses from machine room

50      tbas    1
52      tlen    60
53      tstart  1

60      let     V76=01yp103     ; Flow at neutralization chamber
62      rval    T25='V76'

;++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

;       Calculate the % of each of total raw water flow

10      tbas    1
20      tlen    60
30      tstart  1

40      let     V1=16fc101 av   ; Raw water flow (L/s)

10      tbas    1
20      tlen    1
30      tstart  1

50      cal     V2=('V22'/'V1'*100)'>avMach'
;50     hdbupdate avmach,'V2'
```

```
60      cal     V3=('V64'/'V1'*100)'>avWood'
;60     hdbupdate avwood,'V3'
70      cal     V4=('V47'/'V1'*100)'>avDn'
;70     hdbupdate avdn,'V4'
80      cal     V5=('V98'/'V1'*100)'>avDo'
;80     hdbupdate avdo,'V5'
90      cal     V6=('V34'/'V1'*100)'>avEop'
;90     hdbupdate aveop,'V6'
100     cal     V7=('V18'/'V1'*100)'>avD2'
;100    hdbupdate avd2,'V7'
110     cal     V8=(100-'V2'-'V3'-'V4'-'V5'-'V6'-'V7')'>avOther'
;110    hdbupdate avother,'V8'

;+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

;       Calculate the % of each of total neutralization chamber flow

10      tbas    1
20      tlen    5
30      tstart  1

40      let     V1=01yp103 av   ; Neut. Chamber flow (L/s)

10      tbas    1
20      tlen    1
30      tstart  1

50      cal     V2=('V22'/'V1'*100)'>avMachN'
;110    hdbupdate avmachn,'V2'
60      cal     V3=('V64'/'V1'*100)'>avWoodN'
;110    hdbupdate avwoodn,'V3'
70      cal     V4=('V47'/'V1'*100)'>avDnN'
;110    hdbupdate avdnn,'V4'
80      cal     V5=('V98'/'V1'*100)'>avDoN'
;110    hdbupdate avdon,'V5'
90      cal     V6=('V34'/'V1'*100)'>avEopN'
;110    hdbupdate aveopn,'V6'
100     cal     V7=('V18'/'V1'*100)'>avD2N'
;110    hdbupdate avd2n,'V7'
110     cal     V8=(100-'V2'-'V3'-'V4'-'V5'-'V6'-'V7')'>avOtherN'
;110    hdbupdate avothern,'V8'

;+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

;       Calculate the % of each of total effluent flow

10      tbas    1
20      tlen    1440
30      tstart  1

40      let     V1=17ft096 av   ; Effluent flow at partial flume (L/s)

10      tbas    1
20      tlen    1
30      tstart  1

50      cal     V2=('V22'/'V1'*100)'>avMachE'
```

```
;110    hdbupdate avmache,'V2'
60      cal      V3=('V64'/'V1'*100)'>avWoodE'
;110    hdbupdate avwoode,'V3'
70      cal      V4=('V47'/'V1'*100)'>avDnE'
;110    hdbupdate avdne,'V4'
80      cal      V5=('V98'/'V1'*100)'>avDoE'
;110    hdbupdate avdoe,'V5'
90      cal      V6=('V34'/'V1'*100)'>avEopE'
;110    hdbupdate aveope,'V6'
100     cal      V7=('V18'/'V1'*100)'>avD2E'
;110    hdbupdate avd2e,'V7'
110     cal      V8=(100-'V2'-'V3'-'V4'-'V5'-'V6'-'V7')'>avOtherE'
;110    hdbupdate        avOtherE,'V8'


[End of file]
```

Appendix E

Additional References

The following list of additional references is indicated to provide a list that could be used to help with research in the area of zero liquid effluent discharge and progressive system closure.

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