CRYSTALLIZATION OF MECHANICAL PULP MILL EFFLUENTS THROUGH HYDRATE FORMATION FOR THE RECOVERY OF WATER

by

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ABSTRACT

This work presents data toward the development of a new zero-liquid discharge (ZLD) system, the aim of which is to concentrate a liquid effluent thereby recovering process water. The crystallization technology used in this work is clathrate hydrate crystal formation. A screening of clathrate hydrate formers was performed and three were chosen, propane, carbon dioxide, and a 30-70 mol% propane - carbon dioxide mixture. Experiments were carried out with these substances in a vessel that was immersed in a temperature controlled bath. The effluent samples used in this study were generated at four pulp mills, an unbleached and a bleached thermo-mechanical pulp mill (TMP1, TMP2), a bleached chemi-thermo-mechanical pulp mill (BCTMP), and a combined bleached BCTMP/TMP mill (CTMP).

The aim of this work was two-fold. The prime objective was to study experimentally the formation of clathrate hydrate crystals in these effluents. Experiments were designed to measure: (1) The temperature and pressure conditions at which hydrates form in mechanical pulp mill effluent; (2) The induction time and the growth rate of crystal formation; and (3) The ability of this apparatus to concentrate the effluents *in-situ*. In addition, effluent characteristic tests were performed, and qualitative process characteristics were noted. A secondary objective was to perform a survey on the liquid effluents generated at TMP and CTMP mills. This survey focused on the type, concentration, source, and environmental impacts associated with the contaminants typically present in these effluents, on the current discharge regulations, and on the available treatment options.

It was determined that hydrate crystals can form in these effluents at temperatures above the normal freezing point of water. The measurements were compared with similar hydrate formation data in pure water. It was also found that the presence of impurities did not cause any appreciable change in the hydrate crystal pressure and temperature formation conditions with the TMP and CTMP effluent samples, but that the BCTMP effluent, which had a high electrolyte and organic content, did affect these conditions. It was found that the induction period and growth rate of hydrate crystals are dependent on the driving force and the prior history of the effluent. And finally, that some level of *in-situ* concentration was attainable with our apparatus.

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CHAPTER 1: Introduction

The 1982 report, "Our Common Future", written by the World Commission on Environment and Development clearly stated the need for the development of a sustainable environment, where this is defined as *development that meets the needs of the present without compromising the ability of the future*. This concept, according to Wrist (1993), has four broad principles in relation to the forest products sector: (1) Forestry practices must impart minimal impact on the ecosystem and assure a sustainable forest yield; (2) Within each major forest ecosystem a certain percentage of forest should be set aside as a preserve to protect biodiversity and maintain a representative pool of genetic material; (3) Manufacturing operations must be conducted so as to minimize the impact on the surrounding environment, with the long term objective to close as many of the systems as possible; and (4) The industry must assume a greater responsibility for the disposition of its products after use, e.g. recycling of waste paper products. The third principle, the integration of closed-cycle systems into pulp and paper mill operations, is relevant to the focus of this work.

Pulp production processes are classified as chemical, mechanical, or hybrid according to the technology that they utilize and the pulp yield they produce. Chemical processes (kraft and low-yield sulphite) have the lowest yield at 40 to 55%, mechanical (pressurized groundwood, PGW, and thermo-mechanical, TMP) have the highest at 85 to 95%, and hybrid processes have a 55 to 85% yield (Smook, 1992). The chemicals that are added to the digesters in the chemical processes aid in the degradation of the nonfibrous material in wood. The energy that is added to the refiners in the mechanical processes aid in defibrating the wood resulting in fibres that are literally torn apart. Hybrid processes utilize both chemicals and mechanical energy to produce pulp, e.g. high-yield sulphite (HYS) and chemi-thermo-mechanical (CTMP) mills (CTMP mills may also be classified as mechanical mills because of their high yields, between 80 to 90%). A rapid expansion in the utilization of high-yield mechanical and chemi-mechanical processes has occurred during the past several years (Leask, 1990). This change has partly resulted from the replacement of lowyield sulphite mills by high-yield mills in order to reduce the discharge of biochemically oxygen demanding substances into the environment.

The pulp and paper industry requires a large amount of water to run its unit operations and, as a result, generates a substantial volume of dilute aqueous effluent. According to Statistics Canada (1991) the paper and allied products industry discharges 30% of the total process water (calculated as water intake less water consumption) generated by industrial operations in Canada, including both the manufacturing and the mining sector. In modern mechanical mills approximately 90% of the organics and acutely lethal materials are removed during pulp washing. Therefore, the majority of the water pollution generated by the industry results from the pulp rather than the paper division (McCubbin, 1992). The liquid effluent streams that are typically generated by these mills are dilute aqueous solutions contaminated with organic and inorganic matter which is dissolved and/or suspended. The most common pollution parameters used to control the discharge of these effluents include total suspended solids (TSS), toxicity, and biochemical oxygen demand (BOD). In general, the TSS content results from fibrous matter, the toxicity is mainly attributed to naturally occurring extractive compounds that leach out of the wood during the pulping process, and the BOD load is generated from both fibrous matter and extractives. Until recently, limited information has been available on the characteristics and environmental impacts of mechanical pulp mill effluents (McLeay, 1987).

The conventional end-of-pipe treatment systems used to decrease the pollution load rely predominantly on sedimentation and biological degradation of the contaminants. These systems are capable of complying with the current discharge limits, but they may prove to be inadequate if future regulations become increasingly stringent, as is expected (Beaudoin et al. 1991; Colodey, 1993). Therefore, new and innovative zero-liquid discharge (ZLD), or closed-cycle systems are emerging. These ZLD systems are capable of recovering clean process water from the effluent allowing water to be recycled back into the mill, refer to Figure 1.1. Without a purification step, these effluents can not be reused because dissolved solids will accumulate within the unit operations and compromise both production and quality. Successful implementation of a ZLD system requires a two-fold approach. Firstly, water management strategies that increase the recycle of internal effluent streams, and minimize the volume of effluent generated must be incorporated. And, in parallel with these internal measures, a separation technology(s) which is capable of removing dissolved solids from the effluent is required. The main "environmental" advantage of a ZLD system is the elimination of any potential negative impacts that might occur as a result of continuously discharging an aqueous effluent into the local environment.

Separation technologies that have the potential to be used in a ZLD system include evaporation, membrane separation, and crystallization. These technologies



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are currently at different stages of development for implementation in the pulp and paper industry. There are two industrial scale ZLD systems operating in Canada. Both operate at bleached CTMP (BCTMP) mills and utilize evaporation as their separation technology (Fromson and Leslie, 1993; Arac, 1993). At present, evaporation is the only proven technology, however, both membrane separation and crystallization are considered to be viable options for the future. The work presented here will focus on a crystallization technology, in particular the clathrate hydrate concentration process.

The process which concentrates an aqueous solution by generating ice crystals followed by the physical separation and melting of the resulting crystals, is referred to as freeze concentration (Heist, 1979). The temperature at which liquid water forms ice will depend on the concentration and nature of the other compounds that are present in the solution. Clathrate hydrate concentration, a variant of freeze concentration, generates clathrate hydrates. These hydrates are ice-like crystalline non-stoichiometric compounds. They are formed from a mixture of water and at least one low molecular weight substance. There are over one hundred known compounds which can form these crystals including argon, dichlorofluoromethane (R-21), carbon dioxide, methane, and propane. Hydrate crystals can form at temperatures several degrees above the normal freezing point of water, thereby decreasing the energy requirements compared with the freeze concentration process. Experimental evidence to date has shown that *impurities are not included within ice or hydrate crystal*

The primary goal of this work is to experimentally investigate the formation of clathrate hydrates in effluents generated at TMP and CTMP mills to provide technical data for the subsequent pilot plant and commercial development of a clathrate hydrate concentration process. A secondary goal is to perform a survey on the liquid effluents generated at TMP and CTMP mills.

The specific objectives of this work are to: (1) Determine the type, concentration, source, and environmental impacts associated with the contaminants typically present in TMP and CTMP effluents, present the current discharge regulations, and compare the available treatment options; (2) Outline an effluent treatment selection procedure for TMP and CTMP mills based on the information collected during the survey; (3) Determine the characteristics of interest for the specific mill effluent samples used in this work; (4) Select suitable clathrate hydrate forming substances to be used in the experiments; (5) Qualitatively observe the clathrate hydrate crystal formation process; (6) Determine the minimum pressure, at a given temperature, that hydrate crystals will form; (7) Study the induction period and the growth rate of hydrate formation; and (8) Study the potential for *in-situ* concentration of the effluents.

In Chapters 2 and 3 a survey on the typical characteristics and environmental impacts of TMP and CTMP effluents, the current Federal effluent discharge regulations, and the available treatment options will be presented. Freeze concentration and clathrate hydrate concentration will be discussed in Chapter 4. The experimental apparatus, procedures and materials will be described in Chapter 5. The results and discussion will be presented in Chapter 6, and the conclusions and recommendations will be summarized in Chapter 7.

CHAPTER 2: Mechanical Pulp Mill Effluent I: Source of Pollutants and Characteristics

The first three sections in this chapter present background information required to determine the characteristics of effluents generated at TMP and CTMP mills. The first section will outline the major unit operations and chemicals that are used in the TMP and CTMP processes, and the second will give a general introduction into the composition of wood, the raw material. The third section will define the common water pollution parameters in which contaminants are grouped based on their potential environmental impacts (these parameters will be used throughout this work). The fourth section will discuss the type of contaminants that originate from the raw material, the point source from which individual effluent streams originate throughout the processes, and the effect that certain pulping practices have on the concentration of the contaminants. And the fifth section will summarize the typical characteristics of untreated TMP and CTMP effluents.

2.1 Pulp Production

Pulp mills receive wood chips from local sawmills and/or whole logs directly from logging companies. This wood may be processed within a few days or stored for several months (sometimes longer) prior to use. The whole logs that are received must be debarked and chipped before being pulped in a TMP or CTMP mill.

2.1.1 Debarking

There are two types of debarking equipment those that use water, such as wet

drums and hydraulic jets, and those that do not, for example, dry drums and mechanical debarkers. The wet debarkers produce a "wet" waste which must be dewatered before it can be used as fuel by on-site hog fuel burners. The dry debarkers, on the other hand, produce a dry waste which can be sent directly to the hog fuel burners.

2.1.2 TMP and CTMP Processes

Figure 2.1 shows a simplified flow diagram of the TMP and CTMP processes. The first step in a TMP process is to wash the wood chips in washers which remove grit, sand, and tramp metal based on the differences in their specific gravity and size. The clean chips are placed in a presteaming vessel in which they are softened by pressurized steam. This thermal pretreatment results in a higher strength pulp by softening the lignin to reduce the damage of the long fibre component during mechanical defibration. The chips are defibrated, torn apart to produce a pulp, in one, or more, consecutive disc refiners in which the chips pass between two serrated plates, one, or both, of which are rotating. These refiners operate under pressure at temperatures over 100 °C (McCubbin, 1992). The pulp that is generated is screened to remove the oversized material with coarse screens (which remove knots, slivers, and unground pieces of wood) and fine screens (which remove fibre bundles and other small particles that are up to four times larger than the average fibre length). The pulp which has a consistency around 0.5% is then dewatered to a consistency between 3 to 14% depending on its end-use (McCubbin, 1983).

The CTMP process is similar to the TMP process, but the former impregnates the wood chips, on a dry wood basis, with a 1 to 5% sodium sulphite (Na_2SO_3)

FIGURE 2.1: Simplified Flow Diagram for TMP and CTMP Market Pulp (Branion, 1990)



solution (Smook, 1992). The impregnation occurs in the presteaming vessel, i.e. prior to preheating and refining. The addition of sulphite increases the quality of the pulp as compared to pulp generated by the TMP process, but it also decreases the pulp yield by 5 to 10%. Pulp quality is enhanced because sulphite decreases the temperature at which lignin softens thereby aiding in fibre separation and increasing the long fibre fraction. A further removal of extractives in the pulp can be accomplished by the addition of surface active agents which improve water absorption properties and pulp brightness.

2.1.3 Bleaching

There are two approaches in the chemical bleaching of pulp. The first is to remove the lignin, and the second is to selectively destroy some of the chromophoric groups in the pulp. The latter approach, referred to as brightening, is used with highyield mechanical pulps, i.e. TMP and CTMP. The brightening of these pulps is performed by the addition of a reducing agent, an oxidizing agent, or a combination of the two. The most common commercially used brightening chemicals are sodium hydrosulphite (Na₂SO₄) as a reducing agent, and hydrogen peroxide (H₂O₂) as an oxidizing agent (Smook, 1992). Alkali and chelating agents are added to peroxide brightening units (McCubbin, 1992). The alkali controls the pH and the chelating agent binds to the metal anions present in the pulp that accelerate the catalytic decomposition of peroxide. The most commonly used chelating agent is diethylenetriamine-pentaacetic acid (DTPA).

2.2 Wood Chemistry

The wood species primarily used include the softwoods pine, spruce, fir and hemlock, and the hardwoods birch, aspen, poplar, and maple (McCubbin, 1983). Wood, on a dry weight basis, contains about 60 to 80% polysaccharides (cellulose and hemicellulose), 20 to 30% lignin, and 1 to 5% extractives. Cellulose accounts for about 45% of the wood on a dry weight basis and is a strong, alkali-insoluble carbohydrate. Lignin compounds are hydrophobic, acid-insoluble aromatics located mainly between the wood fibres. They give a tree its structural rigidity.

The extractives include a large number of neutral solvent-soluble extracelluar chemical compounds. The extractive content, i.e. the composition and concentration, varies from species to species and may therefore be used as a fingerprint for the different species. Extractive compounds can be divided into four classes (Sjöström, 1993). These include: (1) Terpenoids and steroids, e.g. resin acids, juvabione compounds, sterols and diterpene alcohols; (2) Fats and waxes, e.g. fatty acids; (3) Phenolic constituents, e.g. lignans; and (4) Inorganics, e.g. metal salts. Extractives are present at specific sites in a trees structure (Sjöström, 1993). For example, resin acids are located in resin canals and fats and waxes are encapsulated in parenchyma cells. The extractives that are present in resin canals are more easily dispersed during pulping than those found in the parenchyma cells. As a result, wood species like Scots pine with 70% of its extractive content present in resin canals will, in general, produce a more toxic effluent than Norway spruce which has only 45% of its extractive content present in resin acid canals (Sjöström, 1993).

2.3 Effluent Discharge Parameters

Because there is a large number of different contaminants present in the liquid effluent the contaminants are grouped according to their environmental impacts. The water pollution categories that are of prime concern to the pulp and paper industry include solids concentration, oxygen demand, and toxicity. The effluent parameters used to regulate these pollution categories include: (1) total suspended solids (TSS); (2) biochemical oxygen demand (BOD); (3) acute and sub-lethal toxicity tests; (4) adsorbable organic halogens (AOX); and (5) dioxin and furan concentrations. The last two parameters, which include the organochloride compounds, will not be addressed here because, in general, TMP and CTMP mills do not practice chlorine bleaching.

2.3.1 Solids

Solids can be categorized as dissolved or suspended particles. The latter can be further categorized as either settleable or non-settleable. Non-settleable suspended solids are usually colloidal or near colloidal in size and can not be removed by sedimentation whereas the settleable portion can (Smook, 1992). The dissolved solids content of an effluent is, in general, not regulated whereas the suspended solids content is. The concentration of total suspended solids (TSS) in an effluent is determined gravimetrically. The TSS load is defined as the total amount of suspended solids discharged per amount of pulp produced.

2.3.2 Oxygen Demand

A large number of organisms that live in aquatic environments depend on a certain level of dissolved oxygen (DO) in the water for their survival. The actual level

required by an organism is very species dependent, e.g. the minimum DO level required by trout is 4 mg/L (Peavy et al. 1985). The DO level in a natural body of water depends on the temperature and the salinity of the water, the rate at which oxygen is replenished (i.e. by surface aeration, aerated tributaries, and photosynthetic oxygen production by aquatic plants and algae), and the demand for oxygen by the oxygen consuming aquatic organisms. The DO level of natural waters at 20 °C is on average 9 mg/L (Smook, 1992).

Aerobic microorganisms, whose population is controlled by the availability of nutrients, can be found in almost any natural body of water. These organisms consume oxygen as they metabolize the available organic matter. An increase in the availability of organic matter will increase the population of these organisms and result in a decrease in the DO level. The increased oxygen demand placed on a body of water by the introduction of an external source of biodegradable organic matter can be determined by a BOD test. The BOD of an effluent stream is determined by placing a sample of the effluent and a culture of microorganisms in a nutrient solution for a specified amount of time, after which the DO level is determined. The time allotted for oxidation to occur is five days in North America and seven days in Europe. The BOD load, like the TSS load, is defined as the total amount of BOD discharged per amount of pulp produced.

2.3.3 Toxicity

The toxicity of a liquid effluent stream can be determined by measuring its ability to kill (lethal or acute toxicity) or interfere with the well being (sub-lethal or chronic toxicity) of an organism by some means other than oxygen deprivation. There are a large number of different bioassays that can be performed to determine the toxicity of an effluent.

The acute toxicity of an effluent can be determined by the median lethal concentration (LC) test. The LC50 test measures the effluent concentration that is required to kill 50% of a specified test species within a given period of time. Two commonly used test species are rainbow trout and *Daphnia magna*, the corresponding exposure periods are 96- and 48-hours respectively.

Another commonly used acute toxicity bioassay is the Microtox test which determines the inhibition concentration (IC) value (also referred to as the effective concentration (EC) value). This test measures light emitted by the bacterium *Photobacterium phosphoreum* before and after exposure to increasing concentrations of an effluent sample. The logarithm of the loss of light caused by the toxicity of an effluent sample is theoretically proportional to the logarithm of the concentration of that effluent sample. The IC50 (or EC50) test measures the toxicity of an effluent sample by determining the concentration at which half the light, 50%, of a standard amount of glowing reagent is lost.

It should be noted that the toxicity of an effluent increases as the LC or the IC value decreases, i.e. an effluent with an LC50 of 50% is more toxic than one with an LC50 of 80%. These acute toxicity tests are known to be ecologically unrealistic because they use short exposure times and are performed with high effluent concentrations, up to 100%. The use of high effluent concentrations does not allow for the mixing and dilution capabilities of a receiving water. Therefore, acute toxicity tests should only be used to rank the relative toxicity of an effluent compared with other effluents.

The results obtained from sub-lethal toxicity tests, which use more realistic effluent dilutions and longer exposure periods, more closely reflect what is actually occurring in the environment. The sub-lethal toxicity level of an effluent is more difficult to determine than the acute toxicity level because sub-lethal toxic impacts may be manifested in several different ways (as will be described in Section 3.2.1).

There are a large number of different bioassays that are used to determine specific sub-lethal toxic impacts. These include: (1) Body burdens resulting from the exposure of fish to compounds such as resin acids, fatty acids, and cholesterol can be determined by analysing the concentration of these compounds in fish bile. These results can then be used to measure the bioconcentration factor (BCF), i.e. comparing the concentration of resin acids in the bile with the concentration of resin acids in the effluent; (2) The impact that an effluent has on the growth and reproduction of a specific species can be determined from the inhibition concentration percentage (ICp) bioassay. This test calculates the concentration of an effluent that would cause a given percent reduction in growth and reproduction for a specified organism relative to a control group; and (3) The stress associated with exposure of an organism to an effluent can be determined by studying changes that occur within the biochemistry of an organism (biomarkers), e.g. the ability of an effluent to induce mixed function oxidase (MFO) enzyme activity in the liver of a fish. A change in MFO activity can be measured by determining the MFO activity of a group of fish exposed to an effluent and comparing this value to the MFO activity level of a control group.

2.3.4 Other Parameters

Other parameters that may be regulated on a mill to mill basis include i) the

pH, colour, temperature, and nutrient content of the discharged effluent; ii) the discharge of fish tainting compounds such as phenols, and low boiling hydrocarbons, resin acids, reduced sulphur compounds, aldehydes and ketones; iii) reduced nitrogen or sulphur compounds such as mercaptans which may result in an unacceptable taste and odour of the receiving water; and iv) the discharge of coliforms into waters that are classified with a bacteriological water quality standard, i.e., public beaches.

2.4 Source of Pollutants

The pollutant load generated by a mill will depend on the wood furnish, the specific process, the operating conditions, and the rate of water consumption. Aqueous effluent streams are generated throughout the mechanical pulping process (refer to Figure 2.1). The potential sources include wet debarkers, chip and pulp washers, screens, presses (plug screw feeders), brightening units, and hydrocyclone condensate (Suckling et al. 1993). The majority of pollutants in these streams, i.e., compounds contributing to the suspended solids, organic, and toxicity loads, originate from the raw material, the wood.

2.4.1 Raw Material

The compounds of most significance from a pollution prevention point of view are the extractive compounds. The extractive content in an effluent will vary with the wood furnish used, the wood storage conditions, and variations within a particular species, i.e. tree-to-tree, seasonal and geographical variations, the age of the tree, and the part of the tree that is being considered. The highest extractive content of a tree is in the bark. This is one reason that dry debarkers are more popular than wet debarkers (Swan, 1973).

The extractive compounds of most concern include resin acids, unsaturated fatty acids, sterols, diterpene alcohols, lignans and juvabione compounds (Carlberg et al. 1993; Walden and Howard, 1981; Wong et al. 1978; 1980; Swan, 1973). Up to 70% of the toxicity in mechanical pulp mill effluents have been attributed to resin acids (Environment Ontario, 1988). Juvabione compounds which have only been detected in fir species contain a juvenile hormone analog and are therefore similar in nature to insecticides (O'Connor et al. 1992). Another juvenile hormone analog of interest is lignan which has been isolated in hemlock (O'Connor et al. 1992).

Wong et al. (1978) determined that effluent produced from softwoods was more toxic than that produced from hardwoods, and that pine produces a more toxic effluent than a spruce/balsam furnish. The reasons being that hardwoods do not contain resin acids, and pine has a higher resin acid concentration than spruce (Swan, 1973). Walden and Howard (1981) reviewed a large number of studies and determined that resin acids accounted for the majority of the toxicity in mechanical pulp mill effluents, diterpene alcohols were intermediate contributors and the unsaturated fatty acids and juvabione compounds were minor contributors (refer to Table 2.1). Suckling et al. (1993) also found that resin acids appeared to be a significant contributor to the acute toxicity of simulated BCTMP effluent streams with the softwood radiata pine as the wood furnish.

O'Connor et al. (1992) determined that the acute lethal toxicity of simulated mechanical pulp mill effluents to both fathead minnows and *Ceriodaphnia* follow the order: white pine > balsam fir > hemlock > black spruce > aspen. The order for the chronic toxicity of these effluents to *Ceriodaphnia* was as follows: balsam fir >

TABLE 2.1:Compounds in Mechanical Pulp Mill Effluents that are
Toxic to Fish (Walden and Howard, 1981; Thakore and
Collins, 1989)

Chemical Compound	Contribution
Resin Acids Abietic, dehydroabietic, isopimaric, laevopimaric, palustric, sandaracopimaric, neoabietic, 7,15- isopimaric, 8,15-isopimaric	Major: M (SW) Major: D
Unsaturated fatty acids Oleic, linoleic, linolenic, palmitoleic	Minor: M (SW,HW) Minor: D
Diterpene alcohols Pimarol, isopimarol, dehydroabietal, abietal	Intermediate: M (SW) Minor: D
Juvabiones Juvabione, juvabiol, ¹ '-dehydrojuvabione, ¹ '- dehydrojuvabiol, dihydrojuvabione todomatuic acid, 3 ¹ -deoxy,3 ¹ -hydro-todomatuic	Minor: M (HW)
Other neutrals Abienol, 12 E-abienol, 13-epimanool, 3',4- divanillyltetrahydrofuran	Minor: D

M: refers to mechanical pulping

- D: refers to debarking
- SW: softwood

HW: hardwood

hemlock > white pine > ~ black spruce ~ aspen. The compound primarily responsible for the low threshold of *Ceriodaphnia*, to balsam fir, was dehydrajuvabione. A breakdown of the important extractives found in the wood species used in these simulated effluents can be found in Table 2.2. The age and storage conditions of the wood furnish will affect the toxicity of an effluent, but not the TSS or BOD load (Wong et al. 1978; 1980). It is known that if wood is stored for longer periods of time the resin and fatty acid compounds will degrade. The extent of degradation will also

TABLE 2.2:	Extractive	Content	of	Several	Different	Wood	Species
	(O'Connor,	1992)					

Wood Species	Total Resin Acids (mg/L)	Free Fatty Acids* (mg/L)	Neutral Compounds** (mg/L)
White Pine (SW)	18.2 - 22.5	2.6 - 6.7	ND
Black Spruce (SW)	4.4 - 6.8	0.4 - 0.7	ND
Balsam Fir (SW)	0.1 - 0.85	ND	15.5
Aspen (HW)	0.7	0.7	ND
Hemlock (SW)			ND

* Subtotal including linoleic and oleic acids.

** Subtotal including juvabione and dehydrajuvabione.

SW: softwood

HW: hardwood

ND: Not Detected

depend on the storage temperature, and whether the wood is stored as chips or logs (Swan, 1973; Leach and Thakore, 1976; Wong et al. 1978; 1980). Resin and fatty acids can undergo isomerization, oxidation, and/or polymerization reactions if stored for a long enough time period. These changes in chemical make-up may result in a decrease in the toxicity of effluents generated with these denatured wood sources (Swan, 1973).

2.4.2 Point Source

The origin of individual effluent streams in the TMP and CTMP processes is shown schematically in Figure 2.1.

TSS. Suspended solids can originate in several of the TMP and CTMP unit

operations. Bark, trace metals and sand particles are found in the effluent streams generated by chip washers and wet debarkers. Fibrous matter, residual bark particles, and grit (produced by the rotating disks) are introduced as part of the effluent produced by pulp washers and dewatering units. Wong et al. (1978; 1980) found that the majority of the TSS originating in the wood during the TMP process was released in pulp washers situated after the first of two consecutive refiners. The lower pulp yield, i.e. fibre loss, that results from the addition of sodium sulphite in a CTMP process increases the TSS load of these effluents as compared to TMP effluents. Suckling et al. (1993) found that in a simulated BCTMP process the TSS loads of the effluent generated by the brightening units was higher than that generated in the refiners and released in the pulp washers.

BOD. The effluent streams with the highest BOD loads in both the TMP and the CTMP processes are generated in the wet debarkers, the refiners, and the brightening units (Wong et al. 1978; 1980; Suckling et al. 1993). The effluent produced by a wet debarker will increase the BOD load due to the high extractive content associated with tree bark (McCubbin, 1983), as will any residual bark that may be present after dry debarking. Stenberg and Norberg (1977) found that wood chips with a bark content of a few percent could increase the BOD load by 3 to 4 kg/tonne of pulp. The major source of BOD generated at an unbleached TMP mill will result from the soluble wood extractives. The other wood components, i.e. cellulose, hemicellulose and lignin, do not add to the BOD of TMP effluents because in their natural form they can not be readily utilized by microorganisms within the 5-day test period. However, the addition of sodium sulphite in the CTMP process aids in the solubilization of these components resulting in oligosaccharides, simple sugars, low molecular weight lignin derivatives, and hemi-cellulosic substituent groups, e.g. acetic acid. These derivative compounds, which can be readily metabolized by microorganisms, result in an increased BOD load in CTMP effluent as compared with TMP effluent. The BOD load generated by a mill is also affected by the use of oxidizing agents. Malinen et al. (1985) found that the addition of peroxide increased the BOD load of CTMP effluents by up to 40%.

TOXICITY. The toxicity of an effluent depends on the amount of solubilized extractive compounds, the metal content, and the presence of residual chemicals. The extractive compounds can be released in the effluent generated by wet debarkers or in the form of residual bark after dry debarking (if present), in the pulp washers situated after the refining operation, and in the effluent generated during brightening (if present). The addition of sodium sulphite and/or oxidizing agents will increase the toxicity of an effluent because these compounds increase the solubility of the extractives in water. As a result, mills that brighten their pulp with peroxides will generate more toxic effluents than those that do not, and CTMP effluent will have a higher toxicity value than TMP effluent.

Metals are known to be toxic. The metals that may found in mechanical pulp mill effluents can originate as trace elements introduced with the wood, e.g. copper, zinc, mercury and cadmium, or associated dirt, as impurities in the pulping chemicals, or from pipe and vessel walls. The presence of metals in these effluents does not result in a significant increase in the overall toxicity because metals require an acidic environment to be readily solubilized and both the TMP and CTMP processes operate under neutral to alkaline conditions.

The presence of residual amounts of process chemicals, i.e. brightening agents,

chelating agents, surface agents, and cooking chemicals, may also contribute to the overall toxicity of an effluent. The actual fate of these chemicals in the environment has not been well documented.

Wong et al. (1978; 1980) found that the majority of the toxic compounds originating from the wood during the TMP process were released in pulp washers situated after the first of two consecutive refiners.

Suckling et al. (1993) studied individual effluent streams from a simulated BCTMP process with the softwood radiata pine as the wood furnish. The streams included chip washer effluent, plug screw feeder pressate (psfp) prior to chip impregnation, psfp prior to primary refining, pulp psfp prior to secondary refining, pulp washer effluent, filtrate following DTPA treatment, and filtrate following peroxide brightening and washing. They found that effluent stream toxicity decreased as follows: psfp prior to chip impregnation > psfp prior to primary refining > filtrate following peroxide brightening and washing > pulp psfp prior to secondary refining > pulp washer effluent > chip washer effluent > filtrate following DTPA treatment. A relationship was found between the toxicity of these effluent streams and their resin acid concentration, with the exception of the brightening plant filtrate which had a higher toxicity than predicted. This increased toxicity could be a result of the residual peroxide remaining in the effluent. It should be noted that the presence of DTPA did not seem to have any significant affect on effluent toxicity.

2.4.3 Other Factors

The process operating conditions and the rate of water consumption will both affect the pollutant load of an effluent generated at a TMP and a CTMP mill. Wong

et al. (1978; 1980) found that the BOD load increased slightly with higher steaming pressures as a result of increased yield loss, but that this did not have an appreciable effect on toxicity, and that neither toxicity nor BOD were affected by small changes in pretreatment times. However, they postulated that with significant increases in pretreatment times the BOD would increase. Several researchers have found that the BOD of TMP effluents increased significantly with operating temperatures above 120 °C (Idner and Norberg, 1976; Stenberg and Norberg, 1977; Järvinen et al. 1980). A similar result was found for CTMP effluents by Malinen et al. (1985) who determined that BOD increased with higher pretreatment temperatures but was not significantly affected by an increase in pretreatment time. Increasing the energy input during the refining stage of a TMP process has had varying results. Idner and Norberg (1976) found that the BOD increased, whereas Stenberg and Norberg (1977) could not find any correlation, and Wong et al. (1978) determined that neither an increase in energy input or a redistribution of this energy between the first and second stage refiners affected the toxicity.

The toxicity of an effluent is also dependent on the pH of the effluent because pH can influence the extent of ionization of toxic compounds, e.g. resin and fatty acids. The pH range that an effluent containing resin and fatty acids will be the least toxic is between 8 and 9.5, with the toxicity increasing with decreasing pH (Walden and Howard, 1981).

The typical water consumption rate for TMP and CTMP processes ranges from 16 to 150 m³/ODt of pulp (Novatec, 1987). However some of the newer mills are now approaching a rate of 10 m³/Adt (Cornacchio and Hall, 1988). The volume of water used by a mill will affect the toxicity but not the TSS or BOD load of an effluent. The reason being that toxicity is regulated based on concentration.

2.5 Summary of Effluent Characteristics

The effluent characteristics of interest include the BOD, TSS, toxicity, pH, temperature, resin acid concentration, fatty acid concentration and flowrate. Typical values of these characteristics for untreated TMP and CTMP mills are given in Table 2.3.

TABLE 2.3:	Untreated	TMP	and	CTMP	Pulp	Mill	Effluent
	Characteris	tics (Co	ornacc	hio and	Hall, 19	88; Ha	bets et al.
	1991; Kovac	s et al.	1992)				

Characteristics	TMP	CTMP
BOD5 (kg/ADt)	12 to 44	21 to 59
TSS (kg/ADt)	20 to 40	3 to 17
96 hr-LC50 Acute Toxicity (v/v)	1.3 to 35.3%	0.8 to 1.8%
pH	5 to 9	7 to 9
Temperature (C)	35 to 40	35 to 70
Total Resin Acids (mg/L)	2 to 21	26 to 559
Total Fatty Acids (mg/L)	0.3 to 6.4	55 to 69.5
Flow Rates (m ³ /ADt)	10 to 150	20 to 30

Summary. The majority of the effluents generated by TMP and CTMP mills will contain suspended solids (colloidal and particulate matter), extractive compounds, lignin, cellulose and hemicellulose fragments, some low molecular weight compounds, metals and some residual chemicals. Of these compounds the extractives are of most concern from a pollution prevention point of view.

The type and concentration of contaminants that will be present in a particular effluent will primarily depend on the following: (1) The wood furnish, i.e. softwoods vs. hardwoods; and (2) The process, i.e. the presence of a debarker (wet vs. dry), the addition of pulping chemicals (TMP vs. CTMP), and the use of brightening agents (brightened vs. unbrightened pulp). The TSS, BOD and toxicity of an effluent depend on the following: (1) The type and concentration of contaminants that are present; (2) The operating conditions, i.e. temperature, residence time, steaming pressure, energy input, and pH; and (3) rate of water consumption. In general, the compounds that are primarily responsible for the TSS of an effluent result from the fibrous matter, the compounds responsible for an effluents toxicity result from the fibrous matter, and the compounds responsible for the BOD are generated from both the fibrous matter and the extractive compounds.

CHAPTER 3: Mechanical Pulp Mill Effluent II: Impacts of Pollutants, Discharge Regulations, and Treatment Options

The first section in this chapter will outline the important site-specific receiving environment data that are required to be able to determine the potential for specific impacts to occur at a particular site. The second section will describe the potential impacts associated with discharging effluents that have high TSS and BOD loads and/or are toxic, summarize the results of several short-term studies that have been performed with untreated TMP and CTMP mill effluents, and discuss the need for long-term, in-depth studies. The third section will present the current Federal effluent regulations and monitoring program requirements. And the fourth and fifth sections will describe and compare the conventional and zero-liquid discharge treatment technologies.

3.1 Receiving Environment

To determine the impacts that result from discharging an effluent into a particular ecosystem a thorough understanding of the following is required (Owens, 1991): (1) The chemistry and variability of the process so as to determine the effluent characteristics (refer to Chapter 2); (2) The history of the site and the upstream sources of pollutants so as to determine all the types of contaminants that are present; (4) The sensitivity of the local ecosystem to enrichment and toxicants by performing lab and field studies; and (5) The chemistry, available dilution, and turnover of the receiving waters.

The location of a pulp mill will determine the water quality of the receiving
waters, i.e. river, tributary, lake, or ocean, into which it discharges its effluent. A receiving water can be characterized by its pH, buffering capacity, temperature, colour, dissolved oxygen level, toxicity, taste, odour, nutrient concentration, productivity (population of microorganisms), and dissolved, suspended and floatable solids concentration (Smook, 1992; Beak, 1987). The characteristic of primary concern to the pulp and paper industry is pH because it can influence the extent of ionization of toxic compounds commonly discharged in TMP and CTMP mill effluents (refer to Section 2.4.3). The pH of the dilution water that is specified in the protocol of a toxicity bioassay may not be the same as the pH of the receiving water. Therefore to determine the "true" toxicity of an effluent the dilution water pH should be adjusted to that of the receiving water. The other receiving water characteristics that were mentioned above may also affect the overall impact that an effluent has on the environment. For example, a body of water with an unusually low dissolved oxygen level, e.g. 5 mg/L, will not be capable of assimilating the biologically degradable matter present in an effluent without having detrimental effects on the aquatic environment.

3.2 Impacts

There are a large number of potential impacts that may result if an effluent is discharged into the environment. The actual impacts will depend on the characteristics of the effluent, the extent of effluent treatment prior to discharge, and the receiving ecosystem at a particular site.

3.2.1 Potential Impacts

TSS. Suspended solids can interfere with the transmission of light in a receiving water. This may decrease the photosynthetic activity of algae, and disturb the predator-prey interactions of aquatic organisms that depend on vision. The discharge of suspended solids can also result in stress, secondary infections, and/or suffocation in fish (if enough material gets trapped within their gills). The settleable portion can cause problems if it forms a sludge blanket on the river, lake, or ocean bottom because this can cause the suffocation of bottom dwelling plants and creatures, as well as interfere with the growth of aquatic plants (if the blanket is not conducive to good root attachment). In the case where the blanket becomes thick enough anaerobic conditions may develop and undesirable organisms such as sludge worms may become prevalent. These anaerobic conditions could lead to the death or migration of desirable life forms such as shellfish due to a lack of oxygen, and the production of toxic and/or foul smelling gases, e.g. reduced sulphur compounds. The production of a gas may cause the sludge mats to float to the surface resulting in an unpleasant sight. The dilution of the non-settleable portion of the suspended solids by the receiving water is, in general, sufficient to ensure that they will have a minimal impact on the environment.

BOD. The major impact resulting from the discharge of BOD into the environment is a decrease in the dissolved oxygen level of a receiving water. In the extreme case, where the BOD load is very high, the level of dissolved oxygen can be depleted to such low levels that both motile fauna which do not leave the area and nonmotile fauna die. At lower BOD loads some aquatic organisms may suffer stress as a result of a lower than normal dissolved oxygen level. For example, a low dissolved oxygen level may decrease an organisms growth rate.

TOXICITY. The potential impact of discharging an acutely toxic effluent is death to those species for which the effluent is acutely toxic. The discharge of a sublethally toxic effluent may lead to a large number of potential impacts, refer to Table 3.1. The extent to which a sub-lethal impact is manifested will depend on the type and the concentration of the contaminants that are present. Sub-lethal toxic impacts can be revealed in one or more ways, within several different species, and at varying organizational levels. The organizational levels include communities, populations, whole organisms, and levels within an organism, i.e. the organ, tissue, cell, subcellular, and molecular levels.

TABLE 3.1:Sub-Lethal Effects (Owens, 1991)

	Sub-lethal Effects
1.	Body burdens: resulting from exposure to toxic compounds, these estimate the toxicant exposure which arises from direct bioaccumulation, food chain biomagnification, environmental transformation (or internal metabolism).
2.	Whole organism effects: including reproductive and early life stage responses.
3.	Within organism effects on histopathology: including pathological effects in either gross morphology (deformities) or histology (tissue structure).
4.	Within organism effects on physiology and biochemistry: due to stress, often referred to as biomarkers.

3.2.2 Short-Term Impact Studies

The studies presented here have examined impacts associated with the toxic compounds present in untreated effluent generated at TMP and CTMP mills. Specific studies on the impacts resulting from the discharge of TSS and/or BOD loads will not be discussed here because the conventional treatment systems, as described in Section 3.4.1, are capable of adequately decreasing both TSS and BOD.

The majority of studies performed on the toxic impacts associated with pulp mill effluent have concentrated on the effluent that is generated at kraft mills (McLeay, 1987). However, in the past three years several short-term laboratory studies have been performed with TMP and CTMP mill effluents. The bioassays that were used in the studies that are presented here were briefly described in Section 2.3.3.

Johnsen et al. (1993) exposed rainbow trout to several effluent dilutions (1:200, 1:400, and 1:1000) to determine the extent of bioconcentration of extractive compounds in the bile of these fish. It was found that the 1:200 effluent dilution was acutely toxic to trout, and as a result could not be used to determine sub-lethal toxic impacts. The fish exposed to the 1:400 dilution were placed in a reference water for a four-week recovery period after being exposed to the effluent for eight-weeks. The bile of the fish exposed to the 1:400 and the 1:1000 dilution had high extractive concentrations, in particular resin acids. Based on these findings it was expected that significant physiological responses would occur. However, this was not the case, as only slight differences could be noted between the exposed fish after a 4-week recovery period, and the control group. It was found that the fish were capable of decreasing the concentration of resin acids in their bile during the recovery period without any physiological impacts. These results imply that rainbow trout are able to adapt to exposure conditions and subsequently recover.

Martel et al. (1993) found that mechanical pulp mill effluent did not increase the mixed function oxidase (MFO) activity in the liver of rainbow trout based on a 96hour laboratory experiment. Suckling et al. (1993) determined from the Microtox test that all the individual effluent streams studied during a simulated BCTMP experiment were toxic. The IC50 values ranging from 0.012 to 21.5% v/v.

Carlberg et al. (1993) determined the toxicity of effluents from three different sources using the Microtox test (with the bacterium *Photobacterium phosphore*um) and the LC50 test (with the water flea *Daphnia magna*). The mills, which all used Norway spruce (*Picea abies*) as their wood source, included: (1) A combined groundwood/TMP mill in which the pulp was bleached with either hydrosulphite (A1) or peroxide (A2, A3); (2) A TMP mill with hydrosulphite bleaching (B); and (3) a combined high-yield sulphite/groundwood/TMP mill with hydrosulphite bleaching (C). All three effluents were found to be toxic to the bacterium. Their IC50 values ranged from 0.7 to 2.2%. The LC50 for the water flea was 3.5% for mill B effluent, 22.5% for mill C effluent, and 100% for mill A effluent, i.e. the effluent generated at mill A was not acutely toxic to this water flea species. In addition to performing the LC50 of mill B effluent with a bacterium and a water flea it was also performed with salmon and an algae (*Selenastrum*). The sensitivity of these species to this TMP effluent in decreasing order was: bacteria > salmon > algae > water flea.

Kovacs et al. (1992) performed several toxicity tests on fifteen different highyield mechanical pulp mill effluents that used various combinations of spruce, fir, and pine as their wood furnish. Results from the three TMP mills will be presented here. The test species used for the LC50 test were rainbow trout, fathead minnows, and *Ceriodaphnia affinis*. The IC50 test was performed with *Photobacterium phosphoreum*, and the IC25 was determined for fathead minnows and *Ceriodaphnia affinis*. The results from these tests can be found in Table 3.2.

TABLE 3.2:Acute and Sub-lethal Toxicity Data for Several Different
Aquatic Species Exposed to TMP Effluent (Kovacs et al.
1992)

Species	Toxicity Tests			
	LC50	IC50	IC25*	
Rainbow Trout	6 - 28% (96-h)			
Fathead Minnows	2 - 42% (48-h)		1.6 - 3.5%	
Water flea	1 - 28% (48-h)	0.01 - 0.39		
Bacterium		1.4 - 17%		

* These researchers considered a 25% reduction in the growth inhibition concentration to be an estimate of the threshold level causing sub-lethal toxicity.

The results in Table 3.1 show the sensitivity of the species used in this study to these TMP effluents. The acute toxicity, i.e. LC50 and IC50, decreases in the following order: *Ceriodaphnia* > minnows/trout > bacteria > algae. And the sub-lethal toxicity, manifested as growth rate, i.e. IC25, shows that *Ceriodaphnia* was more sensitive to these TMP effluents than fathead minnows.

Buckney (1978) studied a TMP effluent and found that it was highly toxic to

rainbow trout, golden perch, murray cod, mussels, daphnia, and shrimp. The 96-h LC50 values ranged from 7.2 to 48%. This study also determined several sub-lethal responses which included mussels closing their values so as to avoid the intake of the effluent, a darkening in the colour of the fish (which is a common response for distressed fish), and a decrease in the moult rate of shrimp with an increase in effluent concentration. Nestmann et al. (1979; 1983) found that the resin acids neoabietic (tested with yeast and bacteria) and 7-oxodehydroabietic (tested with yeast) exhibit mutagenic activity.

Summary. The results found in this section present evidence that untreated TMP and CTMP effluents can be acutely toxic to organisms that are typically found in receiving waters, and that they can result in sub-lethal toxic impacts within these organisms. Therefore, based on these short-term studies, it can be concluded that there is a necessity to implement effluent treatment systems at TMP and CTMP mills that generate toxic effluents so as to preserve the integrity of the environment. The selection of a treatment system that can prevent all of the potentially negative impacts from occurring within a particular ecosystem will depend on the results of long-term impact studies.

3.2.3 Long-term Impact Studies

Several researchers have noted that a general effects model and/or specific long-term impacts can not be inferred from short-term impact studies (Martel et al. 1993; Johnsen et al. 1993; Kovacs et al. 1992). The major limitation of short-term studies is their inability to consider the cumulative sub-lethal effects that may result from the continuous discharge of an effluent. Long-term, in-depth assessments that integrate chemical, toxicological, and biological data at all of the organizational levels are required to determine the actual impacts that will occur within a specific ecosystem. These studies should be performed in both the field and in simulated stream channels or pools, include organisms from different levels of the food-web, and be performed for a long enough period of time so as to include several life cycles of the test species being considered. In addition, the sub-lethal effects that a specific contaminant has on an organism, its food source and its predators, and the season, sensitivity, sex and stage of life cycle of the test organism should be determined (Lehtinen, 1991; Hall, 1992; Owens, 1991; Swanson, 1992). At present no in-depth, long-term ecosystem studies have been performed with TMP or CTMP mill effluent. However, this will soon change as a result of the new discharge regulations that have been set forth by the Federal government (refer to Section 3.3).

3.3 Federal Regulations

The trend of the federal government, spurred on by public opinion, has been to enforce more stringent discharge limits on pulp and paper mill effluents (Environment Canada and Department of Fisheries and Oceans, 1992a; 1992b). Aqueous effluent generated by the pulp and paper industry is regulated by the federal government, however, some provinces have additional requirements. The <u>Fisheries Act</u> which included the first Pulp and Paper Effluent Regulations (PPERs) was legislated in 1971, and amended in May of 1992.

The two major changes that were legislated in the May 1992 amendment of the <u>Fisheries Act</u> required that all of the pulp and paper mills in Canada meet the most current PPERs, and that they all implement an Environmental Effects Monitoring

(EEM) program (Department of Fisheries and Oceans, 1992). The EEM program is two-fold. The first part is a pre-design requirement which includes a description of the receiving environment and mill data (refer to Table 3.3.

TABLE 3.3:	EEM	Pre-Design	Requirements	and	their	Purpose
	(Coloc	ley, 1993)				-

Pre-design Requirements*	Purpose		
Delineation of effluent mixing zone	Integrity of effluent-exposed sites and reference sites		
Habitat inventory	Consistency between reference and exposed sites, identify confounding inputs (rivers, other sources), provide maps		
Resource inventory	Identification of sentinel and resource species		
Historical receiving environment information	Documentation of previous impacts, assist in sampling design		
Effluent quality	Evaluation of effluent quality in relation to PPER		
Mill History	Description of site history and current operations		

* Pre-design information is required once unless mill operations or environmental conditions change substantially.

The second part requires a mill to perform in-depth studies every three years to examine the effects that discharging its effluent is having on fish, fish habitat, and fisheries resources. The required studies and toxicological tests are outlined in Table 3.4.

TABLE 3.4:	EEM Studies	(Environment	Canada	and	Department	of
	Fisheries and	Oceans, 1992)				

Effects on Fish:	Adult fish survey (on selected species) to include: Length, fresh weight, age, gonad weight, egg size, weight of liver and hepatopancreas, external condition (obvious abnormalities, prevalence of lesions, tumours, parasites, etc.)		
Effects on Fish Habitat:	Invertebrate community monitoring to delineate the extent of habitat degradation due to organic enrichment or other forms of contamination, and to provide an evaluation of aquatic food resources for selected fish species.		
Effects on Use of Fisheries Resources:	 a) Tissue analysis (for the presence of chlorinated dioxin and furan congeners) b) Tainting evaluation 		
Toxicological Tests:	 a) Fish early life stage development test b) Invertebrate reproduction test c) Plant toxicity test d) In situ fish lethality e) Amphipod survival (sediment test) f) Invertebrate survival and growth (sediment test) 		

The major advantages of implementing the EEM program are its cyclical and site-specific components. By monitoring the environment every three years the longterm effects, if any, that result from the discharge of mill effluents can be determined. This knowledge can then be used to update the regulations. And, because the program is site-specific the government will be able to implement specific regulations, as required, for mills located in sensitive ecosystems.

The current Canadian PPERs are given in Table 3.5. The test protocol used by the Canadian pulp and paper industry for the determination of TSS and BOD can be found in the CPPA Standard Test Methods H.1 and H.2, respectively (CPPA, 1991a; 1991b). The current protocol used for the acute toxicity test, the 96-hr LC50 test performed with rainbow trout is specified by the <u>Fisheries Act</u> (Department of the Environment, 1990).

TABLE 3.5:Pulp and Paper Effluent Regulations (Department of
Fisheries and Oceans, 1992)

Parameter	Limits	
	Daily	Monthly
BOD5 (kg/ADt)	12.5	7.5
TSS (kg/ADt)	18.75	11.25
96 hr-LC50 Acute Toxicity (v/v)	100%	100%

3.4 Effluent Treatment Technologies

Conventional treatment systems can employ primary, secondary and tertiary technologies. Primary technologies include clarifiers, flotation cells and sedimentation lagoons which can physically remove 85 to 98% of the settleable portion of the suspended solids present in a pulp and paper mill effluent (Beaudoin et al. 1991). These units also reduce some of the BOD load. Secondary technologies utilize biological systems so as to remove dissolved organic material, resulting in a decrease in the BOD and toxicity of an effluent. The objective of tertiary technologies is to further decrease the TSS, BOD, and toxicity of an effluent. Examples of tertiary technologies include chemically assisted coagulation and granular filtration.

An alternative to conventional treatment systems are zero-liquid discharge (ZLD), or closed-cycle, systems which do not discharge any liquid effluent. These ZLD systems recover clean water from the effluent and recycle it back into the mill. It should be noted that the ZLD systems that will be discussed here require primary treatment of the effluent so as to decrease the TSS load.

3.4.1 Biological Systems

Biological systems, which can be either aerobic or anaerobic, decrease BOD and toxicity by utilizing microbes that metabolize the organic matter present in the effluent. These systems add nutrients, such as phosphorous and nitrogen, during the process to aid in this metabolism. Aerated lagoons (aerated stabilization basins), activated sludge, and biofilters are examples of aerobic technologies, whereas anaerobic contact reactors, upflow anaerobic sludge basins (UASB), fixed film reactors, combined reactors (fixed film/UASB), fluidized bed reactors, and anaerobic lagoons are examples of anaerobic technologies. The anaerobic technologies discussed here all require an aerobic polishing step to further reduce the BOD and toxicity levels. The two most commonly used technologies in North America are aerated lagoons and activated sludge, with either pure air or oxygen (Landry, 1993).

Several TMP and CTMP mills in Canada operate full scale aerobic and anaerobic treatment systems. In general, the mills utilizing aerobic systems are capable of consistently reducing the TSS, BOD, and toxicity loads to below the acceptable discharge limits (Black, 1990; Easton et al. 1992; Servizi et al. 1986; Strang, 1992), as are the mills which utilize anaerobic systems (Andersson et al. 1987; MacLean et al. 1990).

In the past three years several lab and pilot scale studies, some of which are presented here, have compared the ability of aerobic and anaerobic systems to treat TMP and CTMP effluents. The results from these studies conflict with one another, some advocate aerobic while others advocate anaerobic systems. Schnell et al. (1990) found that both aerobic and anaerobic systems were capable of reducing both the toxicity and BOD of a TMP effluent, but that the anaerobic systems were not able to decrease the toxicity to an acceptable level on a consistent basis. Lo et al. (1991) found that aerobic systems were more favourable than anaerobic systems in the treatment of CTMP effluent. Habets et al. (1990) found that an aerobic system was not able to reduce the pollutant load of a mixed TMP/CTMP effluent, whereas an anaerobic system was.

3.4.2 Zero-Liquid Discharge Systems

Several separation technologies, such as evaporation, freeze concentration, and membrane separation can be utilized in a ZLD system (Beaudoin et al. 1991; Gerbasi et al. 1993). The ZLD systems that utilize membrane separation and/or freeze concentration require an evaporation step to further concentrate the effluent. This is due to technical limitations with respect to the final water content that membrane separation and freeze concentration can attain.

The developmental stage at which these three technologies are at differs widely. Evaporation is a mature technology, and has been implemented on an industrial scale in a vast number of different industries. As a result, it is the separation technology that is utilized by both of the ZLD mills that are currently operating in Canada.

These two mills have implemented ZLD systems for very different reasons. The first ZLD mill was built by Louisiana-Pacific in Chetwynd, BC. This mill required a ZLD system because the company decided to site the mill as close as possible to the wood supply (thereby decreasing transport costs of the raw material) even though this site did not have a receiving water source. It should be pointed out that this mill initially used a freeze concentration process, however, due to operational problems these units were latter retrofitted to be used as evaporators (refer to Section 4.1.4). The other ZLD mill was built in Meadow Lake, Saskatchewan by Millar Western Pulp Ltd. This mill was first designed to use a conventional biological treatment system. However, this was not considered acceptable to the Saskatchewan government or the public. The reason being that effluent generated by the system would be "cleaner" than that of the receiving water and as a result would change the overall ecosystem (albeit in a "positive" way) (Sagert, 1993). A third mill, planned for Kitimat, BC, also proposes to operate a ZLD system that will utilize evaporation. The proposal is currently being assessed by the BC government (Orenda, 1991).

The use of membrane separation to produce potable water from sea water has been very successful, however, for the treatment of pulp mill effluent it is still at the lab-scale stage of development (Beaudoin et al. 1992; Zaidi et al. 1991). Freeze concentration has been successfully implemented in both the organics and the food industry. The capacity of the freeze units used by these industries are at least 20 times smaller than those required by the pulp and paper industry. The specific

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separation process that is being considered in this work is clathrate hydrate concentration. This process is a variant of freeze concentration and will be discussed in the next Chapter.

3.5 Comparison of Treatment Options

There are advantages and disadvantages associated with the implementation and operation of both conventional (biological) and ZLD systems. The major advantages associated with biological systems are: (1) They include the most cost effective treatment methods currently available; (2) They are capable of attaining the current discharge limits; and (3) They do not affect product quality. The disadvantages associated with the implementation and operation of biological treatment systems include: (1) The increasing concern about the long-term effects associated with discharging high nutrient loads into the environment, especially nitrogen and phosphorous; (2) The high sludge production, the associated removal/disposal costs, and the leachate problems that may occur if this sludge is land filled (these sludges concentrate the metals present in the effluent); and (3) The large land requirements.

The advantages of implementing a ZLD technology include: (1) There is no potential for negative impacts to occur in the aquatic environment because these systems do not discharge any liquid effluent; (2) The high costs associated with extensive and time consuming long-term ecosystem tests will not be incurred, e.g. the EEM program recently introduced by the Federal government; (3) ZLD mills will not be affected by future effluent discharge regulations, which may require the implementation of tertiary treatment technologies and/or more adequate disposal treatments for sludge (both of these will increase the cost of biological systems); (4) These mills are easier to site because they do not depend on a receiving water source, and they are more readily accepted by both the public and the regulatory bodies; and (5) They implement water conservation principles (this is of interest to mills located in areas where water is a commodity and has an associated cost). The main disadvantages of ZLD systems include: (1) Their high capital and operating costs (Gorgol, 1991); (2) The large energy requirements associated with these systems which pose an environmental disadvantage (which results from the environmental impacts associated with generating and transporting the energy required by these systems) (Galloway et al. 1991); (3) Their potential to decrease product quality as a result of water recirculation; (4) The implementation of a ZLD system may result in an increase in the air pollution load (due primarily to the incineration of the concentrate that is produced); and (5) There is a lack of long-term operating knowledge about these systems as they have been on-line for less than two years.

Wearing et al. (1985) found that the energy and associated equipment size requirements could be reduced substantially if mills were capable of decreasing their water-use to flow rates as low as 1.7 m³/tonne pulp. These low flow rates could also make it feasible to physically treat (recover the chemicals) and combust the concentrates that are generated by a ZLD system. It is, however, not likely that the effluent flow will get much below 10 m3/tonne pulp unless new more innovative internal recirculation technologies are developed (Cornacchio et al. 1988).

Several simulations have recently been performed in which the capital and operating costs of different ZLD systems have been determined. Paleologou (1993) found that if the effluent flow rate was reduced to less than 5 m³/tonne pulp the cost

of a ZLD system utilizing a membrane separation technology would be comparable to the costs associated with a conventional biological system. Jantunen (1993) simulated a TMP mill utilizing an evaporation/membrane ZLD system at an effluent flow rate of 6.9 m³/tonne pulp and compared the capital and operating costs with a secondary biological treatment system. The results showed that the capital cost of the ZLD system was greater than for the biological system, whereas the operating costs for the ZLD system were less than those required by the biological system (the author notes that these numbers are very dependent on the volume of water that is to be treated). Gerbasi et al. (1993) also compared the capital and operating costs of a simulated TMP mill with the costs for a conventional biological system. Three different ZLD systems were simulated, a biological/membrane system, a freeze concentration system, and an evaporation system, with the effluent flow rate varying from 5 to 20 m³/tonne pulp. In contradiction to Jantunen and Paleologou, Gerbasi et al. found that conventional biological treatment was the most economical treatment option in each case.

Summary. The main advantage of a ZLD system is the removal of all potentially negative impacts that may occur as a result of continually discharging a conventionally treated effluent. At present the major drawback of ZLD systems is their high capital and operating costs. However, as effluent flowrates decrease, discharge regulations become more stringent, and the ZLD technologies are further developed specifically for the recovery of water from TMP and CTMP effluents these costs will decrease relative to conventional systems. Therefore, it can be inferred that ZLD systems will become a viable effluent treatment option in the near future.

CHAPTER 4: Freeze Concentration and Clathrate Hydrate Concentration

The first section in this chapter describes the unit operations used in the freeze concentration process, reviews the literature on industrial scale applications, and discusses the differences between freeze concentration, evaporation, and membrane separation. The second section introduces clathrate hydrate crystal structure, and a literature review on the clathrate hydrate process and its applications. And the last section discusses the thermodynamics and kinetics of clathrate hydrate formation.

4.1 Freeze Concentration

Freeze concentration refers to the concentration of a solution by crystallization. This process concentrates a solution by generating ice crystals within the aqueous stream followed by the physical removal of these crystals from the solution and subsequent crystal melting (Heist, 1979). The terms freeze concentration and freeze crystallization are often used interchangeably in industry. However, freeze concentration is actually a type of freeze crystallization because the latter includes all the processes in which heat is removed from a mixture resulting in the crystallization of a component. Crystallization processes, including freeze concentration, are based on the formation of pure crystals when a substance changes from the liquid to the solid phase. During crystal formation the impurities present in the original solution will not be contained within the crystal structure. The temperature at which ice crystals form can be determined from freezing point depression data.

4.1.1 Basic Process

There are several process configurations which can be formulated to recover water by freeze concentration. A general process based on desalination is shown schematically in Figure 4.1. The first step in the process is to cool the original solution to a temperature close to its freezing point via a feed-heat exchanger. The solution is then fed into a crystallizer in which ice crystals are formed. These crystals, together with the concentrate, are pumped into a separator. A portion of the cold concentrate is removed and recycled back into the crystallizer to increase the overall conversion. The crystals are removed from the separator and fed into a melter in which they are melted upon contact with a hot refrigerant stream. Heat is removed from the crystallizer and transferred to the melter so as to increase the energy efficiency of this process. The resulting liquid refrigerant is recycled back into the crystallizer, and the product water is removed after exchanging heat with the feed in the feed-heat exchanger. The most important unit operations, when considering the economics of the overall separation process, are the crystallization stage (the formation of the crystals), and the separation and purification stage (the recovery of pure crystals) (Hahn, 1986; Heist, 1979).

4.1.2 Unit Operations

The formation of ice crystals occurs in the crystallizer, and proceeds in two steps: nucleation and growth. The crystals that are formed in the crystallizer may be coated by the impurities that are present in the effluent. Some of the concentrate may also be occluded (entrapped within the interstices) between individual crystals (Bozza et al. 1965; Maguire, 1987; Gorgol, 1991). Both these phenomena are important

FIGURE 4.1: Freeze Concentration Process used in the Desalination of Seawater (Englezos, 1993a)



because the degree to which they occur will determine the ease and extent of complete separation. The reason that the crystals are coated with these impurities is probably due to the low interfacial tension between the crystals and the concentrate (Tleimat, 1980). This surface attraction can be minimized if the surface area to volume ratio of each crystal is small, i.e. crystals are shaped like spheres rather than snowflakes, and both the surface tension and viscosity of the concentrated solution are low (Gorgol, 1991; Douglas, 1989; Barduhn, 1975). It is thought that the extent of occlusion can be minimized if large crystals are grown at a slow rate, thereby minimizing the driving force (Sloan, 1990a; Barduhn, 1975).

Significant progress in the understanding of ice crystal nucleation and growth has resulted from studies on the application of freeze concentration in both sea water desalination (Harriott, 1967; Vlahakis et al. 1972; Udall et al. 1965; Delyannis, 1967; Delyannis and Delyannis, 1970; 1973; 1976; 1978) and the food-industry (Stocking and King, 1976; Shirai et al. 1985; 1987). It has been postulated that the growth of these ice crystals is controlled predominantly by mass and heat transfer processes (Margolis et al. 1971; Shirai et al. 1985; 1987; Stocking, 1976) and to a lesser extent by the residence time in the crystallizer (Shirai, 1987; Smith et al. 1985).

The separation and purification of the crystals requires a separation unit, e.g. a wash column, belt press or centrifuge. The most commonly used separation units in desalination are wash columns. In these units, which operate by gravity or under pressure, clean water is sprayed onto the top of the ice crystal bed, the washed crystals are recovered by scraping them off the top, and the concentrate is collected from the bottom of the column.

The concentration of impurities by the removal of water will eventually result

in the concentrate interfering with the crystallization process by preventing effective separation or exhibiting an excessive freezing point depression. Therefore, it is necessary to select the extent of concentration required by the process at a level low enough such that these maximum limits will not be attained. To concentrate the effluent beyond this limit evaporation must be used.

4.1.3 Technology Systems

Freeze concentration systems can be divided into two groups, indirect (Heist, 1979; 1981; Hahn, 1986) and direct (TechCommentary 1988; Hahn, 1986; Emmermann et al. 1973; Ziering et al. 1974; Heist, 1979; 1981). The system that is chosen to concentrate a particular solution will depend on the characteristics of the solution and the end-use of the product water.

Indirect systems use a refrigerant to lower the solution temperature through a heat exchanger surface in a closed refrigeration cycle. The hot side contains the feed solution and the cold side contains the refrigerant. These systems, which are expensive when compared with the other freeze options, are commonly used by the food industry so as to avoid contamination of the product solution with the refrigerant.

In direct systems a heat exchange surface is not required because the refrigerant acts as the heat-transfer medium. There are two types of direct systems: (a) triple point (vacuum freezing), and (b) secondary refrigerant. The triple point systems use water as the refrigerant by operating the process at the triple point of water. As water evaporates it removes heat from the system allowing the solvent to crystallize. In secondary refrigerant systems the refrigerant is mixed with the solution and acts as the heat transfer medium by evaporation. The refrigerant that is used must be nearly insoluble in water such that it can be removed from both the product water and the concentrate, and be recycled back into the process. These systems are considered for applications where large volumes of water are to be treated and a slight degree of contamination is acceptable. The clathrate hydrate concentration process resembles a secondary refrigerant system.

4.1.4 Industrial Applications

Freeze concentration is currently used in the food industry and in the production of high purity organics. It is well suited to the food industry because it can separate water from a solution without the loss of flavour and aroma often associated with evaporation and distillation processes (Douglas, 1989; Chowdhury, 1988). However, commercial freeze units in the food industry process less than 190 L/min of solution. The freeze process is also used to purify chemicals, e.g. separate p-xylene from a mixture of petrochemicals (Douglas, 1989; Chowdhury, 1988; Heist, 1979). Its primary advantage to the organics industry is its ability to produce high purity products, in some cases, over 99% (Basta and Fouhy, 1993; Chowdhury, 1988).

Barduhn (1968; 1975) has reviewed the work on the application of the freeze process to the desalination of sea water. A commercial desalination unit designed and built by CBI industries in Yanbu, Saudi Arabia is capable of producing 110 L/min of potable water from a freeze concentration process (Douglas, 1989; HPD, 1990). Several researchers have performed small scale testing programs to study the technical and economical feasibility of using the freeze process to concentrate kraft pulping liquor and bleach plant effluent (Rousseau and Sharpe, 1980; Rousseau, 1981; Coleman, 1986). The concentration of black liquor was found to be technically viable but not economical because of the low cost of energy (Coleman, 1986).

A pilot plant freeze concentration unit was designed by HPD Inc. and built in Ontario at Tembec's BCTMP mill during 1991. Kenny et al. (1992) determined that the indirect freeze process used at this pilot plant could reduce the concentration of low molecular weight organics (C1 through C3), resin and fatty acids, the BOD and COD loads, and the electrolyte content in the recovered process water. However, the number of reported results were limited due to operational problems during the test period. The results from this pilot project and the lessons learned from CBI's desalination plant in Yanbu were used to design an industrial scale freeze concentration system. This system was designed by HPD Inc. and built in the fall of 1991 at Louisiana-Pacific Canada Ltd.'s (L-P) Bleached CTMP mill near Chetwynd, BC. Details of the effluent treatment process at the L-P mill are proprietary. However, a general outline of the original process is summarized here (Kelsey, 1990; HPD, 1990). The effluent is clarified, the primary sludge is collected, and used as fuel in the hog-fuel boilers. The clarified effluent enters one of four refrigeration units in which ice is formed. These units utilize an indirect freezing process with ammonia as the refrigerant. The slurry that is produced is pumped into a separator in which the ice is washed, scraped off, and melted before being pumped back into the mill.

This freeze process was designed to treat 4,000 L/min and to concentrate the effluent from 2% solids up to 10% which would approximately result in an 80% recovery of the water present in the effluent stream. The effluent was to be further concentrated up to 50% solids in an evaporation unit that was designed to use wasteheat from the refrigeration cycle. The mill was designed to reuse 75 to 80% of its

process water, the remaining 20% of this water was expected to be lost through evaporation during the drying of the pulp. The make-up water was to be supplied by on-site wells, as there are no other available water sources at the mill site. It was proposed that the concentrate be sold to kraft mills and used for energy and/or chemical make-up in their black liquor recovery boilers, or be incinerated at the mill site (Kelsey, 1990). It should be noted that Basta and Fouhy (1993) determined that the concentrate which would typically be generated by a ZLD system at a mechanical mill would be similar in elemental composition to kraft black liquor, and have a heat of approximately 9000 kJ/kg.

However, several problems with the freeze system built at the L-P mill limited the overall recovery of an adequate volume of clean process water. It was found that once ice started to form in the refrigeration units it was difficult to control the growth such that the whole system would not freeze up. Scale formation in the refrigeration unit was also noted. It was found that the wash columns could not adequately separate the ice crystals from the concentrate. This may have been partly due to the presence of colloidally suspended material which enhanced surface attraction and the degree of occlusion. As a result, the wash columns were replaced with belt-press units (Gorgol, 1992). However, the freeze system was still not capable of recovering more than 40 to 50% of the water present in the effluent (Arac, 1993). Due to all of these problems the mill converted to an evaporation system similar to that used by Millar Western's BCTMP-ZLD mill. However, based on the experience attained at the L-P mill it is believed that with more research freeze concentration has the potential to become a viable option for the future (Arac, 1993).

Some potential future applications of this process have been suggested by

Douglas (1989). These include the remediation of hazardous waste lagoons, the concentration of deep mine reject water, the recovery of process materials from ammunition plants, byproduct recovery from organic chemical and pharmaceutical waste streams, desalination, and the treatment of metal-plating facility wastewater in which the recovery of both valuable plating metals and water can be accomplished.

4.1.5 Comparison of Separation Technologies

Compared with other separation technologies the major advantage of a crystallization process, e.g. freeze concentration, is that at a given temperature and pressure only one component will crystallize and it will do so as a pure crystal. In addition, freeze concentration has several other specific advantages over both evaporation and membrane separation.

The freeze process has a potential energy savings compared with evaporation. Seven times more energy is required to evaporate water than to freeze it (6.008 J/mol vs 40.66 J/mol). However, this energy advantage is substantially reduced when a multiple effect evaporator is considered. Two other important advantages result from the low operating temperatures used in the freeze process. At these low temperatures, i.e. below room-temperature, a large portion of the volatile organics that are known to be present in TMP and CTMP mill effluents will be removed with the concentrate. In comparison, the high temperatures required for evaporation will volatilize these compounds such that they will be present in the recovered water, and as a result ZLD systems which utilize evaporation may require extra separation units, e.g. stripping columns (Burke, 1990). The low operating temperatures used by the freeze process will also decrease the potential for scaling and corrosion problems that can result from the presence of organic and inorganic salts in TMP and CTMP mill effluents. These problems become more prominent at higher temperatures, and as a result more costly materials will be required for the construction of the units used in evaporation.

Freeze concentration has two main advantages over membrane separation. These include: (1) The fouling problems associated with membranes which are exposed to solutions having high organic contents (Zaidi et al. 1991); and (2) The shortened life expectancy of a membrane exposed to phenols, bacteria, fungi, high temperatures, high or low pH values, and scale-forming compounds, e.g. calcium carbonate and calcium sulphate (McCubbin, 1992). In a recent study it has been determined that a ZLD system which incorporates reverse osmosis and ultrafiltration is technically feasible. The development of these technologies is ongoing (Paleologou et al. 1993).

Gerbasi et al. (1993) did a cost comparison between three closed cycle technologies and an aerobic treatment system. It was found that the capital and operating costs increased as follows: biological treatment < membrane separation < evaporation < freeze concentration. However, preliminary results from the freeze crystallization desalination plant in Saudi Arabia have shown that the freeze process can compete economically with membrane separation (Douglas, 1989). HPD Inc. which designs both freeze concentration and evaporation units has determined which of these two systems deals best with the various contaminants present in CTMP effluent (refer to Table 4.1). They found that the freeze process is suitable for most of the contaminants present in CTMP effluents with the exception of solids, and that evaporation does not deal well with the volatile compounds. In conjunction with this they also determined that biological systems are less expensive than evaporation which in turn is more economical than freeze concentration. However, if biological treatment is not acceptable and evaporation can not produce water of an acceptable quality then freeze concentration is a viable option (Gorgol, 1991). HPD Inc. have reported four potential applications: (a) CTMP, BCTMP, and Groundwood effluent; (b) Bleach plant effluent; (c) De-inking waste; and (d) Acid recovery.

TABLE 4.1:Removal Efficiency of Contaminants Typically Present in
CTMP Effluents by Evaporation and Freeze Concentration
(Gorgol, 1991)

Contaminant	Evaporation	Freeze Concentration		
Inorganics	High	High		
Light Organics	Low	High		
Volatile Acids	Low	High		
Fatty Acids	Medium	Medium		
Resin Acids	High	Medium		
Organic Sulphur	Low	High		
Fibre/Suspended Solids	High	Low		

4.2 Clathrate Hydrate Concentration

Clathrates, a type of inclusion compound, were first discovered by Sir Humphrey Davy in 1810, but their "practical" importance did not become evident until 1934 when it was discovered that clathrate hydrates were responsible for the plugging of natural gas pipelines. As a result, the majority of research has focused on limiting their formation. In the mid 1960's vast quantities of methane hydrates were found in the earth's crust. These natural hydrate formations have the potential to become very important energy sources in the future if an economical method to extract them can be found (Holder, 1988). On the other hand, these formations may result in a further warming of the atmosphere if the current atmospheric temperature increases sufficiently such that these hydrates decompose and release methane, a "Green House" gas (Sloan, 1990b).

4.2.1 Crystal Structure

Clathrate hydrate crystals are formed at suitable pressure and temperature conditions by the physical combination of water molecules and one or more hydrate forming compounds. The resulting inclusion compounds contain only water and the hydrate former. The cubic lattice like structures of these compounds are formed by the presence of strong hydrogen bonds between adjacent water molecules. These structures, without the presence of a hydrate former, are thermodynamically unstable. However, if hydrate formers occupy the interstitial vacancies of these cubic structures weak van der Waals type dispersion forces (between the hydrate former and water molecules) stabilize the structure.

The majority of hydrates form one of two structures, referred to as I (body centred cubic) or II (diamond lattice). Each of these structures contain two roughly spherical cavities with different diameters (refer to Figure 4.2). A unit cell of structure I is constructed from 46 water molecules and has 2 small (12-Hedron) and 6 large (14-Hedron) cavities, and structure II has 16 small (12-Hedron) and 8 large (16-Hedron) cavities formed from 136 water molecules (Sloan, 1990a). Each cavity can

FIGURE 4.2:

Cavities and Unit Cells for Clathrate Hydrate Structures (Sloan, 1990a)





contain only one guest molecule, however the number of cavities that are occupied in a hydrate vary with pressure.

4.2.2 Concentration Process

Hydrates can form at several temperatures well above 0°C. These high crystallization temperatures can result in an energy saving compared with freeze concentration. Another advantage of the clathrate process is the increased flexibility due to its dependence on pressure as well as temperature. Pressure, which has a negligible affect on the freezing point of water, can have a large impact on the temperature at which hydrates form. This "extra" process variable may lead to an increased ability to control the crystallization process. However, it will also increase the cost of operating the process and limit the use of hydrate formers that have high formation pressures (due to the energy loss that would result from attaining these high pressures).

The operations required for the clathrate concentration process are similar to those described for freeze concentration. There is, however, one additional operation: the recovery of the hydrate forming substance once the hydrates have decomposed. Refer to Figure 4.3 for a schematic of a conceptual clathrate hydrate concentration process implemented at a pulp mill.

This work will explore *in-situ* concentration and separation. The current procedure used in freeze and clathrate processes is to form crystals in a crystallizer and then move the crystal slurry to a separator. The concept of *in-situ* concentration is to control the crystal formation conditions in such a way that part of the separation step can be performed within the crystallizer unit. This process change could result

Clathrate Hydrate Concentration Process used in the Concentration of Mechanical Pulp Mill Effluent



in a decrease in both the capital and operating cost of the separation step.

4.2.3 Industrial Applications

The concentration of aqueous streams by clathrate hydrate concentration was patented by Glew (1962) and was also investigated by Werezak (1969). Formation of hydrate crystals in seawater was considered as the basis of a process to recover pure water. The process was demonstrated at a pilot plant stage (Knox et al. 1961; Barduhn, 1968; 1975; Tleimat, 1980) but never became commercial due to economic reasons. The application of the process has recently become of interest as a waste minimization operation as well as in the food product industry (TechCommentary, 1988; Heist, 1988; Douglas, 1989).

In the early 1960's research into the application of the clathrate hydrate concentration process to desalinate water was supported by the US Department of the Interior through the Office of Saline Water (OSW). During this time two pilot plants were built, one by the Koppers Company which used F-12 (Cl_2F_2) as the hydrating agent (Knox, 1961), and the other by the Sweet Water Development Company which utilized propane as the hydrating agent (Heem, 1965). One problem that both of these plants encountered was the difficulty in adequately separating the crystals from the concentrate. The crystals that formed were very compressible and difficult to wash using a wash column (Barduhn, 1968). The OSW withdrew their support for the pilot plants in 1968 due to the slow progress in process development (Barduhn, 1968). As a result, an industrial scale desalination unit that utilized the clathrate hydrate concentration process was never built. Rautenbach et al. (1978) determined that it was difficult to produce crystals of adequate size and shape at a

sufficient growth rate, and that the desorption of the hydrating agent(s) from both the concentrate and the recovered water may pose problems. This later problem is especially important in the production of potable water as some hydrating agents are toxic at low concentrations. However, this may not be a problem when recovering pulp mill process water because the quality requirements may not be as high. In 1985 a pilot plant which used a eutectic clathrate hydrate concentration process in which ice and sugar crystals were formed simultaneously (and separated by gravity) was built by the beet sugar refining industry (Heist, 1988). The results from this plant showed that if clathrate hydrate concentration replaced evaporation at several points within the process the overall cost of producing sugar would decrease.

4.3 Clathrate Hydrate Formation

Thermodynamic and kinetic data are required to fully understand the formation of clathrate hydrates. Thermodynamic experiments determine the conditions, i.e. temperature and pressure, at which hydrates will form in a specific system. And kinetic experiments determine the rate of hydrate formation.

4.3.1 Thermodynamics

The temperature and pressure at which hydrates will form in a crystallizer will depend on the type of hydrate former(s) that are used, and the chemical make-up of the solution that is to be concentrated. If these formation conditions, for a given system, are not available in the literature, they can be determined by performing equilibrium experiments. The resulting data points are used to generate phase equilibrium diagrams.

A partial phase equilibrium diagram is depicted in Figure 4.4. The points indicate experimental data for the propane - water system in the hydrate formation region determined by Kubota et al. (1984), whereas the lines are interpolations of these data. Line KL is the vapour pressure line for propane. Line AQ defines the locus of hydrate - vapour, (rich in propane) - liquid, (rich in water) phase equilibrium. At a given temperature the pressure that corresponds to a point on this line is the minimum pressure required for hydrate formation. Propane hydrates are formed at conditions corresponding to pressures and temperatures on the left of line AQ. The temperature corresponding to point Q is the maximum temperature at which propane can form hydrates. This point is called the upper quadruple point. At this point four phases namely, hydrate, vapour, liquid_w and liquid_n (rich in propane) coexist in equilibrium. Line AQ extends down to another quadruple point (not shown on the plot) at 273.15 K (0 °C). At this lower point hydrate, ice, vapour and liquid water coexist in equilibrium. Line QC defines the locus of hydrate - liquid, - liquid, condensed phase equilibrium. Propane hydrates are formed when the pressure and temperature correspond to a point on the left of line QC.

It is well known that the presence of impurities, also referred to as inhibitors (e.g. electrolytes and dissolved molecular species), in an aqueous solution will alter the location of the AQ line by depressing hydrate formation. In particular, at a given temperature, the equilibrium hydrate formation will be higher, or, at a given pressure, the equilibrium hydrate formation temperature will be lower as compared to pure water. For example, in Figure 4.4, the incipient hydrate formation conditions in a 2.5 wt% NaCl solution are shown. These experimental points are on the line A1Q1. The extent of deviation from the formation conditions with pure water


(line AQ) will depend on the type and concentration of the impurities that are present in the solution of interest.

4.3.2 Kinetics

The process of hydrate formation can be divided into two separate stages, nucleation and growth. The first stage involves the formation of hydrate nuclei and is often referred to as the induction period. The formation of nuclei is not well understood. The second stage, the growth period, commences after the nuclei have reached a critical size and are stable, at which point the liquid becomes turbid and the growth stage begins. This stage is more quantifiable than nucleation but it is still difficult to study. Pinder (1964) exposed the difficulties in studying the kinetics of hydrate formation. Some progress has been made since then. Englezos (1993b) has reviewed the literature on clathrate hydrates, including a summary of experimental and modelling studies on the rate of hydrate formation.

The induction time for the nucleation of gas hydrates was experimentally found to depend on the history of water (Vysniauskas and Bishnoi, 1983a; 1983b), stirring rate (Makogon, 1981; Englezos et al. 1987; Skovborg et al. 1993), and the degree of supercooling, i.e. the temperature difference between the experimental temperature and the equilibrium temperature at a given pressure (Glew and Hagget, 1968; Knox et al. 1969; Scalon and Fennema, 1972; Makogon, 1981; Vysniauskas and Bishnoi, 1983a; 1983b; Englezos et al. 1987; Skovborg et al. 1993). Correlations employing the degree of supercooling have been proposed for the growth of hydrate crystals (Glew and Hagget, 1968; Pangborn and Barduhn, 1970). Recently, mechanistic models have been proposed for the growth kinetics (Englezos et al. 1987).

CHAPTER 5: Experimental Section

The experimental objectives of this work were to: (a) Determine the characteristics of interest for the specific mill effluent samples used in the experiments (effluent characterization tests); (b) Observe the clathrate hydrate concentration process (qualitative process characteristics); (c) Determine the minimum pressure, at a given temperature, at which hydrate crystals form (pressure-temperature hydrate formation experiments); (d) Study the induction period and growth rate of hydrate formation (induction and growth rate experiments); (d) Study *in-situ* concentration with the effluents and various salt solutions (*in-situ* concentration experiments).

The first section in this Chapter discusses the effluent sources, and the hydrate formers that were used. The second section outlines the effluent characterization tests. The third section describes the experimental apparatus. And the last section presents the experimental procedures that were used.

5.1 Effluent Samples and Other Materials

Effluent samples were received from four different high-yield mechanical pulp mills in British Columbia. These included a sample of effluent generated by: (1) Fletcher Challenge's unbleached TMP line at Elk Falls (referred to as TMP1); (2) Howe Sound Pulp and Paper's bleached TMP line at Port Mellon (referred to as TMP2); (3) Quesnel River Pulp's combined BCTMP/TMP mill in Quesnel (referred to as CTMP); and (4) Louisiana-Pacific Canada Ltd.'s BCTMP mill in Chetwynd (referred to as BCTMP). Design parameters for these mills are given in Table 5.1.

Mills	Process Capacity (t/d)	Effluent Volume (m³/d)	Wood Species
TMP1	1400	170,000 (estimated)	hemlock, fir, whitewood
TMP2	600	20,000	hemball, fir, pine, spruce
CTMP*	950	17,000	pine, sp r uce
BCTMP	500	5,000	aspen

TABLE 5.1:Design Parameters of the Pulp Mills from which the
Effluent Samples Used in this Study were Generated

* The volume of BCTMP to TMP effluent in the effluent sample used in our experiments was approximately 2:1.

The types of chemicals that are generally added during the production of pulp at these four mills include the following: (1) The TMP1 mill adds sodium sulphite, sodium dithionite, peroxide, sodium hydroxide (caustic), DTPA, and epson salts (the TMP1 effluent stream also receives landfill site leachate, mill yard run-off, and effluent from a kraft specialty paper line which adds alum and Rozonsize (a refined lignin compound)), (Easton, 1992; 1993); (2) The TMP2 mill adds sodium sulphite, talc, DTPA, sodium hydrosulphite, sodium hydroxide, sodium silicate and peroxide (Ling, 1992); (3) The CTMP mill adds sodium sulphite, DTPA, sodium hydroxide, sodium hydrosulphite, sodium sulphite, and hydrogen peroxide (Jackson, 1992); and (4) The BCTMP mill adds sodium sulphite, sodium hydroxide, peroxide and XU82 (a chelating agent) (Morand, 1993).

Four concentrate samples, generated by evaporation in an open beaker under a fume hood, were also used in this work. It was attempted to concentrate these samples by seeding them with an ice cube and placing them in the freezer, but this was not successful. A 50 and an 85% concentrate (referred to as TMP2/50 and TMP2/85) were generated from a portion of the TMP2 effluent sample, i.e. the solution volume was reduced by 50 and 85% respectively. And a 50 and an 80% concentrate (referred to as CTMP/50 and CTMP/80) were generated from a portion of the CTMP effluent sample. In addition, a 1 and 5 wt% salt solutions were used. These solutions were prepared with deionized water and laboratory grade sodium chloride from Fisher Scientific. The appropriate amounts of salt were weighed using an analytical balance.

The hydrate formers selected for this study were: (1) propane (C_3H_8); (2) carbon dioxide (CO_2); and (3) a 30-70 mol% propane-carbon dioxide mixture. All three were Medigas industrial grade gases.

5.2 Effluent Characteristic Tests

The parameters chosen to characterize the effluent samples used in this study included electrolyte content, solids content, carbon content, colour and pH. The electrolyte, solids and carbon content of the effluents and concentrates were monitored to determine the effect, if any, that these had on the hydrate formation pressure-temperature conditions, and the induction and growth rate of the hydrates. The conductivity, and in some experiments the carbon content, were used to determine if *in-situ* concentration was occurring. The colour (which was determined visually) and pH were monitored as additional parameters of interest.

The electrolyte content of a solution, which is related to conductivity, was determined with an Orion Model 160 Conductivity meter. This meter was designed for a \pm 0.5% accuracy for solutions up to 199.99 μ S/cm, and has an automatic temperature compensator.

The solids content of a solution was determined by the total solids (TS), volatile solids (VS), fixed solids (FS), and the total suspended solids (TSS) tests. The TS value represents the mass of suspended and/or dissolved solid matter that is left in a crucible after evaporation and drying at 105 °C. The FS value represents the mass of the solids that do not burn at 550 °C, i.e. the matter remaining in the crucible. The VS value refers to the mass of solids that volatilize at 550 °C and is calculated as: VS = TS - FS. The TSS value represents the portion of the solids present in a solution that is retained by a filter with a selected porosity. Details of these procedures can be found in Appendix A.

The carbon content of a solution was determined with a Shimadzu TOC 500 total organic carbon analyzer. This apparatus determined the total organic carbon (TOC) and total inorganic carbon (TIC) concentration of a solution.

The pH of a solution was determined with a digital pH meter, the Cole Palmer Model OS669-20. This meter was designed for a \pm 0.1% full-scale accuracy and has an automatic temperature compensator. It was calibrated using CanLab pH 4.0, 7.0 and 10.0 reference buffer solutions.

5.3 Experimental Set-up

The experimental equipment included two equilibrium vessels, a glycol-water bath, a refrigerator, three thermocouples, two pressure gauges, a thermometer, and a tachometer.

5.3.1 Apparatus

The experimental apparatus used to study hydrate formation is illustrated in Figure 5.1. The primary component in this set-up is the vessel in which the hydrates form. This vessel was immersed in a large temperature controlled bath. The bath was filled with 100 L of a 50-50 wt% ethylene glycol-water mixture. The temperature of the bath liquid was controlled by an external refrigerator/heater which uses a cooling/heating coil to transfer heat in and out of the bath. The coil was constructed with copper tubing. A uniform temperature was maintained within the bath by a motor driven stirring mechanism. The refrigerator bath was a Forma Scientific Model 2095 bath with a 28.4 L capacity. The refrigerator bath was also filled with a 50-50 wt% ethylene glycol-water mixture. This set-up can maintain a relatively constant temperature (\pm 0.10 K) within the bath over a long period of time. The bath temperature was measured with a Fisherbrand thermometer with 0.1 °C subdivisions.

5.3.2 Hydrate Formation Vessels

Two different equilibria vessels were used, one for low pressure systems (C_3H_8 and the 30-70 mol% C_3H_8 -CO₂ mixture) and the other for high pressure systems (CO₂). Both vessels were machined from solid pieces of a 316 stainless steel cylindrical bar.

A cross-sectional view of the low pressure vessel is illustrated in Figure 5.2. This vessel, with a capacity of approximately 750 mL, has three sight windows. Two were situated across from one another near the base of the vessel and a third was placed at the top of the vessel (the lid). These windows were machined from 1/2" thick

FIGURE 5.1: Apparatus used for Clathrate Hydrate Formation Experiments

Λ







316 STAINLESS STEEL



PLEXIGLASS

Plexiglas plates, sealed with neoprene o-rings and held in place by stainless steel bolted studs. Mixing within this vessel was accomplished with the aid of a magnetic stir bar coupled with a set of magnets rotating beneath the vessel. The set of magnets were mounted on an aluminum housing that was connected to a DC motor (as the set of magnets spin they generate a magnetic force which couples with the stir bar causing it to spin thereby mixing the contents in the vessel). This vessel has two gas and two liquid ports. One of the liquid ports was used to gravity feed the solution into the vessel and the other to drain the solution.

Figure 5.3 shows a cross-sectional view of the high pressure vessel. This vessel, with a volume of 280 mL, has only two site windows. These windows were situated across from one another approximately half way up the vessel and were machined from 1 3/4" thick Plexiglas plates. These windows were friction fit. The lid of the vessel was sealed with a neoprene o-ring and held in place by stainless steel bolts. Mixing was accomplished in the same manner as it was in the low pressure vessel. The high pressure vessel has two inlet and two outlet ports, similar to the low pressure vessel.

The temperature inside both of the vessels was measured with two Omega copper-constantane thermocouples. One thermocouple was situated in the top half of the chamber, to determine the gas phase temperature, while the other was positioed near the bottom, to determine the liquid phase temperature. A third thermocouple was placed outside of the vessel in the bath liquid.

The pressure in the low pressure vessel was measured with a 0-300 psi Bourdon tube Heisse pressure gauge with 1 psi subdivisions. This gauge was calibrated against an Ametek Modcal Pressure Model (pneumatic), traceable to NIST.



The pressure in the high pressure vessel was measured with a 0-14,000 Bourdon tube Heisse pressure gauge with 50 kPa subdivisions. This gauge was also calibrated against an Ametek Modcal Pressure Model (pneumatic), traceable to NIST. The accuracy of the measurements taken with the low pressure gauge are within \pm 0.5 psi or \pm 0.003 MPa, and measurements taken with the high pressure gauge are within \pm 25 kPa or 0.025 MPa.

The speed of the stir bar was approximated with an ADAMS photoelectric Tachometer 5205 set for a 0-1000 RPM range with 10 RPM subdivisions. This tachometer was calibrated to a known source, its accuracy was within \pm 50 RPM. The tachometer was used in the growth and the concentration experiments.

5.4 Experimental Procedures

Different procedures were used for each set of experiments, however the vessels were cleaned using the same procedure. The vessels were washed every time the source of the test solution was changed. The washing procedure included flushing the vessel twice with hot water, once with deionized water, and once with the solution to be tested, prior to injecting the test solution into the vessel. Periodically, the lid of the vessel was removed and the inside of the vessel was wiped with warm water, with methanol, and finally with deionized water.

5.4.1 Qualitative Process Characteristics

The observations made about the clathrate hydrate concentration process were visual, without the aid of any magnifying devices.

5.4.2 Pressure-Temperature Hydrate Formation Conditions

The following outlines the procedure used to determine the hydrate formation pressure at a given temperature in both the low and the high pressure vessels. Approximately 200 mL of the test solution was injected into the vessel. The bath temperature was set to the desired level and the stir bar was set at the maximum speed that would not cause decoupling, approximately 200 rpm. The system was given time to equilibrate, such that the bath temperature and the temperature inside the vessel were stable. At this point the system was purged twice with the chosen hydrate former to remove any remaining air, and the vessel was pressurized (to a level well above the expected incipient pressure) to induce hydrate nucleation. Subsequently, the hydrates were decomposed by venting the gas out of the system. The reason for this procedure was to eliminate the hysteresis phenomena and enhance the structure in the aqueous solution. After these initial procedures, the first incipient hydrate phase equilibrium data point was measured as follows.

The vessel was pressurized to a level well above the estimated equilibrium value to induce hydrate nucleation. The estimated equilibrium value for the first experiment was usually obtained by trial and error for a particular effluent. Then, the deviation of this initial value from the value for hydrate formation in pure water was calculated and used to obtain an estimate for experiments at other temperatures, with the same effluent. Once hydrates had formed the pressure was dropped to a level slightly above the estimated equilibrium value, at the system temperature. The system was then given at least 4 hours to equilibrate. If, at that time, a large amount of hydrates were present the pressure was dropped further, if no hydrates were present the system was renucleated and set at a higher pressure. This process was continued until only a small amount of hydrates were present and the temperature and pressure had remained constant for at least 4 hours. Once these equilibrium requirements had been met the incipient hydrate formation pressure, at the system temperature, was recorded. The next incipient hydrate equilibrium data point was found by selecting a new temperature and repeating the above procedure.

5.4.3 Induction and Growth Rate Experiments

The growth experiments were performed with the propane-carbon dioxide mixture in the low pressure vessel. The low pressure vessel was chosen because it could withstand the experimental pressures required by the C3H8-CO2 gas mixture, and it was easier to visually observe the formation process in this vessel as compared to the high pressure vessel. Before induction and growth experiments could be performed the driving force had to be established. Driving force can be determined from thermodynamic considerations, and the fact that clathrate hydrate formation is a crystallization process. A schematic of a partial three phase diagram for hydrate formation with a pure compound, e.g. propane, and water is given in Figure 5.4. At a given temperature the pressure where the three phases, namely gas, liquid and hydrate coexist is unique. The driving force in a hydrate formation experiment that is performed at a constant temperature, T_{exp} , is: driving force (ΔP) = experimental pressure (P_{exp}) - equilibrium pressure (P_{eq}) . One may also define a driving force at constant pressure, P_{exp} , as: driving force (ΔT) = experimental temperature (T_{exp}) equilibrium temperature (T_{eq}). Other factors, such as stirring rate, liquid and gas phase volume, and the history of a solution, can also affect the induction period and the growth rate of hydrates. Therefore, to be able to study the effect of pressure





Temperature (K)

differences the solution volume, temperature, stirring rate, and prior history were kept constant throughout these experiments. The solution volume was 200 mL, the bath temperature was set at 1 °C, and the stirring rate was set at 200 rpm. At 1 °C the hydrate formation pressure for a 30-70 mol% propane-carbon dioxide mixture in deionized water was expected to be 0.420 MPa, based on experimental results obtained in this work.

The procedure used was as follows: (1) Clean the vessel; (2) Place the test sample in the vessel; (3) Set the bath temperature to 1 °C, and let the system reach thermal equilibrium; (4) Purge the vessel twice with the propane-carbon dioxide mixture to remove any remaining air; (5) Set the pressure to the desired value and start the stop watch; and (6) collect pressure versus time data.

The time it took before hydrate crystals could be observed was recorded (induction period), after which pressure versus time data was recorded for the following hour (initial growth period). After this first hour, the growth of the hydrate crystals was stopped by dropping the pressure to 0.15 MPa and maintaining it there for at least four hours, allowing the hydrates to decompose. The system was then renucleated, the pressure was increased to the next desired value, and pressure versus time data was recorded for another hour (second growth period). The above procedure was repeated three times, each time with a "fresh" sample of the test solution.

5.4.4 In-Situ Concentration Experiments

Several procedures were attempted to try to systematically determine the effect that different formation conditions would have on *in-situ* concentration. The

experiments were performed to try to determine if a part of the hydrate-concentrate separation step could be attained within the vessel.

Three sets of experiments were performed, and two procedures were established, A and B. All of the experiments were performed with the low pressure vessel, the volume of test solution used varied from 200-400 mL. The initial two steps in both procedure A and B were the same. The first step was to form a suitable amount of hydrate crystals such that when they decomposed they would result in at least 50 mL, this is the smallest sample volume required to determine conductivity. The second step was to collect the concentrate by blowing it out of the vessel under pressure. The last two steps in procedure A were to decompose the hydrates, and collect the resultant liquid. The remaining steps in procedure B included venting the gas, i.e. dropping the pressure, removing the lid of the vessel, recovering as much as possible of the hydrates by scooping them out of the vessel and letting them decompose. The final step in both procedures was to determine if any concentration had occurred. In the first two sets of experiments this was done by testing the conductivity of both the concentrate and the decomposed hydrates and comparing this with the conductivity of the original solution. Conductivity was chosen as the initial concentration parameter because it could be determined immediately. In the last set of experiments conductivity, TOC and TIC were determined for the initial effluent and the concentrates.

CHAPTER 6: Results and Discussion

The first section in this chapter will present an effluent treatment selection procedure. The second section will discuss physical characteristics that were determined for the effluent and concentrate samples used in this work. The criteria used to select the hydrate formers, and characteristics of the chosen hydrate formers will be given in the third section. The fourth section will summarize and discuss the qualitative characteristics of the clathrate hydrate concentration process that have been observed during the experimental part of this work. The incipient clathrate hydrate formation pressure-temperature conditions that have been determined for the effluents and concentrates, with the various hydrate formers, will be presented in the fifth section. The results from the induction and growth experiments will be given in the sixth section, and the results from the *in-situ* concentration experiments will be presented in the seventh section. In the last section the results that have been obtained in this work, in addition to the information that was collected during the survey of TMP and CTMP effluents, will be discussed with respect to their relative importance to the development of the clathrate hydrate concentration process.

6.1 Effluent Treatment Options

The practice of directly discharging untreated liquid effluent into the environment will not be acceptable in the future. This was clearly stated in the 1992 amendment to the <u>Fisheries Act</u>. As a result, all of the pulp and paper mills currently operating in Canada will be required to either treat their liquid effluents appropriately, or avoid the discharge of these effluents by implementing a ZLD system.

The effluent treatment systems that will have the least negative impact on the local ecosystem, at a specific site, will be those which implement a ZLD technology (refer to Section 3.5). However, these systems are both expensive and energy intensive in comparison with conventional systems. Therefore, until the volume of liquid effluent that is generated by a mill can be significantly reduced, there will continue to be a need for conventional treatment systems. The objective of the discussion that is presented here is not to determine which treatment option is the best, but rather to present an effluent treatment selection procedure based on the information that was collected during the survey performed on the effluents generated by TMP and CTMP mills, and the current discharge regulations (refer to Chapters 2 and 3).

The first step in selecting an effluent treatment system is to determine: 1) The type, the point source, and the concentration of the contaminants that will be present in the untreated effluent. These can not be determined before the pulp quality, wood furnish(es) and pulping process(es) are selected, refer to Chapter 2; and 2) The sensitivity of the receiving environment and the presence of an adequate receiving water source. These can not be determined before the selected mill site has been studied in-depth, refer to Section 3.1.

The determination of the point source(s) from which a contaminant originates may aid in minimizing both the volume and pollutant load of the effluent that is generated by a mill. There are several different internal measures that can be implemented. In general, these may include: (1) modifying the unit operation(s) that generate large pollutant loads, and/or have high water consumption rates; and (2) recycling effluent streams that have low concentrations of contaminants so as to decrease the overall volume of effluent that is generated (this is of particular importance for ZLD systems).

The next step is to select the treatment systems that are capable of attaining the extent of treatment that they will be required. In the case of a conventional system, the current (and if possible the expected future) discharge regulations will determine the extent of treatment that will be required. And, in the case of a ZLD system, the extent of treatment (or separation) of the recovered water will be determined by the effect that process water has on both product quality and process operations.

The final step in this selection procedure is to determine the capital and operating costs, and any potential long-term negative environmental impacts that may be associated with these systems. Then, based on this information the "best" option can be determined. If the treatment system is part of a proposal for a new mill the anticipated response of the public and local government bodies towards the mill, in particular the environmental impacts, must also be considered. Their opinions are important because if these bodies consider the "environmental" cost of implementing a selected treatment system to be too high they can delay, or stop, the permitting process of a new mill.

6.2 Mill Effluent Characteristics

It is known that the extent to which electrolyte and organic compounds inhibit hydrate formation depends on their concentration in the solution of interest. As a result, the electrolyte content (conductivity) and the organic content (total organic carbon, TOC) of the effluent samples (TMP1, TMP2, CTMP, and BCTMP) and the concentrate samples (TMP2/50, TMP2/85, CTMP/50 and CTMP/80) were determined. In addition, the solids content, the pH, the colour, and the total inorganic carbon (TIC) concentration of each of the samples were determined. Total solids (TS), volatile solids (VS) and total suspended solids (TSS) tests were performed to determine the solids content. The results from all of the aforementioned tests, with the exception of the pH and colour, are shown in Figures 6.1 through 6.6. The arrows, to the right of each test name, indicate which y-axis should be used.

Effluent samples. The conductivity, and the TOC and TIC concentrations of the effluents are shown in Figure 6.1, and the results from the solids content tests are presented in Figure 6.2. The conductivity of the BCTMP effluent was found to be 17,000 μ S. Thus, the conductivity of the BCTMP effluent was about five times that of the CTMP effluent, 20 times greater than the TMP1 effluent, and 40 times that of the TMP2 effluent.

The TOC concentration increased from 60 mg/L in the TMP1 effluent to 7830 mg/L in the BCTMP effluent. And the TIC concentration increased from less than 10 mg/L in the TMP1 effluent to 490 mg/L in the BCTMP effluent.

The TS concentration increased from 710 mg/L in the TMP1 effluent to 26,960 mg/L in the BCTMP effluent, and the VS concentration increased from 240 mg/L in the TMP1 effluent to 11,690 mg/L in the BCTMP effluent. The TSS concentration ranged from 10 mg/L for the TMP1 effluent to 980 mg/L for the BCTMP effluent.

The electrolyte, carbon, and solids content of a TMP or a CTMP effluent all depend on the rate of water consumption, the pulping process (in particular, the chemicals and operating conditions) and the wood furnish that are used. The BCTMP





effluent was generated at the mill with the lowest rate of water consumption. The mills that generated the CTMP, TMP2, and TMP1 effluents used 2.8, 3.3, and 28 times more water than the mill that generated the BCTMP effluent respectively (refer to Section 5.1). Therefore, based on these large differences in water usage it was expected that the electrolyte, carbon, and solids content of these effluents would decrease as follows: BCTMP > CTMP > TMP2 > TMP1. The only exception to this was the electrolyte content of the TMP1 effluent which was greater than that of the TMP2 effluent. The reason for this is not known.

Another factor that could be responsible for the difference in the organic content and the solids content of these effluents is the use of sodium sulphite (Na_2SO_3) and/or hydrogen peroxide (H_2O_2) in the pulping process. As noted in Section 2.4.2, the use of these chemicals will increase the TSS, BOD, and toxicity of an effluent. In general, an increase in the BOD and/or toxicity of an effluent will result in an increase in its TOC concentration because the contaminants that are responsible for both BOD and toxicity are predominantly organic in nature. Therefore, the higher TOC and TSS concentrations of the BCTMP and CTMP effluents, as compared with the TMP1 and TMP2 effluents, may partly result from the addition of large amounts of sodium sulphite.

The higher TOC and TSS concentrations of the TMP2 effluent, as compared with the TMP1 effluent, may be partially due to the addition of peroxide during the bleaching stage at the TMP2 mill. The mill which generated the TMP1 effluent does not have a bleaching stage, however, it does add small amounts of peroxide during its pulping process.

The pH of the TMP1, TMP2, CTMP, and BCTMP effluents were 6.3, 6.2, 6.9,

and 6.8 respectively. These are all below the "ideal" pH range of 8.0 to 9.5, at which the resin and fatty acids are thought to be least toxic. The BCTMP effluent was an opaque, dark orange-brown solution. The CTMP effluent was an opaque, orange solution. And both the TMP1 and the TMP2 effluents were clear, pale orange solutions.

Concentrate Samples. The conductivity, and the TOC and TIC concentrations of the TMP2 concentrates are shown in Figure 6.3, and the results from the solids content tests are presented in Figure 6.4. The conductivity of the TMP2/50 and the TMP2/85 concentrates were 1.9 and 6 times larger than the conductivity of the TMP2 effluent. The TOC and TIC concentrations of the TMP2/50 concentrate were 2 and 3 times greater than those determined for the TMP2 effluent. And the TOC and TIC concentrations of the TMP2 effluent. And the TOC and TIC concentrations of the TMP2/85 concentrate were 8 and 5 times larger than those determined for the TMP2 effluent.

The TS and VS concentrations of the TMP2/50 concentrate were 2.2 and 2.4 times greater than those determined for the TMP2 effluent. And the TS and VS concentrations of the TMP2/85 concentrate were 3.9 and 4.2 times larger than those determined for the TMP2 effluent. The TSS concentration of the TMP2/50 and the TMP2/85 concentrates were 4 and 16.7 times greater than the TSS concentration of the TMP2 effluent.

The conductivity, and the TOC and TIC concentrations of the CTMP concentrates are shown in Figure 6.5, and the results from the solids content tests are presented in Figure 6.6. The conductivity of the CTMP/50 concentrate was 2.5 times greater than the conductivity of the CTMP effluent. And the CTMP/80 concentrate was 3.5 times greater than the conductivity of the CTMP effluent. It

FIGURE 6.3:









should also be noted that the conductivity of the CTMP/80 concentrate was only 1.7 times less than that of the BCTMP effluent. The TOC and TIC concentrations of the CTMP/50 concentrate were 2.8 and 2.5 times greater than those determined for the CTMP effluent. And the TOC and TIC concentration of the CTMP/80 concentrate was 6.8 and 1.2 times larger than the CTMP effluent. The reason for the low TIC concentration of the CTMP/80 effluent is not known.

The TS and VS concentrations of the CTMP/50 concentrate were 1.9 and 1.6 times greater than those determined for the CTMP effluent. And the TS and VS concentrations of the CTMP/80 concentrate were 5.7 and 4.0 times larger than those determined for the CTMP effluent. The TSS concentrations of the CTMP/50 and the CTMP/80 concentrates were 2.5 and 3.6 times greater than the TSS concentration of the CTMP effluent.

The pH of the TMP2/50, TMP2/85, CTMP/50, and CTMP/80 concentrates were 6.6, 5.5, 7.6, and 9.2, respectively. All of the four concentrates were a very dark orange-brown colour, darker than the BCTMP effluent. However, the CTMP concentrates were appeared clear, in comparison to the TMP concentrates.

6.3 Selection of Hydrate Formers

Several criteria were used to determine which of the over one hundred hydrate formers would be most suitable for this study. The initial criteria, referred to as "gate" criteria, were used in the selection of environmentally acceptable hydrate formers. These criteria included selecting hydrate formers that were nontoxic, had a low ozone depletion potential (ODP), low global warming potential (GWP), low explosion potential, and were nonflammable. Flammability was not considered to be a major issue if extensive knowledge on how to properly handle the particular hydrate former on an industrial scale was available.

The next criterion that was used utilized the hydrate formation equilibrium data for the compound of interest in pure water. This data determined which of the environmentally suitable hydrate formers were capable of forming hydrates at temperatures well above 0 °C, and at pressure as close as possible to atmospheric. Thermodynamic models were used to predict these data for those compounds where experimental data was not available. This criterion was of particular importance because the hydrate formation temperature must be well above the freezing point of the solution for the clathrate hydrate concentration process to have an energy advantage over freeze concentration.

The other criteria that were used included the solubility of the hydrate former in water, its cost and its availability. The solubility of the hydrate former in water aids in determining what type of a separation step will be required, if at all, to recover the hydrate former from the water phase once the hydrates have been decomposed. The extent to which the hydrate former must be recovered will depend on both the cost of the hydrate former and the degree of purity that will be required for the recovered water, i.e. the process water. Finally, the cost and the availability of the selected compounds are important criteria because they aid in determining whether the clathrate hydrate concentration process has the potential to become economical.

Based on the above selection criteria the two hydrate formers that were initially chosen for this study were carbon dioxide and propane. Characteristics of interest for both of these compounds can be found in Table 6.1.

TABLE 6.1: Hydrate Former Characteristics for Propane and Carbon Dioxide

CHARACTERISTIC	CARBON DIOXIDE	PROPANE
Maximum equilibrium T & P in pure water (quadruple point)	10.1 °C at 4.5 MPa	5.3 °C at 0.542 MPa
Ozone Depletion Potential (ODP)	0	0
Global Warming Potential (GWP)	1.0	-
Explosion Potential	None	Lower level 2.1% Upper level 9.5%
Flammability	Nonflammable	Autoignition temp. 432 °C
Toxicity	Asphyxiant TLV 5000 ppm	Asphyxiant (no threshold limit given)
Solubility in water at maximum temperature (quadruple point)	6.1 wt. percent	0.06 wt. percent
Structure of Unit Cell	I	II
Maximum number of water molecules per hydrate former molecule in the hydrate phase	7.3	17.95
Hydrate Density (g/cm ³)	1.112	0.88
Heat of hydrate formation (kJ/mol hydrate)	- 55.0	- 134.2

It is known that propane is flammable and has an explosion potential if not handled properly. However, due to its wide spread use in other industries it was decided that procedures known to minimize both of these risks could be implemented. Carbon dioxide falls short in three areas. It requires pressures up to 4.5 MPa to form hydrates, it is more soluble in water than propane, and it is a known greenhouse gas. However, it is nontoxic, poses less of an environmental hazard in comparison with propane, and can form hydrates at temperatures up to 10 °C. Two other hydrate formers were also considered, cyclopropane and the new refrigerant R-134a. It was found that the cost of cyclopropane and R-134a were much higher than the cost of propane and carbon dioxide. In addition, it was difficult to obtain a small quantity of the R-134a refrigerant for lab purposes.

Based on the results from the experiments performed with propane and carbon dioxide, a propane-carbon dioxide mixture was chosen as the third hydrate former. It is well known (from thermodynamic considerations) that the hydrate formation pressure, at a given temperature, will be less with a propane-carbon dioxide mixture, due to the presence of propane, than with pure carbon dioxide. Furthermore, it was assumed that hydrates would nucleate more readily in the presence of a propanecarbon dioxide mixture than in the presence of pure propane. This latter point was verified experimentally.

The make-up of the mixture that was determined from pressure formation predictions. The formation pressures for 100% propane, a 50-50 mol% propane-carbon dioxide mixture, a 30-70 mol% propane-carbon dioxide mixture, and 100% carbon dioxide in pure water at 3 °C were predicted with thermodynamic models. The Peng-Robinson Equation of State model was used to model the vapour phase, Henry's Law Constant was used to model the aqueous phase, and the Van der Waals-Platteeuw model was used to model the hydrate phase. The predicted formation pressures were 0.32, 0.39, 0.48, and 1.23 MPa for 100% propane, the 50-50 mol% mixture, the 30-70 mol% mixture, and 100% carbon dioxide, respectively. Based on these predictions a 30-70 mol% propane-carbon dioxide mixture was chosen.

It was predicted that the maximum hydrate formation pressure attainable with this mixture was between 9 and 10 °C. The formation pressure at 9 °C was predicted to be 1.31 MPa. The propane-carbon dioxide mixture forms structure II hydrate crystals. Carbon dioxide molecules can occupy both the small and the large cavities, whereas propane molecules can only occupy the large cavities. If all of the small cavities are filled with carbon dioxide and the large cavities are filled with propane then a unit cell would contain 136 mol H_2O : 16 mol CO_2 : 8 mol C_3H_8 .

6.4 Qualitative Process Characteristics

The prime objective in visually observing the formation process was to collect qualitative information on the hydrate crystals that formed. However, changes in the pH, colour, and carbon content of several of the effluent samples were noted. The results presented here were observed during the pressure-temperature, induction and growth, and concentration experiments that were performed during this study.

Hydrate Crystal Formation. The crystals that formed in the presence of propane varied in colour. The initial crystals that formed floated on top of the effluent and were white, similar to snow. As the hydrate mass grew all of the visible crystals appeared to have the same colour as the initial effluent. The reason for this colour change is most likely due to occlusion of effluent in the vacant space between individual crystals and/or coating of the crystals with the effluent.

The crystals that formed in the presence of propane did so in a donut shaped solid that formed up the walls of the vessel. It was postulated that the solid that had formed in the bulk of the effluent was not all hydrate crystals but rather a "gel-like" structure which was composed of large amounts of effluent caught in the interstices between individual crystals. This follows from a comparison between the maximum amount of propane that was available in the vessel (determined from the initial pressure - the equilibrium pressure) and the theoretical value, assuming 100% of the large cavities are filled with propane molecules. The results for two separate runs in which the "gel-like" structure formed are shown in Table 6.2. The theoretical value was calculated from the maximum propane to water ratio, i.e. 17 mol C_3H_8 : 1 mol H_2O , for hydrate formation. The large difference between the theoretical values and the experimental values show that the structure which was present could not have used all of the available water molecules, i.e. liquid effluent, is caught between the crystals.

TABLE 6.2:	Moles of Propane Gas Required and Available to Convert
	100% of an Effluent Sample to Hydrates

Volume of Sample (mL)	Temp (K)	Driving Force (AP MPa)	Moles of Propane Required (Theoretical)	Maximum Number of Moles of Propane Available (Experimental)
300	275	0.4	0.136	0.09
350	276	0.19	1.307	0.04

The hydrate crystals that formed in the presence of carbon dioxide at high pressures (i.e. large driving forces) were initially suspended in the liquid phase and appeared to be white, similar to snow. The crystals that formed with small driving forces were more susceptible to forming on the vessel walls initially, and were similar in colour to the effluent. Foaming was observed during these experiments, however the "gel-like" structure was not apparent.

Crystal growth in the presence of the propane-carbon dioxide mixture was very similar to that described for carbon dioxide. However, a "gel-like" structure, similar to that which formed in the presence of propane, was apparent during these experiments. It should be noted that the "gel-like" structure formed slower in the presence of the propane-carbon dioxide mixture than in the presence of propane.

pH, *Colour*, *and Carbon Content*. Changes in the pH and colour of the effluent that was removed from the vessel, after hydrates had been formed and decomposed at least once, were observed during several experiments. There was no change noted in either the pH or the colour of the CTMP effluent after being exposed to propane. Colour changes in the other effluent and concentrate samples, i.e. TMP1, TMP2, BCTMP, CTMP/50 and CTMP/80, that were exposed to propane were not observed.

The colour of the TMP1 and CTMP effluent exposed to carbon dioxide changed from an orange to an orange-grey colour, and a black precipitate formed in both cases. There was no colour change or precipitate formation in the experiment with pure water and carbon dioxide. The grey CTMP effluent returned to a slightly darker shade of its original colour and some of the precipitate dissolved when concentrated NaOH was added to a sample of this effluent. Both pH and colour changes were observed during the five experiments that were performed with CTMP effluent samples in the presence of the propane-carbon dioxide mixture. The initial pH of these samples ranged from 7.0 to 7.7, whereas the final values, after being exposed to the propane-carbon dioxide mixture, ranged from 5.6 to 6.0. The colour of each of the CTMP effluent samples changed from an orange to an orange-grey colour, and a black precipitate was formed. Upon addition of concentrated NaOH the colour changed back to an orange hue, slightly darker than that of the original, and some of the precipitate dissolved. These results were similar to those obtained with the CTMP effluent in the presence of carbon dioxide.

Changes were also noted in the carbon content of a CTMP effluent sample that was exposed to the propane-carbon dioxide mixture. The TOC and TIC concentrations of the sample were determined before the sample was placed in the hydrating vessel, and after it had been exposed to the propane-carbon dioxide mixture for five days, during which hydrates were formed and decomposed twice. The initial TOC concentration was 1159 mg/L and the final concentration was 552 mg/L. The initial TIC concentration was 182 mg/L and the final concentration was 1008 mg/L.

Summary. It was found that hydrate nucleation occurred more readily in pure water than in the effluents in the presence of both carbon dioxide and the propanecarbon dioxide mixture. A "gel-like" structure formed in the presence of both propane and the propane-carbon dioxide mixture.

The pH decreased and the effluent colour changed from an orange to an orange-grey colour in the presence of both carbon dioxide and the propane-carbon dioxide mixture. The TIC concentration increased and the TOC concentration decreased in the presence of the propane-carbon dioxide mixture. Similar changes
were not noted in the presence of propane. Therefore, these results suggest that a chemical reaction may be occurring between the compounds introduced into the effluent during the pulping process, water, and carbon dioxide.

6.5 Pressure-Temperature Hydrate Formation Conditions

Incipient equilibrium hydrate formation pressures, at temperatures above the normal freezing point of water, were determined for several of the effluent and concentrate samples in the presence of the three selected hydrate formers. The results from these experiments are shown on pressure-temperature diagrams. Data for the hydrate formation conditions in pure water with the hydrate former of interest are also shown. It should be noted that at a given temperature the points represent the minimum pressure at which hydrate crystals can form in a particular aqueous solution. Thus, they define the pressure-temperature operating conditions of a clathrate hydrate crystallization unit.

Propane. Formation experiments, in the presence of propane, were performed with each of the four effluent samples and two of the concentrate samples. The results are presented in Figure 6.7 and 6.8, and given in Table 6.3. The formation pressures for the TMP1, TMP2, and CTMP effluents were only slightly above those required for hydrate formation in pure water, at a given temperature. Therefore, the concentrations of the electrolyte and organic compounds present in these effluents were not large enough to significantly alter the hydrate formation conditions. The hydrate formation pressure required by the BCTMP effluent sample at 275.15 K was 12% higher than the corresponding pressure required to form hydrates in the other

FIGURE 6.7: Pressure-Temperature Hydrate Formation Data for the Effluent Samples with Propane



Pressure-Temperature Hydrate Formation Data for the CTMP Concentrates with Propane



Temperature	Pressure (MPa)					
(K)	CTMP	BCTMP	TMP1	TMP2	CTMP/ 80	CTMP /50
273.6	0.183					
274.2	0.224					
274.5	0.241					
275.6	0.301					
276.6	0.377					
277.6	0.481					
278.0	0.529					
275.1		0.287				
276.3		0.398				
277.0		0.501				
274.2			0.225			
276.1			0.324			
277.6			0.467			
274.3				0.225		
276.5				0.356		
277.8				0.501		
273.7					0.212	
276.3					0.377	
277.4					0.501	
274.5						0.230
276.0		54				0.332
277.9						0.515

 TABLE 6.3:
 Propane Hydrate Formation Pressure-Temperature Data

effluent, and at 277 K the required pressure was 26% higher (refer to Figure 6.7). These elevated formation pressures can be attributed to the high electrolyte (conductivity) and organic (TOC) content of the BCTMP effluent, as was discussed in Section 6.2.

It was found that propane hydrates were readily nucleated in the TMP1, TMP2, and CTMP effluents, but that they were more difficult to nucleate in the BCTMP effluent, especially at temperatures above 275.15 K. Nucleation was induced in these experiments by one of the following methods: 1) the pressure was set at a value that was significantly greater than the equilibrium pressure, thereby increasing the driving force (ΔP); 2) the mixing mechanism (the stirrer) was continuously turned on and off (this is known to enhance nucleation); or 3) large amounts of hydrates were formed at a low temperature, then the temperature was increased to the desired set point. The last method, the most time consuming of the three options, was required to nucleate hydrates in the BCTMP effluent at temperatures above 275.15 K.

The two TMP concentrates were not tested because their conductivity and TOC concentrations were less than those determined for the CTMP/80 concentrate. The results from the experiments with the two CTMP concentrates, the CTMP effluent, and pure water with propane are shown on Figure 6.8 and given in Table 6.3. It was found that the nucleation of hydrates in the CTMP/80 concentrate, like the BCTMP effluent, was difficult, especially at the higher temperatures. The results presented in Figure 6.8 show that recovering 50% of the water in the CTMP effluent (CTMP/50) would not affect the formation conditions. However, the recovery of 80% of the water (CTMP/80) would affect the hydrate formation conditions, as shown by the increased

formation pressure required by the CTMP/80 concentrate, at a given temperature, in comparison with that required with the CTMP effluent. As expected, the formation pressure, at a given temperature, increased with increasing electrolyte content, i.e. the formation pressure of the BCTMP effluent was greater than that required by the CTMP/80 concentrate, which was larger than that required for the CTMP effluent. However, a similar correlation was not found with the organic content of these solutions (the TOC concentrations of the CTMP/80 concentrate was similar to that of the BCTMP effluent). These results suggest that hydrate formation in the CTMP/80 concentrate was mostly influenced by its electrolyte rather than its organic content.

Carbon Dioxide. The experiments that utilized carbon dioxide as the hydrate former were performed with pure water, the TMP2 and the CTMP effluents. These pressure-temperature hydrate formation data are presented on Figure 6.9 and in Table 6.4. The results yielded similar conclusions to those obtained with propane. Both effluents formed hydrates at pressures only slightly above those for pure water, at a given temperature. As expected, the formation pressures required, at a given temperature, in the presence of carbon dioxide were larger than those required for hydrate formation in the presence of propane. For example, the pressure requirements for the CTMP effluent at 274.4 K was six times larger with carbon dioxide than with propane. The pure water data determined with carbon dioxide were in good agreement with similar data available in the literature. These pure water data aid in validating the experimental equipment and procedures that were used in this study. It was found that the hydrate crystals formed rapidly in the TMP2 and the CTMP effluents at all of the set point temperatures.

FIGURE 6.9: Pressure-Temperature Hydrate Formation Data for the TMP2 and the CTMP Effluents, and Deionized Water with Carbon Dioxide



TABLE 6.4:Carbon Dioxide Hydrate Formation Pressure-Temperature
Data

Temperature	Pressure (MPa)			
(K)	CTMP	TMP2	Pure water (This work)	
274.4	1.440			
275.9	1.720			
277.3	2.025			
278.4	2.360			
280.0	2.900			
281.5	3.600			
282.6	4.290			
274.5		1.400		
280.3		2.950		
282.1		3.800		
273.6			1.310	
275.1			1.550	
276.8			1.900	
278.2			2.260	
281.3			3.380	
282.8			4.350	

Propane-Carbon Dioxide Mixture. Pressure-temperature data was determined for pure water, the CTMP effluent and the CTMP/80 concentrate in the presence of the 30-70 mol% propane-carbon dioxide mixture. The results are shown on Figure 6.10 and given in Table 6.5. As expected, the hydrate formation pressure, at a given temperature, in the CTMP effluent was very similar to that determined

FIGURE 6.10: Pressure-Temperature Hydrate Formation Data for the CTMP Effluent, the CTMP/80 Concentrate and Deionized Water with a Propane-Carbon Dioxide Mixture



Temperature (K)	Pressure (MPa)				
	CTMP	CTMP/80	Pure water (This work)		
274.6	0.429				
277.2	0.656				
278.0	0.739				
273.8		0.336			
275.0		0.429			
277.5		0.629			
274.4			0.429		
276.5			0.598		
278.2			0.777		

TABLE 6.5:Propane-CarbonDioxideMixtureHydrateFormationPressure-TemperatureData

for pure water. However, it was found that hydrates formed in the CTMP/80 concentrate at pressures below those required by the CTMP effluent and pure water, at a given temperature. The reason for this is most likely due to a difference in the solubility of carbon dioxide and propane in the CTMP/80 concentrate as compared to their solubilities in the CTMP effluent. A decrease in the solubility of propane in the CTMP/80 concentrate will result in an increase in the relative solubility of carbon dioxide in this solution. The reason for this differential change in propane-carbon dioxide solubility can be attributed to the "salting-out" effect caused by the presence of electrolyte and organic compounds. Thus, the propane concentrate than in the one performed with the CTMP effluent. As was mentioned in Section 6.3 the

formation pressure, at a given temperature, will decrease if the propane concentration in the gas phase increases relative to the carbon dioxide concentration. Thermodynamic models predicted that a 50-50 mol% propane-carbon dioxide mixture would require a lower pressure to form hydrates, at a given temperature, than a 30-70 mol% propane-carbon dioxide mixture.

Summary. Hydrate crystals formed more readily in the CTMP effluent with the propane-carbon dioxide mixture than with propane, but not as readily as they formed in the presence of carbon dioxide. And, as expected, the hydrate formation pressure, at a given temperature, decreased as the concentration of propane in the hydrate forming mixture increased. For example, the formation pressure at 3 °C in pure water was determined to be 0.323 MPa (Kubota, 1984) with propane, 0.56 MPa with a 30-70 mol% propane-carbon dioxide mixture, and 1.768 MPa with carbon dioxide.

The overall pressure-temperature results indicate that the TMP1, TMP2 and CTMP effluent samples used in this study did not contain electrolyte and/or organic hydrate inhibitors at concentration levels that could significantly alter the hydrate formation conditions, whereas the BCTMP effluent sample did. It was also found that 50% of the water present in the CTMP effluent sample could be recovered without significantly altering the pressure-temperature hydrate formation conditions, whereas recovery of 80% of the water would affect the formation conditions. As expected, the formation pressure, in the presence of propane at a given temperature, with the CTMP/80 concentrate increased compared with the CTMP effluent. Whereas the formation pressure with the propane-carbon dioxide mixture, at a given temperature, in the CTMP/80 concentrate decreased compared with the CTMP effluent.

6.6 Induction and Growth Rate Experiments

These experiments were designed to determine the length of the induction period and the rate of hydrate crystal growth. Because the mill effluents are complex solutions we wanted to perform a number of kinetic experiments to see if the results would agree with the nucleation characteristics of hydrate formation in well defined systems, i.e. hydrocarbon-water, in which the majority of the previous work has been done. Experiments were attempted with both propane and the propane-carbon dioxide mixture. The point (time and pressure) at which hydrates formed in each of the experiments, Figure 6.11 through 6.15, is indicated with an arrow and the run number.

Propane. The experiments performed with propane were aborted due to operational problems. Propane hydrates plugged both the gas inlet and pressure gauge lines such that the pressure drop could not be accurately monitored.

Propane-Carbon Dioxide Mixture. A temperature of 1 °C was selected to perform the experiments. Higher temperatures could have been chosen but we decided to work with a small induction time, less than one hour, and have more flexibility with an increased driving force, i.e. expressed as a pressure difference ($\Delta P = P_{exp} - P_{eq}$).

Four runs were performed. For each run a fresh 200 mL sample of CTMP effluent was used, and the stirrer bar was set at 200 rpm. The results from the induction period and the first growth period (1a, 2a, 3a, and 4a) are shown on Figure 6.11. The equilibrium pressure, P_{eq} , at 1 °C for the CTMP effluent is 0.420 MPa, determined from Figure 6.10. The initial pressures, P_{exp} , were 0.860, 0.846, 0.736, and 0.598 MPa for runs 1a, 2a, 3a, and 4a respectively. And the corresponding $\triangle P$'s were

FIGURE 6.11: Induction Period and the First Growth Rate Period for Run 1, 2, 3 and 4 with the CTMP Effluent



0.440, 0.426, 0.316, and 0.178 MPa.

It can be seen that for runs 1a, 3a and 4a hydrates formed within 12 minutes, whereas it took 20 minutes for hydrates to form in run 2a. Variation in the nucleation time (induction period) is expected since nucleation is not a completely deterministic process.

In each of these four runs a second growth period was measured (1b, 2b, 3b, and 4b). The results are shown on Figure 6.12, 6.13, 6.14, and 6.15 for runs 1, 2, 3, and 4 respectively. In run 1b and 2b hydrates formed immediately, and in run 3b they formed after 5 minutes, whereas in run 4b hydrates did not form within the one hour test period. The immediate formation of hydrates in run 1b and 2b can be attributed to the history of the effluents. Hydrates were formed and decomposed in these effluents prior to the second growth period and, as a result, the solution had become more structured such that hydrates formed more readily. The reason that hydrates formed later in run 3b and did not form within the one-hour time period in run 4b is most probably a result of the small $\triangle P$ values used in these runs, 0.288 and 0.128 MPa respectively. In summary, these results suggest that both the history of the effluent and the magnitude of the driving force affect the growth pattern of hydrate formation in a manner similar to that observed with well defined systems.

6.7 In-Situ Concentration Experiments

The main objective of these experiments was to try to determine if the hydrate formation conditions (given the configuration of our apparatus) could be controlled such that *in-situ* concentration could be realized. It was hypothesized that if the process could be adequately controlled a layer of hydrates, that did not contain

FIGURE 6.12: Induction Period, and the First and Second Growth Rate Periods for Run 1 with the CTMP Effluent



FIGURE 6.13: Induction Period, and the First and Second Growth Rate Periods for Run 2 with the CTMP Effluent



FIGURE 6.14: Induction Period, and the First and Second Growth Rate Periods for Run 3 with the CTMP Effluent



FIGURE 6.15: Induction Period, and the First and Second Growth Rate Periods for Run 4 with the CTMP Effluent



occlusions and were not coated by impurities, could form on top of the concentrate and grow in a downward motion. In the absence of stirring, this concept is shown schematically in Figure 6.16. Four tests were performed with propane, and four with the propane-carbon dioxide mixture. The stirring rate was set at 200 rpm for each of these experiments.

Propane. In the first experiment 300 mL of the CTMP effluent was used, the temperature was set at 2 °C, and the initial pressure was set to 0.65 MPa. The pressure dropped to 0.61 MPa. The effluent formed into a donut shaped solid up the walls of the vessel, resembling a "gel-like" structure (refer to Section 6.4). No liquid was visible in the vessel, and as a result no concentrate could be collected. In the second experiment, 350 mL of the CTMP effluent was used with the temperature maintained at 3 °C and an initial pressure of 0.47 MPa. It was thought that by increasing the effluent volume and the set point temperature, and decreasing the initial pressure the "gel-like" structure would not form as readily. However, the "gel-like" structure did form. In the third experiment, 400 mL of CTMP effluent was used, the temperature was set at 3 °C, and the initial pressure at 0.54 MPa. The same "gel-like" structure formed.

Based on the results from these initial experiments it was decided to use a 5 wt% salt solution in place of the effluent. The aim of this experiment was to determine whether the "gel-like" structure was associated with the propane or the effluent, and to see if *in-situ* concentration could be attained with a less complex solution. For this test 400 mL of the salt solution was used, the temperature was set at 2 °C, and the initial pressure was 0.412 MPa. The same "gel-like" structure formed with this solution. As a result of the limitations caused by the "gel-like" structure



in-situ concentration in the presence of propane was not observed.

Propane-Carbon Dioxide Mixture. In the last four concentration experiments hydrates were formed in the presence of the propane-carbon dioxide mixture. The first experiment was performed with 400 mL of a 1% salt solution, the temperature was maintained at 2 °C, and the initial pressure was set to 0.62 MPa. The pressure decreased to 0.425 MPa, however only a small amount of hydrate crystals had formed. As a result, a pressure of 0.75 MPa was manually maintained in the vessel to try to promote the growth of hydrates. After five days the majority of the solution had formed hydrates, and only a small amount of liquid, i.e. concentrate, was visible in the vessel. The "gel-like" structure was not apparent in this experiment. The initial conductivity of this salt solution was 17.6 mS, similar to that of the BCTMP effluent which was 17.0 mS. The conductivity of the concentrate that was collected was 19.0 mS, slightly higher than that of the original solution.

The last three experiments were all performed at a temperature of 2 °C with 200 mL of the CTMP effluent. The crystal structure that formed during these experiments appeared to be similar to the "gel-like" structure that formed with propane. However, it did not form as rapidly. As a result, concentrate samples could be collected.

The conductivity, TOC and TIC concentrations of the initial effluents, the concentrates, and the final (decomposed hydrate) solutions are given in Table 6.6. These results show that some *in-situ* concentration did take place. This can be concluded because the concentration of the electrolyte (conductivity) compounds and the concentration of the carbon (TOC and TIC) compounds decreased as follows: recovered water samples (final) < effluent samples (initial) < concentrates.

TABLE 6.6:Conductivity, TOC and TIC of CTMP Effluents Determined
During In-Situ Concentration Experiments

Run #	Conductivity (mS)	Carbon Content (mg/L)	
		TOC	TIC
6	initial : 3.06	1159	182
	concentrate : 3.20	1399	175
	final : 2.89	1433	201
7	initial : 3.07	1159	182
	concentrate : 3.29	1433	163
	final : 2.60	ND	ND
8	initial : 3.04	1159	182
	concentrate : 3.32	1400	182
	final : 2.90	ND	ND

ND: Not Determined

However, the ideal *in-situ* process that was described in Chapter 5 and shown schematically on Figure 5.5, in which the hydrate crystals formed as a layer on top of the solution without the presence of any impurities (either occluded or coating the crystals), did not occur. The reason for the lack of significant *in-situ* concentration that occurred during these experiments may result from the limitations posed on the process by the formation of the "gel-like" structure.

6.8 Overall Discussion

The overall scope of this work was to aid in the development of a clathrate hydrate concentration process that can recover clean water from the liquid effluent stream that is generated at a TMP or CTMP mill such that it can be reused. Similar work has not been reported in the literature. The only relevant previous work was concerned with seawater desalination. However, two major differences are apparent between our system and the systems that are used for desalination: (1) TMP and CTMP effluents solutions are more complex, they contain both organic and inorganic compounds; and (2) The extent of separation required to produce potable water (the objective of clathrate hydrate desalination systems) is much higher than that required for the recovery of process water.

The motivation for performing the survey presented in Chapters 2 and 3 was to determine the "environmental" need to treat TMP and CTMP effluents with a ZLD system. It was found that untreated TMP and CTMP effluents can exhibit both lethal and sub-lethal toxic impacts on organisms present in a receiving water, whereas conventionally (biological) treated effluents are in general not acutely toxic. However, based on the impact studies performed to date it can not be determined whether the continuous discharge of treated TMP and CTMP effluents will result in long-term sub-lethal impacts. Therefore, the "environmental" need for ZLD effluent treatment systems can not be verified.

It has been suggested that the best way to maintain a sustainable environment, with respect to liquid effluent streams, is to implement a ZLD system. Because, in addition to alleviating the potential for impacts to occur in the local environment as a result of discharging a liquid effluent, these systems minimize the use of water, a known commodity. Currently, the only proven ZLD technology available to treat TMP and CTMP effluents is evaporation. Based on the potential economic and operational advantages of the clathrate hydrate concentration process, in comparison with evaporation, this work was performed.

Several observations that will aid in the development of the clathrate hydrate

concentration process have been made. Clathrate hydrates can form readily in both TMP and CTMP effluents. The most concentrated effluent sample, the BCTMP effluent, has similar characteristics to the type of effluent that a clathrate hydrate concentration process would be required to treat. The reason being that the mill which generated this effluent sample has a very low water consumption rate, one of the factors that will affect the economics of a ZLD system. Based on environmental, economical, and operational considerations a propane-carbon dioxide mixture is a very suitable clathrate hydrate former to use in the process. And, results from the batch experiments that were performed can be used to design and operate a continuous system. The specific conclusions of this work, and recommendations for future work are presented in the next chapter.

CHAPTER 7: Conclusions and Recommendations

In an effort to obtain technical data for the development of a process for the concentration of TMP and CTMP mill effluents through clathrate hydrate concentration propane, carbon dioxide and a 30-70 mol% propane-carbon dioxide mixture were selected as suitable hydrate forming substances. Propane hydrates formed readily in all of the mechanical effluents and concentrates that were examined, with the exception of the samples with high electrolyte contents. Carbon dioxide was tested with two effluent samples, and the propane-carbon dioxide mixture was tested with one effluent sample and one concentrate sample. It was found that hydrates formed readily in each of the experiments performed with these hydrate formers.

The pressure-temperature hydrate formation conditions (partial phase diagram) for all three gases were determined. It was found that the presence of the electrolyte and organic compounds, in the less concentrated TMP and CTMP effluents, altered the pressure-temperature equilibrium locus only slightly compared with pure water for each of the three hydrate formers. In the presence of propane the pressure-temperature equilibrium did change with the BCTMP effluent and the CTMP/80 concentrate, which both had relatively high electrolyte and organic concentrations compared with the other effluents. In both cases the locus shifted to a higher formation pressure at a given temperature. However, the pressure temperature equilibrium locus shifted to a lower formation pressure at a given temperature with the CTMP/80 concentrate in the presence of the propane-carbon dioxide mixture. It was found that the induction period and the rate of hydrate formation depend on the driving force, expressed as a deviation in pressure from the equilibrium hydrate formation pressure at a given temperature, and the history of the effluent sample. Overall, these experiments demonstrated that the thermodynamics and kinetics of clathrate hydrate formation in TMP and CTMP effluents exhibit similar behaviour to those of well defined systems, i.e. hydrocarbonwater. In addition, it was found that some *in-situ* concentration could be achieved in our batch apparatus.

Based on the above work, the recommendations for the next step include designing and building a lab-scale continuous clathrate hydrate concentration unit, studying the separation of the crystals from the concentrate, and determining the cause of the reactions that occur in the presence of carbon dioxide and the effluent. The design of a continuous unit should include the following: (a) A mechanical mixer rather than a magnetic stirrer such that the gel-like structure can be more readily controlled and *in-situ* concentration can be further studied; (b) A data acquisition system such that the gas consumption rate during hydrate formation can be measured; (c) A pressure control system such that isobaric experiments can be performed; and (d) A unit in which the gas and effluent can be mixed prior to entering the hydrate formation vessel such that hydrates will not plug the gas inlet lines.

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APPENDIX: Effluent Characteristic Tests

I <u>Total Solids, Volatile Solids and Fixed Solids</u> (TS, VS, FS):

Procedure

- 1. Burn crucibles at 550 ± 50 °C for 1 hour, cool to room temperature, and place in desiccator for 4 hours.
- 2. Weigh the crucibles (A) immediately before use.
- 3. Place the crucibles at 103 105 °C for 48 hours with a known volume of sample. The resulting residue should be between 2.5 to 200 mg, if not the procedure must be redone.
- 4. Let the crucibles cool, and place them in a desiccator for 4 hours.
- 5. Weigh the crucibles (B).
- 6. Burn the crucibles at 550 ± 50 °C for 1 hour, cool to room temperature, and place in desiccator overnight.
- 7. Weigh the crucibles (C).
- 8. Perform triplicates for each sample.

Calculations

TS = VS (Volatile Solids) + FS (Fixed Solids)

TS = (B - A)/Sample VolumeFS = (C - A)/Sample Volume VS = TS - FS

II <u>Total Suspended Solids</u> (TSS):

Whatman Glass MicroFibre Filters GF/A, 1.6 μ m, were used.

Procedure

- 1. Wash the filter apparatus with distilled water.
- 2. Place the filter paper in the apparatus and wash with three successive 20 mL portions of distilled water.
- 3. Remove the filter paper, place in a crucible, and burn at 103 105 °C for 1 hour.
- 4. Cool to room temperature, and place in desiccator for 4 hours.
- 5. Weigh the crucible plus filter paper (A), immediately before use.
- 6. Place filter paper in apparatus, and wet paper with a small volume of distilled water to seat it.
- 7. Filter a known volume of sample through the paper. It may be necessary to dilute the sample to be within the acceptable residue range of 2.5 to 200 mg. If it takes more than 15 minutes to filter the solution, then redo the experiment with a smaller volume.
- 8. Wash the sides of the filter apparatus and the filter paper with three successive 10 mL volumes of distilled water.
- 9. Remove the filter paper and place it in the corresponding crucible and dry at 103-105 °C overnight.
- 10. Let the crucibles cool, then place them in a desiccator for 4 hours.
- 11. Weigh the crucibles (B).
- 12. Perform triplicates for each sample.

Calculations

TSS = (B - A) / Sample Volume