DETOXIFICATION OF BLEACHED KRAFT MILL EFFLUENTS BY FOAM SEPARATION

bу

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ABSTRACT i

Foam separation has been successfully developed on a 4-1 laboratory column, an 80-1 field column installation and a 6000 gal pilot plant trough type system as a novel process for detoxifying bleached kraft mill effluents.

Toxic surface active materials such as resin and unsaturated fatty acids collect at the gas-liquid interface of rising air bubbles and concentrate in the foam. The highly toxic collapsed foam represents 1-2% by volume of the influent and is subsequently detoxified by biological treatment. Process parameters controlling detoxification efficiency are pH, gas-liquid interfacial area, initial toxicity level and mode of operation. The gas-liquid interfacial area and pH are of utmost importance. For a typical effluent with MST of 3-4 hr, approximately 20- $30~\text{m}^2/1$ of interfacial area given to an effluent at pH > 7.0 are required for detoxification.

Foam separation is universally applicable and reliable for detoxifying kraft whole mill effluent. Over 80% of 205 samples from 10 Canadian mills were detoxified. A 1 gal/min, one and two stage continuous flow systems detoxified over 90% of samples at pH 8 and 1-2 hr retention time over 80 days of operation period.

Study of detoxification mechanism indicated that foam fractionation accounts for 77.5% of detoxification, volatization for 5.4% and unidentified mechanisms for 17.1%. Depending on the mode of operation, up to 5% of effluent volume was discharged as foam. The foam volume could be reduced to < 2% by increasing foam retention time and enhancing internal

reflux. Collapsed foam was readily detoxified by a biodisc or aerated lagoon process.

In addition to detoxification, foam separation removed 20-60% of suspended solids, 66% resin acids, 12% BOD_5 (10% TOC), 8% color and 80% foaming tendency. Suspended solids removal could be increased to 88% if an expensive dissolved air system were used for bubble generation.

Commercially available equipment for foam generation and foam breaking was reviewed. Jet aerators and turbine systems were assessed as most suitable for commercial application. Pilot plant evaluation of this equipment indicated that reliable and consistent operation could be obtained. The results were used to establish empirical formulae for use in process scale up.

During a 4 month continuous flow study, approximately $5-7 \text{ m}^2/1$ of gas-liquid interfacial area was provided to detoxify 80-100 gal/min of mill A effluent with MST of 6-10 hr. The detoxification success rate of a large number of samples increased from 50 to 86 and to 100% as the operation changed from 1 to 2 to 3 stages. The foam produced by the pilot plant was collapsed by a 12" diameter turbine at 100% efficiency all the time.

Costs of foam separation were examined for a projected 3 stage foam separation process, treating 25 M gal/day of bleached kraft whole mill effluent. Capital costs for pH control, foam generation, foam breaking and foam treatment were estimated at \$2.26 M. Operating costs were estimated at \$2.35/ton of pulp.

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NOMENCLATURE

| Υ | Surface tension (dynes/cm) |
|--------------------|---|
| μ | Chemical potential (dynes-cm/g-mole) |
| Γ | Surface excess (g-mole/cm ³) |
| а | Activity coefficient |
| R | Gas constant |
| T | Absolute temperature |
| K | Proportionality constant i=1,2,3,4 |
| N | Rotation speed of turbine (rpm) |
| D | Diameter of turbine (cm) |
| $v_{\mathtt{tip}}$ | Tip velocity (cm/sec) |
| Σ_{t} | Foaming tendency (min) |
| $\Sigma_{f s}$ | Foaming stability (min) |
| v | Volume of foam |
| E | Efficiency of foam breaking |
| P | Power consumption (watts) |
| F | Foam breaking capacity (ft ³ /min) |
| d | Bubble diameter (mm) |
| t | Time of aeration (min) |
| Y | Treatment time required |
| X | Influent toxicity (MST:hrs) |
| | |

CHAPTER 1

POLLUTION PROBLEMS IN KRAFT INDUSTRY

The process of manufacturing pulp and paper requires an enormous amount of water. In Canada, a typical bleached kraft pulp mill consumes an average of 30,000 to 40,000 gal of water per ton of pulp produced. Up to 25% of the wood chips may be digested by the cooking chemicals, converted into various chemical compounds and discharged to the receiving waters in dilute form. These chemical compounds are considered as pollutants. The characteristics and types of pollutants however, are highly complex and are still in the process of being identified. Nevertheless, these pollutants can be classified in the form of the following effects:

- pH inbalance
- suspended solids concentration.
- biochemical oxygen demand (BOD)
- toxicity
- color.

The greatest impact of discharging untreated kraft mill eflfuent to the adjacent environment is primarily due to release of tremendous volume of waste at a single point. The cumulative effect of various pollutants will consequently lower the quality of receiving waters and damage the ecology of the surroundings. At present the Federal and Provincial authorities have established effluent discharge guidelines for pH, suspended solids, BOD₅ and toxicity; the degree of removal required for each mill however is set according to individual circum-

stances such as geographical locations, type and age of the mill, etc.

In general, pulp and paper mills across Canada attempt to meet the pH standard by controlled discharge of various acid and alkaline sewers coupled with chemical treatment where necessary, to achieve the permitable pH levels. Suspended solids standards are met by sedimentation with or without chemical aids. The design of these two physical-chemical treatment processes are quite standard and their performances are reasonably consistent (1).

The removal of BOD₅ is accomplished by biological treatment processes where the BOD₅ materials are biodegraded by micro-organisms (2) to CO₂, water and cell mass. Nutrients and other environmental factors must be maintained at suitable levels. A good biological system must also incorporate special designs to provide protection against shock loads such as spills and process changes during pulp mill operations. These are to ensure proper functioning of the biomass.

With regard to detoxification, although several techniques have been proposed, none of them is yet economically viable. The kraft industry presently relies completely on the proper performance of their biological waste treatment system to achieve the side effect of detoxification. Since the bio-processes are not designed for toxicity removal, proper safeguards have not been considered to ensure optimum performance. As a result, removal of toxicity is not always consistent (3).

Kraft mill effluents are highly colored due to the presence of large amounts of lignin derivatives. An adverse effect on fish life has not been demonstrated. Current studies are related mainly to the effects of color discharge (4, 5) on light transmission and in turn on primary productivity of photosynthetic aquatic flora. At present, no standard has been set to regulate the discharge of color compounds. However, in anticipation of the more stringent regulation, several major research studies on color removal have recently been initiated. Most notable are the development of massive lime (6,7,8), ion flotation (9,10) and ozone (11,12) treatment processes. These processes still require substantial development work before commercialization can be achieved.

Considering the effluent guidelines and the technologies available to date, one of the most pressing problems facing the pulp and paper industry is the removal of toxicity. At present the Federal Government toxicity standard calls for discharge of an effluent capable of sustaining 80% fish survival in a 65% effluent over 96-hr. In 1971, the Pollution Control Board of British Columbia established level A and B effluent toxicity guidelines for coastal mills (13). The level A toxicity objective requires 50% fish survival in 45% effluent concentration over 96-hrs, whereas for level B, the effluent concentration is 12.5%. The mills are required to meet the level A standard in the near future. The federal and provincial level A standards can only be met by implementing some form of waste treatment system. Since a biological treatment process is the best known method of simultaneous BOD₅ and toxicity

removal, even though detoxification is not necessarily consistent, the process has been widely adopted by the industry. However, in most coastal mills, BOD5 removal is not compulsory due to the large dilution involved when discharging to marine water and as land is always scarce, a biological treatment process is not a suitable choice. An alternative approach, such as physical separation technique would be more practical.

CHAPTER II

RATIONALE OF FOAM SEPARATION PROCESS AS A MEANS OF DETOXIFYING KRAFT MILL EFFLUENTS

A. TOXIC COMPONENTS OF KRAFT MILL EFFLUENTS

The toxicants in kraft mill effluent have been shown to vary with the type of wood furnish (soft-or hardwood) and process conditions. A large number of chemical compounds are known to contribute to the overall toxicity. In a recent review (14), it has been suggested that toxicants consists mainly of soaps of resin and fatty acids, terpenes; sulphur compounds (hydrogen sulphide, sodium hydrosulphide, sodium thiosulphate, dimethyl sulphide, methyl mercaptan); chlorinated lignin residues; chlorinated guaiacols and catechols; tetrachloro-o-benzo-quinone; trichloroveratrole; 4-(P-tolyl)-1-1 pentanol; acetone; methyl ethyl ketone, pinenes, diterpine and terpineol.

Basically, the toxic materials can be classified as volatile and nonvolatile substances. The volatile compound are mostly sulfur compounds (15). The type, and the concentration lethal to fish (16) are shown in Table 1. The maximum concentrations of volatile toxicants tolerable by fish without causing death range from 0.3 to 1 mg/l. The lethal concentration is approximately 1 - 3 mg/l. The concentrations that exist in fresh effluent normally exceed the lethal level. However they are unstable and can be removed by air or steam stripping. This type of toxicant is not the subject of this study.

^{*} LC50: Concentration of effluent at which 50% of test fish was killed after 96-hr exposure.

TABLE 1
REPORTED TOXIC VALUES (15,16) OF SULPHUR COMPOUND

| Sulphur Compound | Chemical Formula | *Critical Concentration (mg/l) | ** Lethal Concentration (mg/l) | *** LC50-48 hr (mg/1) |
|----------------------|--|--------------------------------------|---|-----------------------------|
| Hydrogen sulphide | H ₂ S | 0.3-0.5 | 1.0 | <u>-</u> |
| Methyl mercaptan | CH₃ SH | 0.5-0.9 | 0.9-1.2 | _ |
| Dimethyl sulphide | (CH ₃) ₂ S | - , | - | 2.3 |
| Dimethyl disulphide | (CH ₃) ₂ S ₂ | - . | | 4.0 |
| Dimethyl sulphoxide | (CH ₃) ₂ SO | - | | 5.4 |
| Sodium sulphide | Na ₂ S | 1.0 | 3.0 | 1.75 |
| Sodium Hydrosulphide | NaHS | 0.3 | 1.8 | - |
| Sodium Thiosulphate | Na ₂ S ₂ O ₃ | 5.0 | - | - |

^{*} Maximum concentration tolerable by test fish without causing death.

^{**} Minimum concentration required to kill 100% of test fish.

^{***} Concentration required to kill 50% of Daphnia after 48 hr of exposure.

Among the non-volatiles, resin acids were first reported as toxic constituents (17). Other toxicants and their contributions to toxicity were not identified until recently. The toxicants are organic in nature. Table 2 shows the types and concentration of toxicants present in individual and combined effluent streams from several Canadian kraft mills. Individual toxicants isolated (18) from these effluents kill fish at 0.2 - 2 mg/l. Most process streams contain more than 2 different toxicants, their combined concentrations (19) in these streams are up to 10 times greater than the individual lethal concentrations (20,21).

In woodroom effluent, the concentrations of toxicants vary widely with the wood furnishes, the degree and nature of water recycle, the extent of debarking and temperature of the wash water. The pH condition at which debarking is undertaken is also important because more resins would be dissolved at an alkaline pH. Approximately 10 - 50 mg/l of resin acids, depending on (22) whether hardwood or soft wood are used, can be found. The resin acids, composed mainly of abietic, dehydroabietic, isopimaric and palustric acids account for about 80% of the toxicity (18) of kraft mill effluents. A small fraction of unsaturated fatty acid and diterpene alcohols were also found to contribute to the overall toxicity. The major unsaturated fatty acids were oleic, lino-leic, linolenic, and palmitoleic. Saturated fatty acids are not toxic at concentrations of up to 20 mg/l (20).

In the pulping effluent (unbleached white water), resin acid concentration ranges from 14 - 20 mg/l, which is also responsible for

TABLE 2 TOXIC COMPONENTS IN KRAFT MILL INDIVIDUAL AND COMBINED PROCESS STREAMS

| | | | Concentration of Toxicants (mg/1) | | | |
|--|---|----------------------|-----------------------------------|--------------------------------|---|---------------------------------------|
| Type of Chemical Compounds* | Lethal Concentration (mg/1) 96-hr LC50 | Woodroom Effluent | Kraft Unbleached Whitewater | Kraft Bleach Plant Effluent | | Maximum Conc. |
| (Sodium salts) | | | | Caustic Effluent | Acid Effluent | in Bleached Kraf Wholemill Effluen |
| Naturally Occuring Resin Acids(abietic, dehydroabietic, palu- stric, pimaric) | 0.4-1.1 | 10 - 50 | 14 - 20 | Trace | 0 | . 8 |
| Chlorinated Lignin | - | - | - . | | 1.3-2.2 Chlorine Atoms/ lignin unit | - . |
| Chlorinated Resin Acids(Mono & dichloro- dehydroabietic) | 0.6 | 1440 | - | (0-6.8) | - | . 2 |
| Unsaturated Fatty Acids (Oleic, linoleic, lino- leric, palmitoleic) | 2.5-8 | 0.3-2 | 7 | _ | - | 2 |
| Chlorinated Phenolics (Tri & Tetrachloro- guaicol) | 0.3-0.8 | - | - | (0.4-2.3) | - | 0.7 |
| Diterpene Alcohols (Pimarol, dehydroabietol, abietol) | 0.3-1.8 | Trace | · - | . - | - | 1 |
| Epoxystearic acid | 1.5 | - | - | 1.5-17 | _ | |
| Juvabiones** | 0.8-2.0 | - | - | | _ | 3 |

^{*} Purification of chlorinated lignin have not achieved.** Present only in fir species.

80% of the toxicity (18). Under vigorous wood digestion conditions, up to 7 mg/l of fatty acids were found in the effluent. These two chemical components account for virtually all the toxicity in unbleached white water.

Two entirely different waste streams, namely caustic extraction and acid bleacheeffluents are discharged from the bleach plant. Toxicants (20) in the caustic extraction effluent are mainly chlorinated resin acids (1 - 6.8 mg/1) chlorinated phenolics (0.4 - 2.3 mg/1) and epoxystearic acid (1.5 - 1.7 mg/1). These compounds are not found in the acid bleach effluent. Instead, significant quantities of chlorinated lignin derivatives are believed to be present and to be responsible for the toxicity of acid bleach effluent. Their chemical structure and concentration have not yet been fully identified. However, it has been reported that 1.2 to 2.2 chlorine atoms were detected for every lignin unit present (23).

Although only limited data are available, the toxicants present in all individual process streams are expected to be present in the total combined effluent. The calculated concentrations of different toxicants in combined whole mill effluent are shown in Table 2. The major toxic components are naturally occurring and chlorinated resin acids (up to 8 and 2 mg/l respectively) and unsaturated fatty acids (up to 2 mg/l). Juvabione derivatives (up to 5 mg/l) although existing in high concentrations, were only found in mills processing fir species (20). For typical kraft whole mill effluent, the total combined concentration of toxicants is estimated to be 18.7 mg/l, approximately 10 - 20 times

greater than the lethal concentration of individual components.

B. EXISTING DETOXIFICATION PROCESSES

In recent years, because of the enforcement of toxicity discharge guidelines, removal of toxicity from effluents has become of concern to the kraft industry. Most detoxification processes have been developed on a trial and error basis and overall have not been very successful. Of those processes which show promise in reliably detoxifying the effluent, only a limited few were economically viable. These processes can be briefly categorized into physico-chemical and biological treatment processes.

1. Physico-Chemical Processes

a. Adsorption

Adsorption is based on operations in which specific substances are separated from solution upon contact with another insoluble phase, the adsorbent solid. Physical adsorption occurs as a result of physical or intermolecular forces of attraction between the gaseous adsorbate and the solid adsorbent. This type of adsorption, also known as "van der Waals" adsorption, is a readily reversible phenomenon. Chemisorption is the result of chemical interaction between the solid and the adsorbed substance. The adhesive force involved is generally greater than that of physical adsorption. Moreover, the process is frequently irreversible and, on desorption, the original substance often will be found to have undergone a chemical change.

Activated carbon is the most common adsorbent used to physically adsorb the pollutants from industrial effluents. This process is characterized by short retention time (< 4 hr), simple operation and it does not generate difficulty in the disposing of sludges (24). Carbon is effective in removal of toxicity from the effluent (25), but very little BOD removal is accomplished. Recently a carbon adsorption process using 300 mg/l of powder carbon and combined with 300 mg/l of alum has been proposed (26). After pH adjustment and followed by aeration, the toxicity, BOD₅ and color of kraft mill effluents were concurrently removed. However, the cost is high and the process may require an alum and carbon regeneration system.

Detoxification studies have also been undertaken with flyash (multiclone rejects from the hog fuel boiler) with a certain degree of success (27). Because of the uncertainties in flyash supply, this method could only be used for selected waste streams and by a limited number of mills. Use of peat moss for toxicity adsorption (27) was not successful.

Polymeric resins, such as Rohm and Haas XAD-2 have been extremely successful in adsorbing toxicity (28). An adsorbent regeneration system and subsequent disposal of the toxic materials are required. The cost of this system would be higher than for the carbon system.

1

b. Coagulation - Flocculation

The words coagulation and flocculation are often used interchangeably in waste water treatment technology. In the treatment of effluents, coagulation usually involves the reduction of surface charges and the formation of complex hydrous oxides. This process is generally instantaneous in the interaction between coagulant and solid particles. Typical coagulants are alum and heavy metals. In most waste water applications, soluble polymers are used as flocculants either solely or after the addition of coagulants. These polymers may be natural products, e.g., guar gum and modified lignosulphones, or synthetic, e.g., polyacrylamide and polyethylenimine. Typically, the molecular weight of these polymers is between $<2 \times 10^6$ and 20×10^6 .

Polyelectrolytes are linear or branched polymer molecules with ionizable functional groups. When these groups dissociate, the polymer molecules become charged either positively (cationic) or negatively (anionic). Nonionic polyelectrolytes are those without ionizable functional groups. At a given temperature, the configuration of the polymer molecule is dependent on the number of potential charge sites on the polymer chain, the extent to which these sites are ionized and the ionic strength of the solution. Unfortunately, because detailed information pertaining to the physical and chemical nature of the commercial products are closely guarded by each manufacturer, the selection of a suitable polyelectrolyte is mostly based on experience and still remains as an art.

A number of studies have been undertaken using several polyelectrolytes (29), and heavy metal compounds, e.g. lime, alum and ferric chloride (30) as flocculants. Removal of toxicity (31,31) can be obtained at a cost of \$5 - \$6/ton of pulp. Sludge handling appears to be the major problem.

c. Chemical Oxidation

Air and molecular oxygen are the most common oxidants for general industrial uses. However, at ambient temperatures and pressures, these oxidants are ineffective for the treatment of pulp and paper effluents. The efficiency of these oxidants can, however, be improved by operations at elevated temperature and pressure. Catalytic oxidation has been tried to improve the oxidation efficiency of organics in dilute aqueous solutions. In general, a catalyst or promoter is used to initiate the oxidative reaction. Ultraviolet and gamma irradiations have been studied as promoters of chemical oxidation of pulp and paper mill effluents. These processes are relatively sophisticated and cannot be justified economically.

Among the gaseous oxidants, ozone has been investigated (11,12,32) most thoroughly for removal of various categories of pollutants from kraft mill effluent. It has been reported that acute toxicity of kraft mill effluents could be removed during ozonation. However, detoxification was attributed to concurrent foam separation rather than chemical degradation of toxicants. Treatment costs were estimated to range

between \$7 - \$45 per ton of pulp. During the process, the color and BOD_5 of kraft mill effluent were also removed by 80% and 70% respectively (12,32).

2. Biological Treatment Processes

Biological processes are primarily designed for BOD_{ς} removal (33) and have become the only practical form of detoxification technique currently in use. The efficiency of detoxification by biological treatment is associated with BOD_5 removal (33,34). In a recent study, it has been shown that most toxicants isolated from kraft mill effluent are biodegradable (35). However, chlorinated constituents except tetrachloroguaiacol compounds are more resistant to biodegradation than resin and fatty acid derivatives. To achieve high success rate of detoxification, biological processes must be operated at suitable retention time with adequate nutrient, dissolved oxygen and mixed liquor suspended solids concentrations (36). The operating cost of these processes ranges from \$2 - 4 per ton of pulp. Experience in pulp and paper mills(e.g. Northwood pulp mill, Prince George, B.C. and Weyerhaeuser Pulp Mill, Kamloops, B.C.) suggests that high detoxification success rate can be obtained consistently by proper operation of the treatment system: most mills, detoxification failures can be related to negligence, lack of suitably trained operators, frequent process changes in the mill and variation of environmental factors.

3. Conclusions

The upper cost limit for a detoxification process to be acceptable to the kraft pulp industry, should not exceed the cost of biological treatment process i.e., \$2 - 4/ton of pulp. Most physico-chemical treatment processes for detoxification are still in the development stage. Treatment costs for all processes are in the \$6 - 20 range, i.e. far beyond the economical level. Moreover, subsequent sludge disposal usually presents a problem. From both economic and technical points of view, none of the physico-chemical methods have developed to a commercially viable process.

In the past, biological detoxification techniques were practised without the full understanding of the chemistry of toxicants. At present, with more toxicants being identified, detoxification performance of biological processes has been improved. The largest drawback of biological process however, is the large land area requirement. For mills which are hampered by shortage of land and for coastal mills who are not required to remove effleunt BOD₅, a rapid detoxification process which can guarantee reliable detoxification is still highly desirable.

C. POTENTIAL ROLE OF FOAM SEPARATION PROCESS FOR DETOXIFICATION OF KRAFT MILL EFFLUENTS

Foaming has always been associated with the pulping process (19,37) and with its effluent discharges. It is a frustrating and troublesome operation characteristic. The foaming tendency of the effluent depends on the pulping process and wood species and varies with each process

stream. Over the years, a great deal of attention has been given to foaming characteristics of pulp and paper mill effluents. Foaming technology has been investigated in several studies for reduction of BOD₅ (38), color (29,39), foaming tendency (38), resin acids (40) and suspended solids with variable degrees of success. Some reduction of toxicity as a result of foaming, but not a substantial one, has also been reported in dilute black liquor (41), sulphite mill effluent (42) and kraft mill effluent (43) in earlier studies. However, the cause of toxicity reduction was not clear when these observations were made.

In recent years, it has been observed that during biological treatment processes, copious amounts of stable foam (accumulating up to depths of several feet) are produced which cover the entire aeration pond during the aeration process (44). These foams are produced, collapsed, dried and redispersed to the pond according to changes in effluent characteristics and climatic conditions. It is now believed that the foams when returned to the effluent will cause irregular detoxification results (45) of the biological treatment system.

To date, among the toxic components identified in kraft mill effluent, major toxicants, such as all naturally occurring (Figure 1) and chlorinated resin acids, fatty acids and chlorinated lignin derivatives belong to the group of carboxylic acids. These are all surface active compounds. Surface active compounds are known to reduce surface tension and promote foaming (46,47) in a solution. Under suitable conditions, they can be separated by foaming as a result of their own surface

CHEMICAL STRUCTURE OF RESIN ACIDS

ABIETIC ACID

CH₃

CH₃ COOH

LEVOPIMARIC ACID

DEHYDROABIETIC ACID

NEOABIETIC ACID

CH3

ĊH₃

17

activity or by reacting with non-surface active materials (toxic or non-toxic) to form new surface active complexes which are then removed from the bulk of the solution by foaming. It is postulated that resin acids, fatty acids and other not as yet identified toxic compounds, surface active or not, may concentrate independently in the foam or react to form a complex prior to attachment to the foam. Removal of foam will result in removal of toxicity. Recent studies have documented the validity of this hypothesis:

- 1. Separation of foam from kraft mill effluent removed up to 65% of the resin acid content (40).
- 2. A non-active biological treatment system (extreme pH and N $_2$ aeration to prevent the growth of microbes) under foaming conditions, detoxified a kraft mill effluent to a degree comparable to an active biodegradation system (48) in the laboratory.

Although the solubility, foaming characteristics and lethal concentrations of individual toxic compound vary and are dependent on pH, temperature and synergistic effect of each toxic component, these surface active compounds can be adsorbed onto the gas-liquid interface (bubble) by providing suitable chemical and physical conditions. Thus their concentration in solution can be reduced to a level which is not toxic to fish. Based on these preliminary data, it is proposed to evaluate and optimize foam separation as an alternative to existing techniques for detoxification.

CHAPTER III

LITERATURE REVIEW OF FOAM SEPARATION PROCESSES

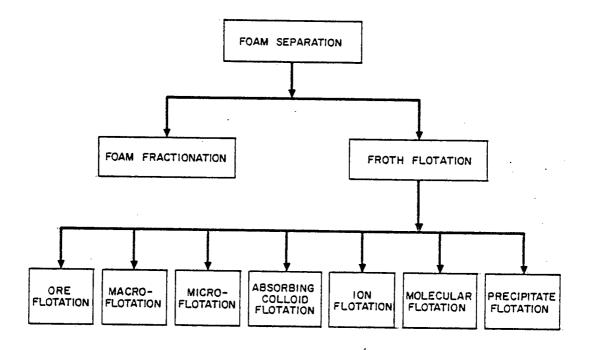
A. CLASSIFICATION OF FOAM SEPARATION PROCESSES

Foam separation is a chemical engineering process that selectively separates the surface active components of a solution at the surfaces of ascending bubbles. Foam separation belongs to the group of "adsorptive bubble separation methods" (49) that may be conveniently classified into foam fractionation and froth flotation (Figure 2). Foam fractionation separates dissolved substances from homogeneous solutions by selective adsorption of one or more solutes with the aid of surfactants on the gas-liquid interface while froth flotation separates insoluble substances from heterogeneous systems.

Froth flotation is further subdivided into seven categories:

- 1. Ore flotation is a solid-solid separation technique. This technique is mainly used for separation of mineral ores.
- 2. Macroflotation is the removal of macrosopic particles by foaming.
- 3. Microflotation is the removal of microscopic particles, especially microorganisms and colloidal materials by foaming.
- 4. Adsorbing colloid flotation is the removal of dissolved material that is first adsorbed on colloidal particles. The major objective being the removal of the dissolved material rather than the colloidal particles.
- 5. Ion flotation is the removal of surface inactive ions (colligend) by the addition of an oppositely charged surfactant (collector) in

Figure 2
CLASSIFICATION OF FOAM SEPARATION



is then floated out. At high concentrations, a precipitate is formed which is subsequently removed by particulate flotation. At lower concentrations, the collector adsorbs on the bubbles and holds the colligend to them.

- 6. Molecular flotation is the removal of surface inactive molecules through the use of a surfactant which yields an insoluble complex which is then floated out.
- 7. Precipitate flotation involves the formation of precipitates prior to addition of surfactant. Since flocculants are used frequently, the overall charge on the material to be removed is reduced. The surfactant is required only to react with outermost layer of the precipitates resulting in surfactant requirement less than stoichiometric amount.

B. PRINCIPLES OF FOAM SEPARATION

1. Film Formation

The most widely believed theory of film formation is the "balanced layer" theory (50). The hypothesis was that below the surface, when two bubbles were formed, a foam film is formed as two bubbles approach each other. In the solution, the mechanical force, that brought these surfaces together encounters increasing resistance as the liquid layer between them becomes thinner. The resistance arises from the difference in concentration between the surface layer and the mass of the solution. Solute is either positively or negatively adsorbed on the surface. This concentration difference is spontaneous, and therefore requires the

expenditure of work on the system to restore the quality of concentration. This theory explains why pure liquids and saturated solutions do not foam. Since adsorption does not occur in these solutions, resisting forces cannot arise to prevent coalescence and the consequent disappearance of surface.

2. Adsorption

The fundamental equation for adsorption (51) was developed by Gibbs. It relates the degree of adsorption at the boundary between 2 phases to the change in interfacial tension at that boundary and composition of the two phases. For equilibrium conditions at constant temperature, and where the radius of curvature of the boundary surface is large compared to the thickness of the interfacial transition layer, the equation is:

$$d\gamma + \Gamma_{\dot{1}}d\mu_1 + \dots + \Gamma_{\dot{i}}d\mu_{\dot{i}} = 0$$

 γ = Surface tension of solution, dynes/cm

 $\mu =$ Chemical potential of the components in the bulk phase, dynes-cm/g-mole

 Γ = Excess surface concentration of components g-mole/cm²
In a system containing one solvent and one solute, the surface excess concentration of the solvent Γ_1 = zero, and the equation becomes:

$$d\gamma + \Gamma_2 d\mu_2 = 0$$
 or $\Gamma_2 = -\frac{d\gamma}{d\mu_2}$

The chemical potential of a solute is defined as:

$$\mu_{i} = \mu_{i} + RT \ln a_{i}$$
 where

 μ_{i} = Chemical potential of component i in the surface phase (dynes-cm/g-mole)

 μ_{i} = Chemical potential of component in the surface phase under standard conditions (dynes-cm/g-mole)

 $a_i = Activity of component i (g-mole/cm³)$

R = Gas constant

T = Absolute temperature

By differentiation:

$$d\mu_i = RT dln a_i$$

hence

$$\Gamma_2 = -\frac{1}{RT} \times \frac{d\gamma}{d\ln a_i}$$

In practice, the difficulties in measuring small changes in γ accurately and the uncertainties in identifying the specific surfactants and evaluating their activity coefficients have severely limited the utilization of this equation as a quantitative tool. However, at below critical micelle concentrations (dilute solution), a_i approaches c_i (concentration of solute).

$$\Gamma_2 = -\frac{1}{RT} \times \frac{d\gamma}{d \ln c}$$

The Gibbs adsorption equation indicates that the surface excess of a solute depends on $\frac{d\gamma}{d\ln c}$. A large negative value of $\frac{d\gamma}{d\ln c}$ will mean high concentrations at the gas-liquid interphase (52).

3. FOAM SEPARATION MECHANISMS

a. Foam Fractionation

Foam fractionation of solutes occurs when gas is dispersed into a solution containing material which has a different surface activity (53)

than the bulk liquid. In an aqueous phase, surface active material possessing hydrophilic (polar groups) and hydrophobic (non-polar groups) properties will migrate to the bubble-liquid interface because this arrangement provides higher stability than the homogeneous solution. Figure 3-a illustrates the orientation of surface active molecules on a bubble. The molecules arrange themselves in such a position that the hydrophilic ends of the molecules remain in the aqueous phase and the hydrophobic ends protrude into the gaseous phase. During continuous operation, bubbles float to the top of the liquid and form a foam blanket. If the foam produced is stable, the surface active material will be accumulated in the foam layer and can be removed from the mother solution.

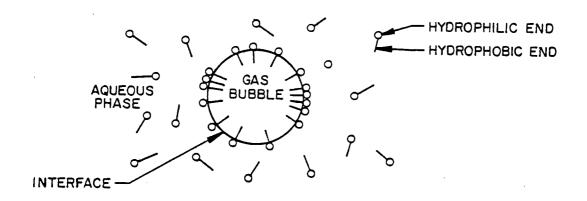
Solutes which by themselves have little or no foaming ability, may be successfully foam fractionated by adding foaming agents. These agents (54) are required to form either electrostatic bonds or chelates with the solutes. For instance, organic (55) and inorganic ions can be foam fractionated (56) by the aid of cationic or anionic surfactants, i.e. by using a surfactant of the opposite charge. In some situations, the charge of a solute may be changed by a change in pH and made susceptible to foam fractionation.

b. <u>Froth Fl</u>otation

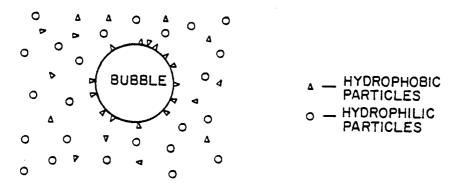
Froth flotation removes insoluble, suspended matter. Air bubbles are introduced into a heterogeneous mixture of liquids and solids. The tiny bubbles serve as sites for the attachment of the suspended matter

Figure 3

a. ADSORPTION OF SURFACE ACTIVE MOLECULES ON GAS-LIQUID INTERFACE



b. MECHANISM OF FROTH FLOTATION



(57) which posesses hydrophobic properties. Figure 3-b illustrates how the operation of froth flotation is effected. Due to differences in density, the bubble-particle conglomerate will rise to the top and concentrate into a froth layer. The froth together with the suspended solids can then be removed.

c. Factors Affecting Foam Separation

The effectiveness of foam separation depends on the adsorptive characteristics of the system and properties of the surfactants. characteristics are frequently described by the following terms (58):

Expansion Ratio Liquid Content

 $= \rho \times \frac{V1}{Vf}$ Foam Density

Foaming Tendency = $\frac{\text{Vf x t}}{\text{Vg}}$ Gas/liquid interfacial area S = $\frac{\text{Vg x 6}}{\text{Vl x d}}$ assumes spherical bubbles

Where: Vf = Volume of foam

= Volume of liquid contained in the foam

= Density of liquid

= Volume of gas introduced at time t

= thickness of liquid film

d = bubble diameter

= gas-liquid interfacial area/unit liquid volume.

The efficiency of foam separation is governed by the ratio of the concentration of the solute in the foam phase to that of the bulk liquid (enrichment ratio). A maximum enrichment ratio corresponds to maximum

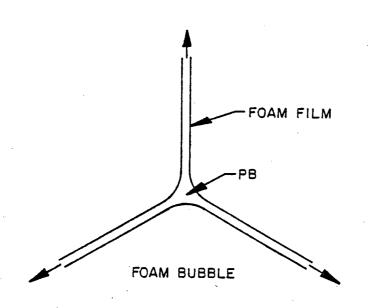
purification and minimum foam production. In order to obtain a high enrichment ratio, the foam on which surfactant is adsorbed must be reasonably stable; the entrained liquid should be easily drained out (53,54).

Foam stability relates to the capability of foam to maintain thick walls of liquid which resist external stresses and to repair random thin spots thus preventing foam breakage by the presence of electrostatic surface forces. Foam persists so long as the liquid films constituting it exist. A stable foam can withstand lamellar thinning without rupturing. Those factors (59) which affect the development and stability of foams are: the nature and concentration of the system components, temperature, pressure and pH. These factors in turn determine the secondary variables such as viscosity, surface tension and bubble size. Their relative contribution and interaction to foam stability are extremely complex. The selection of optimum values for these factors seeks to provide a different surface film concentration from that of the bulk liquid and to create a high surface viscosity in the surface layer.

Foam drainability refers to the formation of a dry foam as a result of suction and gravitational forces. When a foam is formed, liquid drainage (60) occurs instantly within the plateau borders and lamellar walls (Figure 4). Drainability is affected by intralamellar liquid concentration, bubble size, viscosity and surface tension.

Figure 4

THREE FOAM LAMELLAE COMING TOGETHER IN A PLATEAU BORDER AND FORMING ANGLES OF 120° WITH EACH OTHER



Foam stability and drainability can be improved by the following methods (58):

- Increase the bulk viscosity
- Increase the surface viscosity
- Lower the surface tension
- Increase the surface elasticity
- Increase the surface concentration
- Prevent evaporation.

Specific parameters that have an important effect on the degree of separation are presented as follows:

1. Chemical Nature and Concentration

In general, the foaminess of aqueous solutions of inorganic compounds is small compared to aqueous solutions of many alcohols, organic acids, and organic salts. For a single solute, there is an ideal concentration where the most stable foam will be formed. If the concentration of a surfactant is too high, its molecules can group together so that the hydrocarbon chains are close together and away from the solvent liquid (61). Such a grouping is usually referred to as a micelle.

Maximum foam stability occurs at the critical micelle concentration (45). Micelle formation has a detrimental effect on successful separation because of the loss of surface activity (62).

Low concentration of surfactant is also undesirable as the stability of the foam cannot be maintained. For multi-component solutions, foam

stability may increase or decrease as the concentration changes.

2. pH

Almost all investigators refer to the importance of pH on foam separation. In general the effect of pH can be summarized (63,64) as follows:

- pH changes may affect the solubility of the surfactant and surface tension of the solution. The stability of the foam may change leading to redispersion.
- A change may occur in the charge of colligend, due to hydrolosis or formation of other complexes.
- Variation of pH can lead to precipitation of a colligend.
- Changes may occur in the ionization of the collector; (Surface active agent used to form a complex with materials to be removed) acid or amines, may lose their charge at low or high pH values.

 They either then cease to be collectors, or their mode of collection changes.

3. Gas Flow Rate

With a constant bubble diameter, the volume of gas provided determines the surface area available for surfactant adsorption. Increasing air flow increases the rate of surfactant removal. However, this will reduce the retention of the foam in the column, permitting more liquid entrainment and reducing the enrichment ratio (65). The volume of foam generated will also be greater.

4. Bubble Size

In foam separation the gas-liquid interfacial area required for removal of a unit concentration of a specific surfactant is constant. Therefore, the sizes of the bubbles produced dictate the amount of air required (blower capacity) to produce this gas-liquid interface. The bubble sizes should preferably be as small as possible. Small bubbles, however are more costly to produce. The adsorption properties of bubbles of different sizes are basically the same on a per unit area basis but the ascent rates of bubbles are different. As a result, smaller bubbles will have a longer bubble-liquid contact time. In foam separation of toxicity (resin acids and fatty acids removal), it is assumed that adsorption of toxicants on the interface is instantaneous, therefore the ascent rate due to bubble size difference should not be an important factor in determining gas-liquid interfacial area.

5. Temperature

Foam stability usually decreases with increasing temperature. This is due primarily to the decreased viscosity of the surface layers and increased gas pressures within the bubbles. Although it has been known that there is a critical temperature above which a solution containing surfactants will not foam, very little attention has been given to this in most studies. In theory, the behavior of surface active compounds is greatly affected by temperature. Above the critical micelle concentration, the solubility of surfactants increases markedly with temperature. The temperature at which the surfactant solubility is equal to critical micelle concentration is defined as "Kraft-Point" (66). Increased temperature will decrease viscosity and increase the drainage rate in the foam film. Therefore the foams are unstable and easily ruptured. High temp-

atures also cause preferential evaporation within the liquid films. If the liquid is evaporated, the concentration of the solute may be increased until the bubbles collapse.

6. Viscosity

Foam stability is highly dependent on viscosity. High viscosity reduces foam drainage and may reduce enrichment if the foam is removed quickly. However, slow drainage will cause the gas bubbles to remain in contact with the bulk of the liquid longer. This is beneficial to surfactant adsorption.

7. Column Height

The height of the column affects the mass transfer of the surfactants from the bulk solution to the gas-liquid interface. In general, minimum column height will depend on bubble size. Increasing column height permits longer bubble-liquid contact and will enhance foam enrichment. A study conducted by Goldberg (67) suggested that a minimum column height of 10 cm would be sufficient for surfactant absorption.

8. Foam Removal

Removal of surfactant cannot be realized without the formation of foam. Unstable foams must be removed as they are formed, thereby decreasing drainage and enrichment. Moderately stable foams may break and provide internal reflux which increases enrichment. For stable foams

external reflux is required to increase enrichment. So the method of foam removal depends on the foam characteristics and the extent of enrichment desired.

D. Mode of Operation

There are two general configurations for foam separation equipment: the column type and the trough type. For small-scale and laboratory operations, the column type separator is the most common type in use today. The feed liquor is fed to the side of the column just below the foam liquid interface. Porous spargers are placed near the bottom of the column to disperse the gas. The accumulated foam is removed from the top of the column.

From practical considerations the trough system is most suitable for commercial operations because of simpler construction than a tall foaming column. The feed is introduced at one end of a horizontal covered trough and is discharged near the opposite end. Devices generating fine bubbles are spaced along the bottom and the foam accumulates in the space between the foam-liquid interface and the trough cover. A vertical baffle holds the liquid in the trough while allowing the foam to spill over into a chamber for eventual discharge. The foam travels variable distances depending on where it was generated. Froth flotation is done mostly in trough-type systems. Both dissolved air and dispersed air are used to create the required bubble surface.

The column foamer is more versatile than the trough type. Figure 5 shows three additional modes of operation of a column foamer. The operational characteristics and the equations used (51) for estimation of the surfactant concentration in the treated effluent and in the foam are summarized (68) in Table 3. For enriching purposes, (Figure 5-b) a portion of the collapsed foam is returned into the foam fraction of the column as external reflux. This operation will enrich the net overflow and reduce foam production. For stripping action (Figure 5-c) the feed is in immediate contact with the foam. Some of the surfactants are removed before entering the liquid pool. This operation purifies the bottom product but greatly increases the foam volume. The combined enriching and stripping mode (Figure 5-d) is operated by directing the feed through the foam blanket and concurrently returning part of the collapsed foam as external reflux. Consequently, the net overflow is enriched, the bottom product and the volume of foam minimized.

E. Applications

Conventionally, foam separation has been used for the separation (69) and purification of naturally surface active substances, proteins, enzymes (70), fatty acids (71), salts and detergents (72). The use of foam separation in pollution control for the recovery and fractionation of surface inactive materials is a recent development (73,74,75). Table 4 summarizes the types of anions, cations, dyes, fatty acids and detergents, proteins and enzymes that have been removed by foam separation (76).

Figure 5
MODES OF OPERATION OF VARIOUS FOAM SEPARATION SYSTEMS

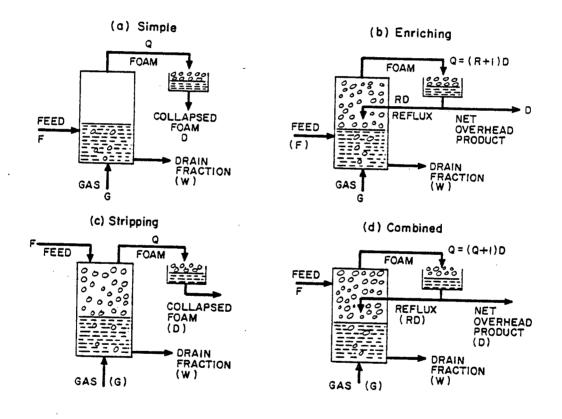


TABLE 3
CHARACTERISTICS OF DIFFERENT FOAM SEPARATION OPERATIONS (51,64)

| Mode of Operation | Features | Résults | Equations for estimation of column performance |
|----------------------|---|--|--|
| Simple | -Feed into liquid pool -Countercurrent contact of gas and feed | -Volume of foam removed is a function of foam height | $C_{Q} = C_{W} + \frac{6 G \tau_{W}}{Q d}$ $C_{W} = C_{F} - \frac{6 G \tau_{W}}{F d}$ |
| Enriching | -Feed into liquid pool -Part of collapsed foam returned to foam layer as external reflux -Countercurrent contact of gas and liquid(feed+ liquid drainage from foam) | Enriches the net foam overflowReduces volume of foam removed | $C_{D} = C_{w} + (6.59 - \frac{0.59}{R+1}) \frac{G\tau w}{Dd}$ $Cw = C_{F} - (6.59 - \frac{0.59}{R+1}) \frac{G\tau w}{Fd}$ |
| Stripping | -Feed into foam blanket -No reflux -Countercurrent gas- liquid contact | -Purifies bottom product -Increases foam volume -Decreases enrichment | $C_{Q} = C_{F} + \frac{6.59 \text{ Gt w}}{Q \text{ d}}$ $Cw = C_{F} - \frac{6.59 \text{ Gt w}}{w \text{ d}}$ |
| Combined | -Feed at lower part of foam layer -Part of collapsed foam returned to foam layer -Countercurrent gas- liquid contact | -Enriches the net foam overflow -Purifies bottom product -Moderate foam production | $C_{D} = C_{F} + \frac{6.59 \text{ Gr}_{F}(R+1)}{Q \text{ d}}$ $C_{W} = C_{F} - \frac{6.59 \text{ Gr}_{F}}{W \text{ d}}$ |

×

C = Concentration of surfactant

 τ = Surface concentration

F = Feed

Q = Collapsed foam flow rate

w = output from column

D = net collapsed foam overflow

R = reflux ratio

d = average bubble diameter

TABLE 4
APPLICATION OF FOAM SEPARATION PROCESS

| Types of Materials Removed | Specific Examples | Surfactant Requirement | Remarks | |
|----------------------------------|---|------------------------|---|--|
| Proteins and Enzymes | Cholinesterase, Dextrins, Diatase Fish scales, Hemoglobin, Hop Resins, Pepsin, Rennin, Tyrosinase, Urease, Metaprotein, Egg Whites; albumin | No | Best separation at isoelectric pH | |
| Anions | 1-Chloromethyl napthalene, 1-Naphthoic acid, Phosphates, ferrocyanide, Silicate, Phenolate | Cationic Surfactant | Recovery of surfactant may be required | |
| Cations | Ag, Be, Ca, Co, Cu, Fe, K, Mg, Mn, Ni, Ra, Sm, Sr, U, V, Th, Zn | Anionic Surfactant | | |
| Fatty acids and detergents | Lauryl sulfate, Sulfonates, Myristic acid, Nonylic acid, Oleic acid, Palmitic acid, Ricinic acid Saponin, Stearic acid, Decanoic acid, Lauric acid, triton. | No | | |
| Miscellaneous | Amyl and Lauryl alcohol. Sugar juices. Apple and beer proteins. Gonadotiopic hormones. Dyes. | No | | |

Examples of commercial applications of foam separation processes are the concentration of proteins from dilute solutions (69) and the removal of detergent compounds in sewage (77,78,79). Foam separation usually is conducted with 5 to 10 min retention times and G/L ratios of 3 to 6. For removal of anions and cations, addition of a surfactant of opposite charge (69, 71) to form a foamable metal-surfactant complex is required. The process therefore is more complicated.

In the pulp and paper industry, foam separation has been investigated for BOD removal (38,80). Froth flotation is widely used for removal of suspended solids (81) and biological solids (82). Foam fractionation is practised for recovery of tall oil (83) from black liquor. An ion flotation process (29,39) has been proposed for the removal of color from kraft mill effluent. Other applications include oil recovery from refinery wastes, grease and suspended solids removal from food processing, removal of colloidal materials (84) and concentration of algae (85) from lagoon discharges.

CHAPTER IV

MATERIALS AND METHODS

A. SCOPE OF STUDY

The research program was carried out in four phases:

- Phase I. Treatability and optimization studies using a 4 l laboratory foam separation system.
- Phase II. Idenfication of process operational problems in a 80 ℓ foam separation column installed at mill site.
- Phase III.- Verification of process conditions and detoxification reliability of foam separation process in a 6000 gal trough type foam separation system.

Phase IV. - Assessment of capital and operating costs.

1. Treatability of Various Process Sewers

During the manufacture of bleached pulp, various process sewers discharge wastes of different characteristics. In general, unbleached white water and caustic extraction effluent are more toxic than acid effluent (86) and combined effluent and also differ in foaming tendencies; in fact, only whole mill effluents possess excessive foaming tendencies. Experiments were designed to assess the amenability of individual and combined waste streams to detoxification by foam separation. The feasibility of using synthetic surfactants for enhancement of the foam separation process was also included in the evaluation program. The most easily treatable individual and combined effluent

streams were selected for subsequent studies.

2. Universal Applicability of Foam Separation Process

Wood furnishes, pulping and bleaching procedures, water usage and other process modifications for production of bleached kraft pulp vary from mill to mill across Canada. Effluent characteristics therefore also differ and may not be equally susceptible to detoxification by foam separation. In order to evaluate the applicability of the process to the entire industry, daily effluent discharges from a large number of Canadian mills were sampled over a one month period. Under standardized conditions, effluents were treated at different time intervals. The success rate and the treatment time required for detoxification were calculated. Attempts were made to identify the reasons for occasional detoxification failures in specific instances.

3. Optimization of Various Process Parameters

Using effluents from several mills, those process variables that were important in foam separation were optimized. Factors studied were pH, aeration rate (G/L), gas-liquid interfacial area, temperature, treatment time, column height and mode of operation. The optimum conditions for detoxification were determined for several mills and the results were used for development of a continuous flow system for onsite operation.

4. Detoxification Mechanisms

The principal mechanisms involved in detoxification by foam separation were studied to gain a better understanding of the process and to control better the process parameters. Several explanations have been postulated for the mechanisms controlling detoxification, namely: stripping, volatization, oxidation and foam fractionation. Attempts were made to determine the relative contribution of various mechanisms by separating the effluent into a foam fraction, a vapour fraction and a treated effluent fraction.

5. Feasibility of Combined Detoxification with Suspended Solids Removal

Dissolved air flotation has been used widely for suspended solids removal. During foam separation, a process similar to flotation, one would expect that the bubbles could be used for concurrent toxicity and suspended solids removal. An assessment was made as to whether the conditions suitable for detoxification were compatible with conditions for good suspended solids removal.

6. Beneficial Side Effects of Foam Separation

Foam separation is known to be capable of concentrating a variety of materials in the foam fraction. During the detoxification process, pollutants other than toxicants may also be removed simultaneously. Pollution parameters of interest that were studied, included BOD, TOC,

foaming tendency, resin acids, and color.

7. Process Reliability

After determination of process applicability and optimum process parameters in the laboratory, the results were verified in an 80-gallon capacity foam separator operated continuously at 1 gal/min for several months at a mill site. Effluents of changing characteristics were continuously fed to the system and detoxification performance was correlated to influent toxicity, operating conditions, mill upsets and mill operating practices.

In the course of the investigation, foam generation rates and operation difficulties were studied and corrected to improve the performance of the process. Collapsed foam was also collected and characterized for foam volume, liquid content and toxicity for foam disposal studies.

8. Selection of Foam Generation Systems

In the foam separation process, sufficient gas-liquid interfacial area must be generated for adsorption of surface active substances. The surface area can be estimated from:

For spherical bubbles,

Interfacial Area =
$$\frac{\text{Vgas x 6}}{\text{Vliq x bubble diameter}}$$
 (m²/1)

This equation suggests that at constant liquid volume, the smaller the bubble diameter, the smaller the volume of gas needed to generate the required surface area for detoxification. However, production of

small bubbles usually requires high energy inputs and may not be economical for commercial operation. Therefore, several types of commercial foam generating equipment were tested and compared with respect to bubble sizes, horsepower requirement and detoxification performance. The data are important for the design of any large scale system and for estimation of operating costs.

9. Reduction and Breaking of Foam

An average 750 tpd kraft mill discharging 25 MGD of effluent will produce large amounts of foam which must be collapsed by some practical means. The suitability of various modes of operation and foam breaking devices available on the market was investigated for application in a foam separation operation. The most efficient and economical system was selected and design parameters pertinent to kraft mill effluent were developed.

10. Disposal of Foam

Hypothetically, if foam fractionation is the main mechanisms of detoxification, the toxic substances will be concentrated in the foam. Further treatment will be required prior to disposal. Assuming that a minimum of 1 - 2% of the influent is converted to foam, the total volume of collapsed foam from a 25 MGD plant is estimated at approximately 250,000 - 500,000 gal/day. Although several approaches are available for treatment and disposal of this highly concentrated material, only

a few are practical. Physical destruction techniques such as evaporation followed by incineration appear to be the most effective from a technical view point, but may be too costly to operate. In consideration of the economics, only the less expensive biological treatment (aerated lagoon or biodisc processes) and chemical treatment techniques (flocculation - coagulation) were studied.

11. Pilot Plant Operation

Following laboratory and field site studies on the feasibility of foam detoxification techniques, the most suitable equipment selected for foam generation and foam breaking was installed in a 100 gal/min pilot plant. After successful demonstrations of the suitability of the selected equipment, a two-month continuous study was conducted to verify the detoxification performance of foam separation process and to obtain design parameters for a large scale installation.

12. Evaluation of Process Potential

After completion of the laboratory, field and pilot plant studies, the technical and economical potential of the foam separation process as a means of detoxification were evaluated. The capital and operating costs were compared to biological treatment processes, in particular to the aerated lagoon treatment which is used most commonly for BOD removal and detoxification of kraft mill effluents.

B. SOURCE AND TYPE OF EFFLUENTS

During the initial phase of laboratory investigation, individual process effluents, obtained from mills A,B,C and D were foam separated. For the remainder of the laboratory study, combined wholemill effluent from 10 Canadian mills (A to J) was used. For field and pilot plant studies, combined wholemill effluent from mills F and A were used throughout.

1. Laboratory Studies

As individual process streams, unbleached white water, caustic extraction stage effluent and acid bleached effluent were obtained.

Wholemill effluent consisting of all the major and minor process streams was obtained from 10 Canadian mills, the code names, location, wood furnishes and type of effluents obtained for the laboratory studies are shown below:

| Mil. | | tion of | Principal Wood Furnish | Type of Effluents Obtained | |
|------|------|----------|--|---------------------------------------|---------|
| A | B.C. | Coast | 18% fir, 46% hemlock 36% cedar | Individual process wholemill effluent | streams |
| В | в.с. | Coast | 43.4% fir 3% hemlock 16.3% cedar | Individual process wholemill effluent | streams |
| С | в.с. | Interior | 50% spruce, 45% pine, 5% fir | Individual process wholemill effluent | streams |
| D | | Interior | 36% spruce, 33% pine 31% others | Individual process wholemill effluent | streams |
| E | B.C. | Coast | Fir, cypress, spruce, pine and hemlock | Wholemill effluent | |

| F | B.C. Interior | 60% spruce, 16% pine 12% balsam and others | Wholemill effluent |
|---|---------------|---|--------------------|
| G | B.C. Interior | 50% spruce, 45% pine 5% others | Wholemill effluent |
| Н | B.C. Coast | 50% hemlock, 32% fir, 18% cedar | Wholemill effluent |
| I | Ontario | 80% jackpine and 20% spruce | Wholemill effluent |
| J | Quebec | 46% poplar, 27% maple, 17% birch and 10% softwood | Wholemill effluent |

The samples were shipped immediately to the laboratory and stored in a 2°C walk-in refrigerator. In order to minimize any deterioration in effluent quality, they were used for experiment as soon as possible.

2. Field Studies

Field studies were conducted at the combined effluent outfall of mill F; an interior B.C. mill. The mill produced an average of 750 tpd of bleached kraft pulp using the CEDED bleaching sequence and discharge approximately 25 MGD of effluent to the Fraser River. The effluents were toxic, possessed good foamability and appeared suitable for foam separation.

The effluent was neutralized in the mill with lime mud and slaked lime to about pH 4.5, then with sodium hydroxide to pH 7. The suspended solids of neutralized effluent were removed in a 4-hr retention primary clarifier; the clarifier overflow was enriched with ammonium phosphate

and urea to a $BOD_5/N/P$ ratio of about 100/2.5/0.7 and discharged to a 5-day retention aerated lagoon system. Wholemill effluent entering the mill's biotreatment lagoon was tapped and pumped to the field foam separation plant.

3. Pilot Plant Studies

Pilot plant studies were conducted at the combined effluent outfall of mill A on Vancouver Island. The mill produced approximately 1000 tpd of bleached kraft pulp and discharged 60 MGD of effluent. The wood furnishes were 18% fir, 46% hemlock and 36% cedar; a CEHCHDED bleaching sequence was used. The effluents were moderately toxic to fish. The pH of the effluent ranged from 3 - 5.

C. FOAM SEPARATION SYSTEMS - EQUIPMENT AND OPERATION

1. Laboratory System

Laboratory studies were done using a dispersed air foam fractionation system, a helical aerator system, a turbine and a high pressure flotation system.

a. Foam Generation

(i) Foam Fractionation Column

Dispersed Air System

A series of foam fractionation columns, 180 cm high, were con-

structed from 7.5 cm diameter methacrylate plastic tubing (Figure 6-a). Two sintered glass tubes (Figure 6-b), 1 inch in length, 1/2 inch in diameter, (45 μ pore size) were inserted in the bottom of the column for dispersion of air into the solution. In Figure 7, the set up of a laboratory system, complete with automatic pH and temperature control, gas and liquid feed and vacuum suction is shown.

Most experiments in the laboratory were done batch-wise. Four litres of raw effluent were adjusted to the desired pH, poured into the foam fractionation column, warmed up to the temperature required and then foam fractionated for a specified length of time.

Foam fractionation was achieved by dispersing air through the effluent at 500 ml/min, unless otherwise indicated. The foam generated was continuously removed at 60 cm foam height by vacuum suction. After treatment, the foam fractionated effluent was sampled for analysis.

Helical Aerator Foam Generation System

A Kenics aerator system consists of a series of alternating right and left hand helices contained in a pipe. These helices are oriented so that each leading edge is at 90° to the trailing edge of the one ahead. A schematic diagram is given in Figure 8.

For bubble generation air is mixed with the liquid and then pumped at high speed through a pipe. Bubble size is controlled by the velocity of the air-liquid mixture.

FIGURE 6-a

OVERALL VIEW OF LABORATORY FOAM

SEPARATION EQUIPMENT

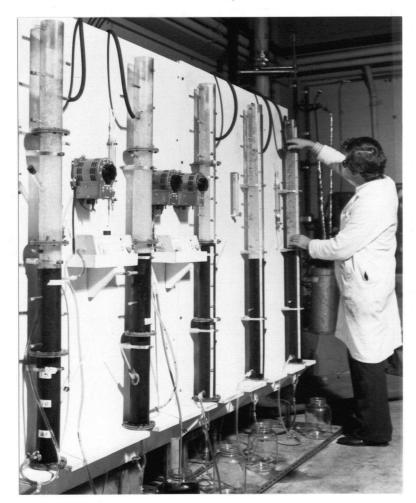


FIGURE 6-b
SINTERED GLASS GAS DISPERSER
INSERTED IN THE BOTTOM OF
THE FOAM SEPARATION COLUMN

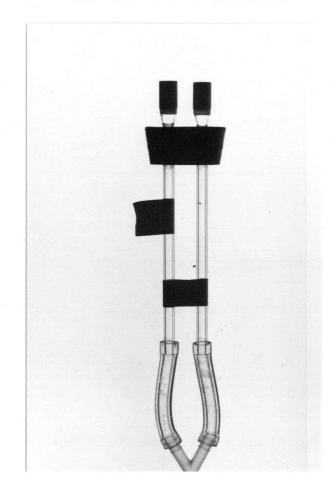


Figure 7

A SINGLE COLUMN USED FOR
LABORATORY FOAM SEPARATION STUDIES

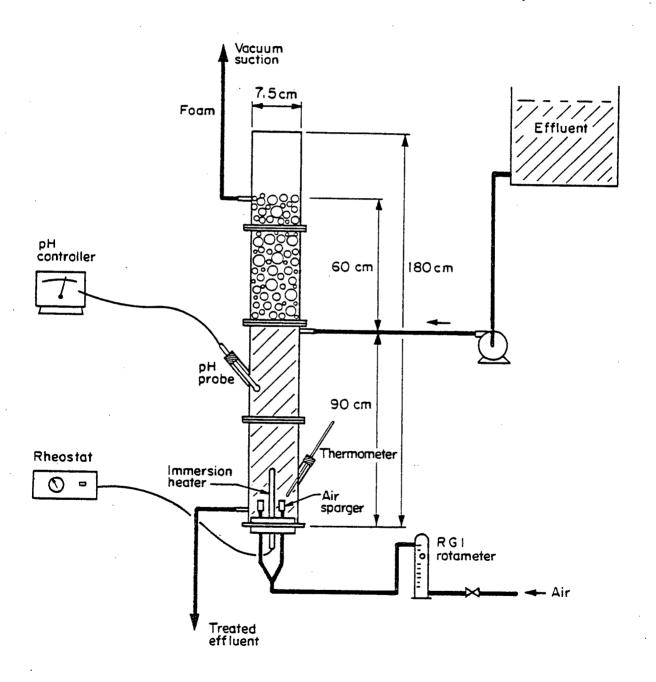
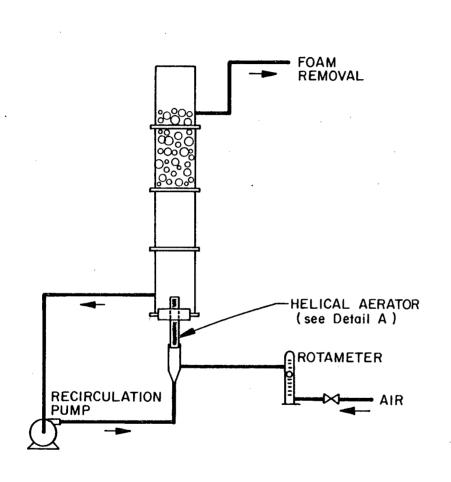
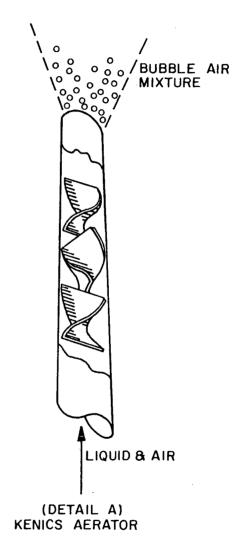


Figure 8
FOAM SEPARATION SYSTEM WITH KENICS AERATOR





For laboratory studies, a 1.25 cm diameter, 30 cm long Kenics Aerator consisting of 6 left- and 6 right-hand helical elements was installed at the bottom of a foam-fractionation column (Figure 7). Four litres of effluent were treated batch-wise. Liquid was drawn from the bottom of the column and pumped at 2 ft/sec through the helical aerator back into the column. Air was metered to the high velocity system at 250 ml/min. Foam was removed continuously by vacuum suction at 60 cm foam height.

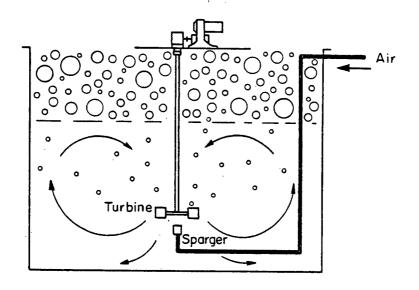
(ii) Trough Type Foam Fractionation Tank

Turbine System

A laboratory-sized turbine system was used. It consisted of a 15 litre glass rectangular vessel, a shaft with a 7.5 cm diameter impeller fitted with four 1.5 cm x 1.5 cm blades and an air feed line leading beneath the impeller (Figure 9). The system disperses air by shearing the air bubbles. Bubble size is controlled by the rotational speed of the impeller.

For each experiment, 10 litres of effluent were treated. Air was metered at 500 ml/min into the system, and dispersed by the impeller at approximately 1000 rpm. Foam was manually removed from the surface of the liquid at 2 min intervals.

Figure 9
MECHANICAL DISPERSION OF AIR BY A TURBINE



(iii) High Pressure Foam Fractionation Column

Dissolved Air Flotation System

Figure 10 shows a dissolved air flotation system used in the laboratory. The batch system consisted of an 8 litre capacity pressurization tank. Under high pressure (20 - 80 psig), air was dissolved into the effluent by splashing the effluent on a 3" diameter plate located 2" below the top of the pressurization tank. After 5 min of continuous circulation the effluent was released very slowly to an 8 litre flotation cell for foam generation.

b. Foam Volume Reduction

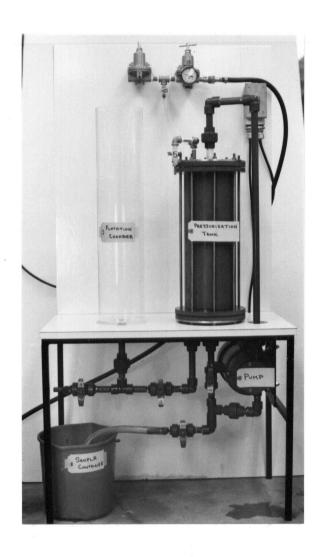
In specific instances, the foam volume to be discharged was considered to be too large therefore subsequent disposal would not be economically feasible. Methods for reducing the volume of foam which were investigated in this study, involved internal and external refluxes of the collapsed foam.

The study of foam reduction was undertaken in a 350 cm high, 7.5 cm diameter foam separation column. The liquid volume treated was 4-1 (90 cm column height). Maximum foam height was 260 cm.

(i) Internal Reflux

The volume of the foam discharged was gradually reduced by increasing the height of the foam retention column prior to draw-off.

FIGURE 10
DISSOLVED AIR FLOTATION SYSTEM



Under normal operating conditions (Air flow = 500 ml/min; air diffuser pore size = 45 μ), all the foam produced was broken spontaneously and resulted in formation of a gummy solid material at a height of 250 cm above the liquid level.

(ii) External Reflux

The external reflux system is also referred to as "enrichment mode operation" in foam separation processes. The set-up of the equipment is shown in Figure 11. The same column designed for internal reflux operation was used except that foam was removed arbitrarily at 60 cm above the liquid level and collapsed externally. A measured flow of collapsed foam was sprayed continuously back into the column on top of the foam layer. The amount of foam returned was controlled at recycle ratios of 0.1 to 1.0.

c. Foam Collapsing

A vacuum system consisting of an eductor and a 4-1 capacity vacuum jar was used (Figure,12). The vacuum line was linked to a foam removal port 60 cm above the liquid surface of a 7-1 capacity foam separation column, exposed to atmospheric condition. The applied suction coupled with continuous aeration forced the foam to flow to the vacuum jar. Foam was collapsed due to the expansion in volume in the vacuum jar and the stirring effect of a magnetic bar. In situations where foaming was excessive, small amounts of chemical defoamers were added to assist foam breaking. The method of vacuum suction was used mainly in the laboratory.

Figure II
REDUCTION OF FOAM BY RECYCLING (ENRICHING MODE)

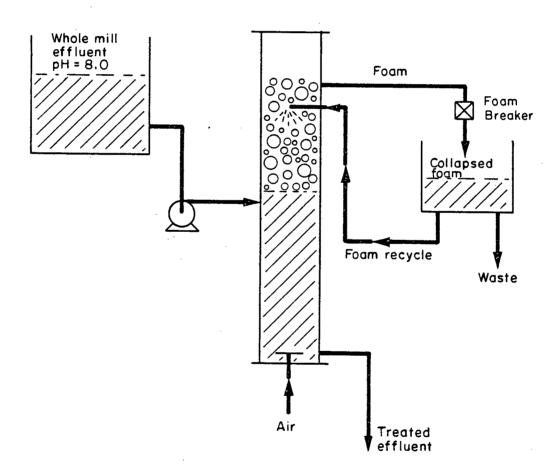
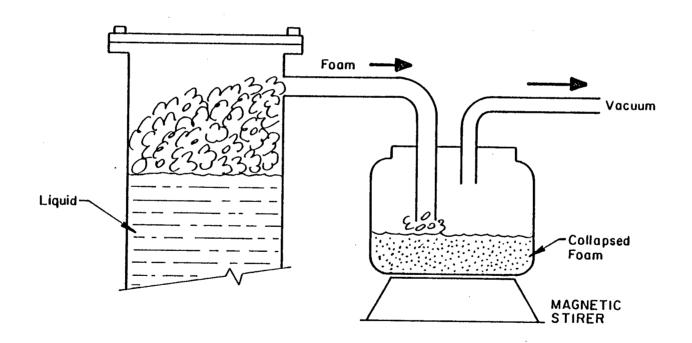


Figure 12
FOAM COLLAPSING SYSTEM USING VACUUM RUPTURE TECHNIQUE



2. Foam Separation System Installed at Mill Site (Field System)

A 1 gal/min continuous flow foam separation plant was installed onsite at the outfall of Mill F at an Interior B.C. Mill. The equipment was installed in a 12' x 50' mobile trailer. The foam separation system consisted of 3 separate columns, each with 80 gal capacity and with individual operational control elements. Supporting equipment included 300-gal and 500-gal pH adjustment tanks, an effluent pumping station with flow control and a $6 \, \mathrm{ft}^3/\mathrm{min}$ compressor. Figure 13 shows a flow sheet of the foam separation process.

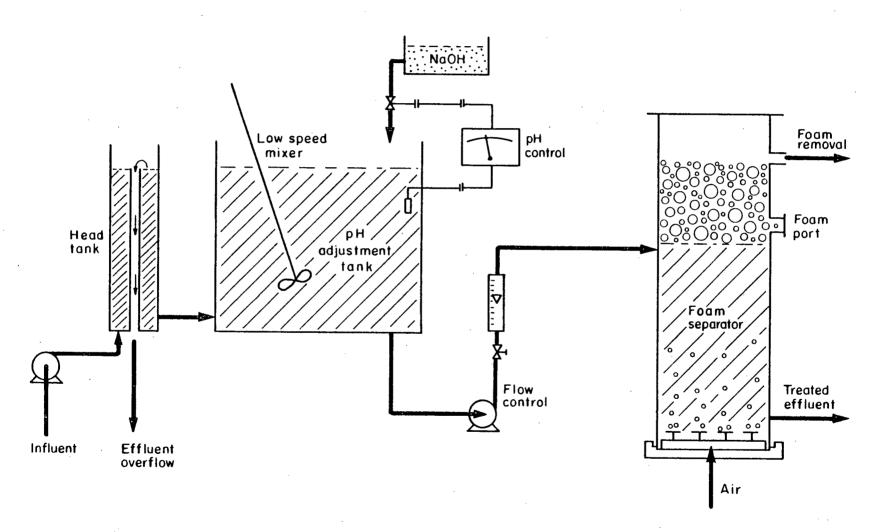
a. pH Control

Raw effluent was pumped from the mill's discharge to a small head tank, which overflowed to the sewer. The head tank gravity fed a 5 \times 5 \times 4 ft wooden tank used for pH adjustment. The operating volume of this tank was 600 gal and retention time was 3 hr. It was equipped with a low speed Lightnin mixer and an automatic pH control system (Great Lakes pH meter, Model 60). The pH of the effluent was maintained at 8 by adding 25% NaOH solution. For standby purpose, a 300 gal pH adjustment tank was kept nearby.

b. Pumping Station

Effluent from the pH tank was delivered by three Jabsco Impeller pumps to the foam fractionation column. Initially the flow rate was

Figure 13
PROCESS FLOW SHEET FOR FOAM SEPARATION AT MILL SITE



controlled by discharging excess liquid through a bypassing system but because of plugging problems in the valves, this control was replaced by an intermittent programmed timer and proper sizing of the pumps. To ensure accurate liquid flow rate entering the system, a Brook rotameter was installed for daily calibration.

c. Air Dispersion System

The air required for foam generation was generated on-site by a 6 $\rm ft^3/min\ compressor$, a 2 $\rm ft^3/min\ system\ was\ used\ as\ stand-by$. The air was delivered by 1/2" diameter high density plastic tubing to the air chamber built at the bottom of the column.

Four different types of porous gas diffusers were inserted in the air chamber for foam generation.

Seven, 5-inch diameter, 1/16-inch thick, porous plastic discs (Bel-Art Products) (Figure 14-a)

- Nominal Pore Size: 65µ
- Total nominal air dispersion area: 0.95 ft^2

Four, 1-ft long, 3-inch diameter, porous ceramic tubes (Norton Company (Figure 14-b)

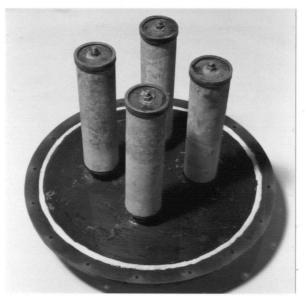
- Nominal Pour Size: <25µ
- Total nominal air dispersion area: 3.14 ft²

FIGURE 14-a
PLASTIC DISC AIR
DISPERSION MEDIA

FIGURE 14-b
CERAMIC AIR DISPERSION
TUBES

FIGURE 14-c
POROUS ALUNDUM PLATE
AIR DISPERSION MEDIA







One, 18-inch diameter, 1 1/2-inch thick porous Alundum plate (Norton Company) (Figure 14-c)

- Nominal Pore Size: 65µ
- Total nominal air dispersion area: 1.77 ft²

Figure 15 shows a foam fractionation column with porous ceramic tubes in place.

d. Foam Fractionation Columns

Three 80 gal capacity foam fractionation columns (1.5 ft diameter, 6 ft height) made of methacrylate plastic were used. The columns were equipped with feed inlet ports, air dispersion media at the bottom and foam discharge ports. The dimensions of each column are shown in Figure 16.

Two systems were operated continuously whereas the third system was held in reserve (Figure 17). The columns were operated at a constant liquid height of 4 ft with a liquid volume of approximately 45 gal. Effluent was fed in at the liquid-foam interface and discharged at the bottom of the system via a stand-pipe level control.

Air was dispersed into the liquid at the bottom of the column via air dispersion media.

FIGURE 15
FIELD FOAM SEPARATION COLUMN INSTALLED WITH
CERAMIC TUBE AIR DISPERSERS

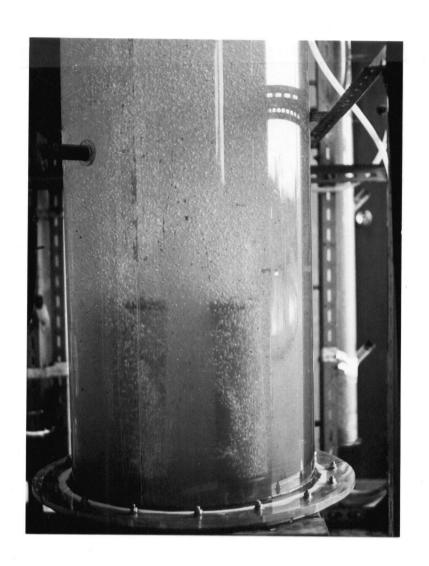


Figure 16
FOAM SEPARATION COLUMN INSTALLED AT MILL SITE

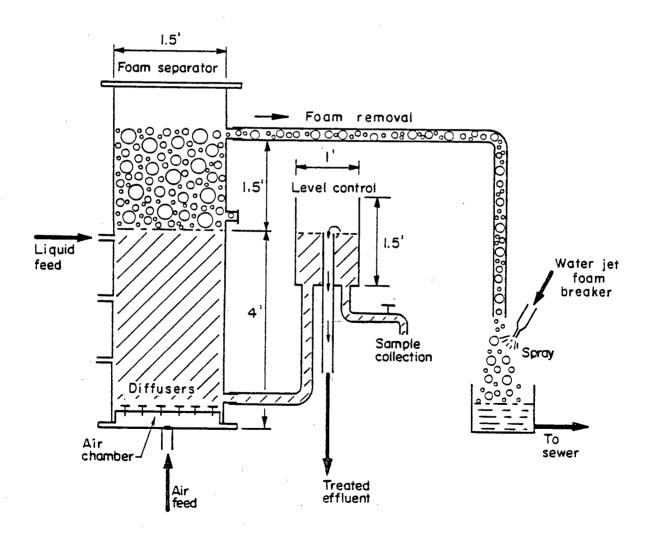


FIGURE 17
PICTURE OF FIELD FOAM SEPARATION COLUMN IN OPERATION



e. Foam Collapsing

The foam separation system operated at the field-site produced up to 30 1/min of foam. In this system, foam was expelled from a 180 1 operating capacity, foam column through a 3-in diameter foam port opened 6-in above the liquid level. The top of the foam column was closed to force the foam to flow out from the system. A water spray nozzle, which was more effective and simpler than a vacuum system, was used for foam collapsing (Figure 18). The impact force of the water jets as they impinged on the foam, and their dilution effects caused the foam to collapse.

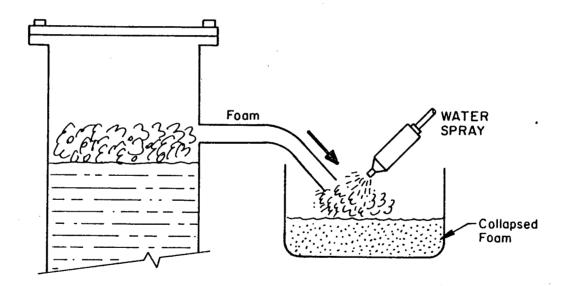
f. Treatment and Detoxification of Collapsed Foam

The foam produced from the field foam separation system was subjected to various chemical and biological treatments. Chemical treatment methods involved flocculation - coagulation of pollutants. Biological treatment methods involved rotating biodisc and aerated lagoon treatments.

(i) Chemical Treatment

The foam removed from the column was collapsed. To the collapsed foam a suitable amount of lime (at pH 10), alum (at pH 5.5), or ferric sulphate (pH 5.5) was added. After addition of the particular chemical, the pH was adjusted to the level optimal for flocculation-coagulation. These studies were conducted with 3-1 of collapsed foam in a Phelps and

Figure 18
FOAM BREAKING BY WATER SPRAY SYSTEM



Birds laboratory flocculator. The wastes were agitated by a 3-inch paddle at 100 rpm for 10 min and 30 rpm for 20 min. The flocs formed were allowed to settle for 2 hr. Clarified effluents were decanted for subsequent toxicity analysis.

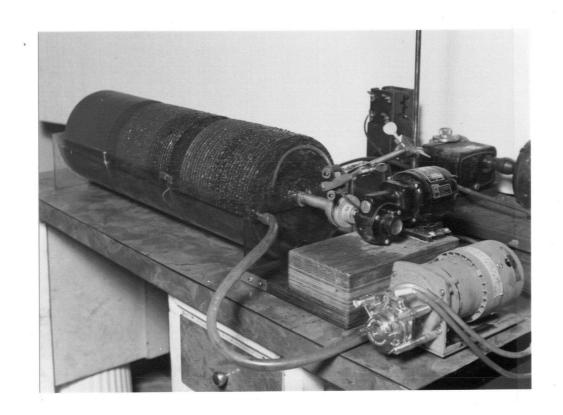
(ii) Biological Treatment

Prior to any experiments, the collapsed foam was adjusted to pH 7 and enriched with ammonium sulphate and phosphoric acid according to $BOD_5:N:P=100:5:1$. Treatment temperature was maintained at 22 ± 3 C. Microbial growth was developed by treating a batch of effluent for one week before the continuous operation was begun. The inoculum was obtained from a near-by activated sludge system.

Rotating Biodisc

An 8-1 capacity, bench scale, continuous flow biodisc unit was used (Figure 19). The unit consisted of a trough divided into three compartments. On the top of the trough, 75 closely spaced discs, 25 in each compartment were supported by a shaft and rotated gently by a low speed, gear drive motor. Each 8-in diameter, 1/8-in thick, plexiglass disc had a surface area of 0.72 ft², giving a total system area of 55 ft². The lower portion of each disc was submerged in the waste being treated, while the upper portion rotated in the air. A biological slime developed on the discs. The waste passing through the discs flows parallel to the adjacent faces of the discs. The drag forces generated by the slow rotation imparted a lifting action to the waste and caused the waste solution near the disc to flow in a circular pattern.

FIGURE 19
BIODISC SYSTEM FOR TREATMENT OF COLLAPSED FOAM



Aerated Lagoon

A 20-1 operating capacity rectangular shaped tank (1 x w x d = 13- x 11- x 10-in) was used as an aerated lagoon. A masterflex pump delivered the collapsed foam to it continuously for biological oxidation. Laboratory compressed air was used to provide oxygen for microbial growth. Approximately $100 \text{ cm}^3/\text{min}$ of air was diffused through three fritted glass tubes submerged at the bottom of the tank. The average dissolved oxygen level was maintained at 3 mg/l and mixed liquor suspended solids were monitored regularly. The aerated lagoon system was operated arbitrarily at 3-day retention times using the same effluent and under the same condition as that used in the biodisc system.

3. Pilot Plant Foam Separation System

The pilot plant was designed to process a maximum of 100 gal/min of effluent. The principle system components consisted of a 500 gal capacity pH control system, a 6000 gal capacity foam generation system and a 300 gal capacity foam collapsing system. Figure 20 gives the dimension of the foam separation system. A 12 x 50 ft trailer was installed (Figure 21) near the pilot plant to house the pH control system, air blowers and laboratory facilities.

a. Effluent Delivery

Approximately 80 - 100 gal/min of wholemill effluent was pumped from the mills' main discharge sewer and delivered through 200 ft of 2-in diameter polyethylene pipe to the pilot plant system. The effluents

Figure 20
PILOT PLANT FOAM SEPARATION SYSTEM (100 gal/min)

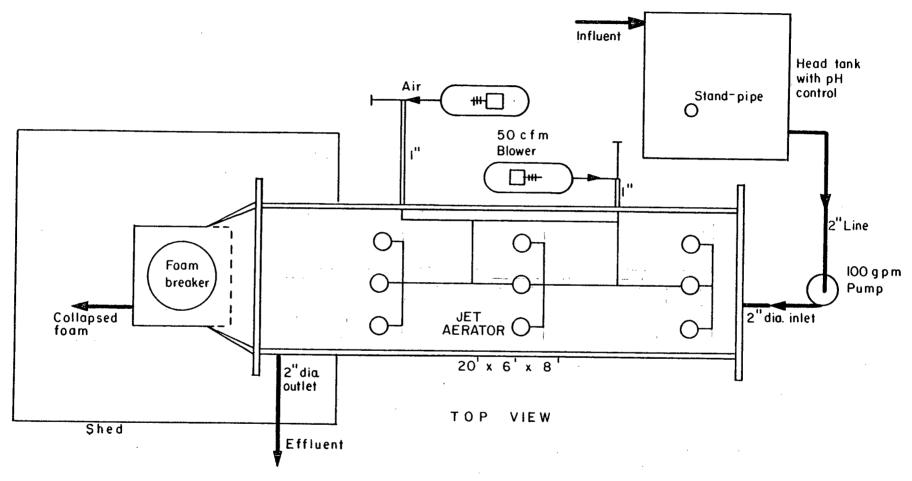


FIGURE 21

OVERALL VIEW OF 100 gal/min FOAM SEPARATION PILOT PLANT INSTALLED AT MILL A



entered a 500 gal capacity head tank (1 x w x d = 4- x 4- x 5-ft) for pH adjustment and were then pumped to the foam separation plant. Excess influents to the pH control system and treated effluents from the foam generation plant were discharged to the ocean.

b. pH Control

The pH of the effluent was adjusted to between 7 and 8 in the head tank prior to foam separation. Overall retention time was 5 - 7 min. pH monitoring and addition of caustic solution (25% concentration) was controlled by a Model 60 Great Lake Industrial pH Monitor. A 1/3 hp Lightnin Mixer activated by a 60-min interval programmable timer provided intermittent agitation (to reduce foaming in pH tank). The pH adjusted effluent was then pumped to the foam generation tank.

Foam Fractionation System

The foam fractionation system comprised a foam generation tank, an air delivery system and foam generation equipment.

(i) Foam Generation Tank

A plywood tank, coated with water proof paint was constructed onsite. The tank measured 20 ft in length, 6 ft in width and 8 ft in height and was operated with a 6 ft depth of liquid. The tank was subdivided with wooden walls into three equal sections. The walls were removable and allowed conversion of the system into a one, two or three stage system as required. Depending on the set-up, the total retention time, the volume of the effluent treated and the number of stages could be varied. The pH adjusted influent entered the tank at a rate of 80-100 gal/min, corresponding to 60-75 min total retention time and 20-25 min retention time per stage.

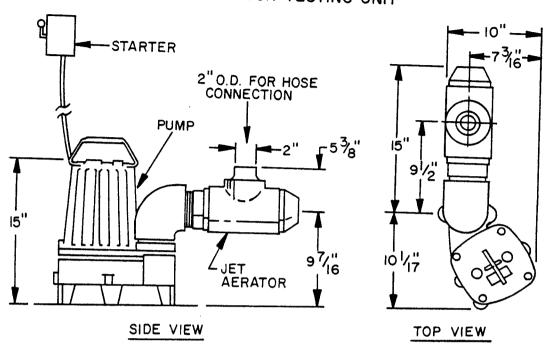
The tank was filled with effluent at all times. However, for single stage operation, only the effluent in the 1st stage was aerated for foam formation. For two and three stage operation, the aerators in the second and third stage were also used. Effluents flowed successively through a $15- \times 61- cm$ opening from the first to the second and then to the third stage.

The top of the foam generation tank was covered by plastic and protected by a shed. The front of the tank was open to allow foam to spill to the adjacent foam breaking system (Figure 21).

(ii) Foam Generating Equipment

Nine, commercial size, 2" diameter, jet aerators were installed in the 3-stage foam generation tank. A diagram of a unit is shown in Figure 22-a. Fibure 22-b shows the formation of a horizontal jet plume (bubble-liquid mixture) by such a jet aerator. The fluid was pumped through the jet nozzle at 2 ft/sec velocity by a 1/2 hp, 20 gal/min capacity recirculation pump attached to the jet. Air was supplied to the jet at 10 psi pressure and mixed with the motive fluid in the

Figure 22a JET AERATOR TESTING UNIT



PRESSURIZED

PRESSURIZED

LIQUID

JET AERATOR IN OPERATION

WIXING CHAMBER

ENTRAINED

LIQUID

VERTICAL

JET FLUX

CONSTANT VELOCITY CONE

HORIZONTAL

JET PLUME

jet chamber. Fine bubbles were produced by shearing action and turbulence and discharged from the jet nozzle to the liquid. Bubble sizes and foam volume were regulated by the air flow rate and the fluid velocity through the nozzle.

(iii) Air Supply System

Two 5-hp, 550 volt rotary vaned blowers were installed to supply air for foam generation. Each blower was rated at 50 cfm, at 1 atm pressure and connected to a 2-in common air line. An orifice plate was installed for air flow measurement. The air line was attached to a manifold to supply air to the nine jet aerators. A non-returnable check-valve was installed in the air line to prevent backflow of liquid.

d. Foam Handling System

(i) Foam Removal

In this system, no mechanical device was installed to assist foam removal. Foam was expelled easily from the system by spillage through a side-opening of the closed top foam generation tank. New foam continuously emerged from the liquid, and pushed old foam slowly to the exit and toward the foam breaking tank. The travel distance varied from 0 to 20 ft depending upon the number of stages used and the location of the stage in the tank where the foam was produced.

(ii) Foam Breaking

The foam breaking system consisted of a 300 gal $(3- \times 3- \times 4-\text{ft})$ wooden tank, fitted with a turbine and was designed to permit discharge of liquified foam only (Figure 23). Foam spilled from the opening of the foam generation system into the foam collection tank and was broken mechanically by turbine due to combination of impact, shear and centrifugal forces.

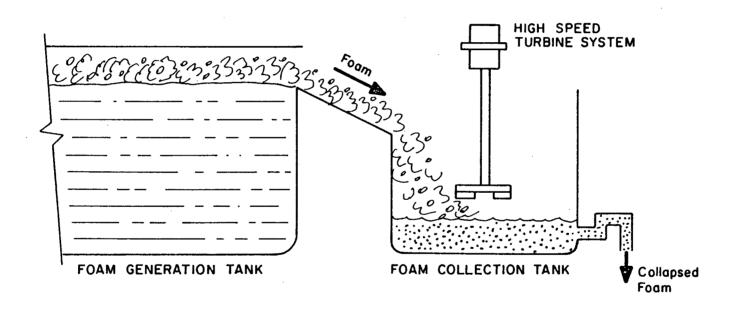
The turbine foam breaker was basically a 3-blade vaned disc driven by a 1/3 hp motor at 1800 rpm. It was mounted centrally, approximately 1-ft above the tank bottom. The size of vaned disc and blade number were changed to accommodate different volumes of foam input.

D. ANALYSES

Toxicity was determined by using juvenile rainbow trout Salmo gairdneri, as the test fish. The fish were taken from a homogeneous population of hatchery-reared fish, acclimated to laboratory conditions of water and temperature. Bioassays were done at $12 - 15^{\circ}\text{C}$, pH 7 ± 0.2 and oxygen saturation. When air was inadequate, pure oxygen was used to maintain oxygen saturation.

Effluent samples from laboratory test were bioassayed with five to tenfish in 3 litre glass jars, at fish loadings of 1 - 1.5 g/l. Effluent samples from the field and pilot plant systems were bioassayed with

Figure 23
MECHANICAL TURBINE FOAM BREAKING SYSTEM



10 - 20 fish in 20 litres of effluent at the same fish loadings as in the laboratory test.

Toxicity was determined according to one of two procedures:

- Median Survival Time (MST) The median survival time of a fish population was determined on 100% effluent concentration over a 24h period. Effluents were classed as non-toxic when all fish survived a 24-h exposure period.
- Static Federal Guideline for Toxicity Fish were exposed to 65% effluent concentrations for 96-h. The effluent met Federal Toxicity requirements, for a static monitoring bioassay, if more than 80% of fish survived.

 $\frac{\text{BOD}}{5}$ was analysed according to the Standard Methods for Waste and Wastewater Analysis (87).

TOC (Total Organic Carbon) was determined by a Beckman Model 905 TOC Analyser.

<u>Suspended Solids</u> were determined by centrifuging aliquots of effluent at 10,000 rpm for 10 min, transferring the solids cake to a GF/A glass fibre filter, rinsing it with distilled water and drying at 105°C for 15-h and weighing.

Resin Acids were determined by a gas chromatographic technique (88).

Color was determined by a spectrophotometric method (89).

<u>Effluent Flow</u> was controlled by using a prerated pump of known capacity and verified by measuring the time required to fill up a tank of fixed capacity.

<u>Air Flow</u> was measured by using rotameters. For high air flow measurements an orifice plate was used. Pressure and temperature of the air measured at the blower discharged were determined and used for conversion of air flow to standard conditions.

Bubble Sizes and Bubble Distributions were determined by photographic technique. In the laboratory and field column installation, bubble sizes were determined by directly photographing the foam liquid interface and crudely estimating an average bubble size. In the pilot plant study, an accurate method was employed. A 1.8- x 0.6- x 1.2-m tank attached with a transparent 40- x 6- x 90-cm rectangular box was used. The aerator was installed in the tank. The bubbles generated by the aerators partially entered the box. Under relatively quiescent conditions, photographs were taken using an Olympus OM-2 automatic aperture controlled, single-lens reflex camera. Strong back and top illumination (2000 watts) and high shutter speed (1/1000 sec) were employed. Picture negatives were projected on a screen for measurement of the bubble diameters. A section of the slide representative to the overall picture was selected and a mean diameter based on at least 200 bubbles was calculated.

Gas/Liquid ratio was determined by dividing gas flow rate by liquid flow rate.

Gas-Liquid Interfacial Area generated by a jet aerator was determined from the air flow rate, liquid flow rate and the mean bubble diameter,

assuming spherical bubbles.

Interfacial area production rate =
$$\frac{\text{Gas flow rate x 6}}{\text{mean bubble diameter}} \times 10^3 (\text{m}^2/\text{min})$$

$$\frac{\text{Interfacial Area Produced}}{\text{Unit volume of effluent processed}} = \frac{\text{Interfacial Area Production Rate}}{\text{Liquid Flow Rate}} (\text{m}^2/1)$$

Foam Flow Rate was calculated from the time required to fill a 5-ft vessel.

<u>Liquid Entrained in Foam</u> was determined by measuring the liquified volume of 20 liters of foam:

Liquid entrained (%) =
$$\frac{\text{V liquid}}{\text{V foam}}$$
 x 100

Conversion of Influent to Foam was determined by the formula

$$% = \frac{\text{Flow rate of foam x liquid content}}{\text{Flow rate of influent}} \times 100$$

Foaming Tendency was measured as the residence time for each foam bubble entrapped in the foam layer (46) by aerating 4 litres of effluent for 4 min at 500 ml/min.

Foaming Tendency :
$$^{\Sigma}t = \frac{V \text{ foam after 4 min of aeration}}{\text{Gas flow rate}}$$

<u>Foaming Stability</u> was determined by measuring the foam volume remaining after 4 min of retention in the foaming column.

Foaming Stability:
$$\Sigma_t = \frac{V \text{ foam after 4 min retention}}{Gas \text{ flow rate}}$$

Foam Breaking Efficiency was defined as the ratio of volume of foam collapsed to original volume.

Efficiency (%) =
$$\frac{V \text{foam} - V \text{residual foam}}{V \text{foam}} \times 100$$

Rotation Speed was determined by using a model 134(3776) Photolastic Inc. stroboscope.

Tip Speed of the turbine was calculated by the formula:

V tip =
$$\frac{\pi \ D \ x \ rpm}{60}$$
 cm/sec.

Power was measured by a model 432 Weston Electric Instrument Watt meter.

E. DETERMINATION OF DETOXIFICATION MECHANISMS

A 7-1 laboratory foam separation column containing 4-1 of liquid, a 3-1 foam collection jar and a 6-1 vapor condensing system were used to separate the treated effluent, collapsed foam and vapor respectively. The set-up of the equipment is shown in Figure 24.

The standard conditions applied for determination of detoxification mechanisms were pH 9.5, room temperatures (22 \pm 3°C) and 500 ml/min aeration rate through 45 μ fritted glass for 1-h. Foam was collapsed by passing through glass wool (foam breaker) to a 3-1 collector. Vapors were condensed in a flask immersed in an acetone-dry ice (CO₂) bath. In all experiments foaming was completely diminished after treatment.

Prior to the experiments a series of dilutions of toxic effluents were bioassayed for toxicity. The MST was plotted against % effluent concentration. Figure 25 shows an example for developing a standard toxicity curve. The relative contribution by various mechanisms was determined by fractionating the same effluent under a standard set of conditions into treated effluent, foam and condensed vapor fractions.

Bioassay was done on treated effluent alone, treated effluent plus the foam fraction, and treated effluent plus both the foam and condensed vapor fractions. The MST of the reconstituted effluents were equated to percent concentration of the raw effluent which yielded the same MST values (Figure 25).

Figure 24
LABORATORY SET-UP FOR INVESTIGATION OF DETOXIFICATION MECHANISMS

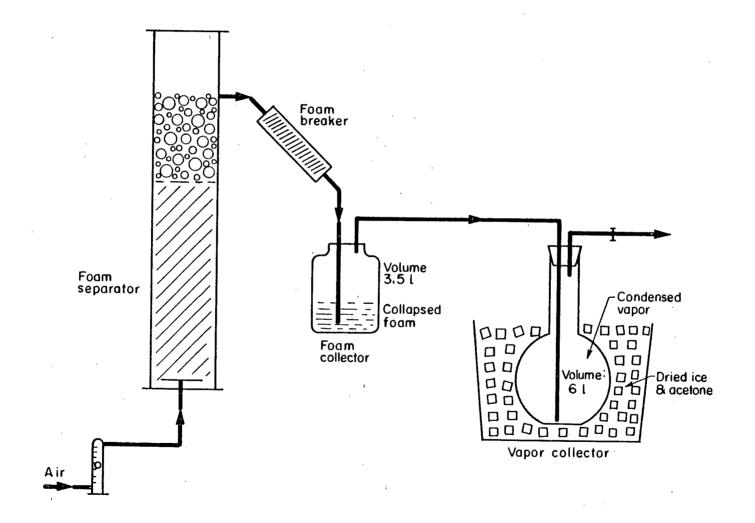
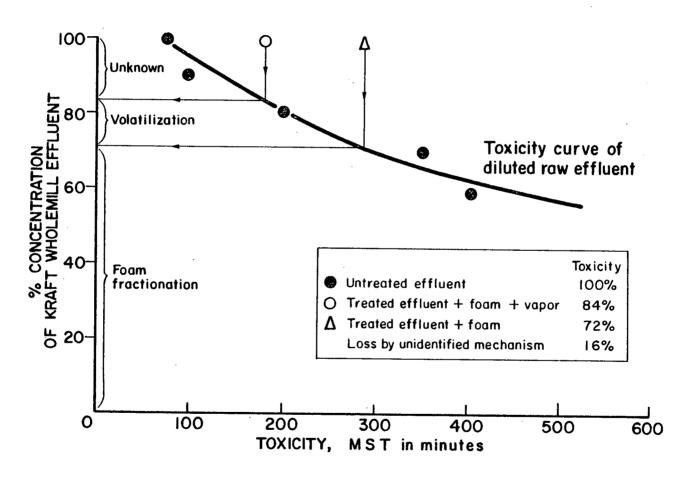


Figure 25

RELATIVE CONTRIBUTION TO DETOXIFICATION
BY FOAM FRACTIONATION, VOLATILIZATION AND UNKNOWN MECHANISMS



Note: The toxicity fractions are determined as percent effluent equivalents, i.e., toxicity of a fraction is compared to the percent dilution of raw effluent, which yields the same toxicity.

CHAPTER V

RESULTS AND DISCUSSION

A. TREATABILITY STUDIES

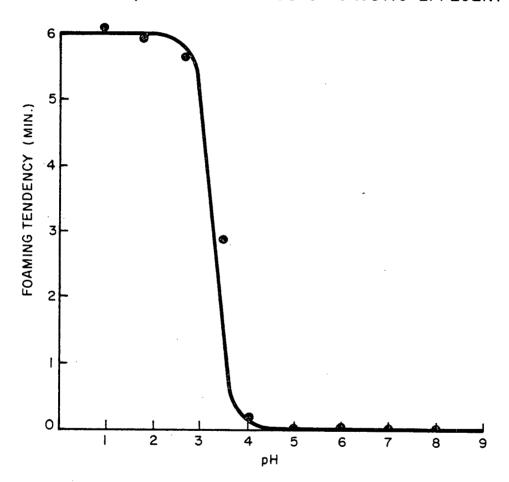
1. Selective Detoxification of Various Process Streams

The three major process streams in a bleached kraft mill are unbleached white water from the pulping discharge; caustic extraction stage effluents and acid bleach effluents from the bleach plant discharge. These three effluent streams differ in waste characteristics and represent up to 75% of the combined wholemill effluent. The toxicity and the foaminess of the effluents measured from a group of samples vary with each process stream in the following manner:

Toxicity Caustic Extraction Unbleached white Acid Bleach (MST:hr) Effluent(1.3-2.1) Water(1.6-2.1) Effluent (0.3-8.5)Foaminess Caustic Extraction Unbleached white Acid Bleach $(\Sigma_{+}:\min)$ effluent (>6) water (4-5) Effluent (2-5)

Caustic extraction effluent is the most toxic of the individual process streams (86). Its foaminess is governed by the pH of the effluent. When the pH was reduced from initial 10 to 4, the effluent was not foamable. However, as the pH decreased further to 3, the foaming tendency of this waste stream increased abruptly to 6 min (Figure 26) and remained constant. The foaminess and toxicity of the unbleached white water are slightly lower than the caustic extraction effluent but higher than the acid bleach effluent. The foaming characteristics of these two streams, however, are not affected as severely as caustic ex-

Figure 26
EFFECT OF pH ON FOAMINESS OF CAUSTIC EFFLUENT



traction effluent by changes in pH. These three individual process streams were subjected to foam separation treatments and assessed for detoxification. The results are presented in Table 5.

a. Unbleached White Water

The major toxic materials in unbleached white water originated from evaporator condensate and residual black liquor (90). The MSTs of the four batches of samples obtained were identical in initial toxicity, and ranged from 1 to 2 hr (Table 5). The effluents were subjected to foam separation at pH 4 and 9.5. During the process of aeration, unstable foams were produced. They collapsed spontaneously and rapidly before reaching the foam removal port. Table 5 shows that after foam separation treatment at both pH the MST remained at 1.1-2.1 and 0.7-3 hrs, i.e. reduction of toxicity was not achieved.

Since foam separation treatment involves the sparging of air through the wastes, volatile toxicants would be expected to be stripped out from the effluent after prolonged aeration. Among the non-volatiles are naturally occuring resin acids which represent 80% of the toxicity (20) and unsaturated fatty acids which are responsible for the remaining toxicity (23). These toxicants are surface active and should be foam separable. However, the foams were not stable enough to facilitate fractionation of toxicants properly. This observation agrees with reported results on the foaminess of commercial sodium abietate and rosin (mainly abietic acid) solution at various pH conditions (91).

TABLE 5

EFFECT OF FOAM SEPARATION ON DETOXIFICATION
OF INDIVIDUAL PROCESS STREAMS

| Individual | Source | Toxicity (MST, hr) | | | | |
|---------------------------|--------------------------|--|--------------------------|--------------------------|--------------------------|--|
| Process Stream | of Effluent (Mill) | Effluent After Foam Raw Separation Waste at pH | | | | |
| | | | 2.5 | 4.0 | 9.5 | |
| Unbleached white water | A B C D | 2.1 1.1 1.2 1.6 | - | 2.2 0.5 0.4 0.5 | 3.0 0.7 1.1 0.8 | |
| Acid bleach effluent | A B C D | 8.5 5.2 0.7 0.3 | 4.8 4.8 0.7 0.2 | 3.7 2.1 0.6 0.8 | NT 24.0 0.6 0.5 | |
| Caustic ext. effluent | A C D | 2.1 0.7 0.3 | NT NT 24.0 | 4.5 1.9 1.1 | 1.8 0.9 0.3 | |

NT: Nontoxic

Treatment Conditions:

Volume

Gas dispersion medium

Pore size

Aeration rate

Treatment time

NT

= 4 liters

= Sintered glass

= 45 µ

= 500 ml/min

= 5 hr

= Nontoxic

b. Acid Bleach_Effluent

Two samples of acid bleach effluent were obtained from Mills A and B (B.C. coast) and the other two were taken from mills C and D (B.C. interior). The coastal mill samples were taken from the mill outfalls and were relatively free of chlorine due to vigorous mixing at the sampling point. These samples were not very toxic (MST = 5-8 hrs) and foaming was moderate. The interior mill samples were taken directly from the bleach plant. The toxicities of these two samples (MST = 1-2hr) approached that of unbleached white water. However, foaming tendency was only a fraction higher. The foam produced by all samples was moderately stable within the tested range of pH 2.5 - 9.5. Most of the foam collapsed before reaching the foam removal port and formed scum on top of the foam. Only a small portion of the foam was removed. less toxic acid bleach effluents from Mills A and B were satisfactorily detoxified at alkaline pHs (Table 5) even though foaming was not satisfactory. In these effluents it would appear that removal of only a fraction of any toxicants reduced the effluent to a non-toxic level. Detoxification can be attributed partially to the air stripping of any volatile materials, including residual chlorine. The formation of scum also suggested that precipitation/ion flotation was partly responsible for detoxification. In contrast, even though foaming was slightly better on highly toxic samples (C and D), detoxification was extremely difficult.

Presently available literature indicates that chlorinated lignin derivatives are the major toxicants (23,92) in acid bleach effluent.

In kraft pulp chlorolignin, the acidic groups of the components are rather strong, which is to be expected for hydroxychloroquinones. They can be neutralized by hydrolysis of the chlorine from the chlorolignin, which requires alkaline conditions (93). At pH 9.5 during foam separation, the chlorine moiety of the chlorolignin can be stripped by aeration and should result in lower toxicity of the effluent. Recent studies (94) have indicated that the toxicity of acid bleach effluent can be completely removed by simply adjusting the pH to basic conditions.

One possible explanation why the more toxic acid bleach effluent samples were not detoxified could be attributed to the grouping of the surfactants into micellar structures. Due to the resultant loss of surface activity, the toxicants would not be removed. This hypothesis, however has not been verified experimentally.

c. Caustic Extraction Effluent

In the alkaline extraction stage of bleaching, saponification of fatty and resin acids into sodium salts takes place as does a micellar solubilization of the more or less hydrophobic constituents of the resins; i.e., the unsaponifiables and the remaining fatty acid esters. This micellar solubilization is effected by surface active fatty and resin acid soaps. The critical micelle concentration (CMC) for resin soaps is reported to be 0.02 moles/1 (95) and 0.002 moles/1 for fatty acids (95,96,97). With a 50 - 50 mixture, the CMC is 0.002 M/1 (98).

Using this figure, it has been calculated that this micellar concentration is exceeded in the kraft cooking of pine. In the caustic extraction stage of the pulp bleaching process half of the soaps are likely to form micelles whereas in a dilute pulp suspension such as in the alkaline washing stage of bleaching after chlorination, no micelles would be formed (99). On this basis and since the wood furnishes in these three mills did not contain pine, it was assumed that micelles were not present in caustic extraction effluent.

The foaminess of caustic extraction effluent (Figure 26) greatly depends on the pH condition. Information available to date indicates that the major toxicants are mainly negatively charged chlorinated phenolics, resin and stearic acid derivatives. Caustic extraction effluent foams copiously at extremely low acid pHs. The acid pHs required to induce foaming suggests the presence of large quantities of non-toxic cationic type, surface active compounds. These cationic type surfactants can react with the negatively charged toxic materials (Table 2) thereby suppressing their foaming capabilities at alkaline pHs.

Caustic extraction effluent is highly responsive to foam separation (Table 5). Detoxification was governed completely by the pH of treatment. As expected, at pH 4 and 9.5 where foaming was not possible, toxicity could not be removed. At pH 2.5, foaming was abundant and large amounts of brownish scum were formed. Foaming still persisted

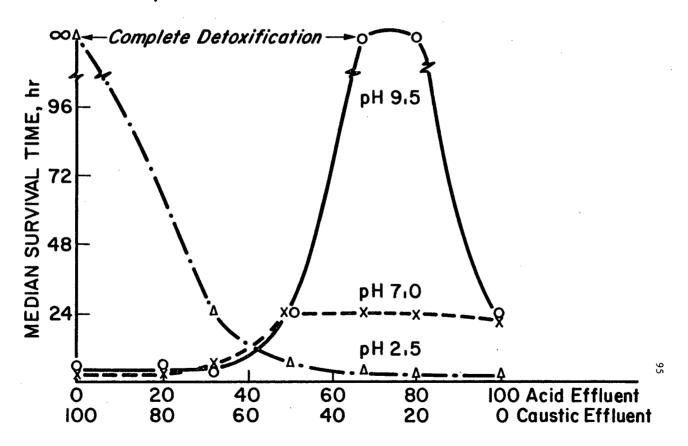
after 10 hr of aeration. Out of three samples treated, two samples were completely detoxified, the third was partially detoxified to a substantially low toxic level (MST increased from 0.3 hr to 24 hr). It appears that if more time were given for removal of residual foam, the third sample would also have been detoxified.

It is speculated that caustic extraction effluent contains a suitable surfactant serving as a collector which forms a colligend with the negatively charged toxic materials. At acid pHs, some toxic components will also be precipitated. The formation of large quantities of scum suggest that precipitate flotation occurs concurrently with ion flotation.

2. Effect of Caustic Extraction Effluent Addition on Detoxification of Acid Bleach Effluent

Caustic extraction effluent is the only individual process stream that could be detoxified by foam separation. It would appear that caustic extraction effluent contains some necessary surfactant which can combine (by means of precipitation, chelation, or complexing) with the toxic surface active compounds and other not yet identified non-surface active materials and make them foamable. An experiment was designed to utilize the surfactants of the caustic extraction effluent for detoxification of acid bleach effluent. Appendix I records the detoxification data of a series of caustic-acid effluent mixtures of different proportions after foam separation treatment at pH 2.5, 7.0 and 9.5. These results are shown in Figure 27.

Figure 27
EFFECT OF EFFLUENT COMPOSITION
ON THE pH REQUIREMENT FOR DETOXIFICATION



The MST of the untreated mixtures varied from 0.3 to 2.8 hr. At pH 2.5, 100% concentration caustic extraction effluent, which foamed copiously, was completely detoxified. Other effluent mixtures did not produce a stable foam. Detoxification decreased as the percentage of acid bleach effluent increased. Toxicity could not be removed in acid-caustic effluent mixtures of proportions greater than 60:40. At pH 7.0 some reduction of toxicity was observed in effluent with < 50% caustic effluent. At pH 9.5 foaming and scum formation were directly proportional to the extent of detoxification. Effluents containing 60 - 80% acid bleach effluent had the greatest foaminess, formed most scum, and detoxified completely.

The relationship of detoxification pH with effluent composition demonstrates the differences in the concentrations and types of surface active toxic materials contained in acid and caustic bleached effluent. Nevertheless, these surface active substances could all be foamed out from the combined effluent by the use of suitable collectors present in the effluent because complete detoxification occurs. It would appear that the collector and colligend are present in at least stoichiometric ratios in the 20 - 35% range of caustic effluent and the 60 - 80% range of acid bleach effluent. Because of the variations in toxicant concentrations due to different process conditions and the ratio of caustic to acid effluent discharge in different mills, it is difficult to determine the exact stoichiometric relationship between collector and colligend in these effluents. Therefore a commercial foam separation

process for removal of toxicity from bleach plant effluent should incorporate sufficient surge capacity to maintain a proper ratio of acidcaustic effluent which would be required to effect detoxification.

3. <u>Effect of Synthetic Surfactants on Detoxification of Unbleached</u> White Water

In mills where only unbleached pulp is manufactured, unbleached white water is the major toxic stream. Under this situation, using caustic effluent as a source of surfactant for flotation cannot be realized. Since most toxic compounds in kraft mill effluents (Table 2) are negatively charged carboxylic organic compounds, addition of a cationic surfactant would most likely aid detoxification. Ideally, such surfactants should be non-toxic and readily biodegradable. Several commercially available cationic surfactants were screened for toxicity at 50 ppm concentration. In Appendix II, it is shown that 5 out of 15 cationic surfactants (tertiary amines and quarternary ammionium salts) tested, were non-toxic. They were added to unbleached white water at 50 mg/l concentration and treated by foam separation at pHs 5, 7 and 9.5. A control sample aerated under the same condition but without surfactant was compared for detoxification. Table 6 shows the results of these experiments.

The control sample foamed modestly. Separation of foam at pH 7 was not effective in detoxifying the sample. In the presence of 50 ppm of

TABLE 6

EFFECT OF SURFACTANT ADDITION ON DETOXIFICATION OF UNBLEACHED WHITE WATER

| · | MST of Foam Separated Effluent (hr) | | | | | | | |
|--------------------------------|-------------------------------------|--|------------|------|--------|--|--|--|
| MST of Raw Effluent (hr) | Without Surfactant | With 50 ppm of Cationic Surfactant | | | | | | |
| | (pH:7.0) | Surfactant Species | рН 5 | рН 7 | pH 9.5 | | | |
| 3 | 5 | Hexadecyl Trimethyl Ammonium Bromide | ** N.T. | 6 | 8 | | | |
| 3 | 5 | Benzyl Hexadecyl- dimethyl Ammonium Chloride | N.T. | N.T. | 24 | | | |
| 0.8 | 1 | Ethomeen 425* | 11 | 8 | 6 | | | |
| 0.8 | 1 | Amine T* | 6 | 1 | 7.0 | | | |
| 0.8 | 1 | Variquat 450* | N.T. | 2.5 | 0.8 | | | |

^{*} Tertiary Amine and Quaternary Ammonium Salts.

Treatment time= 4 hr Aeration rate = 500 ml/min

** NT = Not toxic.

cationic surfactant, however, foaming was greatly enhanced and the extent of toxicity removal improved under most pH conditions. Three surfactants namely: Hexadecyl Trimethyl Ammonium Bromide; Benzyl Hexadecyl-dimethyl Ammonium Chloride and Varriquat 450 detoxified effluent completely at slightly acid pHs. At alkaline pHs, the complexing effect of the surfactants was adversely affected. Removal of the toxicants became ineffective.

The success of using surfactant for detoxification represents an alternative approach for detoxifying effluents which are toxic but not foamable. However, large quantities of surfactants would be required. Supposing that unbleached white water (approximately 4 - 5 M gal/day from a 750 TPD pulp mill) were treated by foam separation and with 50 ppm surfactant dosage at \$1 - 1.50/lb of surfactant cost: then foam separation of unbleached white water would cost \$3.5 - 5.0/ton of pulp; which is uneconomical. Therefore, methods of recovering the surfactant would have to be developed to reduce the treatment cost to an acceptable level.

4. Detoxification of Combined Mill Effluent

A large number of combined mill effluents were taken directly from 5 mills. These effluents were different in terms of make-up of the various waste streams but had in common a caustic extraction effluent. The toxicity of these effluents ranged from 1.3 to 7 hr MST. Since the study was aimed at examining the treatability of effluent obtained

from different sources, foam separation treatment time was arbitrarily chosen at 8 hr, in excess of what would be required for a typical effluent. Detoxification results as a function of effluent composition are presented in Table 7.

In general, all effluents foamed well at both acid and alkaline pHs during the first two hours of experiment. Among the 16 samples, 15 were detoxified by foam separation at pH 9.5. These effluents were obtained from Mills A, B, C, D and E. As indicated in Table 7, although the effluent constituents differed, all combined effluents were detoxified at pH 9.5. Only the Mill C sample which consisted of all major and minor effluent streams except unbleached white water could not be detoxified. However, this effluent was partially detoxified at pH 4.0 (60% fish survival).

Since these effluent samples were obtained directly from the mill discharge pipelines and processed as soon as they were received, the characteristics of these effluents and the response to foam separation are believed to be typical. Thus, it can be assumed that in general, foam separation treatment is effective for detoxifying combined mill effluent waste streams.

TABLE 7 TOXICITY REMOVAL OF COMBINED MILL EFFLUENT BY FOAM SEPARATION

| Mill Type of | Type of Effluent | MST of Raw | MST (hr) of | Treated Effluent at pH | (No.of Detoxified Samples |
|----------------------|--|--|-----------------------|--------------------------------------|---------------------------|
| | | Effluent (hr) | 4.0 | 9.5 | (No. of samples treated) |
| A | Total combined effluent excluding acid bleached effluent | 3.0 | 3.0 | N.T. | 1/1 |
| A Wholemill effluent | | 4.2 2.5 6.0 | _ | N.T N.T. N.T. | 3/3 |
| В | Unbleached white water + acid bleach effluent + caustic extraction effluent | 3.7 | 72 | N.T. | 1/1 |
| | Wholemill effluent | 5.0 4.5 | - | N.T N.T. | 2/2 |
| С | Total combined effluent excluding unbleached | 1.3 | 60% Survival | 1.2 | 1/1 |
| D | Wholemill effluent | 4.8 3.5 | 860 | 80% Survival N.T. | 2/2 |
| E | Wholemill effluent | 7.0 2.5 3.8 4.0 4.5 3.2 | - - - - - | N.T. N.T. N.T. N.T. N.T. | 6/6 |

 $\frac{Process\ condition:}{Sparger\ pore\ size} = 45\mu$ Air flow = $500\ ml/ml$

5. <u>Selection of Most Suitable Process Streams for Foam Separation</u> Treatment

Foam separation results on combined and individual process streams indicate that caustic extraction effluent by itself and other waste streams when mixed with it can be detoxified by foam separation. Since the volumes of kraft mill effluent discharged are enormous, it would be desirable to treat only those combined waste streams which are most responsive to foam separation and can be detoxified rapidly. The viability of a foam separation process is determined by four important factors:

- chemical and pretreatment requirements,
- volume of effluent to be treated and the effectiveness of the foaming technique on detoxification;
- treatment time and land area requirements;
- economics of a foam separation operation.

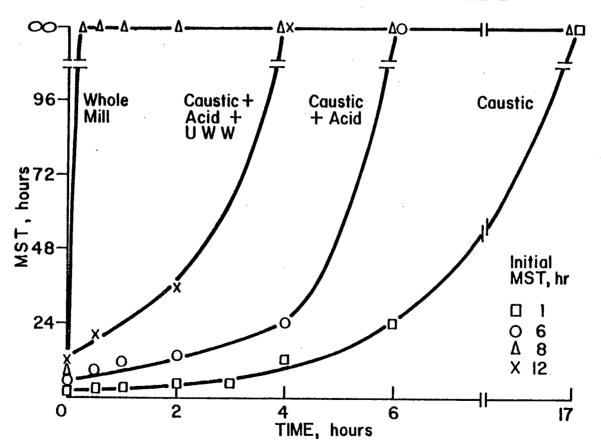
Various process streams were obtained from a pulp mill and mixed according to the proportions in which they are found in the mill to form a combined effluent. The pH's of various effluent were adjusted to conditions where detoxification was most effective. Table 8 shows the relative magnitude of volume discharged, the time required to detoxify these effluent mixtures, the pH requirement for treatment, and the amount of foam removed. Figure 28 plots the MST of the effluent during the progress of foam separation.

TABLE 8

FOAM SEPARATION TIME REQUIRED FOR DETOXIFYING VARIOUS COMBINED EFFLUENTS

| Composition | % of Total Volume Discharged | Initial Toxicity (MST, hr) | pH for Treatment | Time to Complete Detoxification (hr) | Foam Volume removed (% conversion of influent) |
|----------------------------|---------------------------------------|----------------------------------|---------------------|---|---|
| Whole mill effluent | 100 | 8 | 9.5 | 0.25 | 5 |
| Acid:UWW:caustic (2:0.7:1) | 76 | 12 | 9.5 | 4.0 | 4.5 |
| Acid:caustic (2:1) | 67 | 6 | 9.5 | 6.0 | 10 |
| Caustic extraction | 21 | 1 | 2.5 | 17.0 | 20 |
| | | | | | · |

Figure 28
TIME REQUIRED FOR DETOXIFICATION OF VARIOUS EFFLUENT MIXTURES FROM MILL B

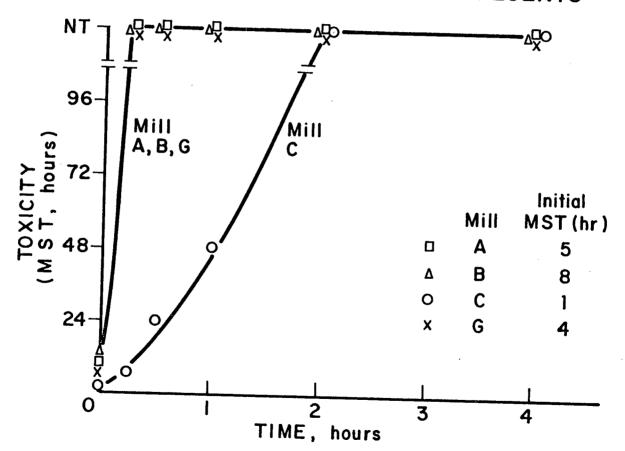


Among the various possible combinations, wholemill effluents were detoxified most readily. After 15-min of treatment, 5% of the effluent treated was removed as foam, toxicity was reduced from 8-hr MST to a nontoxic level. Although the combined acid, UWW and caustic extraction effluents were the least toxic, a treatment time of up to 4-hr was required to effect detoxification. However, because foam formation is less abundant, only 4.5% of the influent was transformed to foam. With combined acid:caustic effluent, about 10% of the effluent was transformed into foam over 6-hr of foam separation. Foam separation effectively produced a nontoxic effluent. Caustic extraction effluent alone was most difficult to detoxify and also produced the most foam (20%). Up to 17-hr of treatment had to be given to achieve a significant level of toxicity reduction.

Four additional experiments were conducted on wholemill effluents with MST's ranging from 1-hr to 8-hr. For the less toxic samples (MST:4-8 hr) treatment time (Figure 29) required for detoxification was in the neighborhood of 0.25-hr. For more toxic effluents (MST = 1 hr) 2-hrs of treatment detoxified the effluent.

In actual operation, it is unlikely that caustic extraction effluent would be treated alone because large amounts of acid would be required to reduce the pH to 2.5. Moreover, after treatment, neutralization would be needed prior to discharge. In addition, the much larger amount of foam produced might present a greater disposal problem. The results (Table 8) clearly indicate that it is more practical to treat

Figure 29
TIME REQUIRED FOR DETOXIFICATION
OF VARIOUS WHOLE MILL EFFLUENTS



combined wholemill effluent because of the following advantages:

- even without foam separation treatment, the effluent would require neutralization to pH 6.5 to 8.0, prior to discharge. Therefore, bringing the pH to the operating condition (pH 7.0 or 9.5) represents only a minor adjustment:
- after treatment, the final pH always remains around 7-8 which would allow direct discharge to the watercourse:
- wholemill effluent detoxified much more rapidly than caustic effluent. This compensates for the larger volumes involved.
- the volume of foam for disposal is substantially reduced:
- all toxic or potentially toxic wastes are included in wholemill effluent and can be treated.

B. PROCESS PARAMETERS FOR OPTIMUM DETOXIFICATION BY FOAM SEPARATION

During the feasibility studies discussed in Section V-A, it was demonstrated that the presence of surfactants is necessary to sustain foaming. The correct effluent composition and suitable pH conditions are essential factors controlling the success of the detoxification of kraft wholemill effluent. Many other variables also affect the performance and efficiency of foam separation. The relative importance of each variable depends on the characteristics of the waste. These variables were examined in a series of batch and continuous experiments. Most parameters were studied in a batch system. Those variables that are interrelated are discussed under the same heading. The batch experiments were done under the following standard conditions with all

operating variables except one held constant.

System = 4 1 laboratory foam separation column

Waste = bleached kraft wholemill effluent

pH = 9.5

Aeration rate = 500 m1/min

G/L = 4-10

Temperature = $30 \pm 2^{\circ}C$

Sparger pore size = 45μ (mean bubble diameter = 1 mm)

Column height = 90 cm

Foam height = 60 cm

Treatment time = 30 min.

1. Effect of pH

Most toxicants contained in bleached kraft, wholemill effluents are negatively charged carboxylic compounds (Table 2). Changes in pH may change the charge on the toxic compounds, enhance hydrolysis of surfactants and/or affect the surface tension and foam properties. As a result, adsorption of toxicants on the bubbles and the extent of toxicity removal can be varied. The interactions of toxic surface active compounds in kraft mill effluents are highly complex. Although the pH effect has been demonstrated quite extensively during the treatability studies (Section V-A-2), to determine the range of pH that would be suitable for removal of the majority of toxic surfactants, foam separation treatments for several more batches of effluents were repeated between pH's of 2 and 10.

The results of foam separation on effluents from three different mills (Figure 30), confirmed that detoxification is pH dependent. The critical pH's for detoxification for Mills D, F and G, were 9 and 7 respectively. The variation in pH reflected the differences in the quantity and characteristics of the constituents of the toxic compounds. Below the critical pH level, although some reduction of toxicity could be achieved, complete detoxification was not obtained. The foaminess also decreased substantially with decreasing pH value. After treatment, the pH of the effluent decreased by 0.5 to 1 pH unit.

The chemicals used for pH adjustment should be selected carefully. In most pulp mills, lime will be used because it is readily available and economical to use. However, the quantity applied should be carefully determined and should not exceed the maximum level where precipitation would occur. Otherwise severe scaling by calcium deposits on the equipment will occur. In consideration of this limitation as well as the economics of the situation it is advisable to add lime to raise the pH to just below the troublesome level (e.g. pH 6). Further pH adjustment should be made by caustic addition.

2. Effect of Temperature

In a solution containing surface active compounds, changes in temperature affect the solubility of the surfactants and surface tension of the solution. Therefore, separation of toxic materials by foam from kraft mill effluents could also be affected by temperature. Figure 31



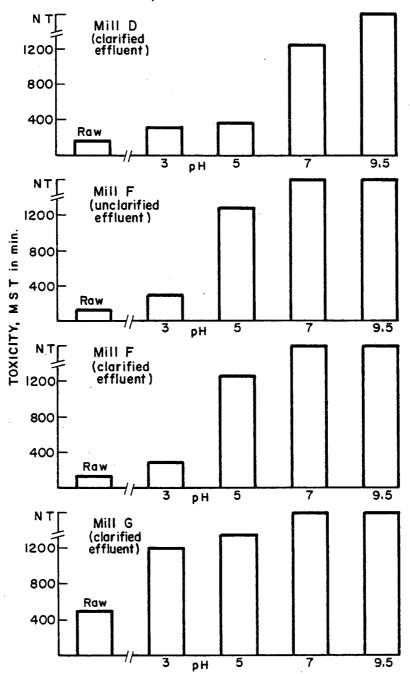
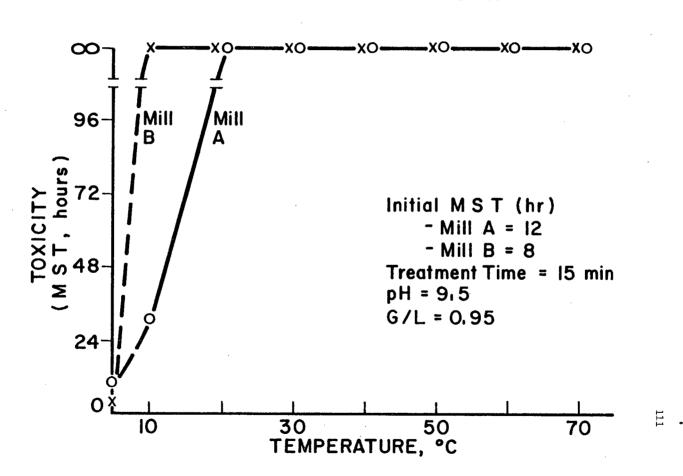


Figure 31 EFFECT OF TEMPERATURE



illustrate the effect of temperature over the range of $10-70^{\circ}\text{C}$ for 2 samples. Other temperatures, which are unlikely to occure in the mill, were not covered in this study. The results indicate that for detoxification of kraft mill effluent, the temperature effect is significant only at low level. At 500 ml/min aeration rate and 15 minutes treatment time, foam separation at temperatures < 10°C was not as effective as treatment at higher temperatures. Between $20-70^{\circ}\text{C}$, effluents were detoxified without difficulty. Other studies on pure surfactants have verified that increases in temperature cause increases in fractionation (100). However, the result is in contradiction to Gibbs adsorption equation ($\tau_{\text{C}} = \frac{-1}{\text{RT}} \frac{\text{d}\gamma}{\text{d} \ln \text{c}}$) where surface excess is supposed to decrease with increasing temperature.

Detoxification by foam separation is a combined process of solute fractionation and solid flotation, as evidenced by the formation of froth and scum in the foam. It is possible that higher temperatures promote formation of precipitates and/or ion complexes. Therefore as long as the temperature is not too high to destroy the stability of the foam film, detoxification will improve. During this experiment, the effect of evaporation on the film became noticeable only at temperatures greater than 70°C. At such high temperatures foams were destabilized and collapsed readily. Since in practice the temperature of kraft mill discharges averages 30 to 40°C, this range of temperature would be suitable to support the formation of stable foam films. Temperature would then not present a problem in foam separation of toxicity.

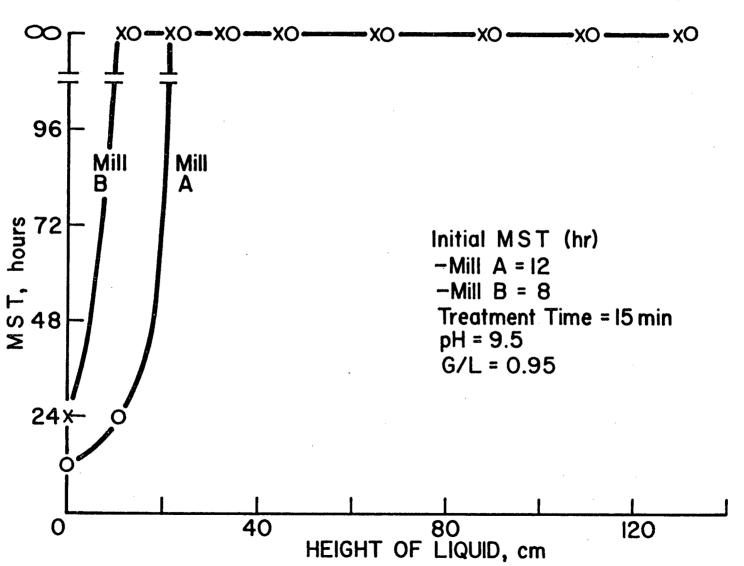
3. Effect of Column Height

The column height of the foam separation system affects the mass transfer and contact time of the bubbles in the liquid. For most pure surfactants, the difference in transfer rates can be great (101). For a two component system, mass transfer can be predicted by using one of several established theoretical principles (102, 103). However, these principles are not applicable to pulp mill effluents which contain a good mixture of surface active substances of different chemical characteristics.

In order to investigate whether column height is of significance in detoxification process, a series of continuous flow experiments were run with liquid heights varied from 11 - 120 cm. The results (Figure 32) indicate that a minimum of 11 cm and 22 cm were all the liquid height required for detoxification of mills A and B effluents having an initial MSTs of 5 hrs (A) and 24 hrs (B) respectively. The liquid height requirement agrees closely with published data (67) on surfactant removal.

In a continuous process, the height of the foam separation column can be divided into 2 regions (65); a mixing zone just around the feed point and a zone below it in which liquid moves countercurrent to the air. It is generally recognized that solute transfer occurs mainly in the countercurrent region. Below a certain height, the countercurrent region disappears, the two regions then become one mixing zone and then height affects separation.

Figure 32
EFFECT OF COLUMN HEIGHT ON DETOXIFICATION

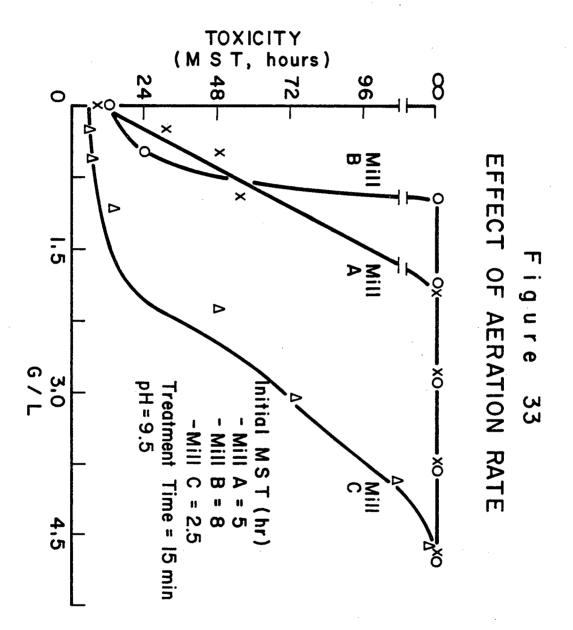


From this study, this condition would appear to occur at liquid heights of 22 cm and 11 cm (Figure 32). The liquid height requirement of a foam separation system is proportional to the effluent toxicity. In general, the average toxicity of pulp mill effluent is seldom less than 2 hr MST and in order to minimize land utilization, commercial foam separation system would be built at least 5 - 10 ft in height, the minimum height of 22 cm and the countercurrent bubble-liquid contact can be met at all time.

4. Effect of Aeration Rate and G/L Ratio

Provided constant bubble diameter (constant gas sparger pore size) are produced, a unit amount of surface active material contained in the effluent would require a constant amount of air bubble surface for complete removal of surfactants from the effluent. Since the toxic materials in kraft mill effluents are surface active, the minimum air requirement should increase with the toxicity. Figure 33 illustrates detoxification results by foam separation treatment for three batches of effluents having MSTs of 2.5, 5 and 8-hrs.

Regardless of initial toxicity level, the results suggest that toxicity reduction was governed by the air flow rate. The critical aeration rate required was controlled by the effluent toxicity. The most toxic effluent from Mill G which had an initial MST of 2.5 hr, required 1000 ml/min of aeration (G/L = 4) to achieve detoxification by foam separation. The less toxic effluent from Mill B (MST - 5 hr) required a minimum aeration rate of 500 ml/min (G/L = 2) whereas the



least toxic effluent from Mill C (MST = 8 hr) was detoxified by aerating a minimum of 250 ml/min (G/L = 1) of air.

The air requirement for a foaming system can also be determined by the G/L ratio (determined by treatment time, gas and liquid flow rates). Each variable determining G/L, i.e. treatment time and air flow rate can be varied and will not affect the amount of surfactants removed. However, it should be realized that high air flow produces wet foam and will lower the enrichment ratio. Moreover, severe turbulence in the foaming column will result. This condition may be detrimental because the toxic foam-scum may be redispersed into the effluent and the foam flow rate may be exceedingly large. Therefore, when large G/Ls are encountered, it would be desirable to consider the advantage of increasing the treatment times slightly so that the aeration rate can be decreased to a more manageable level.

5. Effect of Bubble Diameter and Gas/Liquid Interfacial Area

The gas-liquid interfacial area applied to a foam separation system is controlled by the G/L ratio. The same gas-liquid interface can be created by either sparging large amounts of air in big bubbles or small volumes of air in small bubbles. Thus, the smaller the bubble size produced, the less air blower capacity required. Since it is expected that the total interfacial area required for detoxification should increase with increased influent toxicity level, the extent of toxicity adsorption in foam will be a function of the gas-liquid interface generated per unit time. In a series of batch experiments, the foam

generation system, foam separation time and air flow rates were changed to obtain different bubble diameters and G/L ratios. Although it is recognized that small bubbles ascent slower than big bubbles and this should enhance adsorption of toxicants, this factor was not considered in this study since it was assumed that transfer of toxicants to the interface was instantaneous.

Table 9 shows that with a coarse dispersion medium, producing approximately 4 mm diameter bubbles (estimated crudely by direct photographing of bubbles in the column), a G/L ratio of 30 was necessary to detoxify a typical effluent within 1.5 hr treatment time. By choosing a finer dispersion medium, producing bubbles of approximately 1.5 mm diameter, the necessary G/L ratio for detoxification could be reduced to 10 within a similar treatment time. A third system, producing 1 mm diameter bubbles detoxified waste of similar toxicity even at a lower G/L ratio of 7. Although the three systems operated at different aeration rates, G/L ratios and bubble diameters the total gas-liquid interfacial areas cumulated over the whole experiment was similar within the range of 41 to 46 $m^2/1$. tical experiments using a helical aerator (Kenics System) and a turbine system producing 0.07 mm diameter bubbles (G/L = 3-4) and a dissolved air system producing 0.07 mm diameter bubbles (G/L = 0.3) created a gas-liquid interfacial area of 24 - 33 $m^2/1$ compared to the porous diffuser systems, the variations of gas-liquid interfacial area was less than a factor of 2 whereas the G/L was reduced by a factor of 100 from 30 to 0.3.

The data confirm that the same detoxification results can be obtained by reducing the G/L ratio given and with smaller bubble sizes.

There is a minimum limit however, to which the G/L could be reduced because in commercial aeration systems, the cost of bubble generation usually increases with the reduction in bubble sizes. Therefore, the

TABLE 9

EFFECT OF BUBBLE DIAMETER, GAS-LIQUID RATIO AND INTERFACIAL AREA ON DETOXIFICATION

| Experiment | Toxicity | | Type of | Aeration | Treatment Time | | | Gas/Liquid |
|------------|-------------------------|-----------------------------|---|----------------------------------|----------------------------------|----------------------------|----------|--------------------------------------|
| No. | Influent MST (hr) | Treated Effluent (hr) | Sparger Used | (1/min) | Required For Detoxification (hr) | Bubble Diameter (mm) | Ratio | Interfacial Area (m ² /1) |
| 1 | 4.3 | NT** | Seven 5" diameter 65µ pore size plastic discs | 60 | 1.5 | 4.0 | 30 | 46.3 |
| 2 | 4.7 | NT | Four 5" diameter 25µ pore size plastic discs | 30 | 1.0 | 1.5 | 10 | 41.2 |
| 3 | 2.0 | NT | Four 1' long <25µ pore size ceramic tubes | 10 18 | 2.0 1.0 | 1.0 1.0 | 7 6 | 41.1 37.0 |
| 4 | 1.8 | NT . | Seven l'long 0.5" diameter helical aerators | 4 | 3.0 | 0.75 | 4 | 32.9 |
| 5 | 1.4 4.8 | NT NT | 3" diameter 4-blade turbine | 1 1 | 0.5 0.75 | 0.75 | 4 . 3 | 32.9 24 |
| 6 | 5.0 | NT | 40 psi, dissolved air flotation system (4 passes) | Air sat- uration at 40 psi | | 0.07 | 0.3 | 25.2 |

^{*} Bubble diameter and gas-liquid interface were estimated from photographs (Section IV-D) and literature data.

** NT = Non-toxic; 100% fish survival in 100% effluent concentration after 24 hrs.

Note: Experiments No. 1 - 4 done in 180 1 columns at field site; batch operation Experiment No. 6 done in laboratory using a 4 1 flotation unit.

G/L ratio could be reduced only to that minimum below which further reduction of bubble sizes would not be economical. The above indicates that detoxification efficiency depends on the total interfacial area produced per unit volume of waste treated. The production of interfacial area can be controlled initially by selection of a gas dispersion system, which produces gas bubbles of the required diameter and then, by adjusting the G/L ratio accordingly.

6. Effect of Influent Toxicity Level on Treatment Time and Gas-Liquid Interfacial Area Requirement

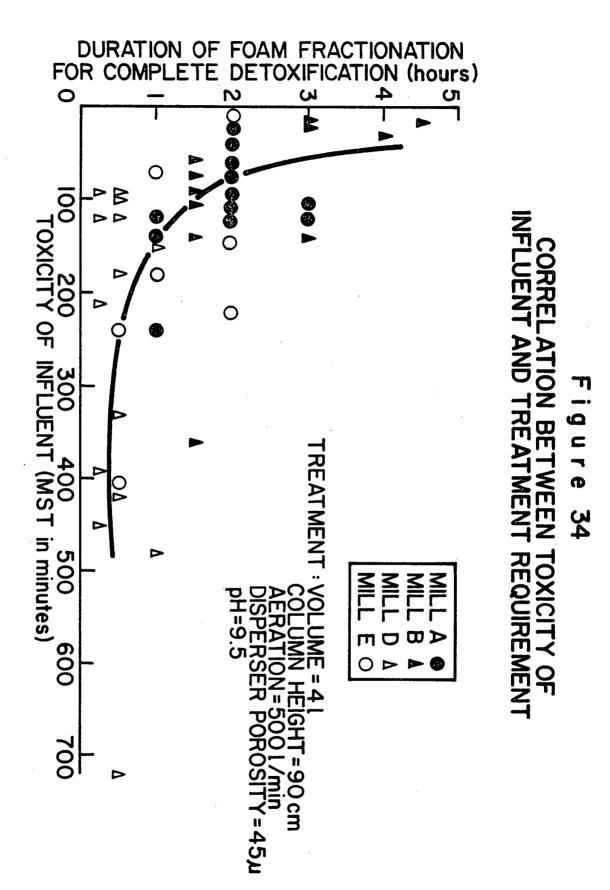
Under a given set of conditions, treatment time required in a batch operation appears to depend on the initial toxicity of the effluent. In Figure 34, the time necessary to detoxify effluents by foam separation is plotted against the initial toxicity. Regression analysis indicates that the data fits the form of a power curve. The correlation coefficient was calculated as r = 0.81.

$$Y = 41.84 X^{-0.71}$$

where X = influent toxicity in MST (min)

Y = treatment time

The expression could be used to predict treatment time required for detoxifification. Using this equation and calculating the worst cases where effluents of 100 min and 50 min MSTs are foam separated, the predicted treatment times for detoxification are 1.6 and 2.6 hrs.



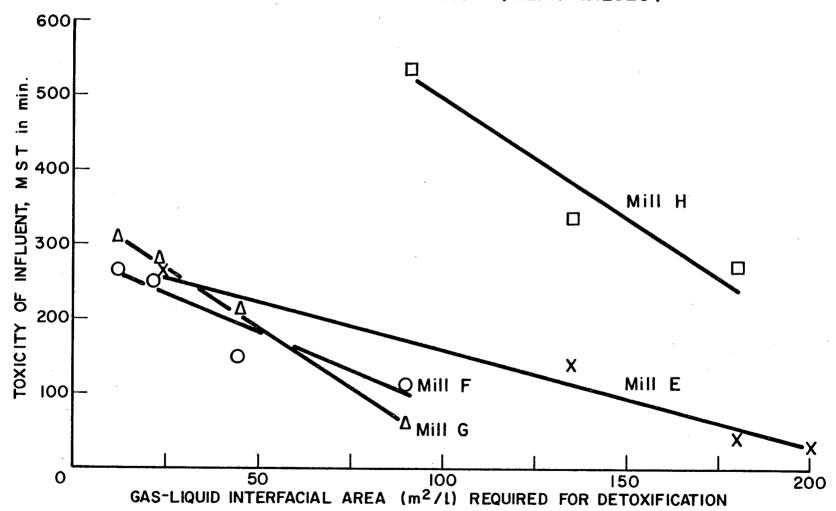
In general, the MST of the majority of the effluents exceeds 100 min and seldom falls below 50 min. Therefore, maximum treatment time required is not expected to be greater than 3 hrs.

At the specific air flow rate given and assuming bubbles of 1 mm mean diameters were produced, the total gas-liquid interface generated over the period of treatment time required for detoxification was calculated for a group of samples from Mills E, F, G and H (Appendix III). Figure 35 plots the gas-liquid interfacial area generated as a function of the mean toxicity of the various sample groups. The results produce a series of straight lines but not parallel to each other. In general, it was found that gas-liquid interfacial area requirement increased linearly with the initial toxicity of the effluent. However, the slopes of the curves varied from mill to mill indicating that the detoxification requirements for foam separation are different for each mill. For example, effluents from Mills E and G with an MST of 3 hr required 50 m²/l interfacial area. whereas Mill E effluent with the same initial toxicity needed $100 \text{ m}^2/1$. In contrast, this interfacial area was not sufficient to detoxify Mill H effluent where large quantities of defoamer were present when the samples were obtained from the mill. Thus, requirement for detoxification by foam separation needs to be assessed for each mill. Determination of the minimal gas-liquid interfacial area is an important design consideration of the foam separation process.

Typical MST values of most bleached kraft mill effluents vary from 100 - 800 min; with an average of 200 - 300 min. A foam separation system designed to provide only sufficient interfacial area for removing average toxicity loads will fail to detoxify when influent toxicity

Figure 35

CORRELATION BETWEEN TOXICITY AND GAS-LIQUID INTERFACIAL AREA REQUIRED FOR DETOXIFICATION (MEAN VALUES)



exceeds the average. Thus for a proper design some measure of toxicity variation as well as average values are required. For attainment of a satisfactory detoxification rate, which meets regulatory requirements, the system therefore will have to be designed to handle toxicity well in excess of the average loads. For example, if a system for Mill E was designed to handle toxicity levels of MST - 100 min instead of 250 min, the interfacial area required would be 145 m 2 /1 instead of 30 m 2 /1; a five fold increase. Such a drastic increase of interfacial area requirement might prove to be prohibitively costly. Thus, utilization of surge capacity and minimization of the frequency with which excessively toxic loads have to be handled probably will be essential to eliminate the need for impractically high interfacial area generation requirements.

7. Effect of Mode of Operation and Retention Time Required

Three different modes of foam separation operation, namely: simple, stripping and enriching modes (Section III) were investigated. Total reflux, a special case of enrichment operation was also studied to determine what type of operation would be most suitable for detoxification of kraft mill effluent. The experiments were conducted using effluent having an original MST of 305 min. The system was operated under continuous flow conditions for 8 hrs in a 4 1 laboratory column, at retention times of 10 min, 15 min, 25 min and 40 min. Foam was withdrawn 60 cm above the liquid level.

Among these various modes of operation (Table 10) effluents were detoxified more readily using a stripping mode. A retention time of 15 min permitted 80% fish survival. At 25 min retention time, the effluent was completely detoxified. Under the same conditions, simple mode and enrichment mode operations both allowed 20% and 80% fish survival at 15 min and 25 min retention time and complete detoxification at 40 min retention time.

An interesting result was obtained by operating the column at total reflux where foams were returned completely into solid gummy materials. Detoxification results at 25 min and 40 min retention time were comparable to the simple mode operation.

The overall results suggest that a stripping mode operation would appear to have slight advantage because of the lower retention time requirement. However, because the effluents were fed on top of the foam, large amounts of liquid were entrained in the foam. By increasing retention time, the foam volume discharged could be reduced quite substantially (from 30 to 12% as retention time increased from 10 to 40 min) as a result of better liquid drainage. Even at the highest retention time (40 min) tested, the foam volumes were still 4 - 12 times greater than simple mode (3% volume) and enriching mode (1.2% volume) operations.

In designing a commercial foam separation plant, stripping mode operation is not recommended because of the large foam volume involved.

TABLE 10

EFFECT OF OPERATION MODE AND RETENTION TIME ON
CONTINUOUS DETOXIFICATION OF KRAFT MILL EFFLUENTS

| | Operation | Process C | ondition | MST of Effluent | Foam Volume |
|----------------------|---|-------------------------|----------|-----------------------|--|
| Mode | Feed Position | Retention Time (min) | G/L | after Treatment (min) | (%) Discharged (60 cm foam height) |
| | | 10 | 1.2 | 800 | 8.5 |
| Simple | Influent: feed at | 15 | 2 | 5000 | 7.0 |
| Бішріс | gas-liquid interface | 25 | 4 | ** 80% Survival | 5.3 |
| | | 40 | 4.8 | Nontoxic | 3.0 |
| | | 10 | 1.2 | 1000 | 30 |
| Strinning | Influent: feed on top of foam layer | 1.5 | 2 | **80% Survival | 21 |
| ottipping | | 25 | 4 | Nontoxic | 16 |
| | | 40 | 4.8 | Nontoxic | 12 |
| | Influent: feed at gas-liquid interface | 10 | 1.2 | 600 | 6.7 |
| Enriching (Normal | Collapsed foam: | 15 | 2 | 5000 | 4.5 |
| operation |)50% returned to)foam layer | 25 | 4 | **80% Survival | 2.3 |
| | Toum Tuyer | 40 | 4.8 | Nontoxic | 1.2 |
| Enriching | Influent: feed at | 10 | 1.2 | 500 | (Scum formation) |
| (Total | gas-liquid interface Collapsed foam: . | 15 | 2 | 1000 | (Scum formation) |
| reflux) | 100% returned to | 25 | 4 | ** 70% Survival | (Scum formation) |
| | foam layer | 40 | 4.8 | Nontoxic | (Scum formation) |

Volume of foam separation column:4 1 MST of untreated effluent: 305 min

Note: **MST cannot be determined when fish survival exceeds 50% after 96 hrs exposure.

The total reflux system offers the advantage of converting large volumes of foam to a small volume of scum. However, the system must be operated with care because of the collapsed foams are highly concentrated in toxic material. When returning to the foam layer for reflux, there is always a danger of liquid channelling within the foam. Once this occurs, the toxic materials will be redispersed into the solution.

In comparing the complexities and disadvantages of various operation modes, detoxification efficiencies and foam volume, it seems logical to use only the simple or the enriching modes for large scale foam separation operations.

8. Effect of Staging

In order to investigate the necessity of staging in a continuous foam separation, a two stage system using two 180-1 columns connected in series was operated at the lowest possible G/L ratio and assessed for detoxification performance. A single stage column operated under similar conditions was run subsequently for comparision. The system was operated continuously for 15 days. In the two-stage system, the air flow and retention time in each column was 2.3 1/min and 30 min respectively: these were approximately half of the single stage system, i.e. the overall G/L and retention time were identical. The operating conditions and daily toxicity data for each column are presented in Appendix IV a-b. Detoxification results for the two systems are compared in Table 11.

TABLE 11

DETOXIFICATION PERFORMANCE (MEAN VALUE) OF A SINGLE STAGE VERSUS 2 STAGE SYSTEM

| D | Single Stage | | Two Stage S | System |
|---|--------------|-----------|-------------|----------------|
| Parameter | System | lst Stage | 2nd Stage | 0veral1 |
| Retention time (min) | 58 | 29 | 29 | 58 |
| G/L | 8 | 4.65 | 4.65 | 9.3 |
| Influent MST (min) | 252 | 277 | _ | . - |
| (No. of Samples Detoxified) (No. of Samples Treated) | 5/8 | 0/14 | 13/14 | 13/14 |
| % of Treated effluent meeting Fed. Toxicity standard. | 63 | 0 | 91 | 91 |
| Foam Production (% volume discharged) | 6.8 | 3.7 | 0.9 | 4.6 |

Gas diffuser: Four fine bubble ceramic diffuser, 1' long, 3"diameter Operation Elapsed Time: 15 days.

The single stage system operating at an average G/L of 8 and 58 min retention time detoxified 63% of the samples (5 out of 8 samples). The foam discharged (collapsed volume) averaged to 6.8% of the influent volume. With a 2-stage system, detoxification rates improved dramatically to 91% (13 out of 14 samples were detoxified). Moreover, overall foam discharged was only 4.6% of influent, about 30% less than that of the single stage system. The reduction in foam discharge was due to increased foam retention as a result of lower air flow (G/L = 4.6) in each The average foam generation in the first stage was 3.7% against 0.9% in the second stage. Although the first stage removed most of the foamable materials, detoxification was incomplete. This is indicated by the poor fish survival rate. The second stage removed the remaining small amounts of toxic materials and brought the effluent to the nontoxic level. The results indicate that although on the overall, the same G/L and retention time were applied to the single stage system, the two-stage achieved a far better detoxification rate (92% vs 63%) and lower foam discharge rates. Staging of a foam separation system assures complete removal of foam and thus prevents the toxic scums and residual foams to return to the liquid phase. Each foam separation column resembles a back mix reactor, although the concentration is uniform in each reactor, there is nevertheless a change in concentration as fluid moves from reactor to reactor, i.e. the concentration drops to a lower value. As the number of back mix reactors increased, the system approaches a plug flow system (104).

Since the effectiveness of the foam separation process is concentration (toxicity) dependent, a plug flow reactor would be more efficient because the concentration of reactants (in this case MST) decreases progressively as fluid passes through the system.

C. EFFECT OF VARIABILITY IN EFFLUENT CHARACTERISTICS ON DETOXIFICATION

The waste characteristics of bleached kraft mill effluents obtained from various Canadian mill differ according to wood furnishes and modification in the various mills process conditions. An extensive sampling program therefore was conducted to investigate the effect of effluent variability on foam separation of toxicity. A total of 205 batches of samples were obtained at different times from eight B.C., one Ontario and one Quebec mills. Wood furnishes used in these mills included fir, hemlock, cedar, spruce, pine, cypress, balsam, poplar, maple and birch. None of the mills processed exactly the same wood furnishes. Water usage ranged from 29,000 to 48,000 gal/ton of pulp. Additives in the effluent were mostly chemical defoamers and usually consisted of more than two different types. Almost all samples obtained were toxic to fish. Over 90% of the MSTs were in the range of 2 - 6 hr.

Each batch of sample was subdivided and treated under established foaming conditions with treatment times of 0.25 - 5 hr. For the majority of the samples, foam ceased to occur after treatment. The reductions in toxicity are shown in Appendix V a-j and are summarized in Table 12.

TABLE 12 SUCCESS RATE IN DETOXIFYING BLEACHED KRAFT WHOLEMILL EFFLUENTS BY FOAM SEPARATION

| Mill | Principal Wood Furnish | No. of | Toxicity Influen | • | Treatment Time Required to | No.of Samples Detoxified 100% 65% | | * Success Rate(%) of Detoxification 100% 65% | |
|---------|--|---------|---------------------|---------|-------------------------------|-----------------------------------|---------------|--|---------------|
| | Futilish | Samples | Mean ± SD | Range | Detoxify (hr) | Test conc. | Test conc. | Test conc. | Test conc. |
| A | 18% Fir, 46% Hemlock 36% Cedar | 8 | 9.7±6.5 | 1.2-24 | 0.25 | 7 . | 8 | 88 | 100 |
| В | 43.4% Fir, 40.3% Hemlock, 16.3% Cedar | 18 | 9.8±7.4 | 0.5-24 | 0.5 - 3 | 12 | 15 | 67 | 83 |
| С | 50% Spruce, 45% Pine, 5% Fir | 19 | 1.4±0.9 | 0.2- 4 | 1 - 3 | 16 | - | 84 | - |
| D | 36% Spruce, 33% Pine, 31% others | 20 | 2.3±1.6 | 0.3-6.5 | 0.25 - 2 | 13 | - | 65 | _ |
| Е | Fir, Cypress, Spruce, Pine and Hemlock | 20 | 1.2±1.3 | 0.2-6.0 | 0.5 - 4.5 | 16 | _ | 80 | _ |
| F | 60% Spruce, 16% Pine, 12% Balsam & Others | 64 | 4.2±4.8 | 0.5-NT | 0.25 - 2 | 54 | - | 84 | _ |
| G | 50% Spruce, 45% Pine, 5% others | 18 | 4.2±3.0 | 0.7-12 | 0.25 - 1 | 22 | 22 | 100 | 100 |
| Н | 50% Hemlock, 32% Fir and 18% Cedar | 19 | 6.0±4.1 | 0.5-17 | 2 - 5 | 17 | - | 100 | - |
| I | 80% Jackpine and 20% Spruce | 10 | 1.8±1.0 | 0.5- 4 | . 2 | 10 | 10 | 100 | 100 |
| J | 46% Poplar, 27% Maple, 17% Birch & 10% Softwood | 9 | 3.4±3.5 | 0.1-NT | 1 - 5 | 6 | 7 | 77 | 89 |
| 0verall | | 205 | | | 0.25 - 5 | 173 | 52 | 83 | 93 |

Note: Mills A - H from B.C.; Mill I from Ontario; Mill J from Quebec.

^{*} Based on no. of samples with 100% fish survival on 100% effluent after 24 hr .

** Over 80% fish survival in 65% effluent after 96 hr of exposure (Federal Toxicity Test).

The majority of the samples, regardless of when and where they were taken were detoxified within 3 hr as a result of foam separation. For highly toxic effluent, detoxification could be achieved by extending the treatment time to 5 hr. The percentage of the samples detoxified from each mill differed slightly. At 100% test concentration, the best results were from mills G, H, and I where 100% success was achieved. Four mills (A, C, E, and F) achieved an 80 - 90% success and the remaining three achieved à 65 - 80% success. Overall 173 out of 205 samples were detoxified and an overall success rate for all 10 mills of 83%.

Additional bioassays were done on samples from 5 mills (A, B, G, I and J) using the Federal Toxicity standard (80% survival in 65% effluent over 96 hr). Detoxification success rates on this basis reached 94%, about 11% higher than with the more stringent MST test in 100% effluent concentration.

Among those samples which did not pass the toxicity tests, substantial toxicity reduction was achieved (MST >1000 min). In most of these samples, foaming was still possible after 5-hr of treatment. This indicates that if longer treatment time were given to permit complete foam removal and if all samples were tested in 65% effluent, they would have passed the federal toxicity test.

In a few isolated instances, a detoxification failure could be traced to black liquor spills and bleach plant breakdowns. Under such

conditions, the effluent composition would not be compatible with the established foam separation process and would probably require completely different conditions for detoxification.

In general, the results lead to the conclusion that the variability of wood furnishes, process modifications, water usage and other factors relating to pulping and bleaching do not seriously affect the amenability of the effluent to detoxification by foam separation. However, these variations affect the toxicity level of the effluent and thereby affect the treatment conditions required. Overall, this sampling program has confirmed the effectiveness and universal applicability of the foam separation process for detoxifying kraft whole mill effluent.

D. DETOXIFICATION RELIABILITY OF A FOAM SEPARATION PROCESS

The characteristics of pulp mill effluents are not constant due to the complexity of mill operation, occasional spills and bleaching changes. For commercial application a foam separation process must produce effluents which meet toxicity standards all the time on effluents of everchanging characteristics. In order to assess the reliability of the process, a 180 l capacity, continuous flow, foam separation column was installed in Mill F and operated continuously over a 63 day period. The system was operated as a single stage column in the simple mode throughout the study. The G/L ratio and gas-liquid interfacial areas were varied by changing the design of the aeration system to provide different bubble sizes. Samples were taken and bioassayed daily on-site.

The operating data with different aerators and aeration rates are given in Appendix VI a-c.

The influent toxicity covered a wide range, (MST = 0.8 - 24 hr) and averaged 4 hr. The results of detoxification under different process conditions are summarized in Table 13. When the system was operated at G/L of 33 - 48 and at 1.6 - 2.1 hrs retention time, the corresponding gas-liquid interfacial areas (>40 m²/1) estimated by simple photographic technique exceeded the minimum requirement for effluents of averaged toxicity (mill E of Figure 24). During the 28 days of continuous operation, all samples met the toxicity standard 100% of the time. As the G/L ratio was decreased to the 8 - 12 range the interfacial area generated became only marginally sufficient. At this initial level, the detoxification success rate dropped to 75 and 63% indicating that the system was operating under sub-optimal conditions.

Over the 63 days of elapsed operation time, it has been documented that if adequate G/L ratios, gas-liquid interfacial areas and retention times were provided, consistent detoxification of effluents of varying characteristics could be obtained. However, adequate safety margins in gas-liquid interfacial area have to be designed into the system, to maintain high operating reliability.

E. MECHANISMS OF DETOXIFICATION

Foam separation involves adsorption of surface active materials onto the gas-liquid interface. During the progress of foam separation, several other mechanisms such as air stripping, volatilization, and

TABLE 13
DETOXIFICATION RELIABILITY OF A SINGLE STAGE CONTINUOUS
FOAM SEPARATION SYSTEM OVER 63 DAYS OF OPERATION

| 0 | Ор | Operating Conditions | | | Gas- | | | day 6 | | |
|-------------------------------|----------------------------------|-----------------------------|-----------------------------------|---------------------------|------|---|----------------------------------|----------------------------|---------------------------------------|---|
| Operation Period (days) | Air Diffuser | Gas Flow Rate (1/min) | Liquid Flow Rate (1/min) | Retention Time (hr) | G/L | Liquid Interface Generated (m ² /1) | Influent Toxicity (MST:hr) | No. of Samples Taken | *No. of Samples Detoxi- fied | Success Rate of Detoxi- fication |
| 12 | 65 μ pore size plastic discs | 65 | 1.5 | 2.1 | 48.0 | 72 | 3.0 | 12 | 12 | 100 |
| 16 | 65 μ pore size plastic discs | 60 | 1.8 | 1.6 | 33.0 | 49 | 3.0 | 17 | 17 | 100 |
| 24 | 25 μ pore size plastic discs | 45 | 3.1 | 1.0 | 12.5 | 42 | 8.0 | 24 | 18 | 75 |
| 11 | <25 µ pore size ceramic tubes | 25 | 3.0 | 1.0 | 8.0 | 30 | 4.2 | 8 | 5 | 63 |

Note: All numbers indicated are mean values of all the samples taken.

Operation: Mill F bleached kraft wholemill effluent.

Continuous on-site study

180 1 column

Treatment pH = 8.0

* Assessed for Federal toxicity standard: over 80% of fish survived in 65% effluent over 96 hr.

oxidation of toxicants could also occur and contribute to the reduction of toxicity. The relative importance of these various mechanisms was investigated in a series of experiments designed to identify the major mechanisms controlling the detoxification process and the problems associated with subsequent disposal of foam. The raw effluents were treated under conditions where the effluent would be detoxified. Preliminary experiments examined the effect of gas used and the toxicity of the various fraction collected during foam separation. Subsequent experiments determined the relative contribution of the various mechanisms and the concentration of toxic surface active materials in the foam.

1. Effect of Gas on Detoxification

The times required to detoxify two samples of bleached kraft whole-mill effluent with influent MST values of 222 and 360 min were determined on parallel systems using air, oxygen and nitrogen as the foam producing gases. After 1-hr of treatment all the foamable materials had been removed. Table 14 shows that all samples were detoxified regardless of the gas used for foam separation indicating that oxidation is of minor significance. When the foam fraction was returned to the treated effluent, the reconstituted effluent became toxic with MST ranging from 281 - 430 min. The loss of toxicity was small and could be due to some chemical degradation of toxicants or to stripping. Since the reconstituted effluents were toxic again and the variations in MST were insignificant, separation of foam was presumed to be the major reason

TABLE 14
FOAM SEPARATION OF BLEACHED KRAFT MILL EFFLUENT WITH DIFFERENT GASSES

| | Toxicity (MST in min) | | | | | | | |
|----------|-----------------------|----------|-----------------------------------|---|--|--|--|--|
| Gas | Untreated Effluent | Treated | Reconstitut | ed Effluent | | | | |
| | Lilluent | Effluent | Treated Effluent + Foam Fract. | Treated Effluent + Foam Fract. + Cond. Vapor Fract. | | | | |
| Air | 222 | NT | 281 | 208 | | | | |
| | 360 | NT | 400 | 400 | | | | |
| Oxygen | 222 | NT | 317 | 350 | | | | |
| · | 360 | NT | 380 | 380 | | | | |
| Nitrogen | 222 | NT | 317 | 337 | | | | |
| | 360 | NT | 430 | 380 | | | | |

NT - Non toxic (100% survival of fish in 100% effluent for 24 hr)

for toxicity reduction. With the addition of the condensed vapor fraction to the reconstituted effluent, the effluents became slightly more toxic (208 - 400 min) and were also not affected by the gas species used. These variations, however may be attributed partially to the errors of the bioassay technique employed.

2. Relative Contribution of Foam Separation, Volatization and Other Mechanisms to Detoxification

The relative contribution of various mechanisms to detoxification (Section IV-E) was determined for 20 samples taken from two B.C. mills and one Ontario mill. The samples were subjected to foam separation until detoxified. The conditions of treatment for individual mills and the toxicities of various reconstituted effluents are given in Appendix VII a-c. The results are sumamrized in Table 15.

Although the relative contribution of various detoxification mechanisms varied from sample to sample, in general the bulk of toxicity was concentrated in the foam. Foam separation responsible for an average of 77.5% of toxicity reduction, ranging from 60 - 90% and 85 - 95% for mill F, G and I samples respectively. In kraft mill effluent, the concentrations of toxic surface active toxicants (Table 2) seldom exceed 20 mg/l and yet copious foaming is an inherent characteristic of kraft mill effluent. It would appear that the foam is produced by surfactants in the effluent of which the toxic surfactants are probably only a minor fraction.

TABLE 15

RELATIVE CONTRIBUTION TO DETOXIFICATION BY VARIOUS MECHANISMS

| | No. of | | Initial | Foam Removed | Relative Contrib | ution to Detoxif | ion to Detoxification by (%) | | |
|---------|---------------------|-----------|-----------------------|---------------------------|------------------|------------------|------------------------------|--|--|
| MILL | Samples Analyzed | · | Toxicity MST (min) | To Detoxification % (v/v) | Foam Separation | Volatilization | Unknown Mechanisms | | |
| F | 10 | Range | 70 - 450 | 3.1 - 9.1 | 60 - 95 | 1 - 13 | 3 - 39 | | |
| | | Mean ± SD | 307 ± 135 | 6.5 ± 9.3 | 71 ± 12 | 5 ± 4 | 24 ± 12 | | |
| G | 5 | Range | 30 - 120 | 7.9 - 20.8 | 70 - 90 | 0 - 14 | 10 - 29 | | |
| | | Mean ± SD | 58 ± 36 | 15.7 ± 5.8 | 79 ± 9 | 4.6 ± 5 | 17.2 ± 11 | | |
| I, | 5 | Range | 60 - 105 | 10.0 - 25.1 | 85 - 95 | 5 – 9 | 0 - 8 | | |
| | | Mean ± SD | 78 ± 17 | 18.2 ± 5.8 | 89 ± 4 | 7 ± 2 | 4 ± 3 | | |
| OVERALL | 20 | Range | 30 - 450 | 3.1 - 25.1 | 60 - 95 | 0 - 14 | 0 - 39 | | |
| | | Mean ± SD | 188 ± 155 | 12.2 ± 7.1 | 77.5 ± 13.0 | 5.4 ± 4.0 | 17 ± 14.0 | | |

Gas stripping of toxic materials (volatilization) which removed only 5.4% of the toxicity is of minor importance. It has been reported (105) however, that in a fresh effluent volatile compounds are major toxicity contributors. Conceivably, these volatile compounds could have escaped during shipment and the 1-day of average storage time before processing.

Approximately 17% of the toxicity, removed by foam fractionation, could not be accounted for in reconstituted treated effluents. sumably some form of chemical change is primarily responsible. the toxic constituents constitute a relatively minute fraction on a weight basis, it is difficult to rule out virtually any possibilities. For example, molecular rearrangement of the resin acid, abietic acid, to the more thermodynamically stable dehydroabietic acid, would result in a diminution of toxicity (18, 20, 106). Oxidation of unsaturated fatty acid to the corresponding oxy or peroxy forms, presumably also would achieve the same result. However, both toxic moieties, i.e. resin and unsaturated fatty acids, presumably would collect in the foam. recently, it has been shown that the toxicity of chlorolignin, the major offender in acid bleach effluent decreased quite substantially when the solution was made alkaline (94). Combination of all these factors is believed to be responsible for the 17% loss of toxicity. Although bioassay values are less accurate than most chemical assays, a cumulative error in bioassay procedures would be expected to show an increase in toxicity for some reconstituted samples. This did not occur within the limits of variability in the toxicity test.

In conclusion, overall results suggest that foam fractionation, i.e. concentration of toxicity in the foam, is the major detoxification mechanism and accounts for about 77% of toxicity removal.

3. Cumulation of Resin Acids in Foam

Eight samples were analyzed for resin acids content before and after foam separation (Table 16). The average resin acids content of the raw effluents, having initial MSTs of 100 - 600 min, was 3.4 mg/1. There appeared to be no direct relation between the resin acids concentration and the toxicity of the effluent. This, probably is due to the presence of many other toxicants which also contribute to the toxicity of the effluent. After a sample was detoxified by foam separation, a 60% reduction in resin acids was achieved; the average resin acids concentration was reduced to 1.4 mg/l. The resin acids contents of the foams were not analyzed. There is no doubt however, that the resin were transferred together with many other surface active materials into the foam fraction. A recent analysis of a foam-scum sample obtained from a kraft mill aerated lagoon indicates that resin acids had accumulated to concentrations of up to 9000 mg/1 (45). This foam sample also contained up to 6000 mg/l of organic substances including alcohols, aldehydes, and ketone derivatives. The lethal concentration (LC50) of these organics is between 2 - 13 mg/1.

TABLE 16
EFFECT OF FOAM SEPARATION ON RESIN ACIDS REMOVAL

| | TOXICITY | (MST) | | RESIN ACIDS | | | |
|-----------|----------------|------------------------------|-----------------|-------------------------------|--------------|--|--|
| EFFLUENT | Influent (min) | Treated Effluent (min) | Influent (mg/1) | Treated Effluent (mg/l) | % Removed | | |
| | 255 240 | NT NT | 2.8 | 1.0 | 64.3 | | |
| Mill F | 160 | NT | 3.2 | 1.1 1.2 | 57.7 62.5 | | |
| | 120 100 | NT NT | 5.1 3.3 | 1.9 1.7 | 62.7 48.5 | | |
| | 600 | NT | 3.4 | 1.4 | 58.8 | | |
| Mill A | 600 | NT | 3.6 | 1.2 | 66.7 | | |
| | 500 | NT | 3.0 | 1.0 | 66.7 | | |
| No of | | | | | | | |
| Samples | 8 | 8 | 8 | 8 | 8 | | |
| Mean ± SD | 322±211 | - | 3.4±0.8 | 1.3±0.3 | 61±6 | | |

F. COMBINED DETOXIFICATION AND FIBRE REMOVAL BY FOAM SEPARATION PROCESS

There is a similarity between the mechanisms of fractionation of solubilized components and flotation of suspended particles by foaming. In both processes, air bubbles are allowed to rise through the solution and produce a foam-froth on the liquid surface. The fractionation process involves adsorption of surface active toxic substances at the gas-liquid interface. The flotation process attracts the hydrophobic suspended particles to the bubbles and separates them from the solution by floating them to the surface (108). Foam fractionation process if properly operated could be made compatible with concurrent suspended solids removal.

At present, the pulp and paper industry is required to reduce the suspended solids level in their waste discharges to < 50 mg/l prior to discharge. Installation of a clarifier is necessary. If foam separation were adopted for commercial application, combined toxicity — suspended solids removal in one process would be of interest. Since the suspended solids in kraft mill effluent consist of large amounts of fibrous materials and because of economics any foam separation would most likely be operated using a dispersed air foam generation system, this study was undertaken with particular emphasis on fibre removal by a dispersed air foam separation system. For comparison, a dissolved air system was also operated.

1. Dispersed Air System

Known amounts of fibre were added to an effluent which had an original suspended solids level of 116 mg/l. This gave a series of effluent samples with suspended solids ranging from 116 to 738 mg/l. These effluent samples were foam separated for removal of suspended solids under the same conditions which would detoxify the effluent.

Removal of fibres after 1-hr of treatment time ranged from 19% to 62% (Table 17). In general when the suspended solids level was below 200 mg/1, a maximum of 39% removal was achieved. Residual SS levels still ranged from 94 - 108 mg/l and could not meet the effluent discharge guidelines. At higher suspended solids levels (260 - 739 mg/l), the degree of removal improved to about 60%; however, the suspended solids remaining in the effluent increased up to 380 mg/l.

In Table 18, the results of similar experiments undertaken in the field using various types of air dispersion media and on fresh primary clarified effluents are shown. The bubble diameter produced ranged from 0.75 - 3 mm diameter. However foam separation yielded similar low percentages of SS removal. Suspended solids of the influent ranged from 87 to 121 mg/1; they were reduced to 51 - 83 mg/1 and averaged 65 mg/1 after 1-hr treatment; i.e. a reduction of 21 - 55% (38% average reduction). Although the removal of suspended solids was substantial, the final concentration still exceeded the discharged guideline.

TABLE 17

REMOVAL OF FIBROUS SUSPENDED SOLIDS AT

DIFFERENT LOADINGS BY A DISPERSED AIR SYSTEM

| Experiment | Suspend | ed Solids (| mg/1) |
|------------|---------------------|--------------------|--------------|
| Experiment | Before Treatment | After Treatment | % Removal |
| 1 | 116 | 94 | 19 |
| 2 | 145 | 108 | 26 |
| 3 | 162 | 105 | 35 |
| 4 | 174 | 106 | 39 |
| 5 | 260 | 166 | 36 |
| 6 | 486 | 183 | 62 |
| 7 | 498 | 210 | 58 |
| 8 | 608 | 380 | 46 |
| 9 | 738 | 306 | 59 |

Operating Conditions: Batch operation

Volume: 4 litre

pH: 8

Air Diffuser: 45μ pore size sintered glass

Retention Time: 1 hr G/L: 7

Toxicity (MST): Before Treatment = 300 min

After Treatment = Non-toxic

TABLE 18

REMOVAL OF SUSPENDED SOLIDS BY A DISPERSED AIR,
FOAM SEPARATION SYSTEM AT MILL SITE

| Air Dispersion System | Estimated Bubble Size | l ('Onditione'' | | Suspended Solids (mg/l) | | |
|---|----------------------------|-----------------|--------------|-------------------------|----------------|-----------------------|
| | (mm) | Time (hr) | G/L | Initial | Final | % Removal |
| Four 5 inch diameter plastic discs (25µ pore size) | 3 | 1. | 7 1.4 | 115 87 | 75 56 | 35 36 |
| Four 1 ft length 3 inch diameter ceramic tubes (<25µ porosity) | 1 | 0.5 1 1 | 6 6 12 | 87 115 .115 | 56 57 51 | 35 50 55 |
| Seven 1 ft long 1/2 inch diameter helical aerator | 0.75 | 1 1.5 | 1.4 2.1 | 121 96 | 83 76 | 31 21 |
| | Range Mean Std. Dev. | | | | | 21-55 37.7 11.5 |

* Batch Operation Volume: 180 litre

pH: 8.0

Effluent: Bleached kraft wholemill effluent
Before treatment: MST = 0.8 - 2 hr

After treatment : Nontoxic.

The capacity of the dispersed air foam separation process for removing fibre depends on the foaming characteristics of the influent; i.e., surfactant concentration. In an experiment with 500 mg/l fibre in suspension, a reasonable relationship between initial foaming tendency and percent fibre removal under a given set of operating conditions was observed (Figure 36). As the foaming tendency (\(\Sigma\)t) increased to 5.0 min which is typical for bleached kraft wholemill effluents, the removal of suspended solids improved to 43%. But, as in the previous experiments, residual fibre levels in the treated effluent remained high (> 250 mg/l) in the treated effluent. Generally, fibrous suspended matter can be floated by a dispersed air system, as long as some foaming tendency remains in the substrate. When all foaming tendency is removed, further removal of fibre becomes impossible.

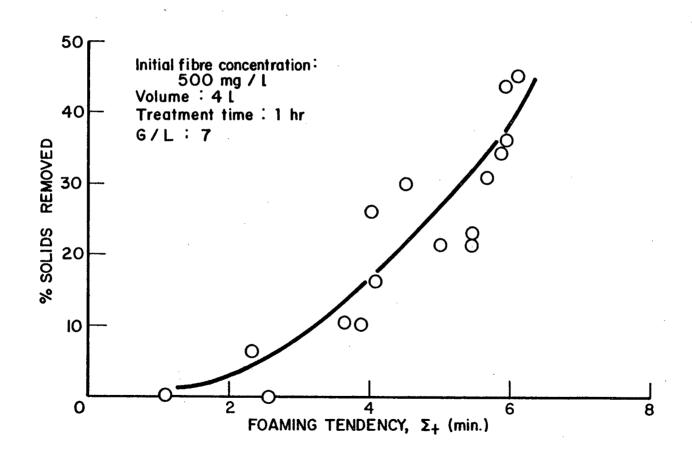
In conclusion, foam separation by a dispersed air system can remove a substantial amount of fibres during the detoxification process. However, the extent of fibre removal depends on the foaming tendency and the suspended solids level of the waste. Sufficient reduction of suspended solids to meet effluent discharge guidelines was not achieved in any instance.

2. Dissolved Air Flotation System

It has been shown in Section B-5 that dissolved air flotation can also be used to create foam for the purpose of separating toxicity from kraft mill effluents. Therefore, dissolved air flotation systems may be

Figure 36

EFFECT OF FOAMING TENDENCY ON SUSPENDED SOLIDS REMOVAL BY A DISPERSED AIR FOAM SEPARATION SYSTEM



more suitable for combining primary clarification with detoxification than dispersed air foam separation systems.

A series of samples with suspended solids ranging from 70 - 450mg/1 were subjected to dissolved air flotation. The results of suspended solids removal are presented in Table 19. During the first pressurization and flotation cycle, suspended solids could be reduced to less than 56 mg/l regardless of initial SS level; the reductions ranged from 53 - 88%. Further treatment of the clarified effluent by a second flotation cycle produced more bubbles and interfacial area. However, only marginal reduction in residual SS levels was achieved; i.e. a second cycle is useful only for reducing toxicity. Overall, removal of suspended solids by dissolved air flotation was far more effective and reliable than by the dispersed air foam separation. The dissolved air flotation applied in this experiment also detoxified the effluent during the pressurization and flotation process. In Figure 37, the reduction of toxicity is plotted against gas-liquid ratio, pressurization cycles and interfacial area applied. In the first cycle, toxicity was reduced from an MST of 150 - 200 min to 1000 - 1200 min. In the second and third cycle, corresponding to 10 and 15 $m^2/1$ of total interfacial area, effluents were completely detoxified. The number of pressurization cycles needed for detoxification is related to the influent toxicity and gasliquid interface requirement (Appendix VIII). Preliminary results clearly indicate that this process is capable of reducing suspended solids to low levels and of removing toxicity in the same operation.

TABLE 19 REMOVAL OF FIBROUS SUSPENDED SOLIDS FROM BLEACHED KRAFT WHOLEMILL EFFLUENT BY DISSOLVED AIR FLOTATION

| | Suspended Solids in Effluent After | | | | | |
|------------------------------|------------------------------------|--------------|--------|--------------|--|--|
| Suspended Solids in Effluent | lst | Cycle | 2nd | Cycle | | |
| (mg/1) | (mg/l) | % Removed | (mg/1) | % Removed | | |
| 70 | 33 | 53 | 27 | 61 | | |
| 106 | 33 | 69 | 28 | 74 | | |
| 141 | 56 | 60 | 43 | 70 | | |
| 215 | 50 | 77 | 50 | 77 | | |
| 334 | 54 | 84 | 57 | 83 | | |
| 450 | 55 | 88 | 55 | 88 | | |

Operating Conditions:

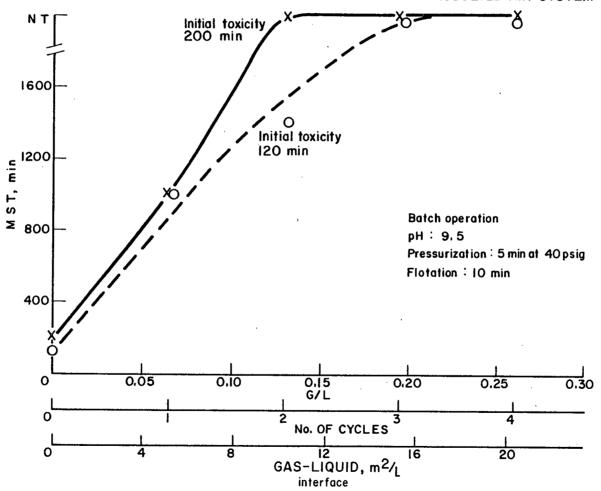
Pressure: 40 psig

5 min pressurization 10 min flotation

Toxicity: Initial MST: 350 min

1st Cycle: 1440 min 2nd Cycle: Non-Toxic

Figure 37
DETOXIFICATION OF BLEACHED KRAFT MILL EFFLUENT BY A DISSOLVED AIR SYSTEM



However, the energy requirements for producing interfacial area by a dissolved air system probably would be too high compared to dispersed air system.

G. BENEFICIAL SIDE EFFECTS OF FOAM SEPARATION PROCESS

Other than detoxification, foam separation could effect removal of a large number of other pollutants. In the course of this study, numerous samples were taken from batch and continuous runs and analyzed for several pollution parameters. Some results have been presented in earlier sections.

1. Resin Acid Removal

As documented earlier in Table 16, the resin acid content of the treated effluent ranged from 2.6 - 5.1 mg/l and averaged 3.4 mg/l. After foam separation, resin acid content was reduced to 1 - 1.9 mg/l and averaged 1.3 mg/l. The average resin acid removal was 62%. Since the lethal concentration of resin acid is in the range of 1 - 2 mg/l, the results of this analysis partly explain the mechanism of detoxification.

2. Suspended Solids Removal

The effect of foam separation on suspended solids removal has been covered in Section F. A dissolved air system is more effective than a dispersed air system. Removal of suspended solids by a dispersed air system ranged from 19 - 62% (Table 17 and 18) and depended on foaming

tendency and initial suspended solids concentration. However, with a more sophisticated dissolved air system, suspended solids were reduced to 52-88% (Table 19) and met the effluent discharge guidelines.

3. BOD₅ and TOC Removal

Among eight samples analyzed (Table 20) foam separation reduced the BOD_5 from an average of 170 mg/l (range = 70 - 278 mg/l) to 150 mg/l, a 12% reduction. The reduction of total organic carbon averaged 11% (from 317 to 285 mg/l). The BOD_5 (or TOC) removed during foam separation process appears to be insignificant and agrees with published data (37, 42).

4. Color Removal

The results of color removal trials are shown in Table 21. The color was reduced from an initial value of 3540 - 5510 to 2990 - 4960 units and average 12.3% removal. The reduction of color was probably caused by partial removal of turbidity as a result of suspended solids removal. The reductions are too small to have any practical significance.

5. Foaming Tendency Removal

The foaming tendency of industrial effluents, particularly pulp mill effluents is aesthetically, an undesirable characteristic. During the process of detoxification, the foaming tendency $(\Sigma_{_{\! +}})$ was reduced

TABLE 20 $$\operatorname{BOD}_5$$ AND TOC REDUCTION BY FOAM SEPARATION

| Before | Before Treatment | | eatment | % Removal | | |
|-----------------------|------------------|-----------------------|---------|------------------|------|--|
| BOD ₅ ,ppm | TOC,ppm | BOD ₅ ,ppm | TOC,ppm | BOD ₅ | TOC | |
| 205 | 449 | 184 | 395 | 10.2 | 12.0 | |
| 130 | 317 | 110 | 288 | 15.3 | 9.1 | |
| 220 | 573 | 195 | 535 | 16.8 | 6.6 | |
| 125 | 195 | 115 | 164 | 8.0 | 15.9 | |
| 160 | 340 | 150 | 325 | 6.2 | 4.4 | |
| 170 | 185 | 160 | 167 | 5.8 | 9.7 | |
| 278 | 293 | 230 | 244 | 17.2 | 16.7 | |
| 70 | 190 | 58 | 165 | 17.1 | 13.1 | |
| | | | | | | |

Process Conditions:

4 1 batch system

500 ml/min aeration

pH = 9.5

Treatment fine: 60 min.

TABLE 21

COLOUR REMOVAL BY CONTINUOUS FOAM SEPARATION SYSTEM

| Colour of * Feed Stream* (APHA Units) | G/L | Colour of Effluent Stream (APHA Units) | % Removal |
|---------------------------------------|------|--|--------------|
| 3540 | 0.83 | 3230 | 8.7 |
| | 0.83 | 2990 | 15.5 |
| | 0.83 | 3190 | 9.8 |
| | 0.83 | 3310 | 6.5 |
| | 0.83 | 3230 | 8.7 |
| 5510 | 2.5 | 4170 | 24.3 |
| | 2.5 | 4330 | 21.4 |
| : | 2.5 | 4720 | 14.3 |
| 5310 | 2.5 | 4960 | 6.6 |
| | 2.5 | 4720 | 11.1 |
| | 2.5 | 4890 | . 7.9 |
| | | | Av:12.3 |

* Mill A whole mill effluent
Operation: 4 l continuous flow system
Retention time: 30 min.

substantially. Figure 38 shows an example of the effect of foam separation on foaming tendency during laboratory batch treatment for toxicity removal.

A sample with an initial MST value of 240 min could be detoxified within 20 min of treatment. During the same period, the foaming tendency of the effluent decreased from an initial value of $\Sigma_{\rm t}=6.0$ min to 3 min; and after 30 min of treatment it was reduced to $\Sigma_{\rm t}=1.0$ min. this same pattern of foaming tendency reducion was observed with all samples examined. As Appendices IX a-b and Table 22 indicate, the foaming tendency of raw mill effluents ranged from $\Sigma_{\rm t}=0.9$ to $\Sigma_{\rm t}=6.0$ min. After toxicity was removed by foam separation, the foaming tendency invariably was less than 1.0 min. At this level, foams were unstable and collapsed rapidly.

During continuous operation, the foaming tendency of the treated effluents discharged was slightly higher than those treated by batch system. Figure 39 shows that at steady state operation, the foaming tendency was reduced from 2.5-6 min to 0.8-1 min.

H. TREATMENT OF FOAM

1. Foam Characteristics

The quality of foam discharged from a foaming system is determined by a number of operating parameters such as air flow, bubble size, and foam height. In Appendices X-a and X-b the daily foam flow rates of

Figure 38
REDUCTION OF FOAMING TENDENCY DURING TOXICITY REMOVAL

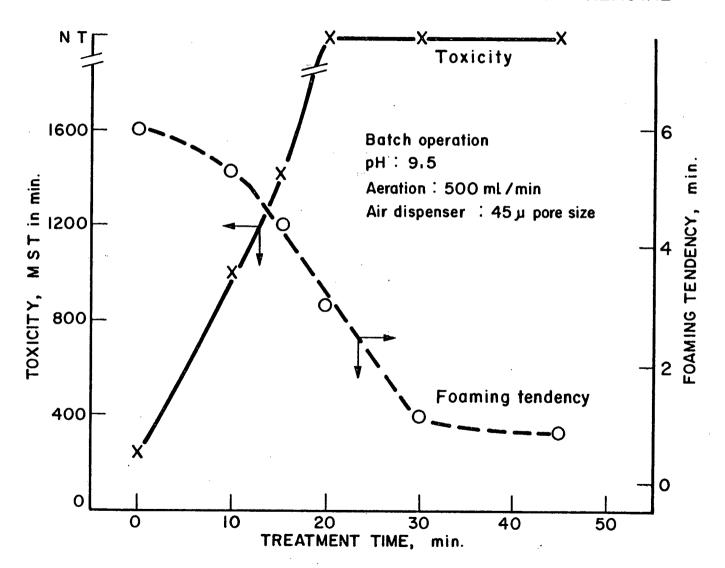


TABLE 22

EFFECT OF FOAM SEPARATION ON

FOAMING TENDENCY REDUCTION

| Foam Separation System | Source of Samples | No. of Samples | TOXICITY (MST:hr) | | FOAMING TENDENCY, min | |
|---|-------------------------|-------------------|----------------------------------|---------------------|--------------------------------|-------------------------------|
| | | | Influent (mean±S.D.) | Treated Effluent | Influent (mean±S.D.) | Treated Effluent (mean) |
| BATCH OPERATION Vol: 4 litre Gas Disperser: 45 μ sintered glass pH: 7.0 Aeration: 500 ml/min Treatment time: 0.25-2 hr | Mill B | . 11 | 8 ± 4.8 (Range: 2.5- 18) | Nontoxic | 3 ± 1.6 (Range: 0.5-3.0) | 1.0 |
| BATCH OPERATION Vol: 4 litre Gas Disperser: 45 μ sintered glass pH: 9.5 Treatment time: 0.25-2 hr | Mill F | 10 | 4.8 ± 2.4 (Range:3.2- 9.0) | Nontoxic | 4.6 ± 0.8 (Range: 3.2-5.8) | 1.0 |

Figure 39 REDUCTION BY CONTINUOUS TENDENCY **FOAMING** FOAM SEPARATION 6.0 Z + (min) 5.0-Mill A Wholemill Effluent pH = 9.54.0 FNDENCY 3.0 ΔΔΔΔ FOAMING 2.0 G/L = 2.51,0-00 = 0.833 24 20

HOURS AFTER INITIATION OF CONTINUOUS OPERATION

two, continuous foam separation systems installed with plastic and ceramic diffusers were measured. The volume of foam produced by plastic diffusers when removed at 30 cm foam height was equivalent to an average of 6.3% of the influent flow. With a fine ceramic diffuser producing 1 mm bubbles, even though the operating G/L was reduced to 4.5 (50% of the plastic diffuser system), the foam volume was 5.6% of the influent flow volume. The collapsed foams were also characterized for BOD_5 and toxicity. As Table 23 indicates, BOD_5 contributing materials are enriched by a factor of 1.2 to 1.5. The low enrichment ratio suggest that the majority of the BOD_5 materials are not surface active. The increase in BOD_5 was due, at least in part to the concentration of suspended solids.

In comparison, toxicity increased by a factor of 4 to 8 (in terms of MST decrease) from initial 4.5 to 7.5 hr in the influent to 0.5 to 2 hr in the foam. These results directly confirm that the toxic, surface active compounds are not degraded. Thus further treatment of the foam prior to discharge would be required.

2. Reduction of Foam Volumes

Using the system, described in this thesis, detoxification of bleached kraft mill effluents transforms 5 to 6% of the influent flow into a highly toxic waste stream. Treatment of 25 MGD of effluent typical of a 750 tpd pulp mill would produce 125,000 - 150,000 gal of collapsed foam for ultimate disposal. Reduction of the foam volume to 1 - 2% of the influent (25,000 - 50,000 gal/day) is considered

TABLE 23

AVERAGE CHARACTERISTICS OF INFLUENT AND COLLAPSED FOAM

| Foam Separation System | | Number | | | Waste Characteristics | | | |
|--|-------------------------|---------------------------|----------------|-----------|-------------------------|-------------------------|-------------------|---------------|
| Air Dispersers | Operating Conditions | of Samples Obtained | Type of Sample | | Suspended Solids (mg/1) | BOD ₅ (mg/1) | Toxicity (MST:hr) | conversion to |
| | w <u>-</u> | | | Range | 17 - 80 | 215-265 | 2.5-5.0 | - |
| Four 25µ 1 ft long, | Retention time = | _ | Influent | Mean±S.D. | 42 ± 25 | 230± 22 | 4.5±1.2 | _ |
| 3 in diameter ceramic tubes 30 ± 6 min $G/L=4.4\pm1.0$ | 5 | * Collapsed | Range | - | 214-290 | 0.3-3.2 | 2.4-13.2 | |
| | 0/11 4141110 | | Foam | Mean±S.D. | | 253± 38 | 2.1±1.0 | 5.6±4.8 |
| Four 25µ | Retention | | | | 38-99 | 122-293 | 0.5-24 | |
| 5 in diameter plastic discs | 5 in diameter time = | 10 | Influent | Mean±S.D. | 57±17 | 220±61 | 7.5± 9 | - |
| G/L=12.2 4.0 | l lco: | *Collapsed | Range | - | 227-450 | 0.2-1.7 | 1.5-13.2 | |
| | | | Foam | Mean±S.D. | _ | 346±88 | 0.6±0.5 | 6.3±4.2 |

^{*} Foam obtained under conditions which detoxified all samples in a 180 1 column at mill site.

practical and acceptable by most mills for subsequent treatment.

Because of this several factors such as the effects of foam height, and of foam recycling on the total foam volume reduction were investigated.

a. Effect of Foam Height

The foam height above the liquid at which foam is removed determines the degree of internal reflux in the foam layer and controls the "dryness" and the volume of foam to be removed. A series of experiments with a 7 litre foaming column was run, in which the foam height (distance from the liquid-foam interface to the foam discharge port) was varied from 30 to 60, 80, 120 and 150 cm. Additional experiments were also conducted by increasing the foam height to a level (250 cm) where the rate of foam destruction by coalescence and drainage is equal to the rate of foam production i.e. no foam was removed. The foam removed during treatment was collapsed and the liquid volume measured. Then the percent of the total treated liquid volume was calculated. Table 24 shows that foam separation detoxified all samples, regardless of foam height. However, the volume of foam removed during this experiment decreased from an average 5.2% at the lowest foam height (30 cm) to 2.1% at the highest foam height (150 cm).

Table 24 also shows that at a foam height of 250 cm, the condition of total reflux was achieved i.e. no foam was discharged. Even at this extreme condition, complete detoxification was achieved. The total reflux column is theoretically an infinitely long reflux column. A foam height of 250 cm was sufficient to achieve this goal. Foams

TABLE 24

EFFECT OF FOAM HEIGHT ON FOAM VOLUME

| Foam Height | *Toxicity After Treatment MST (min) | | Collapsed F | | Influent Conversion to Foam % (v/v) | | |
|----------------------|--|---------|-------------|---------|-------------------------------------|---------|---------|
| (Cin) | Run # 1 | Run # 2 | Run # 1 | Run # 2 | Run # 1 | Run # 2 | Average |
| 30 | NT | NT | 200 | 220 | 5.0 | 5.5 | 5.25 |
| 60 | NT | NT | 175 | 180 | 4.3 | 4.5 | 4.40 |
| 80 | NT | NT | 140 | 160 | 3.5 | 4.0 | 3.75 |
| 120 | NT | NT | 100 | 110 | 2.5 | 2.8 | 2.65 |
| 150 | NT . | NT | 75 | 95 | 1.8 | 2.4 | 2.10 |
| 250(Total Reflux) | NT | NT | 0 | 0 | . 0 | 0 | 0 |

NT = Non-toxic (100% Survival of fish in 100% effluent for 24 hr)

*Influent Toxicity: MST = 1.5 hr

Operating Conditions: Volume: 4 litres

Aeration rate: 500 ml/min

Air disperser: 45µ pore size sintered glass

G/L: 4 pH: 8

Treatment time: 30 min

were turned completely into solid gummy materials and detoxification was equivalent to systems which discharged foam. In the batch system, the concentration of surfactant in the foam never reached a constant value. The concentration of toxicity in the liquid pool decreased with time until eventually it was so low that no foam could reach the top of the column. Practically all surfactants were concentrated in the scum.

In conclusion, then by allowing the liquid content of the foam to drain into the foam column, the net volume of foam to be removed from the system could be minimized. It would appear, that by properly controlling the foam height over the liquid, the dryness and thereby the volume of foam requiring disposal could be significantly reduced.

b. Effect of Foam Recycling

Recycling of collapsed foam also concentrates the toxicants in the foam phase and thereby reduces the volume requiring disposal. The effect of recycling foam and operating the continuous foam separation system in an "enriching mode" (Figure 7) was studied on effluents at four levels of toxicity. Foam was recycled at ratios of zero to 1.

Table 25 shows that for effluents of all levels of toxicity, a foam recycling ratio as high as 0.8 can be operated without sacrificing detoxification efficiency, i.e. all effluents were detoxified. At this condition, the net foam discharged ranged from 0.5 - 1.2% of the influent compared to 2.5-6% discharged when foam was not recycled.

TABLE 25 EFFECT OF FOAM RECYCLING ON DETOXIFICATION IN A CONTINUOUS SYSTEM

| Foam Recycling | MST.of Effluent | at Steady State | Net Foam |
|-------------------|-----------------|-----------------|----------------|
| Ratio | Untreated, min | Treated,min | discharged (%) |
| 0 | 600 | NT | 2.5 |
| | 240 | NT | 3.75 |
| | 180 | NT | 6.00 |
| 0.4 | 840 | NT | 0.45 |
| 0.6 | 840 | NT | 0.30 |
| | 240 | NT | 1.50 |
| 0.8. | 600 | NT | 0.5 |
| | 240 | NT | 0.75 |
| | 180 | NT | 1.20 |
| *1.0 | 840 | NT | 0 |
| | 600 | NT | 0 |
| | 240 | 960 | 0 |
| | 180 | 1620 | 0 |

^{*} Total reflux = no foam was discharged

Operation:

Capacity = 31

Aeration = 750 ml/min

G/L = 7.5

Air dispenser = 45 μ pore size Retention time = 30 min Foam height = 60 cm

Operation with a recycle ratio of one approaches a total reflux system. Detoxification of effluents of relatively low toxicity, e.g. 600 - 800 min MST, was not affected by the complete return of the collapsed foam.

All toxicants accumulated as gummy scums floating on the top of the foam during the process. Presumably, the 100% recycling system remained non-toxic only because the duration of the test was short. For longer operation, it is probable that dispersion of toxic scum into the effluent would occur.

With the more toxic effluents (MST:180 - 240 min) up to 80% of the collapsed foam could be recycled without any toxicity break-through.

The net volume of collapsed foam was less than 1.2%. When 100% of foam was recycled, treated effluents were marginally toxic.

These experiments were done on a continuous scale under controlled laboratory conditions. The reduction of foam volume by operating large-scale systems in an enriching mode may be less effective. Nevertheless, by combining the two techniques, i.e. operating foam separation systems at a maximum foam height and recycling part of the collapsed foam, it appears technically feasible to reduce the net volume of foam to 1-2% of the influent.

3. Breakage of Foam

As the quantity of foam dealt with in the laboratory was small, foam breakage was easily achieved by vacuum suction or by passing the

foam through a packed bed filled with glass or steel wool. Mechanical breakage by a rapidly spinning magnetic bar or agitator was also effective.

The collapsed foam volume produced in the field unit amounted to $0.5 - 1.0 \text{ ft}^3/\text{min/column}$. Breakage of foam was most effectively done by means of periodic addition of a chemical (silicone) defoamer coupled with continuous spraying with a strong jet of water. However, both methods seriously changed the properties of the collapsed foam, and could not be applied if foam recycling were practiced for reduction of foam volume. In view of the tremendous volume of foam produced in a commercial size foam separation plant and the possibility of operating a foam recycling system, an efficient and commercially acceptable means of foam breaking is desirable. Of those methods evaluated (109) a mechanical turbine was assessed as most useful.

Foam breaking by a turbine system was examined briefly in an onsite continuous flow experiment. Foam was produced at a rate of 6-42 ft³/min, containing 2-3% of liquid. Experiments were conducted with a variable speed 1/3 hp motor fitted with 15 to 38 cm diameter vaned disc turbines.

a. Effect of Rotation Speed and Tip Speed of Turbine on Foam Collapsing Efficiency

In theory, foam collapsing efficiency should increase with the rotational speed (109). There is a critical rotational speed at which

100% of the foam will be collapsed. Appendix XI presents this critical speed requirement for four different turbine sizes at 5 foam loads. results (Figure 40) show that the critical rotation speed required to collapse 100% of the foam ranged from 700 to 1700 rpm. It decreased with increasing turbine diameter, but increased as foam load increased. The corresponding mean critical tip speed ranged from 1430 cm/sec to 2200 cm/sec as foam flow varied from 6.2 to 42 ft³/min. However, at constant foam flow, this critical tip speed (Table 26) did not vary significantly as a function of rpm and disc diameter (for 23-38 cm turbine). The maximum tip speed requirement was approximately 2200 cm/sec. It would appear that tip speed, which is determined by rotation speed and turbine diameter is the major controlling parameter for foam break-In Figure 40, it has been shown that plots of critical rpm as a function of disc diameter are straight lines with the same slope (30 rpm/cm) for various foam loads. This family of virtually parallel curves allows tentative extrapolation to values not measured in the pilot plant. An empirical equation relating rpm, foam flow and disc diameter was developed based on this observed relationship:

N = 390 F - 30 D + 1850 or

 $F = 2.6 \times 10^{-3} N + 7.7 \times 10^{-2} D - 4.7$

where $F = foam breaking capacity in <math>m^3/min$

N = rotation speed in rpm

D = diameter of turbine in cm.

Although this equation was developed with turbines ranging from 15 to 38 cm in diameter, operating between 700 - 1700 rpm, it can with

Figure 40
CRITICAL R. P. M. REQUIREMENT FOR VARIOUS TURBINE SIZES

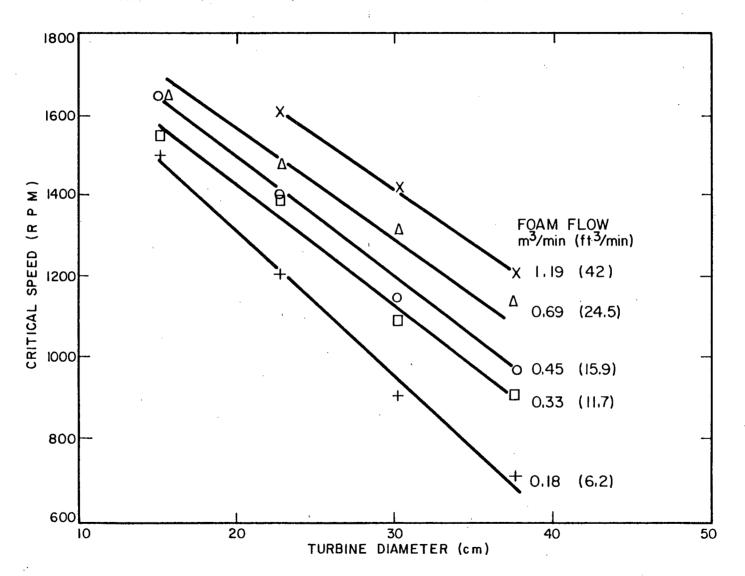


TABLE 26
CRITICAL TIP SPEED*FOR FOAM COLLAPSING

| Foam Flow m ³ /min | | Critical Tip S | peed (cm/sec) | of Turbine | |
|-------------------------------|-----------------------|------------------------|------------------------|------------|-------------|
| (ft ³ /min) | 23 cm (9")diameter | 31 cm (12")diameter | 38 cm (15")diameter | Range | Mean ± S.D. |
| 0.18 (6.2) | 1436 | 1436 | 1396 | 1396-1436 | 1432 ± 23 |
| 0.33 (11.7) | 1675 | 1914 | 1795 | 1675-1914 | 1795 ± 120 |
| 0.45 (15.9) | 1795 | 1818 | 1914 | 1795-1914 | 1842 ± 63 |
| 0.69 (24.5) | 1854 | 2233 | 2393 | 1854-2393 | 2160 ± 277 |
| 1.2 (42.0) | 1914 | 2300 | 2500 | 1914-2393 | 2180 ± 244 |

 $[\]ensuremath{^{\star}}$ Speed at which all foams entering the system were collapsed.

caution be used to estimate the foam breaking capacity of turbines of different diameters and rotational speeds provided these are not too different from the ranges tested.

b. Power Consumption

During the study of foam breaking efficiency with various foam loads, the power consumed by a 31 cm and a 38 cm turbine operating at 100% foam breaking efficiency (all foam collapsed) was measured. The results are presented in Appendix XII. A typical power curve for a 38 cm turbine is plotted in Figure 41. The power consumed was found to depend on rpm, foam flow rate and turbine diameter. For scale up purposes, the power data were fitted to different equations. Linear regression analysis produced the following dimensional relationship:

$$\frac{P}{F}$$
 = 51.7 x 10 ⁻¹⁷ x N³D⁵ + 51.2

where P = Power in watts

F = Foam flow in m³/min

N = rpm

D = Turbine diameter in cm

as the best fit, with a correlation coefficient of 0.81 (Figure 42).

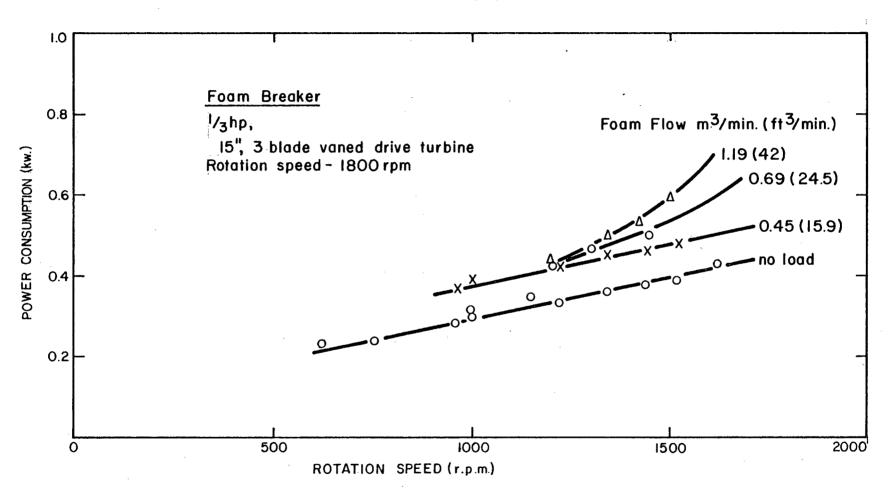
This equation may serve as a basis for predicting the power requirements for a commercial size plant.

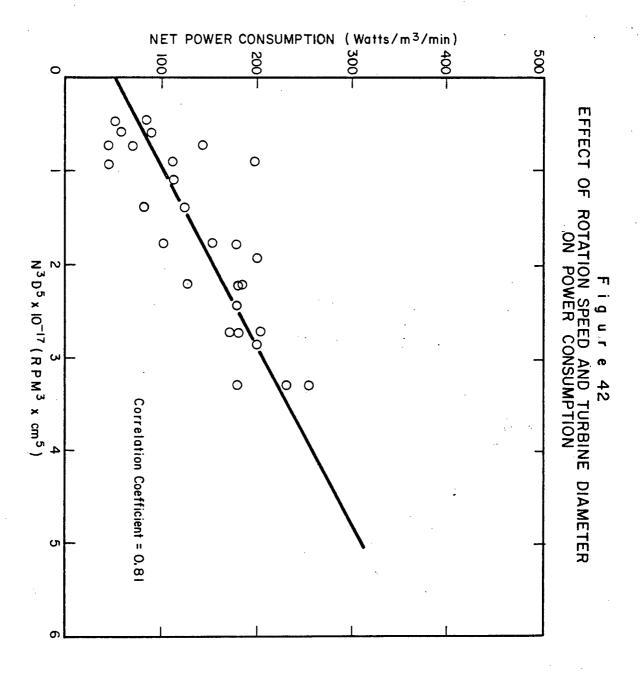
4. Foam Disposal

Several methods were examine for ultimate disposal of collapsed foam. Selection of suitable method depends greatly on the volume and

Figure 41

POWER CONSUMPTION BY A 38cm (15") TURBINE FOAM BREAKER





characteristics of the foam.

a. Incineration

The foam could be incinerated provided its volume was low and the solid content was high enough to justify the cost. The economic feasibility of incineration would depend on the volumes to be handled, on the characteristics of the collapsed foam, the availability of sufficient evaporation and incineration capacity, and other factors. This approach has not been evaluated in detail.

b. Chemical Treatment

Although chemical flocculants were reported to be effective in detoxifying kraft mill effluent at reasonably low dosage (Appendix XIII) Table 27 shows that application of up to 10 g/l of lime, 1 g/l of alum or 1 g/l of ferric sulphate was ineffective in detoxifying the collapsed foam (Table 26). The main reason could be attributed to insufficient dosage due to the high initial toxicity of the collapsed foam.

c. Biological Treatment

In the field column installation, approximately 5% of the influent was converted to foam having an MST value of 0.7-1.8 hr. The foams were collected and subjected to biodegradation. Table 28 summarizes the results of detoxification of collapsed foam by an aerated lagoon and a rotating disc system (Figure 9). The daily data are presented in Appendix XIV a-b.

The aerated lagoon treatment detoxified satisfactorily when operated at 3-day but not a 1-day's retention time. The 1-day reten-

TABLE 27

CHEMICAL TREATMENT OF COLLAPSED FOAM

| | | Tourising | | | |
|--------------------|--------|-----------------------|--------------|--|--|
| Chem | ical | Toxicity of Collapsed | | | |
| | | Foam, MST (hr) | | | |
| Type | Dosage | Before | After | | |
| | (g/1) | Treatment | Treatment | | |
| | 1 | 0.25 | 0.60 | | |
| Lime | 2 | 0.40 | 0.50 | | |
| (pH:12) | 7 | 0.40 | 0.70 | | |
| | 10 | 0.40 | 0.80 | | |
| | 0.1 | 0.40 | 0.60 | | |
| Alum | 0.2 | 0.40 | 0.75 | | |
| (pH:6.5) | 0.4 | 0.25 0.25 | 1.30 2.30 | | |
| | 0.1 | 0.40 | 0.75 | | |
| Ferric Chloride | 0.2 | 0.40 | 0.90 | | |
| (pH:6.5) | 0.4 | 0.25 | 1.00 | | |
| | 1.0 | 1.00 | 4.00 | | |

TABLE 28

TREATMENT OF COLLAPSED FOAM BY AN AERATED LAGOON AND BIODISC SYSTEM

| - | | В | OD ₅ (mg/1) | | Tox | icity, MST (| hr) |
|-----------------------------------|-------------------|---------------------|------------------------|--------------|---------------------|---------------------------------|--------------------------------|
| Biological Treatment System | No. of Samples | Before Treatment | After Treatment | % Removal | Before Treatment | No. of Samples Detoxified | Detoxification Success Rate |
| Aerated lagoon 1-day retention | 7 | 178 | 51 | 71 | 1.8 | 2 | 28 |
| 3-day retention | 9 | 370 | 16 | 95 | 0.7 | 9 | 100 |
| Rotating biodisc 2-hr retention | 7 | 178 | 13 | 92 | 1.8 | 1 | 14 |
| 4-hr retention | 9 | 214 | 20 | 91 | 0.8 | 9 | 100 |

tion, aerated lagoon treatment reduced BOD₅ from an average of 71%, from 178 to 51 mg/1; 3-day retention, aerated lagoon treatment by 95%, from 370 to 16 mg/1. However, the 1-day system detoxified only 28% of the foam samples compared to 100% for the 3-day system.

The rotating biological disc treatment detoxified 14 and 100% of the samples after 2 (hydraulic load:0.45 $\mathrm{gal/ft}^2/\mathrm{day}$) and 4-hr (hydraulic load: 0.22 $\mathrm{gal/ft}^2/\mathrm{day}$) retention times respectively. Corresponding BOD_5 removal was 91 and 92% respectively.

The results indicate that both biological treatment processes are feasible for the treatment of collapsed foam. However, the collapsed foam is concentrated with surface active toxicants, if aerated lagoon is installed for removal of BOD₅ and to dispose of toxicity, foaming can be excessive in a large scale operation. as a result, a suitable method of foam control, such as addition of chemical defoamers or installation of mechanical foam breaking system would be required.

In certain systems, where reflux of collapsed foam is practiced, the foam discharged should be more toxic e.g. MST: 10 - 20 min, biodegradation technique for foam detoxification would still be applicable in view of the high detoxification success rate documented in Table 28. However, the retention time of the lagoon may have to be increased (or hydraulic loading of the biodisc system decreased) to increase the detoxification capability

CHAPTER IV

THEORETICAL ASSESSMENT OF MAJOR OPERATING EQUIPMENT

Design of a commercial size separation plant involves two key unit operations, namely; foam generation and foam breaking. From an engineering standpoint, the equipment should be readily available, rugged, unsophisticated, requiring minimal maintenance and be economical to use.

A. ASSESSMENT OF FOAM GENERATION SYSTEM

1. Specific Criteria for Equipment Selection

The following design characteristics are considered critical for foam generation equipment:

Rate of gas-liquid interface generation = $20 \text{ m}^2/1$ (Figure 35)

Bubble size = 1 mm

Gas/liquid ratio calculated = 7

Bubble-liquid contact time = long(up to 1 hour)

Detoxification of typical kraft mill effluent requires about 20 $\rm{m}^2/1$ of gas-liquid interface and less than 1-hr of retention time. The required interfacial area can be achieved by either sparging large quantities of coarse air bubbles or smaller volumes of fine air bubbles. The bubble size produced by the equipment is expected to be controllable at a mean bubble diameter of 1 mm. Systems producing smaller bubbles

are not considered economically feasible due to the large energy requirement. In order to enhance adsorption of toxic materials onto the gas-liquid interface, long bubble contact times are highly desirable. Furthermore, redispersion of the produced foam should be minimized.

2. Selection of Most Promising Foam Generation System

Foam is generated by dispersing a gas into a liquid. Commercial gas dispersion equipment (aerators) has been manufactured primarily for oxygen transfer in biological waste treatment systems. In designing an aerator (110) oxygen transfer is maximized by (i) generating the largest practical interfacial area between a given liquid volume and air, (ii) preventing build-up of thick interfacial films or by breaking them down to keep the transfer coefficient high, (iii) maintaining the longest possible exposure time. The above considerations are compatible with design of a foam generating device. On the basis of mechanical design, five different types of gas dispersing principles can be applied to foam generation. The characteristics of operation of each are summarized in Table 29. The equipment representative of each system and its potential application for foam generation have been assessed based on performances and operation principles.

a. Forced Air Diffusion

Air is bubbled into water through orifices, nozzles in the air piping, diffuser plates, or spargers. Diffused aeration equipment (Figure 6-b and 14) can be classed into two general types, namely: coarse

TABLE 29 CHARACTERISTICS OF VARIOUS FOAM GENERATING EQUIPMENT

| Characteristics | Foam Generator | | | | | | | |
|--|--|---------------------------------------|---------------------------------------|---|---|--|--|--|
| | Forced Diffusion (fine bubble diffuser) | Surface | Mechanical Shear | Hydraulic Shear | High Pressure | | | |
| Bubble size range (mm) | 0.5 - 1.5 | - | 0.5 - 1.5 | 0.5 - 1.5 | 0.03 - 0.1 | | | |
| Air Requirement (x10 ³ ft ³ /min)* | 3.6-10.8 | | 3.6 - 10.8 | 3.6-10.8 | 0.22 - 0.72 | | | |
| hp/100 gal of effluent** | 0.1 - 0.13 | 0.04 | 0.2 | 0.10 | 0.40 | | | |
| Plugging Problem | Serious | None | None | None | None | | | |
| Maintenance Required | | Frequent servicing of gear box, motor | Frequent servicing of gear box, motor | Routine inspection of circulating pumps | Frequent inspection of pressurization system, compressor. | | | |
| Installation | Simple | Simple | Simple | Simple | Sophisticated | | | |
| Operation | Simple | Simple | Simple | Simple | Sophisticated | | | |
| Relative Cost Magnitude | Economical | Economical | Moderately expensive | Med1um | Expensive | | | |

^{*} to produce 20 m²/1/h of gas-liquid interfacial area. ** from literature (4) and plant operator.

bubble diffusers and fine bubble diffusers. Only the fine bubble devices are suitable for production of the gas-liquid interfacial area required for foam detoxification. These types of diffusers are generally fabricated of a porous medium such as carborundum, plastic or tightly wrapped saran. Bubble sizes as small as 0.5 mm diameter can be The fine bubble diffuser is economical to use and simple to operate, however, plugging of pores occurs readily as a result of inadequate filtration of air, growth of biomass, or suspended solid deposits and scaling. A high degree of maintenance may be required to keep the units operative. These diffuser systems are generally available in the form of 2-ft long, 3-in diameter tubes (Figure 14-b) or 6-in diameter domes/discs (Figure 14-a). Fine bubble generation is usually most effective when the diffusers are installed at the bottom of a long narrow basin. This configuration promotes plug flow and increases gasliquid contact time. However, the construction cost of the waste treatment system may increase.

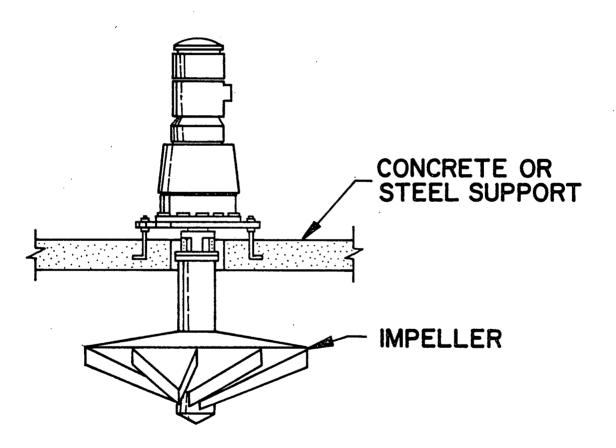
Despite several advantages, fine bubble diffusers require frequent cleaning and replacement. Thus their performance is not consistent.

This limitation seriously restricts the use of porous diffusers in foam generation.

b. Air Entrainment

This type of device is best represented by a surface aerator which brings waste water to the surface for contact with air. Figure 43 shows a typical design of surface aerator (111). The bladed or paddle-surface

Figure 43 SURFACE AERATOR



aerator pumps liquid from beneath the blades and sprays the liquid across the water surface. The brush aerator utilizes a rotating steel brush which sprays liquid from rotating blades with mixing achieved by an induced velocity below the rotating element. A draft tube is employed in some design. The surface aerator offers high oxygen transfer with low horsepower requirements (0.04 hp/1000 gal). Maintenance is mainly related to servicing of the gear box and motor. A surface aerator requires sufficient area for proper aeration and therefore is most effective in a shallow basin.

The major drawback of the surface aerator for use as a foam generator is the mechanism of bubble production. In most systems, air is entrained and foam is created as the spray re-enters the contents of the tank. The stream of air-liquid mixture will impinge on the foam surface. Similar to a liquid spray, the toxic foam will be collapsed and returned to the liquid. This mechanism is detrimental to detoxification. Limited data is available on the size and volume of bubbles produced. However, because air is not introduced directly into the effluent, foam generation capacity is low.

c. Mechanical Shear

The most promising mechanical shear type gas-dispersion device (Figure 8) is the submerged turbine mixer. This system is widely used in fermentation and sewage treatment systems. The gas is discharged from a pipe or sparger ring beneath the rotating blades of an impeller. The design objectives are to provide, by mechanical shear and

fluid shear action, sufficient forces to create a fine bubble distribution and maximize the air retention in the system. The mechanical action is necessary to keep the system fully mixed as well as to inject air to create the gas-liquid interface. Balance between air flow and impeller speed is critical. Under suitable air load and rotation speed (tip speed) of the blade, bubble sizes of 0.5 - 1.5 mm can be produced.

A submerged turbine system is a fixed unit aeration device and usually is installed in a deep basin. The system is most suitable for short retention time, waste treatment plants where land is at a premium. These advantages must be traded off against higher horsepower requirements (0.2 hp/1000 gal). The maintenance requirements are similar to surface aerators.

Turbine systems are easy to operate, reliable in producing fine bubbles and are non-plugging. They would be good systems for foam generation.

d. Hydraulic Shear

The hydraulic shear force developed by turbulent action of water in a tube is an effective means of gas dispersion. Bubble size is controlled by the loading of air and the velocity of the liquid travelling inside the tube. To produce 1 mm mean bubble diameters, the pumping system should be installed to maintain the liquid velocity at >5 ft/sec through the tube. The power requirement (0.1 hp/1000 gal) is lower than for turbine system but higher than for porous media and surface

aeration systems. Some designs are capable of producing bubbles of 0.1 mm diameter (112). The best hydraulic shear system can be represented by helical (Figure 8) and the jet aerators (Figure 22). Both systems are non-plugging, simple to use and generate large interfacial areas. Maintenance requirements are much lower than for air diffusers and turbines. These aeration systems would be suitable for foam generation.

e. High Pressure Aerator

The most common system is based on the principle of dissolved air process. Air and liquid are pressurized together at 40 to 80 psi and due to its greater solubility at higher pressures, the air dissolves. Upon release of the pressure, the air becomes insoluble producing bubbles and, if conditions are right, foam would be created. Bubble size ranges from 30 to 120 μ in diameter according to the pressure applied, surfactant concentration and mode of operation. The process utilizes very small amounts of air but requires an extremely large energy input (0.4 hp/1000 gal). Compared to other alternatives, operating costs are considered high. The dissolved air system is quite sophisticated to build and operate. This system would not be economical to operate.

3. Selection of the Best Foam Generation System

Preliminary examination indicated that the turbine (mechanical shear system), or helical and jet aerators (hydraulic shear system)

would be the most promising systems for foam generation. The size of bubbles produced by all three systems can be varied by changing the operating conditions. With resonable power inputs, a bubble diameter of 1 mm and 20 m²/1 of gas-liquid interfacial area can be achieved. The effectiveness of detoxification with turbine systems or with helical systems (Table 10) has been documented earlier in Chapter IV. The bubble sizes (Figure 44) produced by the jet aerator are much smaller (0.57-1.16 mm diameter using an accurate photographing technique as described in Section IV-D). Thus, the detoxification efficiency of the foam separation process using jet aerators is expected to be at least comparable to a turbine or helical system.

To select the best system for commercial installation, these systems are compared in detail in Table 30 in terms of consistency in producing fine bubbles, equipment reliability and costs.

a. Bubble Size

Laboratory experiments indicated that turbine aeration produced a consistently narrow range of bubble sizes (Table 30) with approximately 50% of them < 1 mm bubble diameter. Due to turbulent condition, bubble-effluent contact was adequate during the operation.

In contrast, actual testing using a regular-type helical aerator produce bubbles ranging from 1 - 3 mm in diameter (Table 30) which quickly rose to the surface. To produce the same gas-liquid interfacial area as a turbine system, a large number of additional aerators and

FIGURE 44

BUBBLE SIZES AT 5 ft 3 /min AIRLOAD PER JET AERATOR

(in bleached kraft wholemill effluent) $\frac{0}{2}$ $\frac{2}{4}$ $\frac{4}{6}$ $\frac{8}{8}$ $\frac{10}{9}$ Scale (mm)

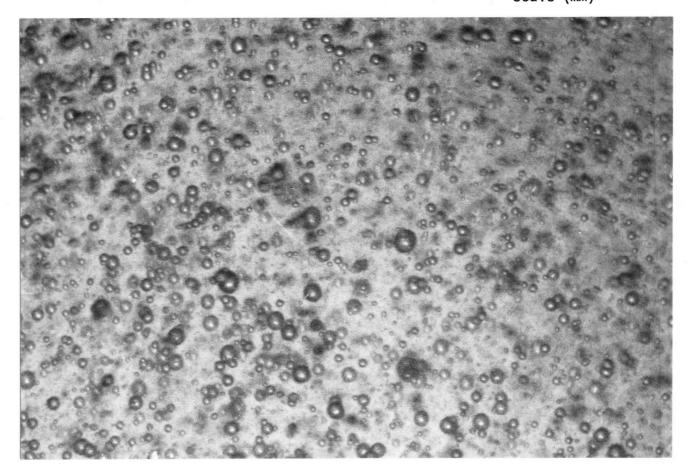


TABLE 30

COMPARISON OF MOST PROMISING FOAM GENERATING EQUIPMENT

| Operating Characteristics | Turbine Aerator | Helical Aerator | Jet Aerator |
|--|------------------------------------|--|------------------------------|
| Probability of producing 1 mm bubble diameter under normal operating conditions | >50% | <50% | 100% |
| Verification of bubble size | Laboratory Experiment | Demonstration of test model | Verification by a test model |
| Possibility of producing >1 mm diameter bubbles due to poor performance | Slightly possible | Highly possible | Slightly possible |
| Consequence of producing >1 mm diameter bubbles | Increase aeration rate | Increase the No. of aerators and aeration rate | Increase aeration rate |
| Gas-liquid contact time | Long | Short | Longest |
| RELIABILITY Simplicity of the system | More sophisticated | Simple | Simple |
| Installation | Sophisticated | Easy | Easy |
| Ease of operation | Easy | Easy | Easy |
| Possibility of breakdown | Highly possible | Minimal | Minimal |
| Maintenance required | On gearbox, bear- ing and motor | Minimal | On pump |
| Possibility of corrosion | On all mechanical components | None | On pump |
| ECONOMY of foam generating equipment (25 MGD plant) | | · | |
| No. of aerators required * | 15 | 312 | 12 |
| hp required | 1430 | 680 | 1328 |
| Capital Cost (\$) | 375,000 | 250,000 ** | 550,000 |
| Operating Cost (\$/ton of pulp) | 0.49 | 0.21 | 0.42 |

Assuming 1 mm bubble diameter are produced.

^{**} Cost based on production of 1 mm mean bubble diameter. According to actual testing, mean bubble size is >2 mm and the capital cost will be at least doubled.

blowers would be required to compensate for the large bubble size and short bubble retention time. This would create design and installation problems. Although the bubble size can be reduced by pumping the effluent through the aerator, with a 2-ft diameter, 5-ft long commercial size aerator, a pumping capacity of 6000 gal/min would be required for each aerator to bring the liquid velocity to the 5 ft/sec required for fine bubble production. The additional cost cannot be economically justified.

Demonstration of the jet aerator showed that this system produced the most uniform and smallest bubbles. In Table 31, the mean and range of bubble sizes in kraft mill effluent are given as a function of air load per jet. Mean bubble diameter remained virtually unchanged at 0.6 mm (Figure 44) when the air load was < 5 ft³/min. At higher air loads, the bubble sizes increased and reached a constant size of approximately 1.2 mm. When the kraft mill effluent was replaced by water, the bubble size increased approximately by 300%. These fine bubbles are discharged in a strong plume (Figure 44). The contact time of the bubbles is extended because the bubbles travel horizontally before rising vertically to the surface.

Of the three systems considered, the jet aerator appears most consistent in producing fine bubbles.

b. Reliability of Equipment

The turbine aerator is the most sophisticated of the three systems compared in terms of design and installation. Without proper care, the large number of mechanical components could cause mechanical failure.

Routine servicing is required. The system is constructed of metal.

TABLE 31

AVERAGE AIR BUBBLE SIZES PRODUCED BY A JET AERATOR

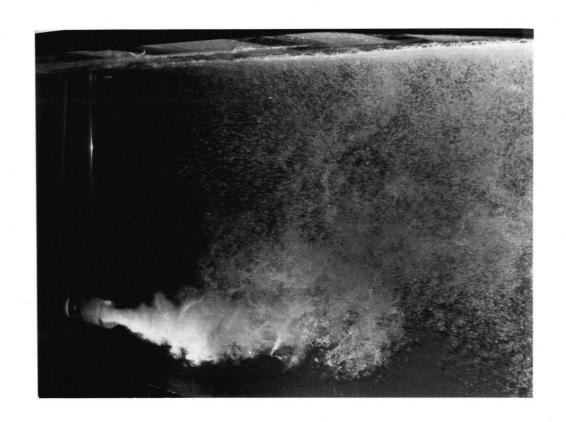
IN BLEACHED KRAFT WHOLEMILL EFFLUENT

| Air flow/jet | Bubble Di | ameter (mm) |
|----------------------------|-----------|-------------|
| (std ft ³ /min) | Range | Mean ± S.D. |
| 1.1 | 0.43-0.86 | 0.57 ± 0.11 |
| 1.8 | 0.47-0.70 | 0.63 ± 0.10 |
| 3.1 | 0.4-0.80 | 0.58 ± 0.10 |
| 3.9 | 0.44-0.89 | 0.61 ± 0.14 |
| 5.0 | 0.48-0.71 | 0.61 ± 0.13 |
| 5.5 | 0.59-0.78 | 0.74 ± 0.09 |
| 6.0 | 0.56-1.94 | 0.88 ± 0.18 |
| 14.3 | 0.76-1.01 | 0.85 ± 0.11 |
| 21.5 | 0.38-2.01 | 1.24 ± 0.35 |
| 50.0 | 0.56-1.45 | 1.16 ± 0.17 |
| | | |

Operating condition: Jet: 5 cm diameter nozzle 1/2 hp, 20 gal/min recirculation pump

FIGURE 45

JET AERATOR IN OPERATION



therefore expensive alloys or stainless steels must be used. Consequently, labour costs and depreciation based on the service life expectancy of the equipment will be high.

The design of the helical system is the simplest and most dependable. It is made of plastic material with no mechanical moving parts.

Operation is trouble free and requires minimum maintenance. It is non-corrosive and unlikely to break down. Addition or replacement of helical aerators is easy.

The jet aeration system also offers simple, easy operation and minimum maintenance expenses. The jets are made of fiberglass and are also non-corrosive. The recirculation pump will require periodic inspection. With advances in pump engineering over the past few decades, continuous reliable operation is almost assured.

c. Economy

Based on the present information and assuming that 1 mm bubble diameter can be produced by all three foam generation systems, the number of units required to produce $20 \text{ m}^2/1$ of gas-liquid interface and capital cost of each system were obtained from various manufacturers. Installation of the turbine aerator, with requirement of 1,430 hp, is estimated at \$375,000. The helical system is the cheapest to install (\$250,000) and operate. It requires the least horsepower (680 hp). However, this system most likely will produce 2 - 3 mm diameter bubbles.

Under this assumption, the estimation will be several times higher. The jet aerator system, requiring 1328 hp is estimated to cost \$550,000. Operating costs are estimated at \$0.49/ton of pulp for turbine aeration, \$0.21/ton for the helical system and \$0.42/ton for the jet aeration system. Although having a higher capital cost, the operating cost of jet aeration is slightly lower than for turbine aeration because of lower depreciation.

d. Conclusion

Among the three most promising aeration systems, the jet aerator produces small bubbles most reliably and provides the longest contact time between bubbles and effluent. Mixing of the tank contents is most complete. The system is easy to install, reliable in operation and the cost is comparable to a turbine system. Therefore, a jet aerator system is recommended for commercial operation.

B. ASSESSMENT OF FOAM BREAKING SYSTEMS

1. Specific Criteria for Selection of Foam Breaking Systems

A 25 MGD plant will produce at least 2000 ft³/min of foam (1-2% liquid content) which spreads evenly over a large liquid surface. Foams flow poorly and must be collapsed as soon as they are produced in order to prevent the redispersion of the toxic materials. The equipment for collapsing such huge quantities of foam should be able to cause the

foam to flow into the foam breaking area, remove the foam from the tank and effectively convert the foam into a freely flowing liquid.

2. Selection of Most Promising Foam Breaking Systems

Several foam destruction techniques have been discussed in the literature. Many of these discussions are concerned only with laboratory experimental work. Some of these techniques have never been tested on a large scale. The principles of operation, application, and their suitability for installation in foam separation plant are summarized in Table 32.

a. Air Jet

Foam can be broken by exposure to a strong current from an air jet (112, 113). Bursting of the bubbles in the foam occurs as a result of evaporation and impact forces. For a large scale installation, it would not be mechanically feasible to subject a large foam surface to the number of air jets, operating at extremely high air flows which are necessary to break the foam. At present, this method is exclusively used for laboratory work.

b. Sonic Pressure

Sound waves of the proper frequency can collapse foam by means of a combination of acoustic pressure, radiation pressure, induced resonant vibrations and turbulence produced by the sonic wave (114). Usually

TABLE 32

COMPARISON OF VARIOUS FOAM BREAKING DEVICES

| Foam Breaking System | Operating Principle | Commercial Installation | Practicability for Pulp Mill Application |
|-------------------------|---|---------------------------------------|--|
| Air | Impact force, Evaporation | None | Impractical |
| Sonic Pressure | Various acoustic pressures | None | Impractical |
| Thermal | Evaporation, Chemical degradation | None | Impractical |
| Orifice | Impact force | None | Impractical |
| Liquid Spray | Sudden pressure change, dilution | Yes | Impractical |
| Mechanical Forces | | | |
| - Whirling Paddle | Shear, Impact, Compression and | None | Impractical |
| - Centrifugal | Tension Forces | Fermentation | Suitable |
| - Turbine | | industry and Pulp and Paper industry. | Suitable |

sirens with a wide frequency range, and whistles tuned to a particular band are effective (115). Acoustic vibrations e.g., 0.7 or 11 kc at 150 db are reported to disintegrate foam. At present, it is not economical to use sonic techniques for controlling large volumes of foam.

c. Thermal Method

Foam may be collapsed by heating it. The high temperature will decrease the surface viscosity which weakens the bubble film. In some instances, degradation of surfactants present in foam film may also occur. Evaporation of the solvent will result in thinning of the film and a change in the concentration of the foaming substances (116). In actual practice, foam is collapsed by heating elements placed directly over the surface of foam (117). Heat treatment is indirect, and less effective on an energy input basis, than other systems. In view of the huge volume of foam (2000 ft³/min) produced from kraft mill effluents, thermal treatment cannot be regarded as an economically viable method.

d. Liquid Spray

Spraying foam with a strong water jet, in most cases is an effective means of foam collapsing. Foam breakage is caused by a combination of various forces and progressive dilution of the foam liquid (118). This technique, however, is only suitable in situations where recovery or reflux of foam is not required and where dilution of foam does not constitute a disposal problem. The system has been applied successfully in the Los Angeles County Sanitation District Water Reclamation Plant

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(119) and in a field scale kraft mill foam separation process (Figure 17). For large scale foam separation of kraft mill effluent, as a means of detoxification, foam must be collected for subsequent treatment. Liquid spray is therefore not suitable.

e. Orifice Foam Breaker

The effectiveness of foam breakage by an orifice is attributed to the sharp pressure changes as the foam passes through the orifice. At a pressure difference of 7 psi, foam drawn through a 2.5 mm diameter orifice is collapsed effectively (120). However, this system is not economically viable for large scale foam breaking due to the large power requirements for pumping gas. In addition, the small orifice used may cause plugging problems.

f. Mechanical Forces

Subjecting the foam to sudden pressure changes can cause it to coalesce, become unstable and burst (121). These pressure changes can be achieved by compression, shear, compaction and tension forces through various kinds of commercially available equipment. For dry and unstable foam, a whirling paddle or rotating rod (122) can create sufficient impact and shear forces for foam collapsing. For wet and stable foam a perforated, centrifugal basket (123) is effective. The foam is broken by sudden pressure changes as the foam leaves the basket. Properly selected turbine blades, rotating at high speed (2000 rpm) can create sufficiently high stresses on the foam to cause rupturing.(124). Turbine

type foam breakers are available in the market and have been reported to reliably collapse foams from black liquor oxidation towers (125). Foam breaking is instantaneous and effective. This system appears suitable for a foam separation plant.

3. Selection of best Turbine Foam Breaking System

Preliminary analysis indicates that mechanical forces created by turbine blades were able to collapse foam successfully. The effectiveness of a turbine for foam breaking has also been verified at a field site (Table 26) as described in Chapter V. Foams were broken by a combination of at least three major forces: Suction, centrifugal and shear forces (126). These forces are determined by the rotational speed and diameter of the blade, as indicated by the following formulae:

Suction force = $K_1 \text{ ND}^3$ Shear rate = $K_2 \text{N}^{1.5} \text{ D}^{2.5}$ Centrifugal force = $K_3 \text{ N}^2 \text{D} = K_4 \frac{\text{V}^2 \text{tip}}{\text{D}}$

where Ki = Constant, i = 1,2,3,4

N = Rotation speed

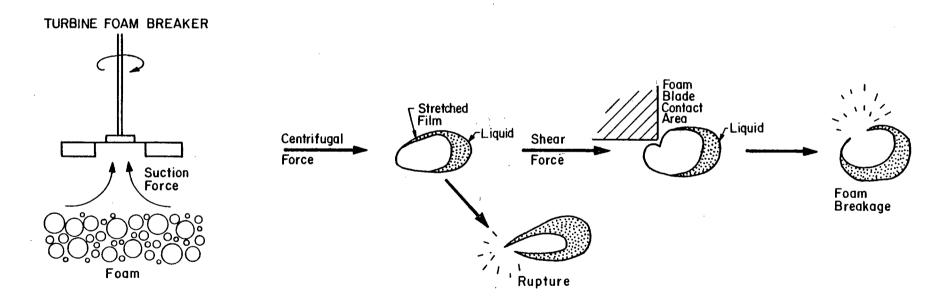
D = Diameter of blade

Vtip = Tip speed

All three forces are concurrently involved in foam breaking.

Figure 46 illustrates the mechanism by which the principal forces involved in breaking foam act. The blades rotating at high speed produce a suction force which draws the foam into the disc. Near the impeller

Figure 46 PRINCIPAL FORCES INVOLVED IN BREAKING FOAM BY TURBINE

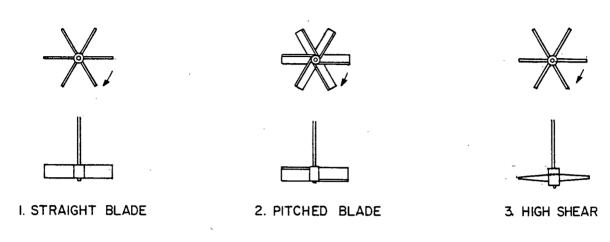


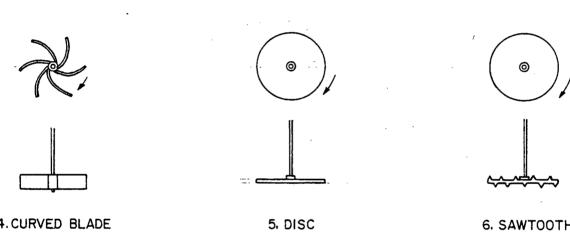
is a zone of rapid radial and tangential currents, high turbulence, and intense shear. The foams are spun and accelerated as they leave the disc. Due to centrifugal force, the liquid content of the foam is accelerated faster than the gas and so is separated. The foam film is stretched and a weak region consisting of thin foam films is created. As the foam circulates and travels along the blades, these weak regions will eventually rupture under tension or be beaten by the blades and then rupture. The combined effect of the various forces causes foam to break within seconds. During mechanical foam breaking, several other factors are also responsible for some foam breaking. These include collisions among the foams, smashing of foams on the walls of the foam tank etc. These factors, however, are not considered as significant as suction, shear and centrifugal forces.

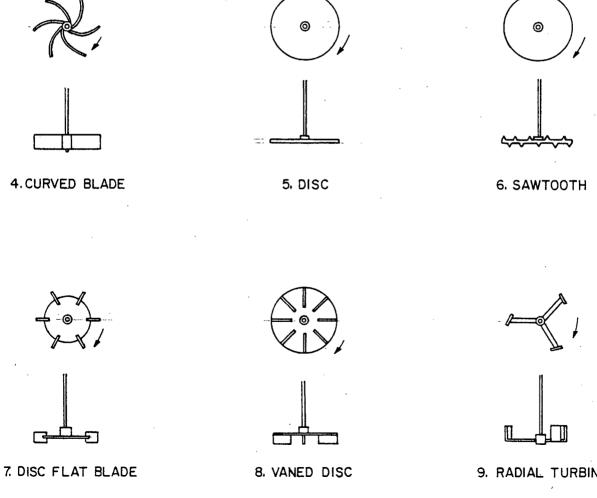
A turbine impeller operates like a pump without a casing. Conventionally, turbines are used for liquid mixing and gas dispersion. They can be classified into two basic designs; the axial discharging type and the radial discharging type. Both types contain many variations and subtypes for specific applications. The blades may be straight or curved, pitched or vertical. The impeller may be open or semi-open. Figure 47 illustrates some of the conventional turbines and more popular modifications (127).

The axial flow type turbines, e.g. straight blade, pitched blade, high shear and curved blades are not desirable. These systems discharge the foam directly, reduce the foam-blade contact time and shear rate, which are essential for foam breaking. Among the radial discharge type

Figure 47 TURBINES OF VARIOUS SHAPES







9. RADIAL TURBINE

turbines, the disc, sawtooth and radial turbines are not suitable because of poor suction and low centrifugal forces. The best systems are the disc flat blade and the vaned disc turbines. They combine good pumping, high shear and centrifugal force during high speed rotation.

Table 33 compares the performance of various types of turbine foam breaking systems. The results indicate that there are no real differences between performance of turbines. However, a vertical 3-blade vaned disc system is considered the best choice in terms of foam breaking efficiency, power consumption and simple design. This system would be suitable for commercial operation.

TABLE 33

EFFECT OF IMPELLER GEOMETRY OF A 3 BLADE TURBINE ON FOAM
COLLAPSING EFFICIENCY AND POWER CONSUMPTION

| Design of Impeller | | Foam Collapsing Efficiency (%) | Power Consumption (KW) Loaded |
|--|----------|---|--|
| Vaned disc (vertical blade) | | 81 | 0.35 |
| Vaned disc (45° pitch) - clockwise | | 82 | 0.35 |
| Vaned disc (tappered blade) | | 77 | 0.35 |
| Curved vaned disc | 9 | 81 | 0.38 |
| Disc flat blade turbine | → | 80 | 0.50 |

Operating Conditions:

Disc ϕ = 31 cm(12")

No. of blades = 3

rpm = 1800

Operation = Continuous

Foam flow = $0.50 \text{ m}^3/\text{min}$ (17.6 cfm)

Liquid entrained = 1.4%

CHAPTER VII

PILOT PLANT OPERATION

Data established during laboratory and field studies were used for designing a 6000 gal capacity foam separation pilot plant. The main intent was to verify the detoxification principles previously discussed and to assess the suitability of the selected foam generating and foam collapsing equipment. This information is required for sizing and costing of a full size commercial foam separation plant. The pilot plant selected was equipped with a jet aeration system for foam generation, and a turbine for foam breaking. It was located near the outfall of Mill A on Vancouver Island.

A. PILOT PLANT FOAM SEPARATION PROCESS

The pilot plant was a 3-stage, trough type design (Figure 20) which processed 80 - 100 gal/min of bleached kraft whole mill effluent. Retention time and air flow rates of the system varied from 20 - 80 min and 50 - 100 ft³/min respectively. The pH of the effluent was controlled only when detoxification performance was being monitored. The variations in gas and liquid flow rates, retention time and pH produced foams of different characteristics. The pilot plant was operated over a period of 8 months. Throughout the study, influent characteristics, foam breaking efficiency and detoxification in each stage were determined at regular intervals.

B. INFLUENT CHARACTERISTICS

During the first month of pilot-plant operation, influent and foam samples were taken each day at convenient intervals. The influent was analyzed for pH and foaming tendency; foam was analyzed for volume, density, stability and liquid content. The toxicity of the influent was determined less frequently. The data are tabulated in Appendix XV and summarized in Table 34. The pH of the mill effluent varied widely from 3.0 to 9.5 depending upon mill operation, and over the experimental period averaged 4.8. The foaming tendency of the effluent was influenced by pH. It varied from 4.2 to 6.5 min and averaged 5.3 min.

Out of a total of 43 samples, ten were analyzed for toxicity. MSTs ranged from 200 to 800 min and averaged 433 min. Using this effluent, and with the foam separation plant operating at an average retention time of 67 min and a G/L of 9.8, approximately 30 m²/liter of gas-liquid interface was produced. Foam production averaged 18.4 ft³/min. The liquid content of the foam averaged 1.5% and foaming stability averaged 4.2 min. The foaming tendency and the foaming stability of the influent were typical of and similar to those observed on effluent from other western Canadian kraft mills (40). Conversion of influent to foam was 3%, lower than the range observed during an earlier feasibility study (up to 5%(Section V-D) on effluents from an interior B.C. mill, foam separated in a 180 1 column). This was due to the design of the pilot plant which permitted longer retention times resulting in better foam drainage.

TABLE 34 INFLUENT CHARACTERISTICS DURING PILOT PLANT OPERATION

| | | Influent Characteristics (mean±S.D.) | | Process Conditions (mean±S.D.) | | Foam Characteristics (mean±S.D.) | | | | |
|-----------------|-------------------|--------------------------------------|------------------------------|--------------------------------|--------------|-------------------------------------|----------------------------------|----------------------------|-------------------------------|---------------------------------------|
| No. of Weeks | No. of Samples | pН | Foaming Tendency (min) | Toxicity (MST, min) | G/L | Retention Time (min) | Foam Flow (ft ³ /min) | Liquid Entrained (%) | Foaming Stability (min) | Influent Conversion to Foam (%) |
| lst week | 6 | 6.9 ±2.4 | 5.6 ±0.3 | _ | 12.2 ±0.5 | 74.8 ±2.8 | 18.55 ± 3.15 | 1.7 ±0.4 | 5.0 ±0.3 | 3.7 ±0.9 |
| 2nd week | 9 | 4.4 ±1.1 | 5.5 ±0.7 | - | 11.1 ±0.6 | 67.8 ±3.6 | 18.9 ± 3.85 | 1.6 ±0.5 | 4.7 ±1.0 | 3.3 ±1.3 |
| 3rd week | | 4.7 ±1.1 | 5.1 ±0.6 | 506± 220 | 8.5 ±2.8 | 65.4 | 17.5 ± 10.85 | 1.4 ±0.2 | 4.0 ±1.0 | 2.6 ±1.8 |
| 4th week | 9 | 3.6 ±0.7 | 5.4 ±0.5 | 277±198 | 9.7 ±2.4 | 65.4 | 19.25 ± 4.9 | 1.5 ±0.3 | 3.6 ±1.1 | 3.2 ±1.1 |
| Overall | 43 | 4.8 ±1.6 | 5.3 ±0.6 | 433±210 | 9.8 ±2.6 | 67.2 ±3.7 | 18.36 ±7.77 | 1.5 ±0.3 | 4.2 ±1.1 | 3.0 ±1.5 |

C. OPTIMIZATION OF OPERATIONAL PARAMETERS FOR DETOXIFICATION OF MILL A"S WHOLEMILL EFFLUENT

In a foam separation process, maximum gas-liquid interfacial area generation is desirable for adsorption of toxic surface active components. However, in terms of economics, the number of foam generating units required to produce that interfacial area and the related foam volume discharged must be reduced to a minimum. Critical design considerations affecting these two factors are the jet aerator distribution and the staging of the system.

1. Gas-Liquid Interfacial Area and Number of Jets Required

It has been reported that under the conditions where bubble coalescence and air pocket formation did not occur, maximum interfacial area (1450 m^2/min) was generated with 5 ft $^3/\text{min}$ of air load per jet (128). Since changes in bubble sizes are not very sensitive to treatment time or jet submergence (128), then operation at an optimum air load of 5 ft $^3/\text{min}$ per jet is independent of the position of the jet in the foam generation tank and staging of the system.

According to earlier studies, the gas-liquid interfacial area requirement for detoxification is directly proportional to the initial toxicity of the effluent (Figure 35). For Mill A's wholemill effluent and with influent toxicity ranged from MST: 360 - 600 min, the reduction of toxicity after foam separation and the gas-liquid interfacial area

applied were calculated (refer to Materials and Methods section) and given in Appendix XVI. In Figure 48 the toxicity of the treated effluent is plotted against G/L ratio and gas-liquid interfacial area. With increasing gas-liquid interfacial area applied, the toxicity was progressively reduced. Most of the samples were completely detoxified at or above 6 m²/1 of gas-liquid interfacial area (at G/L of 1). This interfacial area requirement agrees with earlier results obtained in a laboratory system (Section V-B).

The pilot plant system was operated at 80 gal/min of effluent flow. At an operating air loading of 5 ft 3 /min per jet, bubbles of 0.6 mm mean diameter, were produced giving approximately 1450 m 2 /min (or 3.5 m 2 /1) of interfacial area. Two aerators ($\frac{6}{3.5} = 1.75$), therefore would appear to be adequate to generate sufficient gas-liquid interfacial area.

2. Foam Minimization

If two jet aerators were operated at an air load of 5 ft³/min per jet in a single stage system, processing 80 gal/min of Mill A wholemill effluent they would produce 22.5 ft³/min of foam (Table 35). It has been documented that in a multiple stage system the majority of the foam is produced in the first stage with less being produced in the 2nd and 3rd stages (Section V-A-8). As a result, increasing the foam travelling distance either by staging or proper distribution of the jets would reduce the foam volume discharged. Table 35 also shows that if one aerator was installed in each stage, thereby increasing the foam path

Figure 48
EFFECT OF GAS-LIQUID INTERFACIAL AREA ON DETOXIFICATION OF KRAFT MILL EFFLUENTS

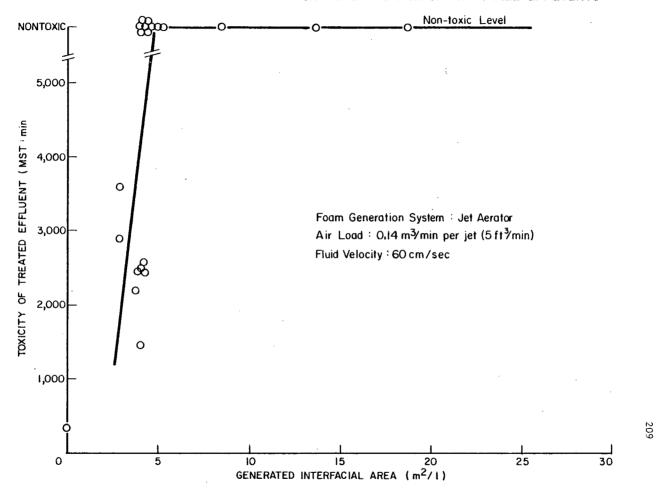


TABLE 35

AVERAGE FOAM GENERATION CHARACTERISTICS OF A 1-3 STAGE FOAM SEPARATION SYSTEM

Influent Characteristics:

- Bleached kraft whole mill effluent
- pH adjusted to 7.0 8.0
- Flow = 100 gal/min

Operation Characteristics:

- Foam generation system with 1 to 3 equally sized stages
- Air load per jet = 3.5-23.1 (ft $^3/min/jet$)

| 1 Stage System | | | 2 S | 2 Stage System | | | 3 Stage System | | | |
|-----------------|------------------------|---------|------------|------------------------|--------------------------------|-----------|------------------------|--------------------------------|-----------|--|
| Total Number | (0-6 ft Foam | Travell | ing Dist.) | (0-12 ft F | (0-12 ft Foam Travelling Dist) | | | (0-18 ft Foam Travelling Dist) | | |
| of Jet Aerators | Maximum | Foam | Influent | Maximum | Foam | Influent | Maximum | Foam | Influent | |
| in the System | Foam | Liquid | Converted | Foam | Liquid | Converted | Foam | Liquid | Converted | |
| | Production | Content | to Foam | Production | Content | to Foam | Production | Content | to Foam | |
| | (ft ³ /min) | (%) | (%) | (ft ³ /min) | (%) | (%) | (ft ³ /min) | (%) | (%) | |
| | | | | | | | | | | |
| 2 | 23 | 1.20 | 2.46 | 14.1 | 1.38 | 1.81 | - | - | - | |
| 3 | 24 | 1.27 | 2.71 | 23.7 | 1.08 | 2.08 | 17.3 | 0.90 | 1.13 | |
| 4 | - | | - | 20.8 | 1.13 | 2.16 |]4.8 | 0.84 | 0.98 | |
| 6 | - - | - | - | 26.5 | 0.68 | 1.47 | 18.0 | 0.75 | 1.26 | |
| | | | | | | | | | | |

from 0 - 6 ft to 0 - 12 ft, the quantity of discharged foam could be reduced by 40% to 14.1 ft³/min. Additional experiments using 3 - 6 jets in a 3 stage operation (increasing the foam path from 0 - 12 to 0 - 18 ft) also showed an additional 20 - 30% foam reduction (Table 35) when compared to a 2-stage system. Staging of the foam fractionation system will also decrease the foam's liquid content. The average foam liquid content in a two stage system was 1.1%, while the average foam liquid content in a single stage system was 1.5%. The reduction of foam production and foam liquid content achieved by using a 3-stage system instead of a single stage system reduced the percentage of influent converted to foam from 2.45 - 2.71% to 0.98 - 1.26% thus minimizing the foam handling problem. The overall results suggest that for detoxifying Mill A effluent, a 2-jet, 2-stage system is satisfactory to provide the critical interfacial area and to minimize foam output.

D. EFFECT OF STAGING ON DETOXIFICATION SUCCESS RATE AND FOAM CHARACTERISTICS

In the previous section, it was established that, processing of 80 gal/min of Mill A wholemill effluent requires two jet aerators operating at an assumed air load of 5 $\rm ft^3/min$ per jet. This condition would provide 6 m²/l of interfacial area (G/L<1) sufficient for detoxification by foam separation. In addition, design considerations suggest that staging of the system; i.e. with one jet installed per stage is beneficial for foam reduction. In order to determine the compatibility of staging with detoxification and foam minimization, the pilot plant was

operated as a 1, 2 and 3 stage system. Air flows and jet configurations were adjusted to maintain 5-7 m $^2/1$ of gas-liquid interfacial area. Grab and composite samples were taken from each stage for bioassay analysis and foam characterization. The data are tabulated in Appendix XVII and summarized in Table 36.

The results suggest that at a selected critical gas-liquid interfacial area (6 $m^2/1$), consistent detoxification was achieved. Detoxification success rate, however was dependent upon the number of stages in operation. It increased from 50 to 86 to 100% as the operation stages increased from 1 to 2 and then to 3 stages. The low detoxification rate in the single stage operation may be partially attributed to the variability of the influent toxicity and the low number of samples examined. If the number of samples were doubled, a slightly higher detoxification rate may be obtained.

Concurrent with the improved detoxification success rate, foam output decreased with increasing stage number, from 13.8 ft³/min in a 1-stage system to 12.4 and 10.9 ft³/min in a 2- and 3-stage system. As documented in Section VII C-2, the reduction in foam flow is attributed to an increase in foam travelling distance (increased time for foam drainage) with an increase in number of operation stages.

Table 36 also lists the MST values of collapsed foam. MSTs ranged from 15 - 20 min in a single stage system to 10 - 20 min in a three stage system. The results confirmed earlier findings that the toxic materials are concentrated in the foam.

TABLE 36

DETOXIFICATION SUCCESS RATE OF VARIOUS CONTINUOUS FOAM SEPARATION SYSTEMS

| System in Each Stage S | No. of Jets | No. of | Interfacial | Foam Characteristics | | Detoxification Success Rate (%) | | |
|------------------------|-------------------------|--------|--------------------------------------|-------------------------------|--------------|---------------------------------|----------------|-----|
| | | | Flow Rate (mean:ft ³ /min | Toxicity (MST :min) | lst Stage | 2nd Stage | 3rd Stage | |
| 1-Stage | 1/0/0 | 4 | 6.2 (Range: 5.5-7.8) | 13.8 (Range: 10.6-17.7) | 15-20 | 50 | . - | - |
| 2-Stage | 1/1/0 | 14 | 7.1 (Range: 5.5-7.8) | 12.4 (Range: 0.4-14.1) | 15-30 | 57 | 86 | - |
| 3-Stage | 1/1/1 2/1/1 3/3/3 | 4 | 7.5 (Range: 7.3-7.6 | 10.9 (Range: 0.7-14.1) | 10-20 | 50 | 100 | 100 |

^{*} Various jet configurations.

For detoxification purposes, staging of the system is crucial for achieving a high success rate. It permits progressive reduction of toxicity from stage to stage and encourages better gas-liquid contact in the effluent. This condition is completely compatible with the requirement for foam minimization.

The MST of Mill A effluent usually ranged from 6 - 10 hr. A two jet system (5 ft³/min air load per jet) operating in a two stage foam separation plant would provide minimum conditions for detoxification of 80 gal/min of whole mill effluent. However, in order to ensure a consistently high success rate and still maintain minimum foam output, it is recommended that a two stage system, with two jets in the 1st stage and one jet in the 2nd stage be used. For effluents from other mills and higher toxic loads, a similar study would be required to determine the proper number of jets and staging requirements of the system.

In this pilot plant system, the jet aerators were operated at an air load of 5 ft³/min per jet, producing 1450 m²/min of interfacial area (0.6 min mean bubble diameter) in order to demonstrate the fine bubble production capability of the jet. This air load is still well below the design air load of jets (50 ft³/min of air flow) available for production of gas-liquid interfacial area (128). The remaining air load capacity per jet could have been utilized to produce more interfacial area to detoxify more toxic effluents without changing other operating parameters. In commercial operation, the jet ought to be operated at maximum design air load of 50 ft³/min(128). At this air load, the dispersed

air bubbles average 1.2 mm (128) and gas-liquid interfacial area would be produced at a rate of $4500 \text{ m}^2/\text{min}$ (assuming 60% of the air entering the jet was dispersed into fine bubbles).

E. FOAM BREAKING PERFORMANCE

The foam separation pilot plant produced a maximum of 23 ft³/min (0.94 m³/min) of foam containing 1 - 1.5% of liquid. This large amount of foam had to be liquified for better handling and subsequent treatment. Throughout this study, the technical and economical feasibility of a 3-blade vaned disc turbine in breaking foam was studied. The foam breaker was fitted with a 30 cm diameter disc and powered by a 1/3 hp motor rotating at 1800 rpm. The corresponding tip velocity was 3600 cm/sec exceeding the previously established minimum requirement for effective foam breaking (Section V-H-III). The foam properties and foam breaking efficiency were monitored over 40 days of operation. The results of foam breaking are presented in Appendix XVIII.

In Table 37, the range and mean values of the foam breaking data are presented. Foam feed rate varied from 3.2 - 23 ft³/min, liquid content varied from 1.06 - 2.92% and foaming stability ranged 3.1 - 5.6 min. Regardless of foam characteristics. foam was effectively and consistently broken by the turbine achieving 100% breaking efficiency over 40 days of operation. No operating problem was ever encountered. The results verified that the turbine foam breaker is reliable, rugged and effective for large scale foam breaking.

TABLE 37

AVERAGE EFFICIENCY OF FOAM BREAKING
BY A 3-BLADE VANED DISC TURBINE SYSTEM

| Day of | Foam | Foam | | |
|-----------|------------------------|-------------------|-------------------|------------------------|
| Operation | Flow Rate | Liquid Content | Foam Stability | Breaking Efficiency |
| | (ft ³ /min) | (%) | (min) | (%) |
| 1 | 2.22 | 2.56 | 11.2 | 100 |
| 2 | 10.91 | 1.88 | 4.0 | 100 |
| 3 | 12.64 | 1.33 | 9.6 | 100 |
| 5 | 13.59 | 2.92 | - | 100 |
| 6 | 18.04 | 2.04 | 10.2 | 100 |
| 8 | 18.00 | 1.32 | - | 100 |
| 10 | 21.00 | 1.5 | 10.7 | 100 |
| 14 | 21.04 | 1.26 | 11.1 | 100 |
| .22 | 14.47 | 1.51 | 11.2 | 100 |
| 26 | 23.76 | 1.06 | 10.2. | 100 |
| 30 | 20.72 | 1.06 | 10.9 | 100 |
| 35 | 16.31 | 0.62 | 6.2 | 100 |
| 40 | 16.31 | 0.62 | 11.3 | 100 |

Operation: Type: 3 blade, 30 cm diameter vaned disc turbine Rotation Speed: 1800 rpm

Rotation Speed: 1800 rpm Tip velocity: 3600 cm/sec.

F. SUMMARY OF PILOT PLANT OPERATION

The pilot plant work covering the operation and performance of the foam separation process over an 8 month operating period, indicated that the equipment selected for foam generation and foam breaking was suitable for large scale operation. The following conclusions are drawn:

- Operation of the foam detoxification process is easy, simple and requires little operator attention;
- Jet aerators produce sufficiently fine bubbles that are necessary for good and practical foam generation;
- Foam breaking is achieved efficiently by a turbine;
- Detoxification is consistent and reliable;
- The foam produced is highly toxic.

The results indicate that foam separation is a technically viable process for detoxification of kraft mill effluent.

CHAPTER VIII

PROPOSAL AND ECONOMICS OF A FOAM SEPARATION PLANT FOR DETOXIFYING KRAFT MILL EFFLUENT

Based on the results obtained from laboratory and pilot plant operation, a foam separation plant has been proposed for a 750 ton/day Canadian bleached kraft mill discharging 25 MGD of effluent. The economics of the plant are assessed in terms that are as relevant to Canadian operating conditions as possible. The major and auxiliary operating equipment required for effective toxicity removal and foam breaking were used as the basis for estimating capital and operating costs.

A. PROCESS DESCRIPTION

Detoxification by foam separation involves the adsorption of toxic surface active components on a gas-liquid interface. The adsorption is to be carried out on a continuous basis in a trough type foam separation tank with provisions for refluxing the collapsed foam. Staging is required to promote gas-liquid contact and enhance the separation of toxicants. The foam separation plant designed for a 750 ton/day bleached kraft mill detoxifying effluents of 3 - 4 hrs MST is described as follows:

Capacity = 25 MGD

Process Cycle = Continuous flow

Reactor = 3 stage trough type complete with foam generation and collapsing systems.

Process elements:

Effluent pumping

pH control

Screening

Air supply

Foam generation

Foam collapsing

Foam treatment.

Operating conditions:

Effluent flow rate: 17,000 gal/min

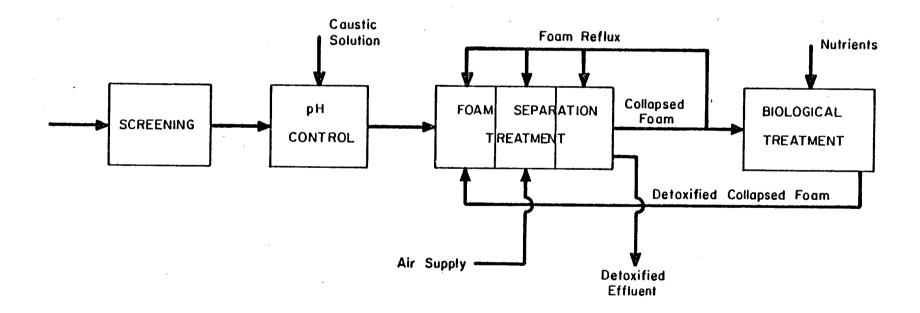
Retention time: 60 min

G/L interface : $20 \text{ m}^2/1$ (Figure 35).

Figure 49 shows the flow sheet of the proposed 25 MGD foam separation plant. Wholemill effluent is discharged at acidic pH conditions and is adjusted by lime mud and slaked lime to pH of 5 to 6. The effluents flow through a travelling screen for removal of chips and knots and enter the foam separation system.

Prior to generation of foam, the pH is increased to 7 - 8 by addition of lime mud and slaked lime followed by caustic solution. The pH adjusted effluent flows to the first stage of a 3-stage rectangular foam generation tank by gravity. The tank provides a total retention time of 1 hr, (20 min/stage). Foam is generated at a G/L ratio sufficient to provide $20 \text{ m}^2/1$ of gas-liquid interface for average toxicity loads. The system should be designed to provide complete detoxification in 2 stages. The 3rd stage would serve as a protection against unusually high toxicity loads and to provide further separation of foam if required.

Figure 49
FLOW SHEET OF FOAM SEPARATION PLANT FOR DETOXIFYING KRAFT MILL EFFLUENT



The foams rise to the chamber above the liquid surface and are continuously pumped and collapsed by mechanical foam breakers installed on top of the foam separation tank. Beneath the tank cover, a fine spraying system is used for reflux operation. Collapsed foam is pumped to a 3-day retention lagoon for biological detoxification. Should the foam volume become excessive, it would be recycled to the foam layer in the foam separator for internal reflux. The total amount of foam should not exceed 2%, by volume, of the influent. Detoxified foam is recycled to the foam separation system for the purpose of protecting effluent quality should biodegradation fail.

B. SPECIFICATIONS AND DESIGN CONSIDERATIONS OF VARIOUS PROCESS ELEMENTS

The principle operations in the foam separation process are effluent pumping, pH control, foam generation, foam breaking and foam handling. The data and specifications for each operation are shown in Table 38.

1. Effluent Screening and Pumping System

Inevitably, pulp mill effluent will occasionally include large and small pieces of woody materials. Large particles such as chips or knots may cause equipment failure. For safety measures, it would be advisable to install a coarse travelling screen. Fine particles such as fibres (approximately 100 mg/l) are flotable by foam. Moreover, they will pass through most commercial size equipment without causing operating problems. Therefore, installation of a clarifier for fibre removal is not

TABLE 38

PROCESS SPECIFICATION FOR A 25 M GAL/DAY INTEGRATED FOAM SEPARATION PLANT

Principal Design Purpose: Removal of acute toxicity from bleached kraft mill

effluent to meet Federal toxicity Standard.

Side Benefits: 10-15% BOD₅ removal

50-60% foaming tendency reduction.

Influent:

Flow: 25 M gal/day (17,000 gal/min)

3 - 5 30-35°C pH: Temperature: 5.9 - 12 min Foaming tendency: MST 180-240 min Toxicity: BOD₅: 100 - 200 mg/1

Suspended solids: 70 mg/l

pH Control:

Method: Lime mud, slaked lime followed by NaOH

End point: 7.0-8.0

Mixing: mechanical agitation.

Foam Separation Process:

Design: 3 stage trough type system

Flow rate: 17,000 gal/min Retention time: 60 min (20 min/stage) Volume of tank: 5,500 ft 3 (1,840 ft 3 /stage) Gas-liquid interface requirement: 20 m 2 /1

Foam generation equipment: Jet aerators (50 ft³/min air load per jet)

Bubble diameter: 1.2 mm

Gas to liquid ratio: 6 (Gas flow rate: 13,600 ft³/min) Rate of gas-liquid interface generated: $1.36 \times 10^6 \text{ m}^2/\text{min}$.

Foam Collapsing:

Foam breaking equipment: Mechanical agitator (1800 rpm) with 3 blade vaned

disc turbine (61 cm diameter)

Restricted liquid draw-off system Design:

 $1800 \text{ ft}^3/\text{min}$ Foam flow:

Foam liquid content: 1.5%

Collapsed Foam Treatment:

Treatment System: 3-day aerated lagoon

Flow rate: 200 gal/min Volume of tank: 4600 ft³

MST = 15 - 30 minToxicity of influent:

 BOD_5 of influent: 400 mg/l

Treated Whole Mill Effluent:

Flow: 17,000 gal/min pH: 7.0 - 8.02 - 6 min Foam tendency: 30 - 35°C Temperature: Toxicity: Non toxic 130 - 150 mg/1 BOD₅:

mandatory. The screened effluent can be handled by a conventional pumping system. Practical experience suggests that the effluent quality is such that it can be processed by foam separation without sophisticated pretreatment.

2. pH Control

The foam separation process must be operated at pH of > 7 in order to effect detoxification. The pH can be brought to the desired level by lime or caustic. However, if the process is operated at higher pH (above 8), the calcium level must be kept below the concentration where precipitation occurs. In most Canadian mills, effluent pHs are adjusted to 5 with lime prior to discharge. This calcium level has not created operation problems in the pilot plant. To ensure trouble free operation and to minimize detoxification failure, it is recommended that the pH of the effluent should be adjusted with lime to pH 5 - 6 and caustic used for further neutralization.

3. Foam Generation System

a. Foam Separation Tank

Staging of the system is recommended. It permits sequential removal of toxicants and would be beneficial to detoxification. The retention time of the process controls the amount of foam discharged. Short retention times, although reducing the volume of the foam separator, will increase the gas-liquid contact time and increase the

volume of foam drastically. Experimental results indicate that a 3-stage system (1st and 2nd stages for detoxification, 3rd stage for protection) with a retention time of 1 hr (20 min/stage) suits all requirements.

The foam separator should have a closed top with a minimum 3-ft foam height to allow for liquid drainage. Provision should also be made for the installation of a foam breaker on top of the cover. To install the directional jet system, a channel type foam separation tank, semicircular at both ends is preferred. This will allow the plume of the air-liquid mixture (Figure 45) to flow freely in the channel and extend bubble retention in the liquid phase. Transfer of toxicants to the gas-liquid interface would be enhanced.

b. Foam Generator

For the average kraft mill effluent, approximately 20 m²/1 of gasliquid interfacial area is required for toxicity adsorption. The air capacity requirement is minimum with equipment that produces the finest bubbles. However, most fine bubble producing equipment is high in capital and energy costs, therefore, economic factors should be considered in order to decide what bubble size is most suitable. Most of the commercially available equipment can produce bubble sizes in the range of 0.5 - 3 mm. Production of an average 1 mm diameter bubble appears to be a reasonable objective, in terms of energy and economy. Theoretical assessment of various aerators (Chapber VI) suggested that a jet aerator system would be most suitable for producing 1 mm diameter bubbles. A jet aerator system depends on pumps, blowers and a series of jet mixing systems to produce bubbles. The sizes are inversely proportional to the energy input and are affected by the following factors:

| Factor | Controlling Parameters |
|----------------------|--------------------------------------|
| Number of jet units | Gas-liquid interfacial area to be |
| | generated, |
| Blower capacity | Amount of air required, |
| Pumping capacity | Shear force, bubble size and power |
| | consumption, |
| Liquid submergence | Bubble size and gas-liquid contact |
| | time, |
| Geometry of the tank | Pattern of the plume of fine bubbles |
| | and gas-liquid contact. |

The first three factors are interrelated and must be determined for a performance optimum where at economical cost, a maximum gas-liquid interfacial area is produced. For most industrial applications the liquid velocity at the jet outlet (50 ft/sec) is critical for producing fine bubbles; a liquid submergence of 15 ft is considered adequate to promote air dispersion and to provide adequate gas-liquid contact time. Among the various models available the directionally mixed jet aerator system is the preferred design. This system ejects fine bubbles horizontally and retains the bubbles in the liquid for the longest possi-

ble retention time. The bubble sizes produced are small and mixing is complete.

c. Blower Capacity

To produce $20 \text{ m}^2/1$ of gas-liquid interfacial area and using jet aerator systems, the air requirement for bubbles of 1.2 mm diameter is estimated to be 4 times the liquid flow rate. To be conservative the foam separation process should be operated at a G/L of 6. The total air requirement is estimated to be $13,600 \text{ ft}^3/\text{min}$ for a 25 MGD plant.

The pressure drop across the jet (1-in diameter) is negligible.

Only liquid head and friction in the air piping and air header contribute significantly to pressure drop. Conventional centrifugal type air blowers rated at operating pressures of 10 to 15 psi would appear to be suitable.

4. Foam Handling

Based on the results of the pilot plant tests, it is reasonable to assume that 1.2% of the influent will be transformed to foam containing 1.5% of liquid, i.e. not more than 2000 ft³/min of foam will be produced. The foams must be removed, collapsed and treated prior to disposal.

a. Foam Breaking System

To eliminate the installation of an expensive foam scraping system and assuming that the foam does not flow, a foam breaker should be mounted on top of the foam separator. It must pump, collapse and discharge the liquified foam to a treatment system.

Three factors should be considered for selection of a suitable system:

| <u>Factor</u> | Controlling Parameter |
|-------------------|---|
| Suction force | Rate of pumping the foams for contact of blade. |
| Centrifugal force | Stretching the film, create thin spot for foam rupture. |
| Shear force | For rupture of foam film. |

The pilot plant system used to evaluate mechanical foam breakers indicates that a 3-blade, turbine, vaned disc system operating at >2200 cm/sec tip speed is efficient for foam breaking. Foam load and power requirement of a 3-blade turbine were given by (Section V-H-3)

F =
$$(2.6 \times 10^{-3} \text{N} + 7.7 \times 10^{-2} \text{D} - 4.7)$$

where: F = foam load (m³/min)
N = rotation speed (rpm)
D = diameter of turbine (cm)
P = F x (51.7 x 10⁻¹⁷N³D⁵ + 51.2)
P = watts

For commercial installations, a 24-in (62 cm) diameter vaned disc turbine positioned on the top of the foam separator would be most suitable.

Should foaming become excessive and the volume of foam exceed 2%, reflux of foam would be required. Increased foam height is in general effective in promoting foam coalescence, self destruction and reducing the total flow rate. Alternatively, the spacing and position of the foam breaker could be altered to increase the travel distance of foam to the effective suction region. Nevertheless, installation of a fine spray foam recycling system on top of the foam layer would be advisable in the event that foaming became excessively high.

b. Foam Treatment System

The collapsed foam is concentrated in BOD₅, suspended solids, toxicity and is highly foamable. For a 25 MGD plant, collapsed foam is discharged at a rate of 250,000 to 500,000 gal/day. A biological treatment process is preferred because of its high detoxification efficiency and low operating cost. Treated effluents are pumped back to the foam generation tank to protect the system against operation failure.

C. PROPOSAL FOR A 25 MGD FOAM SEPARATION PLANT

A 25 MGD foam separation plant, based on the most up-to-date design data, has been proposed in a recent study (129). The major and auxiliary operating equipment required, the power consumption, and the capital cost estimated for detoxifying typical kraft mill effluent of MST: 3 - 4 hrs are reproduced in Appendices XIX a-d for reference. This system would be installed with a directional jet aerator for foam generation and a turbine for foam breaking. Cost figures were

obtained from equipment suppliers. Figure 50 shows a schematic diagram of the proposed system. Figure 51 shows the layout of the foam generation tank with a jet aerator and a turbine foam breaker. The power requirements and installed capital costs are extracted from Appendix XIX a-d and summarized as follows:

| Process Elements | Capacity | No. Required | HP <u>Total</u> | Cost <u>Installed</u> |
|---|-------------------------------|-----------------|--------------------|--------------------------|
| Pumping Station (A | Appendix XIX-a) | | | |
| Effluent Collection Tank C/W Screen | | 1 | _ | 200,000 |
| Pump | > 5,000 gal/min | 5 | 200 | 250,000 |
| pH_Control_System | (Appendix XIX-b) | | | |
| to | control pH at 7 | 1 | | 200,000 |
| Foam_Separation (| Appendix XIX-c) | | | |
| Foam Tank | 1.23 M Gal | 1 | - | 330,000 |
| Jet Aerator (Directionally mixed) | 24 jets/unit | 12 | _ | 350,000 |
| Recirculation Pum | p 5000 gal/min | 13 | 540 | 200,000 |
| Blower | 4500 ft ³ /min | 3 | 900 | 2.50,000 |
| Foam Treatment (A | ppendix XIX-d) | | • | |
| Foam breaker | $170 \text{ ft}^3/\text{min}$ | 13 | 240 | 180,000 |
| 3 day aerated lagoon | 2.2 M gal | 1 | 45 | 300,000 |
| | | Total | 1,925 | \$ 2,260,000 |

The plant cost is estimated at \$2.3 M with 1925 horsepower requirement. For comparison purposes, the calculation was repeated assuming effluents were twice as toxic (MST:1.5-2 hr) and half as toxic (6-8 hr) as the typical effluent, i.e. MST: 3-4 hr. The corresponding capital costs are estimated at \$3.06M(3365 Hp) and \$1.46 M(1205 hp) respectively.

Figure 50
SCHEMATIC DIAGRAM OF FULLY INTEGRATED FOAM SEPARATION PILOT PLANT

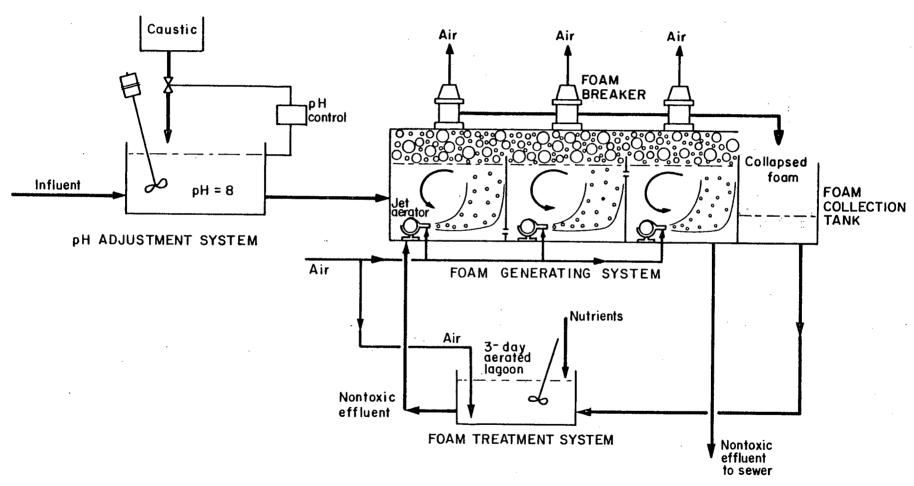
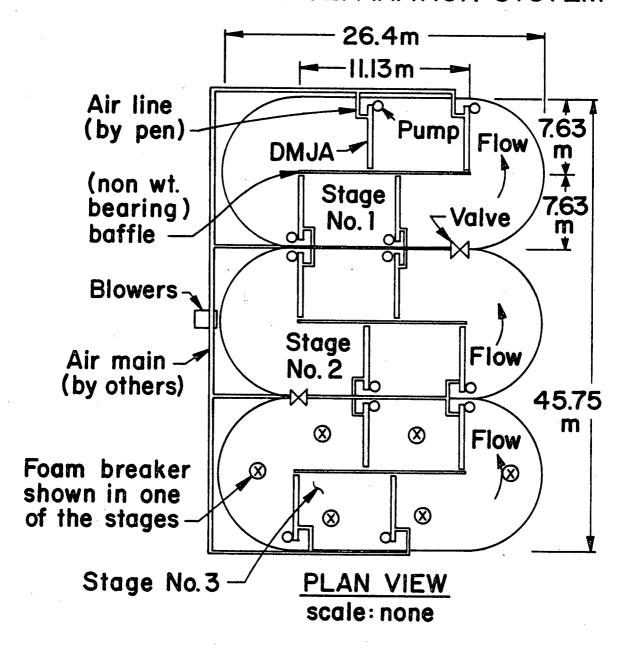


Figure 51 LAYOUT OF FOAM SEPARATION SYSTEM



D. ESTIMATION OF OPERATING COST

| The operating cost of detoxifying of a 3-4 hr MST is estimated as fo | | \$/day |
|---|--------------------------|-------------|
| Plant Cost: \$2,260,000 Capital with 15 years life Capital Recovery factor Taxes and Insurance | 13.5% 3.0% | |
| | 16.5% | 1,021.6 |
| Power Cost* (1¢/Kwh) | | 354.9 |
| Chemical Cost = 1.1¢/100 gal(129) | | 303.0 |
| Maintenance = (5% of capital) | | 51.1 |
| Labor (include overhead = 4 hr/day | at \$16/hr) | 32.0 |
| | Total | 1,762.6 |
| Operating Cost | = \$2.35/ton of pulp (7) | ¢/1000 gal) |

Repeating the same procedure, the operating costs for detoxifying a more toxic effluent (MST:1.5 - 2 hrs) and a less toxic effluent (MST:3-6 hrs) are estimated at \$3.20/ton of pulp (9.6¢/1000 gal) and \$1.66/ton of pulp (5¢/1000 gal) respectively. The operating cost of a foam separation system for detoxifying typical effluent is estimated at \$2.35/ton of pulp or 7¢/1000 gal. The estimated cost is comparable to an aerated lagoon system (\$2.5 - 3.0/ton of pulp) currently widely used for BOD₅ and concurrent toxicity removal.

Table 39 compares the characteristics of the two processes. An aerated lagoon is a biological treatment process, designed primarily

^{*} Power Cost/day = 1985 Hp x 0.745 $\frac{KW}{HP}$ x 24 hr x 1c/KWH

TABLE 39

COMPARISON OF FOAM SEPARATION PROCESS TO AERATED LAGOON PROCESS

| Nature of Process | Aerated Lagoon (Biological) | Foam Separation (Physico-chemical) |
|---|-----------------------------------|------------------------------------|
| | | |
| pH of operation | 7 - 8 | 7 - 8 |
| Retention time | 3 - 5 days | 1 - 2 hr |
| Operating temperature | 10 - 40 C | 10 - 70 C |
| Nutrient requirement | BOD ₅ :N:P= 100:5:1 | None |
| Recovery to shock load | slow | Rapid |
| Simplicity of operation | Simple | Simple |
| Performance BOD ₅ removal Toxicity removal | 60 - 85 % 80 - 100% | 10 - 20 % 90 - 100 % |
| Cost (per ton of pulp) for detoxifying average effluent of 3 - 4 hr MST | \$2.5 - 3.0 | \$2.35* |

For effluents of MST: 1.5 - 2 hrs : Cost = \$3.20/ton of pulp

MST: 6 - 8 hrs : Cost = \$1.66/ton of pulp

to remove 60-80% of BOD_5 , detoxification is a beneficial side effect. The system requires 3-5 days retention time, addition of nutrients and is susceptible to shock load. The success rate of detoxification can reach 80-100% if operated properly.(33). The distinct advantages of a foam separation process, (a physical separation technique) are the short retention requirement (<1 hr), the high success rate of detoxification (90 - 100%), and the rapid recovery from shock loads. However, the process only removes 10-15% of BOD_5 .

Since the cost of this foam detoxification process, (\$2.35/ton) detoxifying effluents of >3 - 4 hr MST is comparable to that of an aerated lagoon process (130), it would appear that for those mills which are not required to remove BOD₅, such as is the case for those located on the coast, foam separation is a suitable process for toxicity removal. For more toxic effluent, cost of foam separation is slightly higher (\$3.20/ton) than an aerated lagoon process. In a situation where land supply is a problem, foam separation still represents a viable salternative.

CHAPTER IX

SUMMARY AND CONCLUSIONS

- 1. The pollutants discharged from a bleached kraft mill consist of numerous organic and inorganic materials. Nevertheless, they can be summarized as:
 - pH inbalance
 - suspended solids
 - Biochemical Oxygen Demand (BOD)
 - toxicity
 - color.

A large number of pulp mills in Canada have already installed neutralization systems, clarifiers, and biological treatment processes for meeting the Federal and Provincial pH, suspended solids and BOD discharge guidelines. The technology for toxicity and color removal are still under development.

2. At present, toxicity removal in the kraft industry relies completely on the proper performance of their biological treatment system (for removal of BOD_5) to achieve concurrent detoxification. Conditions for optimal BOD_5 removal are not necessarily compatible with detoxification; therefore detoxification success rates are not always satisfactory. For coastal mills which are not required to remove the BOD_5 and for mills with land shortage problems, biological treatment pro-

cesses (e.g. 5-day aerated lagoon and 24-hr low rate activated sludge systems) are not suitable. An alternative rapid, reliable detoxification process is desired.

At present, the impact of kraft mill effluent color to the receiving water has not been well established. Removal of color therefore is of low priority.

3. The major toxic compounds in kraft mill effluents are naturally occuring and chlorinated resin acids (up to 8 and 2 mg/l respectively) and unsaturated fatty acids (up to 2 mg/l). Other toxicants include chlorinated lignin, phenolics, alcohols, epoxystearic acids and juvabiones. A typical combined wholemill effluent contains toxicants, 10 - 20 times greater than the lethal concentration of individual compounds.

These toxic materials are mostly organic carboxylic compounds and can be destroyed by chemical or biological means. Several processes e.g. carbon adsorption, chemical flocculation and ozonation have been proposed as alternatives to biological detoxification processes. However, the costs, estimated at \$6 - 20 per ton of pulp, are 2 - 5 times greater than the costs of biological treatment. Thus these processes are not economically viable.

4. The toxicants (mainly carboxylic compounds) are surface active compounds. Surface active compounds are known to reduce surface tension and promote foaming in a solution. Under suitable conditions, they can be separated by foaming as a result of their own surface activity.

Removal of foam should result in removal of toxicity. This hypothesis was verified in a study where a non-active biological treatment system (extreme pH and N_2 aeration) under foaming conditions, detoxified kraft mill effluent to a degree comparable to an active biological system in the laboratory.

Based on these preliminary data and theoretical considerations, a foam separation process was developed as an alternative to existing techniques for detoxification. The feasibility and process parameters were studied in a 4-1 laboratory foaming columns and a 180-1 field site column installation. The results were verified in a 6000 gal capacity 3-stage pilot plant at a B.C. coastal mill.

5. Detoxification by foam separation was investigated on three individual process streams, namely: unbleached white water, acid bleached effluent and caustic extraction effluent plus various combined effluents. Only caustic effluent and its combined effluents were responsive to foam separation treatment. Caustic extraction effluent contained the necessary surfactant and could be used to facilitate detoxification of other effluent streams. However, the proportion of various effluent streams present in the combined effluent was important. For acid bleached effluent, detoxification was effective in the presence of 20 - 35% of caustic effluent. Two synthetic cationic surfactants (quarternary ammonium and amine salts) could replace caustic effluent for collection of toxic materials in unbleached white water.

6. Various combined effluents were assessed in a batch system with variable treatment times, pH and % of total volume treated. The operating conditions required to achieve detoxification are presented as follows:

| Effluent Stream | Treatment Time (hr) | pH Requirement | % Total Effluent Treated |
|---|------------------------|-------------------|-----------------------------|
| Caustix extraction | 17 | 2.5 | 20% |
| Caustic Ext + Acid Bleach effluent | 6 | 9.5 | 50% |
| Caustic Ext + Acid B1. Eff. + U.W.W. | 4 | 9.5 | 67% |
| Combined Wholemill | 0.25 | 9.5 | 100% |

Combined wholemill effluent was selected for all subsequent treatment because of the very short treatment time (0.25 hr) required to effect detoxification. In addition, since 100% of the effluent discharged is treated, the processed effluent may comply with effluent toxicity discharge objectives.

7. Process parameters for detoxification of whole mill effluent were investigated on a large number of samples. For an average effluent, the following conditions were necessary to effect detoxification.

| Process Parameter | Condition |
|-----------------------------|-----------------------|
| pH | >7.0 |
| Temperature | >10°C |
| Column height | >20 cm |
| G/L | 7 - 10 |
| Gas/liquid interfacial area | >20 m ² /1 |

- 8. Results of a continuous study led to several important conclusions.
- a. Gas-liquid ratio, bubble size and aeration rate are interrelated. These factors can vary but will not affect detoxification
 efficiency provided the required gas-liquid interfacial area is produced.
- b. The amount of toxicants present is reflected in the MST value of the effluent. The gas-liquid interfacial area required to effect detoxification is directly proportional to the MST value. On a typical effluent of 250 350 min MST, $20 30 \text{ m}^2/1$ of interfaceial area are required.
- c. A simple mode is recommended for normal operation of the foam detoxification unit. If foaming becomes excessive, an enrichment mode with its built-in foam reflux system is preferred. A stripping mode is not suitable due to large volumes of foam production.
- d. Detoxification by foam separation is concentration dependent. Therefore staging will be beneficial to toxicity removal. A 2-stage system detoxified 91% of a large number of samples compared to 63% with a single stage system.
- 9. The effect of variability in effluent characteristics on foam detoxification was studied on 205 samples obtained from 10 Canadian kraft mills. Under the established foam separation conditions, 170 (80%) samples were detoxified regardless of effluent variation. The treatment time required could be expressed by:

 $Y = 41.84 \text{ X}^{-0.71}$ where Y = treatment time X = effluent MST

The results suggest that foam separation of toxicity from kraft mill effluent is a process universally applicable to the bleached kraft industry.

- 10. A 180-1 capacity column, operated for 3 months in field site, consistently and reliably detoxified the effluents. At G/Ls of 33 48 and 1.6 to 2.1 hr of retention time, 100% of the samples were detoxified. Under sub-optimal operation (G/Ls of 8 12 and 1 hr retention time) 65 75% of the effluents were detoxified.
- 11. Investigation of the detoxification mechanism on twenty different samples obtained from three mills showed that foam fractionation accounted for 77.5% toxicity removal; volatilization for 5.4% and unknown mechanisms for 17.1%.
- 12. Foam separation of toxicity can be combined with removal of fibrous suspended solids. The most suitable system for a combined process is the dissolved air flotation system. Laboratory studies indicate that suspended solids could be reduced from 450 mg/l to less than 55 mg/l (88% removal) in one pressurization cycle operating at 40 psig; complete detoxification of typical effluents of MST values of 5 6 hr was achieved after 2 3 repressurization cycles. However, treatment costs are not economically justifiable.

Dispersed air foam generating systems were less effective in removing suspended solids. Under conditions which provided for complete detoxification, only 19-62% of fibrous suspended solids could be

removed; the residual suspended solid level in treated effluents, however, still exceeded 90 mg/1.

The foam separation process also removed 66% of resin acids, 12% of BOD_5 (10% TOC), 8% of color and 80% of the foaming tendency.

13. Foam separation of toxicity yields foam as a by-product. A single stage process produces about 4 - 5% of the effluent volume as foam. The foam volume which must be removed depends on the operation mode of the system. However, effluents with higher toxicity, require greater volumes of foam removal for detoxification. The volume of foam can effectively be reduced to less than 1 - 2% by increasing the foam height in the foaming column, improving internal reflux, or by recycling collapsed foam to the foaming column.

The foam, is enriched in BOD_5 and toxicity. BOD_5 of the foam ranged from 214 - 450 mg/1; toxicity MST values from 13 - 192 min. The enrichment ratio is 1.2 and 8 respectively. Treatment by a 3-day retention aerated lagoon and by a 4-hr retention time rotating biological disc system detoxified the collapsed foam. Chemical treatment by precipitation did not remove toxicity.

14. Commercially available foam generating and foam collapsing equipment were evaluated for a proposed application to a 25 MGD (750 tpd) plant.

a. Foam Generation

Five categories of foam generation equipment were assessed:

- forced air diffusion system hydraulic shear aerator
- surface aerator
 high pressure aerator.
- mechanical shear aerator

A jet aeration system (hydraulic shear aerator) is recommended. It is simple to operate, easy to maintain and economical to use. The bubble sizes produced are approximately 1.2 mm in diameter and remain in contact with the solution for a long time.

b. Foam Collapsing

With regard to foam collapsing, the following systems were assessed:

- air jetliquid spray
- sonic pressure
 orivice foam breaker
- thermal treatment mechanical forces.

In view of the copious quantities of foam produced from kraft mill effluents foam collapsing by mechanical forces such as impact, compression and shear forces would be most suitable. Commercial systems which are being successfully applied, and are available in the market are of the centrifugal-turbine type. They are widely applied for foam control in the fermentation and the pulp and paper industry. The foam breaking

capacity and power consumption can be predicted by the following relationships established during this study:

Foam breaking capacity:
$$F = 2.6 \times 10^{-3} \text{N} + 7.7 \times 10^{-2} \text{D} - 4.7$$

Power consumption: $\frac{P}{F} = 51.7 \times 10^{-17} \text{N}^3 \text{D}^5 + 51.2$

where N = rpm

F = foam breaking capacity (m³/min)

D = turbine diameter (cm)

p = power (watts)

15. A pilot plant study was undertaken to assess operational reliability. A jet aerator system and a turbine system were installed in a 6000 gal capacity foam generation tank, processing 80 - 100 gal/min of mill A combined effluent. The system was operated over 4 months as a 1, 2 and 3 stage system. The gas-liquid interfacial area generated was kept constant at $5 - 7 \text{ m}^2/\text{L}$ (G/L = 1).

The jet aerator produced a copious amount of fine bubbles consistently and reliably. With an influent toxicity of 2.5 - 6 hr MST, the gas-liquid interfacial area provided resulted in a detoxification success rate of 50, 86 and 100% as the number of operational stages increased from 1 to 2 and then to 3 stages. The foam was highly concentrated in toxic materials, its MST ranged from 15 to 20 min.

During the process of detoxification, a 3 blade, 12-in diameter vaned disc turbine (1800 rpm, 300 cm/sec tip speed) reliably collapsed up to 42 ft³/min of foam over 8 months of continuous operation. Fibres collected in the foam did not cause operational problems.

- 16. A 25 MGD fully integrated foam separation plant consisting of foam generation, foam collapsing and foam disposal was designed and the operating equipment selected. Capital cost installed and operating costs were estimated to be \$2.3 M and \$2.35/ton of pulp. The cost is comparable to that of an aerated lagoon process and lower than the high rate biological processes.
- 17. It is concluded that for those mills located in coastal locations where BOD_5 removal from the effluent is not required and for those mills which have a land shortage problem, foam separation is a viable alternative detoxification process to the existing biological treatment systems.

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APPENDIX I EFFLUENT COMPOSITION VS pH REQUIREMENT FOR DETOXIFICATION

| Efflu Composi | | MST of Untreated Sample | MST of E | ited | |
|------------------|------|----------------------------|---------------|--------|---------------|
| Caustic | Acid | (hr) | рН 2.5 | pH 7.0 | pH 9.5 |
| 100 | 0 | 1.4 | *80% Survival | 2.2 | 1.0 |
| 80 | 20 | 2.2 | 72 | 4.2 | 2.4 |
| 67 | 33 | 0.3 | <24 | 4.6 | 4.9 |
| 50 | 50 | 0.3 | 5.7 | 24 | 24 |
| 33 | 67 | 1.7 | 4.2 | 24 | *80% survival |
| 20 | 80 | 2.7 | 3.7 | 24 | NT** |
| 0 | 100 | 1.7 | 6.3 | 24 | 24 |

 $^{^{\}star}$ MST value cannot be obtained because over 50% of fish survived after 96 hrs exposure.

^{**} NT = Not toxic.

APPENDIX II

TOXICITY OF SELECTED CATIONIC SURFACTANTS TO FISH AT 50 ppm CONCENTRATION

Toxic Non-toxic *

1-Hexadecylpyridinium Chloride Hexadecyl trimethyl Ammoniumbromide

Ethomeen S/20 Benzylhexadecyldimethyl Ammonium Chloride

Arquad 2HT-75 Ethomeen C/25

Dehyquart CDB Amine T.

Hyamine 2389 Variquat 450

Roccal MC-14

Ammonyx1 T

^{*} The surfactants are considered non-toxic at test concentration when over 80% of the fish survived after 96 hrs exposure.

APPENDIX III

CORRELATION BETWEEN INITIAL TOXICITY AND GAS-LIQUID INTERFACIAL AREA REQUIRED FOR DETOXIFICATION

| | | | • |
|------------------------------|---------------------|--|---|
| Treatment Time (hr) | No. of Samples | Initial MST, min (mean±S.D.) | Interfacial Area Required for Detoxification* (m ² /1) |
| MILL E | | · | |
| 0.50 3.00 4.00 4.50 | 1 7 3 9 | 255 147± 97 40± 10 33± 22 | 22.5 135.0 180.0 202.5 |
| | | | |
| MILL F | | | |
| 0.25 0.50 1.00 2.00 | 28 4 10 17 | 265±177 257±156 150± 79 110± 65 | 11.25 22.50 45.00 90.00 |
| | | | |
| MILL G | | | |
| 0.25 0.50 1.00 2.00 | 7 7 4 4 | 309±111 281±230 217±176 53± 21 | 11.25 22.50 45.00 90.00 |
| | | | |
| MILL H | | | |
| 2.00 3.00 4.00 | 6 6 5 | 538±299 343±132 283±175 | 90.00 135.00 180.00 |

^{*} Air dispersion system: sintered glass 45 μ pore size

average bubble diameter, 1.5 mm

APPENDIX IV-a
OPERATING DATA OF A SINGLE STAGE CONTINUOUS FOAM SEPARATION SYSTEM

Volume: 180 litres, Four 1' length, 3" Diameter Ceramic tubes,

Pore size: < 25 μ

| Day of | Tre | atment Condition | າຣ | | Toxicity | Foam Volume |
|--------------------|-------------------|---------------------------|------------|----------------------|--|-----------------------------------|
| Operation | pН | Retention time (hr) | G/L | Influent* (MST, min) | Treated effluent (% Survival in 65% effluent over 96 hr) | (% of Influent converted to foam) |
| Nov. | | | | 700 | 00 | 0.7 |
| 1 | 8.8 | 1.0 | 8 | 702 | 80 | 2.7 |
| 4 | 9.6 | 1.0 | 9 | 120 | 90 | 7.7 |
| 5 | 8.3 | 1.2 | 9 | _ | 100 | 8.01 |
| 7 | _ | _ | - | 300 | 100 | - |
| 8 | 9.2 | 0.97 | 7 | 150 | 0 | 7.01 |
| 9 | 10.0 | 0.97 | 7 | 252 | 100 | 3.6 |
| 10 | 9.4 | 1.0 | 9 | 48 | 0 | 10.7 |
| 11 | 8.1 | 0.8 | 8 | 192 | 60 | 8.5 |
| Range Mean ± SD | 8.1 - 10 9±0.7 | 0.8 - 1.0 0.97 ±008 | 7-9 8±1 | 48-702 252±215 | 0-100 | 2.7 - 10.2 6.8±2.7 |

 $^{^{*}}$ 50% of fish were killed at the specific mean survival time indicated

APPENDIX IV-b
OPERATING DATA OF A 2 STAGE CONTINUOUS FOAM SEPARATION SYSTEM

Volume: 180 litres each, Four 1' Length 3" Diameter Ceramic Tubes,

Pore Size: <25 μ

| | Tre | atment Con | ditions | | Toxicity | Toxicity Treated Effluent | | Foam Volume (% of influent | |
|---------------------|---------|------------|----------------------------------|------------------|-----------|---------------------------|------------------|-------------------------------|--|
| Day of Operation | pН | G/L | Total | Influent | | n 65% effluent | converted 1st | to foam) 2nd | |
| | • | · | Retention _* Time (hr) | MST (min) | 1st Stage | 2nd Stage | Stage | Stage | |
| Dec. | | | | | | | | | |
| 6 | 6.0 | 9.4 | 0.88 | 600 | 40 | 100 | _ | _ | |
| 7 | 8.0 | 7.3 | 0.85 | 402 | 10 | 100 | - | - | |
| 8 | 8.0 | 7.3 | 0.85 | 300 | 0 | 100 | - | _ | |
| 9 | 8.0 | 9.5 | 0.92 | _ | - | - | _ | - | |
| 10 | 8.0 | 9.5 | 0.92 | 180 | 0 | 70 | - | - | |
| 11 | 8.1 | 8.2 | 0.95 | 300 | 0 | 100 | 2.5 | 0.8 | |
| 12 | 8.0 | 8.8 | 0.90 | 350 | 20 | 100 | 2.8 | 0.7 | |
| 13 | 8.0 | 7.6 | 0.80 | 210 | 0 | 100 | 5.2 | 1.7 | |
| 14 | 8.0 | 8.6 | 0.83 | 252 | 0 | 100 | - | - | |
| 15 | 8.0 | 10.8 | 1.15 | 300 | 10 | 80 | 3.9 | 0.9 | |
| 16 | 8.2 | 10.6 | 1.33 | 220 [.] | 0 | 100 | 2.5 | 0.3 | |
| 17 | 8.8 | 11.4 | 1.10 | 120 | 0 | 100 | - | _ | |
| 18 | 8.0 | 11.0 | 1.17 | - | - | 100 | 4.7 | 1.0 | |
| 19 | 8.0 | 9.2 | 0.96 | 240 | 30 | 100 | 3.1 | 0.9 | |
| 20 | 8.0 | 10.0 | 0.98 | 192 | 0 | 100 | 5.0 | 1.1 | |
| Range | 6.0-8.8 | 7.3-11.4 | 0.80-1.17 | 120-600 | 0-40 | 70-100 | 2.5-5.2 | 0.3-1.7 | |
| Mean ± SD | 8.0±0.6 | 9.3± 1.3 | 0.97±0.14 | 277±125 | _ | - | 3.7±1.1 | 0.9±0.4 | |

Retention time and G/L in each stage is 50% of the total.

 $^{^{\}star\star}$ 50% of fish were killed at the specific mean survival time indicated.

APPENDIX V (a)

DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT

FROM MILL A BY FOAM SEPARATION

| Date | Treatment | Toxicity in Concentratio | | % of Fish | *Treated Effluent |
|------------|--------------|-----------------------------|--------------------|--|--------------------------------|
| | Time (hr) | Before Treatment | After Treatment | Survived in65% Effluent over 96 hr | Meets Toxicity Standards |
| July | | | | | |
| 24 | 0.25 | 1440 | NT | 100 | Yes |
| 25 | 0.25 | 90 | 1440 | 100 | Yes |
| 27 | 0.25 | 480 | NT | 100 | Yes |
| 28 | 0.25 | 600 | NT | 100 | Yes |
| 30 | 0.25 | 450 | NT | 100 | Yes |
| - | 0.25 | 450 | NT | 100 | Yes |
| _ | 0.25 | 720 | NT | 100 | Yes |
| August | | | | | |
| 18 | 0.25 | 420 | NT | 100 | Yes |
| Range | - | 90 - 1440 | 1440-NT | - | - |
| Mean ± S D | 0.25 | 581 ± 390 | - | 100 | - |

 $[\]mbox{\ensuremath{\star}}$ Federal toxicity standard is met when over 80% of fish survived in 65% effluent over 96 hrs.

APPENDIX V (b)

DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT

FROM MILL B BY FOAM SEPARATION

| Date | Treatment | Toxicity of 100% Test Cond | Effluent in c.(MST:min) | % of Fish Survived in | * Treated Effluent |
|----------------|--------------|-------------------------------|-------------------------|----------------------------|-------------------------------|
| <u> </u> | Time (hr) | Initial (min) | Final (min) | 65% Effluent over 96 hr | Meets Toxicity Standard |
| <u>October</u> | | | | | |
| 31 | 1.5 | 1440 | NT | 100 | Yes |
| 25 | 1.5 | 1080 | NT | 100 | Yes |
| 29 | 1.5 | 150 | NT | 100 | Yes |
| November | | | | | |
| 5 | 3 | 600 | NT | 100 | Yes |
| 6 | 0.5 | 420 | NT | 100 | Yes |
| 8 | 0.5 | 360 | NT · | 100 | Yes |
| 9 | 0.5 | 600 | NT | 100 | Yes |
| 12 | 3 | 30 | NT | 100 | Yes |
| 13 | 3 | 1320 | 1440 | 100 | Yes |
| 15 | 0.5 | 1440 | NT | 100 | Yes |
| 18 | 3 | 600 | 1200 | 80 | Yes |
| 19 | 1 . | 420 | NT | 100 | Yes |
| 20 | 3 | 120 | 1080 | 0 | No |
| 21 | 0.5 | 500 | NT | 100 | Yes |
| 22 | 3 | 270 | 1080 | 20 | No |
| 25 | 3 | 330 | 1200 | 70 | No |
| 26 | 3 | 300 | 1080 . | 80 | Yes |
| 27 | 1 | 600 | NT | 100 | Yes |
| Range | 0.5 - 3 | 30 - 1440 | 1200-NT | 0 - 100 | - |
| Mean ± SD | 1.9 ± 1.2 | 588 ± 442 | - | - | - |

^{*} Federal toxicity standard is met when over 80% of fish survived in 65% effluent over 96 hrs.

APPENDIX V (c)

DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT

FROM MILL C BY FOAM SEPARATION

| Date | Treatment | Toxicity of 100% Test Con | |
|--------------|-----------|---------------------------|-----------|
| Date | Time | Before | After |
| | (hr) | Treatment | Treatment |
| Jan. | | | |
| 16 | 1 | 240 | NT |
| 17 | 3 | 60 | NT |
| 18 | 3 | 150 | NT |
| 19 | 3 | 30 | NT |
| 24 | 3 | 30 | NT |
| 26 | 3 | 40 | 500 |
| 29 | 3 | 25 | 600 |
| 30 | 3 | 15 | NT |
| 31 | 3 | 60 | NT |
| <u>Feb</u> . | | | |
| 1 | 2 | 105 | NT |
| 2. | 3 | 75 | 1200 |
| 5 | 2 | 90 | NT |
| 6 | 2 | 100 | NT |
| 7 | 2 | 120 | NT |
| 8 | 2 | 165 | NT |
| 9 | 2 | 90 | NT · |
| 12 | 3 | 65 | NT |
| 13 | 3 | 65 | NT |
| 14 | 3 | 105 | NT |
| Range | 1 - 3 | 15 - 240 | 500-NT |
| Mean ± S D | 2.5 ± 0.5 | 86 ± 55 | - |

APPENDIX V (d)

DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT

FROM MILL D BY FOAM SEPARATION

| Date | Treatment | | of Effluent in Conc.(MST:min) |
|------------|--------------|---------------------|-------------------------------|
| | Time (hr) | Before Treatment | After Treatment |
| May | · | | |
| 9 | 1 | 240 | NT |
| 10 | 1 | 180 | NT |
| 14 | 1 | 240 | NT |
| 15 | 2 | 405 | NT |
| 16 | 2 | 140 | 1080 |
| 18 | 2 | 255 | 702 |
| 22 | 2 | 105 | NT |
| 23 | 2 | 100 | NT |
| 24 | 1 | 120 | NT |
| 25 | 1 | 75 | NT |
| 28 | . 2 | 20 | 195 |
| . 29 | 2 | 65 | 720 |
| 30 | 2 | 120 | 1080 |
| 31 | 2 | 15 | NT |
| June | | | |
| 1 | 1 | 150 | NT |
| 4 | 2 | · 45 | NT |
| 5 | 0.25 | 240 | NT |
| 6 | 2 | 40 | 1080 |
| 7 | 2 | 150 | 1080 |
| 11 | 2 | 90 | NT |
| Range | 0.25 - 2 | 20 - 405 | 195 - NT |
| Mean ± S D | 1.5 ± 0.5 | 140 ± 97 | _ |

APPENDIX V (e)

DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT

FROM MILL E BY FOAM SEPARATION

| Date | Treatment Time | Toxicity of Ef | fluent in .(MST:min) |
|--------------|-------------------|---------------------|----------------------|
| | (hr) | Before Treatment | After Treatment |
| Jan. | | | |
| 16 | 4.5 | 45 | NT |
| 17 | 4 | 30 | NT |
| 18 | 4 | 50 | NT |
| 19 | 4.5 | 45 | NT |
| 22 | 4 | 40 | NT |
| 25 | 4.5 | 20 | NT |
| 26 | 4.5 | 15 | NT |
| 29 | 4.5 | 15 | NT |
| 30 | 3 | 360 | NT |
| 31 | 3 | 140 | NT |
| <u>Feb</u> . | | | |
| 1 | 3 | 120 | NT |
| 2 | 3 | 105 | NT |
| 5 | 3 | 75 | NT |
| 7 | 3 | 90 | NT |
| 8 | 4.5 | 70 | 1200 |
| 9 | 4.5 | 60 | 1200 |
| 12 | 3 | 140 | NT |
| 13 | 0.5 | 255 | NT |
| 14 | 4.5 | 10 | 1080 |
| 15 | 4.5 | 20 | 1080 |
| Range | 0.5 - 4.5 | 10 - 360 | 1080 - NT |
| Mean ± S D | 3.5 ± 1.0 | 74 ± 79 | - |

 $\frac{\text{APPENDIX V (f)}}{\text{DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT}}$ FROM MILL F BY FOAM SEPARATION

| Date | | Treatment Time | Toxicity | (MST) |
|----------|----------|-------------------|---------------|-------------|
| | | (hr) | Initial (min) | Final (min) |
| February | 3 | 0.5 | 250 | NT |
| | 11 | 2 | 30 | NT |
| | 12 | 2 | 95 | NT |
| | 15 | 2 | 95 | 1200 |
| | 17 | 1 | 250 | NT |
| | 18 | 1 | 80 | NT |
| | 19 | 2 | 50 | NT |
| | 20 | 1 | 65 | NT |
| | 21 | 2 | 75 | NT |
| | 22 | . 2 | 80 | NT |
| | 24 | 2 | 150 | 1320 |
| | 25 | 1 | 150 | NT |
| | 28 | 1 | 135 | NT |
| March | 1 | 0.5 | 150 | N/T |
| | 7 | 1 | 120 | NT NT |
| May | 8 | 0.25 | 840 | NT |
| | 9 | 0.25 | 1080 | NT |
| | 11 | 0.25 | NT | NT |
| | 14 | 0.25 | 300 | NT |
| | 15 | 0.25 | 120 | NT |
| | 16 | 0.25 | 270 | NT |
| | 17 | 0.25 | 255 | NT |
| | 18 | 0.25 | 240 | NT |
| | 19 | 0.25 | 240 | NT |
| | 21 | 0.25 | 150 | NT |
| | 22 | 0.25 | 180 | NT |
| | 23 | 0.25 | 540 | NT |
| | 24 | 0.25 | 150 | NT |
| | 26 | 0.25 | 300 | NT |
| | 28 | 0.25 | 60 | NT |
| | 29 | 2 | 110 | 1440 |
| | 30 | 1 | 210 | NT |
| | 31 | 2 | 200 | 1320 |
| June | 2 | 2 | 90 | 1320 |
| | 4 | 0.25 | 240 | NT |
| | 5 | 0.25 | 120 | NT |
| | 6 | 0.25 | 30 | NT |
| | 7 | 0.5 | 150 | NT |
| | 8 | 1 | 100 | NT |
| | 9 | 0.25 | 30 | NT |
| | 11 | 2 | 60 | 1440 |
| | 12 | 2 | 45 | NT |
| | 13 | 2 | 50 | NT |
| | 19 | 0.25 | 240 | NT |
| July | 11 12 | 2 | 240 | 1440 |
| | 13 | 0.25 | 240 | NT |
| | 13 | 0.25 | 360 | NT |
| | 15 | 0.25 | 180 | NT |
| | 16 | 2 | 240 | 1440 |
| | 16 | 0.5 | 480 | NT |
| | 18 | 0.25 | 150 | NT |
| | 18 | 0.25 | 390 | NT |
| | 20 | 0.25 | 180 | NT |
| | 21 | 0.25 | NT | NT |
| | 22 | 0.25 | 1440 | NT |
| | 22 23 | 2 0 25 | 150 | 360 |
| | 24 | 0.25 | 360 | NT |
| | 24 25 | 0.25 0.25 | 210 540 | NT NT |
| October | 1 | . 0.25 | 450 | NT |
| | 4 | 0.25 | 1440 | NT |
| | 11 | 1 | 300 | NT |
| | 16 | 2 | 120 | 1080 |
| Range | 17 | 1 | 90 | NT |
| RATIO A | | 0.25 - 2 | 1440 - NT | 360 - NT |

APPENDIX V (g)

DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT
FROM MILL G BY FOAM SEPARATION

| Date | | Treatment 100% Test (| | Effluent in onc. (MST:min) | % of Fish Survival in | Treated Effluent Meets |
|-------|----|-----------------------|---------------------|----------------------------|----------------------------|---------------------------------|
| | | Time (hr) | Before Treatment | After Treatment | 65% Effluent over 96 hr | Federal Toxicity Standard |
| May: | 14 | 1 | -120 | NT | 100 | Yes |
| | 15 | 0.25 | 450 | NT | 100 | Yes |
| | 17 | 1 | 480 | NT | 100 | Yes |
| | 18 | 1 | 150 | NT | 100 | Yes |
| | 22 | 1 | 120 | NT | 100 | Yes |
| | 23 | 0.25 | 420 | NT | 100 | Yes |
| | 24 | 0.50 | 105 | NT | 100 | Yes |
| | 25 | 0.50 | 120 | NT | 100 | Yes |
| | 28 | 0.50 | 420 | NT | 100 | Yes |
| | 29 | 0.50 | 90 | NT | 100 | Yes |
| | 30 | 0.25 | 220 | NT | 100 | Yes |
| | 31 | 0.50 | 720 | NT | 100 | Yes |
| June: | 1 | 0.25 | 210 | NT | 100 | Yes |
| | 4 | 0.50 | 180 | NT | 100 | Yes |
| | 5 | 0.25 | 390 | NT | 100 | Yes |
| | 6 | 0.50 | 330 | NT | ` 100 | Yes |
| | 7 | 0.25 | 290 | NT | 100 | Yes |
| | 8 | 0.25 | 180 | NT | 100 | Yes |
| Nov: | 15 | 2 | 100 | NT | 100 | Yes |
| | 16 | 2 | 80 | NT | 100 | Yes |
| | 19 | 2 | 40 | NT | 100 | Yes |
| | 21 | 2 | 40 | NT | 100 | Yes |
| Range | | 0.25-2.0 | 40-720 | - | - | - |
| Mean | | 0.76±0.58 | 252±179 | - | - | - |

 $[\]star$ Federal toxicity standard is met when over 80% of fish survived in 65% effluent over 96 hrs.

APPENDIX V (h)

DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT

FROM MILL H BY FOAM SEPARATION

| Date Treatment Time (hr) | | Toxicity of Effluent in 100%Test Conc.(MST:min) Before After Treatment Treatment | | |
|--------------------------|----------------|---|-----------|--|
| Jan. | | | | |
| 23 | 5 | 35 | 1440 | |
| 24 | 5 | 30 | 1440 | |
| 25 | 4 | 375 | NT | |
| <u>Feb</u> . | | | NT | |
| 1 | 4 | 360 | NT | |
| 2 | 4 | 480 | NT | |
| 5 | 3 | 180 | NT | |
| 6 | 3 | 300 | NT | |
| 7 | 2 | 1080 | NT | |
| 8 | 3 | 540 | NT | |
| 9 | 2 | 600 | NT | |
| 12 | 2 | 540 | NT | |
| 13 | 2 | 360 | NT | |
| 14 | 2. | 210 | NT | |
| 15 | 2 | 435 | NT | |
| 16 | 3 | 435 | NT | |
| 21 | 4 | 70 | NT | |
| 22 | 4 | 130 | NT | |
| 23 | 3 | 360 | NT | |
| 26 | 3 | 240 | NT | |
| Range Mean ± SD | 2 - 5 3 ± 1 | 30 - 1080 357 ± 246 | 1440 - NT | |

APPENDIX V (i)
DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT
FROM MILL I BY FOAM SEPARATION

| Date | Treatment Time (hr) | Toxicity of 100% Test Co Before Treatment | Effluent in onc.(MST:min) After Treatment | % of Fish Survival in 65% Effluent over 96 hr | *Treated Effluent Meets Federal Toxicity Standard |
|-----------|---------------------------|--|--|--|---|
| Nov. | 2 | 150 | NT | 100 | yes |
| 28 | 2 | 150 | NT | 100 | yes |
| 29. | 2 | 150 | NT | 100 | yes |
| Dec. | | | | | |
| 3 | 2 | - 30 | NT | 100 | yes |
| . 4 | 2 | 90 | NT | 100 | yes |
| 5 | 2 | . 60 | NT | 100 | yes |
| 6 | 2 | . 75 | NT | 100 | yes |
| 10 | 2 | 105 | NT | 100 | yes |
| 11 | 2 | 75 | NT | 100 | yes |
| 18 | 2 | 75 | NT | 100 | yes |
| 19 | 2 | 240 | NT | 100 | yes |
| Range | _ | 30-240 | _ | <u>-</u> | |
| Mean ± SD | - | 105± 60 | | _ | - |

Federal toxicity standard is met when over 80% of fish survived in 65% effluent over 96 hrs.

APPENDIX IV (j) DETOCIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT FROM MILL J BY FOAM SEPARATION

| Date | Treatment Time (hr) | | Effluent in onc.(MST:min) After Treatment | % of Fish Survival in 65% Effluent over 96 hr | *Treated Effluent Meets Federal Toxicity Standard |
|------------|---------------------------|---------|---|--|---|
| Nov | | | | | |
| 28 | 1 | 600 | NT | 100 | yes |
| 30 | 3 | 180 | NT | 100 | yes |
| <u>Dec</u> | | | | | |
| 3 | 5 | 4 | 1080 | 0 | yes |
| 4 | 3 | 5 | NT | 100 | no |
| 5 | 3 | 5 | 1440 | 80 | yes |
| 18 | 1 | 210 | NT | 100 | yes |
| 19 | 1 | 240 | NT | 100 | yes |
| 20 | 1 | 360 | NT | 100 | yes |
| Range | 1-5 | 4-600 | 1080-NT | 0-100 | - |
| Mean±SD | 2±2 | 201±209 | | - | |

^{*} Federal toxicity standard is met when over 80% of fish survived in 65% effluent over 96 hr

APPENDIX VI(a)

CONTINUOUS DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENTS BY FOAM SEPARATION IN A SINGLE STAGE SYSTEM (With Seven 5" Diameter 65µ pore size Plastic Air Diffusers in a 180-1 column)

| | | Treatmen | t Conditions | | | | Toxicity of | Effluent |
|----------------|---------|---------------------|------------------------|-------|------------------------|---------------------|-------------------------------------|---------------------|
| Date (June) | рН | Gas Flow (1/min) | Liquid Flow (1/min) | G/L | Retention Time (hr) | Before Treatment | After Trea % of Fish Survived in | Meets Federal Toxi- |
| | | | | | | TI Cacment | 65%Effluent over 96hr | city Standard |
| | | : | | | | | | |
| 14 | 8.5 | 39 | 1.55 | 25.8 | 1.92 | 250 | 100 | yes |
| 15 | 8.0 | 39 | 1.50 | 26.6 | 1.97 | 60 | 100 | yes |
| 16 | _ | 60 | · <u>-</u> | _ | - | 60 | 100 | yes |
| 18 | 8.0 | 60 | 1.65 | 36.4 | 1.80 | 160 | 100 | yes |
| 19 | 8.2 | 59 | 1.60 | 36.2 | 1.83 | 150 | 100 | yes |
| 20 | 8.0 | 79 | 1.60 | 48.2 | 1.83 | 516 | 100 | yes . |
| 21 | 8.4 | 80 | 0.80 | 98.0 | 3.66 | 100 | 100 | yes |
| 22 | - | | - | - | - | 720 | 100 | yes |
| 23 | 8.0 | _ | 1.40 | - | 2.10 | 90 | 100 | yes |
| 24 | 8.0 | 80 | 2.05 | 39.0 | 1.45 | 210 | 100 | yes |
| 25 | 8.0 | 80 | 1.20 | 66.5 | 2.47 | 75 | 100 | yes |
| 26 | 8.0 | 80 | 1.40 | 57.0 | 2.10 | 120 | 100 | yes |
| | | <u>.</u> | | | | | | |
| Range | 8.0-8.5 | 39-80 | 0.8-2.05 | 25-98 | 1.45-3.66 | 60-720 | 100 | - |
| Mean±S D | 8.1±0.2 | 65±16 | 1.5±0.3 | 48±23 | 2.1 ±0.6 | 210±205 | 100 | _ |

APPENDIX VI(a) Continued

CONTINUOUS DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENTS BY FOAM SEPARATION IN A SINGLE STAGE SYSTEM

(With Seven 5" Diameter 65µ Pore Size Plastic Air Diffusers in a 180-1 column)

| | | Trea | tment Condit | ions | | | Toxicity of | Effluent |
|----------------|-----------------|---------------------|------------------------|-----------|------------------------|---------------------|---|---------------------|
| Date (July) | _. рН | Gas Flow (1/min) | Liquid Flow (1/min) | G/L | Retention Time (hr) | Béfore Treatment | After Treat % of Fish Survived in 65%Effluent over 96hr | Meets Federal Toxi- |
| 11 | 8.0 | 60 | 1.90 | 31.8 | 1.53 | 120 | 100 | Yes |
| 12 | 8.0 | 60 | 1.80 | 33.2 | 1.62 | 330 | 90 | Yes |
| 13 | 8.0 | 59 | 1,80 | 33.3 | 1,62 | 120 | 100 | Yes |
| 14 | 8.0 | 60 | 1,90 | 31.8 | 1.53 | 220 | 100 | Yes |
| 15 | 8.0 | 61 | 1.85 | 32,4 | 1.58 | 576 | 100 | Yes |
| 16 | 8.5 | 60 | 1.85 | 32.4 | 1.58 | 220 | 100 | Yes |
| 17 | 8.0 | 60 | 1,85 | 32.4 | 1.58 | 100 | 90 | Yes |
| 18 | 8.0 | 60 | 1.84 | 32.8 | 1.58 | 282 | 100 . | Yes |
| 19 | 8.0 | 60 | 1.80 | 33.4 | 1.62 | 260 | 80 | Yes |
| 20 | 8.5 | 60 | 1.80 | 33.4 | 1.62 | 132 | 80 | Yes |
| 21 | 8.0 | 64 | 1.76 | 35.8 | 1.65 | 1000 | 90 | Yes |
| 22 | 8.0 | 60 | 1.75 | 34.0 | 1.67 | _ | 100 | Yes |
| 23 | 8.0 | - | 1.80 | - | 1.62 | 350 | - | - |
| 24 | 8.0 | 60 | 1.60 | 37.5 | 1.83 | 360 | .100 | Yes |
| 25 | 8.0 | 60 | 1,80 | 33.3 | . 1.62 | 180 | 100 | Yes |
| 26 | 8.0 | 60 | 1.90 | 31.5 | 1.53 | 120 | 100 | Yes |
| 27 | 8 0 | 60 | 1.60 | 33.3 | 1.62 | - | 100 | Yes |
| Range | 8.0 -8.5 | 5964 | 1.60-1.90 | 31,5-37.5 | 7.53-1.83 | 102-1000 | 80 - 100 | 4.0 |
| Mean±S D. | 8.05±0.16 | 60.25± 1.06 | 1.80±0.08 | 33 ± 1.5 | 1.60±0.07 | 294± 238 | - | ~ |

APPENDIX VI(b)

CONTINUOUS DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENT BY FOAM SEPARATION IN A SINGLE STACE SYSTEM

(With Four 5" Diameter 25µ Pore Size Plastic Diffusers in a 180-1 column)

| | | | Treatment Cond | itions | | | Toxicity of | Effluent |
|-----------|----------|---------------------|---------------------|-----------|------------------------|---------------------|--|---------------------------------------|
| | | | | | | | After Tro | eatment |
| Date | pfl | Gas Flow (1/min) | Liquid Flow (1/min) | G/L | Retention Time (hr) | Before Treatment | % of Fish Sur- vived in 65% Effluent over96h | Meets Federal Toxicity Standard |
| Aug. | | | | | | | | |
| 23 | 8.0 | 60 | 2.9 | 10.4 | 1.00 | 180 | 90 | Yes |
| 24 | 8.0 | 60 | 2.9 | 10.4 | 1.00 | 1080 | 100 | Yes |
| 25 | 8.0 | 60 | 2.9 | 10.4 | 1.00 | 300 | 0 | No |
| 26 | 8.8 | 60 | 2.9 | 10.4 | 1.00 | 1440 | 80 | Yes |
| 27 | 8.0 | 60 | 2.9 | 10.4 | 1.00 | 800 | 100 | Yes |
| Sept. | | İ | İ | | | ļ | | |
| 25 | 8.2 | 29 | 4.0 | 7.3 | 0.73 | 120 | 100 | Yes |
| 26 | 10.0 | 29 | 4.0 | 7.3 | 0.73 | 582 | 100 | Yes |
| 27 | 9.2 | 27 | 3.2 | 8.5 | 1.10 | 680 | 40 | No |
| 28 | 8.0 | 33 | 4.2 | 7.8 | 0.70 | 120 | 90 | Yes |
| 30 | 8.0 | 25 | 3.2 | 7.8 | 0.92 | 360 | 90 | Yes |
| Oct. | ļ | | | | | | | |
| 1. | 8.2 | 31 | 3.2 | 9.7 | 0.91 | 500 | 50 | No |
| 3 | 8.0 | 36 | 2.4 | 15.0 | 1.20 | 250 | 100 | Yes |
| 4 | 7.4 | 50 | 2.0 | 17.8 | 1.04 | 160 | . 100 | Yes |
| 5 | 8.0 | 48 | 3.0 | 16.0 | 0.98 | 120 | 100 | Yes |
| 6 | 8.0 | 48 | 2.9 | 16.6 | 1.01 | 350 | 0 | No |
| 8 | 8.0 | 50 | 3.1 | 16.2 | 0.94 | 190 | 80 | Yes |
| 10 | 8.7 | 50 | _ | 16.0 | 1.00 | 138 | 100 | Yes |
| 11 | 8.2 | 47 | 3.2 | 14.7 | 0.91 | 108 | 80 | Yes |
| 13 | 8.2 | - | _ | _ | _ | 300 | 100 | Yes |
| 15 | 8.1 | 46 | 3.0 | 15.3 | 0.97 | 120 | 0 | No |
| 16 | 8.4 | 45 | 2.8 | 16.0 | 1.05 | 1440 | 100 | Yes |
| 17 | 8.6 | 50 | 2.8 | 17.8 | 1.05 | 162 | 0 | No |
| 18 | 8.2 | 48 | , - | _ | _ | 600 | 100 | Yes |
| 19 | 8.4 | 52 | · - | - | _ | 1440 | 100 | Yes |
| Range | 7.4-10.0 | 25 -60 | 2.8-4.2 | 7.3-17.8 | 0.70-1.22 | 108-1440 | 0-100 | |
| Mean ± SD | 8.3± 0.5 | 45.4±11.6 | 3.1±0.5 | 12.5± 3.8 | 0.96±0.12 | 480± 446 | - [| - |

APPENDIX VI(c)

CONTINUOUS DETOXIFICATION OF BLEACHED KRAFT WHOLEMILL EFFLUENTS BY FOAM SEPARATION IN A SINGLE STAGE SYSTEM

(With Four 1' Length, 3" Diameter 25µ Pore Size Ceramic Tubes in a 180-1 column)

| | | Treatment | Conditions | | | Toxicity of Effluent | | | | |
|----------|--------|---------------------|---------------------|-----|-----------|----------------------|---|--------------------------------------|--|--|
| Date | | | | | | | After Treatm | ient | | |
| | pН | Gas Flow (1/min) | Liquid Flow (1/min) | | | Before Treatment | % of Fish Survived in 65%Effluent over 96hr | Meets Federal Toxi- city Standard | | |
| Nov. | | | | | | | | | | |
| 1 | 8.8 | 25 | 2.8 | 8 | 1.00 | 702 | 80 | yes | | |
| 4 | 9.6 | 27 | 2.9 | 9 | 1.00 | 120 | 90 | yes | | |
| 5 | 8.3 | 27 | 2.9 | 9 | 1.02 | - | 100 | yes | | |
| 7 | _ | - | - | _ | - | 300 | 100 | yes | | |
| 8 | 9.2 | 20 | 3.0 | 7 | 0.97 | 150 | 0 | no | | |
| 9 | 10.0 | 22 | 3.0 | 7 | 0.97 | 252 | 100 | yes | | |
| 10 | 9.4 | 26 | 3.0 | 9 | 1.00 | 48 | 0 | no | | |
| 11 | 8.1 | 30 | 3.6 | 8 | 0.80 | 192 | 60 | no | | |
| Range | 8,1-10 | 25-30 | 2.8 - 3.6 | 7-9 | 0.80-1.00 | 48-702 | 0-100 | - | | |
| Mean±S D | 9 ±0.7 | 25± 3 | 3.0 ± 0.3 | 8±1 | 0.97±0.08 | 252±215 | _ | _ | | |

APPENDIX VII(a)

DETERMINATION OF DETOXIFICATION MECHANISMS - MILL F

| | MS | r (min) of | f Diluted | Raw Influ | ient | | , , | of Various ed Fractions | 1 | Contrib | oution to on (%) | Foam |
|---------|---------|------------|-----------|-----------|--------|----|------------------------------------|--|-------------------------|---------|----------------------------|--------------------|
| SAMPLE | 100% | 90% | 80% | 70% | 60% | | Treated Efflu- ent + foam | Treated Effluent + foam + vapour | Foam Separa- tion | | Unknown Mechan- isms | Removed % (v/v) |
| 1 | 435 | 555 | 1275 | - | 1215 | NT | 525 | 510 | 90 | 2 | 8 | 5.8 |
| 2 | 330 | 285 | - | 870 | 1110 | NT | 1230 | 1170 | 60 | 2 | 39 | - |
| 3 | 420 | 630 | 780 | 960 | NT | NT | 540 | 480 | 72 | 1 | 27 | - |
| 4 | 70 | 80 | - | 110 | 250 | NT | 250 | 200 | 60 | 2 | 38 | - |
| 5 | 300 | 330 | 270 | 330 | 540 | NT | 405 | 120 | 70 | 8 | 22 | 4.3 |
| 6 | 300 | 420 | 690 | 870 | NT | NT | 1440 | 990 | 62 | 7 | 31 | 3.1 |
| 7 | 420 | 240 | 210 | 1140 | 1200 | NT | 135 | 300 | 71 | 9 | 20 | .6.3 |
| 8 | 240 | 135 | 160 | 285 | 780 | NT | 360 | 150 | 67 | 13 | 20 | 6.3 |
| 9 | 450 | 720 | 960 | 1200 | NT | NT | 1320 | 1320 | 68 | 5 | 27 | 9.1 |
| 10 | 105 | 120 | 135 | 180 | 330 | NT | 105 | 75 | 95 | 2 | 3 | 7.0 |
| Range | 70-450 | 80-720 | 135-1275 | 110-1200 | 250-NT | _ | 150-1440 | 75-1320 | 60-95 | 1-13 | 3-39 | 3.1-9.1 |
| Mean±SD | 307±135 | 352±235 | 560± 428 | 660± 447 | - | - | 631± 505 | 531± 463 | 71±12 | 5± 4 | 24±12 | 6.5±1.3 |

APPENDIX VII(b)

DETERMINATION OF DETOXIFICATION MECHANISMS - MILL G

| | MST | (min) o | f Diluted | Raw Infl | uent | MST (min) of Various Reconstituted Fractions | | | Relative Contribution to Detoxification (%) | | | Foam |
|-----------|--------|---------|-----------|----------|---------|---|-------------------------------|---------------------------------|---|---------------------|----------------------------|-------------------|
| Sample | 100% | 90% | 80% | 70% | 60% | Treated Effluent | Treated Effluent + Foam | Treated Effluent + Foam + Vapor | Foam Separation | Volatil- ization | Unknown Mechan- isms | Removed %(v/v) |
| 1 | 120 | 140 | 195 | 320 | 480 | NT | 200 | 220 | 71 | 0 | 29 | |
| 2 | 60 | 55 | 90 | 125 | 165 | NT | 120 | 75 | 70 | 14 | 16 | 14.9 |
| 3 | 40 | 50 | 120 | 180 | 330 | NT. | 80 | 50 | 84 | 6 | 10 | 7.9 |
| 4 | 40 | 50 | 60 | 75 | NT | NT | 50 | 40 | 90 | 0 | 10 | 20.8 |
| 5 | 30 | 70 | 75 | 110 | 120 | NT | 95 | 85 | 76 | 3 | 21 | 19.2 |
| Range | 30-120 | 50-140 | 60-195 | 75+320 | 120-NT | - | 50-200 | 40-220 | 70-90 | 0-14 | 10-29 | 7.9-20. |
| Mean ± SD | 58± 36 | 73± 38 | 108± 53 | 162± 96 | 274±143 | - | 109± 57 | 94± 72 | 78± 9 | 4.6± 5 | 17.2±11 | 15.7± 5. |

APPENDIX VII(c)

DETERMINATION OF DETOXIFICATION MECHANISMS - MILL I

| | | MST (min) | of Dilute | d Raw Inf | luent | ı. | | of Various ed Fractions | Relative Contribution to Detoxification (%) | | | |
|---------|--------|-----------|-----------|-----------|-------|--------------------------|------------------------------------|--|--|--------------------------|-----------------------|----------------------------|
| Sample | 100% | 90% | 80% | 70% | 60% | Treated Efflu- ent | Treated Efflu- ent + foam | Treated Effluent + foam + vapour | Foam Separa- tion | Volat- iliza- tion | Unknown Mechanisms | Foam Removed % (v/v) |
| 1 | 60 | 75 | 130 | 160 | 270 | NT | 95 | 65 | 85 | 9 | 6 | 15.5 |
| 2 | 75 | 90 | 140 | 240 | _ | NT | 110 | 105 | 86 | 6 | 8 | 18.7. |
| 3 | 75 | 105 | 150 | 180 | - | NT | 95 | 75 | 95 | 5 | 0 | 10.0 |
| 4 | 105 | 120 | 150 | 180 | - | NT | 120 | 110 | 90 | 7 | 3 | 21.8 |
| 5 | 75 | 90 | 90 | 210 | - | NT | 90 | 80 | 90 | 7 | 3 | 25.1 |
| Range | 60-105 | 75-1.20 | 90-150 | 160-210 | - | - | 90-120 | 65-110 | 85-95 | 5-9 | 0-8 | 10.0-25.1 |
| Mean±SD | 78± 17 | 96± 21 | 132± 25 | 194± 30 | - | _ | 102± 13 | 87± 20 | 89± 4 | 7±2 | 4±3 | 18.2± 5.8 |

APPENDIX VIII

TOXICITY REMOVAL BY A DISSOLVED AIR FOAM SEPARATION SYSTEM

| Toxici | ty (MST) | No of Cycles | Total Air* | | Foam |
|----------|---------------------|-----------------------------|------------|------------|---------|
| Influent | Treated Effluent | Required for Detoxification | Dissolved | G/L | Removed |
| (min) | (min) | | (1) | 6/1 | % (v/v) |
| 105 | NT | 4 | 1.024 | 0.26 | - |
| 210 | NT | 3 | 0.768 | 0.19 | 3.8 |
| 300 | NT | 2 | 0.512 | 0.13 | 2.8 |
| 420 | NT | 2 | 0.512 | 0.13 | 2.5 |
| 580 | NT | 2 | 0.512 | 0.13 | 3.3 |

Operation

4 1 Dissolved Air Batch Operation

pH: 8.0

Pressurization: 5 min at 40 psig

Flotation time: 10 min Bubble Size: 0.3 mm

^{*}Total dissolved air has been calculated, based on ml of air dissolved at 40 psig and number of pressurization cycles applied.

APPENDIX IX(a)

EFFECT OF FOAM SEPARATION ON FOAMING TENDENCY REDUCTION OF MILL B EFFLUENTS

| Date | MST of 100% E (min) | ffluent | Foaming Te Σ _t (mi | |
|-------------|---------------------|--------------------|----------------------------------|-----------|
| | Before Treatment | After Treatment | Initial | Final |
| October | | | | |
| 25 | 1080 | NT* | 3.66 | <1.0 |
| 29 | 150 | NT | 3.66 | <1.0 |
| November | | | | |
| 5 | 600 | NT | 3.54 | <1.0 |
| - 6 | 420 | NT | 4.58 | <1.0 |
| 8 | 360 | NT | 3.55 | <1.0 |
| 9 | 600 | NT | 1.64 | <1.0 |
| 12 | 30 | NT | 1.42 | <1.0 |
| 15 | 720 | NT | 1.42 | <1.0 |
| 19 | 420 | NT | 0.92 | <1.0 |
| 21 | 300 | NT | 3.12 | <1.0 |
| 27 | 600 | NT | 6.06 | <1.0 |
| Range | 150 - 1080 | _ | 0.92-6.06 | ; |
| Mean ± S.D. | 480 ± 287 | _ | 3.12 1.68 | - |
| | | | | |

*

NT: Non-toxic

Operation:

Volume: 4 liters Aeration: 500 ml/min

pH: 7.0

Treatment Time: 0.5-3 hr

APPENDIX IX(b)

EFFECT OF FOAM SEPARATION ON FOAMING TENDENCY REDUCTION OF MILL F EFFLUENTS

| Date | MST of 100% Et (min) | ffluent | Foaming Te Σ _t (mi | |
|----------------|----------------------|---------|----------------------------------|------------|
| | Before | After | Initial | Final |
| July | | | | |
| 15 | 240 | NT | 5.22 | 1.0 |
| 17 | 150 | NT | 4.58 | 1.0 |
| 18 | 390 | NT | 5.50 | 1.0 |
| 19 | 180 | NT | 4.76 | 1.0 |
| 23 | 360 | NT | 4.76 | 1.0 |
| 24 | 210 | NT | 5.86 | 1.0 |
| 25 | 540 | NT | 5.40 | 1.0 |
| <u>October</u> | | | | |
| 1 | 450 | NT | 3.26 | 1.0 |
| 11 | 300 | NT | 4.20 | 1.0 |
| 17 | 90 | NT | 3.20 | 1.0 |
| Range | 90 - 540 | - | 3.20 - 5.86 | · - |
| Mean ± S.D. | 291 ± 143 | - | 4.66 ± 0.90 | - |
| | | | | |

NT = Non-toxic

Operation:

Volume: 4 liters Aeration: 500 ml/min

pH: 8.0

Treatment Time: 0.25 - 2 hr

Operating Condition: Column: 180 1, Gas Disperser: Four 25μ pore size, 5" diameter plastic discs, pH: 8.0, Retention Time: 59 ± 2.5 min, G/L: 12.2 ± 4.0 .

| | | Raw Influent | | | parated uent | Collaps | ed Foam Char | |
|---|--|--|---|----------------|---|---|---------------------------|---|
| Date | BOD5 (mg/1) | Susp. Solids (mg/1) | Toxicity MST (min) | BOD5 (mg/1) | Toxicity | BOD ₅ (mg/1) | Toxicity MST (min) | Influent Conversion to Foam |
| October 8 9 11 13 16 19 20 November 5 6 7 10 13 15 | 250 165 - 218 144 - - - 293 122 212 285 291 218 | 50 57 40 65 41 - - 54 64 58 99 38 61 | 190 60 110 300 1440 1440 - - 300 48 348 30 | - | N.T. N.T. N.T. N.T. N.T. N.T. N.T. N.T. | 260 445 375 450 267 - - 388 243 310 462 227 375 | 25 100 | 5.6 4.0 6.1 - 1.5 - - 8.0 - 13.2 8.5 - |
| Range Mean ± S.D. No. of Samples | 122 - 293 220 ± 61 10 | 38 - 99 57 ± 17 11 | 30 - 1440 447 ± 538 10 | - | <u>-</u> | 227 - 450 346 ± 88 11 | 13 - 100 38 ± 27 10 | 1.5 - 13.2 6.3 ± 4.2 7 |

N.T. = Non-toxic Foam height : 30 cm

Estimated bubble diameter: 1.5 mm

APPENDIX X (b)

CHARACTERISTICS OF FOAM PRODUCED BY A 25µ CERAMIC DIFFUSER IN A FOAM SEPARATION SYSTEM

Operating Condition: Column: 180 litres, 1st stage of the 2 stage system, Gas Disperser: Four $<25\mu$ pore size, 1 ft long Ceramic Tubes, pH: 8.0, Retention Time: 30 \pm 6.0 min, G/L: 4.4 \pm 1.0

| | | Raw Influent | Foam Separated Effluent | | Foam Characteristics | | | |
|--|--------------------------------------|----------------------------------|--|--------------------------------------|--------------------------------------|----------------------------------|---------------------------------------|---------------------------------------|
| Date | BOD ₅ (mg/1) | Susp. Solids (mg/1) | Toxicity MST (min) | BOD5 (mg/1) | Toxicity | BOD ₅ (mg/1) | Toxicity MST (min) | Influent Conversion to Foam |
| December 8 11 12 13 15 16 | 230 265 210 230 - 215 | 61 31 20 45 80 17 | 300 300 350 150 300 220 | 180 200 175 210 - 160 | N.T. N.T. N.T. N.T. N.T. | 290 255 - 214 - - | 120 120 18 192 144 144 | 13.6 6.2 - 3.2 2.4 2.4 |
| Range Mean ± S.D. No. of Samples | 215 - 265 230 ± 22 5 | 17 - 80 42 ± 25 6 | 150 - 300 270 ± 72 6 | 160 - 210 185 ± 20 5 | | 214 - 290 253 ± 38 3 | 18 - 192 123 ± 58 6 | 2.4 - 13.6 5.6 ± 4.8 5 |

N.T. = Non-toxic Foam height: 30 cm

Estimated bubble diameter: 1 mm

APPENDIX XI

CRITICAL ROTATION SPEED (RPM) AND TIP SPEED* REQUIREMENT FOR FOAM COLLAPSING

| Foam Flow | Turbine Diameter cm (in) | | | | | | | | | |
|---|--------------------------|-----------|------|-----------|------|-----------|----------|-----------|--|--|
| m ³ /min (ft ³ .min) | 15 | (6") | | 23 (9") | 31 | (12") | 38 (15") | | | |
| | rpm | Tip Speed | rpm | Tip Speed | rpm | Tip Speed | rpm | Tip Speed | | |
| 0.18 (6.2) | 1500 | 1197 | 1200 | 1436 | 900 | 1436 | 700 | 1396 | | |
| 0.33 (11.7) | 1550 | 1236 | 1400 | 1675 | 1200 | 1914 | 900 | 1795 | | |
| 0.45 (15.9) | 1640 | 1308 | 1500 | 1795 | 1140 | 1818 | 960 | 1914 | | |
| 0.69 (24.5) | - | _ | 1440 | 1854 | 1400 | 2233 | 1200 | 2393 | | |
| 1.20 (42.0 | _ | - | 1600 | 1914 | 1450 | 2300 | 1250 | 2500 | | |

Liquid Content = $1.5 \pm 0.3\%$

Foam Collapsing Efficiency = 100%

^{*}Tip Speed in cm/sec.

APPENDIX XII
POWER DATA OF FOAM BREAKING SYSTEM

| Foam Flow | Rotation | Turbine | Po | wer Consum | ption | N ³ D ⁵ | |
|------------------------|-----------------|-------------------|---|-------------------------------|---|--|------------------------------------|
| F(m ³ /min) | Speed N(RPM) | Diameter D(cm) | Loaded Turbine P _L (Watts) | Unloaded Turbine (Po(W) | Net Power Cons. P=P _L -Po(W) | (RPM ³ x cm ⁵ x 10 ¹⁷) | P/F Watt m ³ /min |
| 0.18 | 1200 | 31 | 225 | 210 | 15 | 0.46 | 83 |
| 0.18 | 1300 | 31 | 230 | 220 | 10 | 0.58 | 56 |
| 0.18 | 1400 | 31 | 240 | 228 | 12.5 | 0.72 | 69 |
| 0.18 | 1500 | 31 | 260 | 240 | 20 | 0.89 | 111 |
| 0.18 | 1600 | 31 | 280 | 260 | 20 | 1.08 | 111 |
| 0.69 | 1400 | 31 | 270 | 230 | 40 | 0.72 | 58 |
| 0.69 | 1520 | 31 | 270 | 230 | 40 | 0.92 | 58 |
| 1.19 | 1200 | 31 | 270 | 210 | 60 | 0.46 | 50 |
| 1.19 | 1300 | 31 | 325 | 220 | 105 | 0.58 | 88 |
| 1.19 | 1400 | 31 | 400 | 228 | 170 | 0.72 | 143 |
| 1.19 | 1500 | 31 | 475 | 240 | 235 | 0.89 | 197 |
| 0.45 | 1300 | 38 | 435 | 355 | 80 | 1.77 | 178 |
| 0.45 | 1340 | 38 | 450 | 360 | 90 | 1.93 | 200 |
| 0.45 | 1400 | 38 | 455 | 375 | 80 | 2.2 | 178 |
| 0.45 | 1440 | 38 | 460 | 380 | 80 | 2.43 | 178 |
| 0.45 | 1500 | 38 | 475 | 395 | 80 | 2.71 | 178 |
| 0.45 | 1520 | 38 | 480 | 390 | 90 | 2.85 | 200 |
| 0.45 | 1600 | 38 | 495 | 415 | 80 | 3.29 | 178 |
| 0.69 | 1200 | 38 | 420 | 335 | 85 | 1.38 | 123 |
| 0.69 | 1300 | 38 | 460 | 355 | 105 | 1.77 | 152 |
| 0.69 | 1400 | 38 | 500 | 375 | 125 | 2.20 | 181 |
| 0.69 | 1500 | 38 | 535 | 395 | 140 | 2.71 | 203 |
| 0.69 | 1600 | 38 | 590 | 415 | 175 | 3.29 | 254 |
| 1.19 | 1200 | 38 | 430 | 335 | 95 | 1.38 | 80 |
| 1.19 | 1300 | 38 | 475 | 355 | 120 | 1.77 | 101 |
| 1.19 | 1400 | 38 | 525 | 375 | 150 | 2.20 | 126 |
| 1.19 | 1500 | 38 | 600 | 395 | 205 | 2.71 | 172 |
| 1.19 | 1600 | 38 | 690 | 415 | 275 | 3.29 | 231 |

APPENDIX XIII EFFECT OF FLOCCULATION ON DETOXIFICATION OF KRAFT MILL EFFLUENTS

| | Flocculant | MST of | MST of Effluent (min) | | | | |
|----------|----------------------|-----------|--|--------------------------|--|--|--|
| Species | Conc. (mg/1) | Untreated | Treated | Volume (% v/v) | | | |
| Ferric | 100 200 500 | 210 | 80% Survival 100% Survival 80% Survival | Poor Settling* 0.3% 1.3% | | | |
| Chloride | 100 500 | 240 | 60% Survival 100% Survival | - | | | |
| T do | 1000 2000 | 210 | 100% Survival 100% Survival | 7% 7.2% | | | |
| Lime | 1000 2000 5000 | 240 | 1000 min(20% Survival) 80% Survival 80% Survival | - | | | |
| Alum | 100 500 | 240 | 420 min 800 min (20% Survival) | Poor Settling* | | | |

^{*} Flocs in colloidal form.

APPENDIX XIV (a)

TREATMENT OF COLLAPSED FOAM BY 1-DAY AND 3-DAY

RETENTION AERATED LAGOONS

Retention Time: 1 day

| | | Collaps | ed Foam | |
|----------------|-------------------------|-------------------|-------------------------|-------------------|
| Day | Befor | e Treatment | Afte | r Treatment |
| , | BOD ₅ (mg/1) | Toxicity MST (hr) | BOD ₅ (mg/1) | Toxicity MST (hr) |
| 1 | 140 | 2,0 | 20 | NT |
| 3 | 140 | 1.5 | 5 | 2 |
| 4 | 255 | 2.0 | 90 | 20 |
| 5 | 175 | 0.25 | 85 | 1 |
| 6 | 180 | 2.3 | 55 | 4 |
| 7 | - | 0.45 | - | 60% Survival |
| 8 | _ | 4.0 | - | NT |
| Range | 140 - 255 | 0.25 - 4.0 | 5 - 85 | 1 - NT |
| Mean ± S D | 178 ± 47 | 1.8 ± 1.3 | 51 ± 38 | - |
| Retention Time | e: 3 days | | | |
| 1 | 445 | 0.6 | 8 | NT |
| 3 | 375 | 0.6 | 48 | NT |
| 5 | . 450 | 0.4 | 15 | NT |
| 7 | 300 | 0.4 | 12 | NT |
| 8 | 267 | 0.2 | 10 | NT |
| 11 | - | 0.5 | - | NT |
| 12 | - | 1.5 | - | NT |
| 13 | - | 1.5 | - | NT |
| 28 | 388 | 0.4 | 6 | NT |
| Range | 267 - 450 | 0.2 - 0.6 | 6 - 48 | |
| Mean ± S D | 370 ± 75 | 0.7 ± 0.5 | 16.5 ± 15.8 | - |

Note: MLSS \sim 1000 mg/1

APPENDIX XIV (b)

TREATMENT OF COLLAPSED FOAM BY 2-HR AND 4-HR ROTATING BIODISC SYSTEMS

Hydraulic Load: 0.45 gal/ft²/day Retention Time: 2 hr

| | Collapsed Foam | | | | | | | |
|------------------------|--------------------------|--------------------------|-------------------------|------------------------------|--|--|--|--|
| Day* | Befor | e Treatment | After Treatment | | | | | |
| | BOD ₅ (mg/1) | Toxicity MST (hr) | BOD ₅ (mg/1) | Toxicity MST (hr) | | | | |
| 1 | 140 | 2.0 | 30 | 20% Survival after 24 hrs | | | | |
| 3 | 140 | 1.5 | 15 | 40% Survival | | | | |
| 4 | 255 | 2.0 | 10 | 24 | | | | |
| 5 | 175 | 0.25 | 10 | 10% Survival | | | | |
| 6 | 180 | 2.3 | 3 | 20% Survival | | | | |
| 7 | _ | 0.45 | - | 24 | | | | |
| 8 | - | 4.0 | - | NT | | | | |
| Range | 140 - 255 | 0.25 - 2.3 | 3 - 30 | 24 - NT | | | | |
| Mean ± S D | 178 ± 47 | 1.8 ± 1.3 | 13.6 ± 10.1 | - | | | | |
| Hydraulic Retention | Load: 0.22 Time: 4 hr | gal/ft ² /day | | | | | | |
| 1 | 267 | 0.5 | - | NT | | | | |
| 2 | _ | 1.5 | - | NT | | | | |
| 3 | _ | 1.5 | - | NT | | | | |
| 18 | 243 | 0.4 | 23 | NT | | | | |
| 19 | 200 | - | 45 | NT | | | | |
| 22 | 262 | - | 16 | NT | | | | |
| 25 | 227 | 0.8 | 12 | NT | | | | |
| 27 | 175 | 0.25 | 11 | NT | | | | |
| 30 | 125 | _ | 14 | NT | | | | |
| Range | 125 - 267 | 0.25 - 1.5 | 11 - 45 | - | | | | |
| Mean ± S D | 214 ± 51 | 0.83 ± 0.55 | 20.2 ± 12.9 | - | | | | |

 $^{^{}f *}$ The system was operated for 7 days, prior to taking any samples.

APPENDIX XV INFLUENT CHARACTERISTICS UNDER VARYING PROCESS CONDITIONS

| Date | Influe | nt Charact | | | Process Conditions | | | | | Foam Characteristics | | | |
|--|----------------------|-----------------------|--------------------------------|------------------------------------|---------------------------------------|-----------|----------------------------|-------------------------------------|---------------------------------------|-------------------------------|-----------------------------------|--|--|
| | Нę | Toxicity (MST:min) | Foaming Tendencies (min) | Air Flow (ft ³ /min) | Liq Flow (ft3/min) | G/L | Retention Time (min) | Flow Rate (ft ³ /min) | Liquid Entrained in Foam(%) | Foaming Stability (min) | Conversion of Influent to foam(%) | | |
| 10/2 | | ` | | 98 | | | | | | | | | |
| 19/2 | 7.2 9.5 | | 5.6 | 98 | 7.77 8.54 | 13.1 | 80.5 73.7 | 13.77 20.47 | 1.3 | 4.7 5.0 | 2.6 3.9 | | |
| -,- | | | | | | | | | | | | | |
| 20/2 | 7.0 | - | 5.2 | 98 98 | 8.54 | 12.0 | 73.7 | 23.30 17.65 | 1.4 | 5.2 | 3.9 | | |
| " | 3.9 | | 5.7 | 98 | 8.54 | 12.0 | 73.7 | 19.06 | 2.0 | 4.7 | 4.5 | | |
| 17 | 4.0 | | 5.7 | 98 | 8.54 | 12.0 | 73.7 | 16.94 | 2.4 | 5.4 | 4.8 | | |
| D | | | | | | | | | | | | | |
| Range Mean | 4.0 - 9.5 | | 5.2 - 5.7 5.6 | 98 98 | 8.47 | 12.0-13.1 | 74.8 | 13.77-23.30 | 1.5-2.4 | 4.7-5.4 | 2.6-4.8 | | |
| S.D. | 2.4 | | 0.3 | 0 | 0.35 | 0.5 | 2.8 | 18.71 3.18 | 0.4 | 5.0 0.3 | 0.9 | | |
| 23/2 | 4.1 | | 5.9 | 98 | 8.12 | 12.4 | | | | | | | |
| 11 | 3.6 | | 5.7 | 98 | 8.85 | 11.3 | 76.3 69.0 | 21.18 | 1.9 | 5.4 | 5.0 | | |
| 1, | 3.0 | - | 6.5 | 98 | 8.85 | 11.3 | 69.0 | 21.18 | 1.4 | 4.3 5.6 | 3.4 | | |
| 24/2 | 6.4 | | 5.9 | 98 | 8.87 | 10.7 | 65.4 | 20.47 | | | | | |
| 11 | 4.5 | | 4.3 | 98 | 8.87 | 10.7 | 65.4 | 19.06 | 2.5 | 5.6 3.7 | 5.0 | | |
| <u>,, </u> | 6.0 | | 5.9 | 98 | 8.85 | 11.2 | 69.0 | 13.77 | | | | | |
| -,, | 4.0 | | 5.4 | 98 | 8.87 | 10.7 | 65.4 | 12.36 | 1.5 | 5.6 | 1.4 | | |
| 7, | 3.7 | | 4.4 | 98 | 8.87 | 10.7 | 65.4 | 17.65 | 1.3 | | 2.4 | | |
| 25/2 | 4.0 | | 5.8 | 98 | 8.87 | 10.7 | 65.4 | 24.0 | 1.4 | 5.2 | | | |
| _ | | | | | | | | | | | 3.5 | | |
| Range | 4.0 | | 5.4-6.5 | 98 98 | 8.12-8.87 8.30 | | | 12.36-24.0 | 1.1-2.5 | 3.1-5.6 | 1.4-5.0 | | |
| Mean S.D. | 1.1 | | 0.7 | 98 | 0.25 | 0.6 | 76.8 | 19.06 | 0.5 | 4.7 | 3.3 | | |
| 8/3 | 3.3 | - | 5.5 | 98 | 9.30 | 10.7 | 3.6 65.4 | 3.88 | | 1.0 | 1.3 | | |
| 11 | | 200 | | | · · · · · · · · · · · · · · · · · · · | | | 30.71 | 1.2 | 5.4 | 3.9 | | |
| | 4.0 4.5 | 200 | 5.1 | 98 98 | 9.50 9.50 | 10.7 | 65.5 | 30.71 | 1.2 | 4.4 | 3.9 | | |
| 9/3 | 4.1 | 800 | 4.4 | 98 | 9.50 | 10.7 | 65.4 | 30.71 | · · · · · · · · · · · · · · · · · · · | | 3.9 | | |
| 9/3 | 6.5 | | 4.2 | 100 | 9.50 | 11.2 | 65.4 | 10.94 | 1.1 | 3.8 | 1.3 | | |
| " | 3.5 | | 4.4 | 100 | 9.50 | 11.2 | 65.4 | 10.94 | 1.1 | 4.0 | 1.3 | | |
| 10/3 | 4.5 | 480 | 5.9 | 100 | 9.50 | 11.2 | 65.4 | 10.94 | 1.1 | 5.8 | 1.3 | | |
| 11/3 | 4.5 | - | 5.4 | 105 | 9.50 | 11.7 | 65.4 | 40.96 | 1.8 | 4.5 | 7.7 | | |
| " | 3.9 | _ | 5.8 | 50 | 9.50 | 5.6 | 65.4 | 20.47 | 1.5 | 4.8 | 3.2 | | |
| 11 | 3.9 | 600 | 5.8 | 50 | 9.50 | 5.4 | 65.4 | 13.06 | 1.5 | 4.8 | 2.1 | | |
| 11 | 3.9 | - | 5.8 | 50 | 9.50 | 5.5 | 65.4 | 7.77 | 1.5 | 4.8 | 1.2 | | |
| 12/3 | 4.1 | - | 5.1 | 50 | 9.50 | 5.5 | 65.4 | 8.47 | 1.5 | 4.4 | 1.3 | | |
| " | 4.1 | • | 5.1 | 48 | 9.50 | 5.4 | 65.4 | 6.35 | 1.5 | 4.4 | 1.0 | | |
| 11 | 4.1 | • | 5.1 | 48 | 9.50 | 5.3 | 65.4 | 6.35 | 1.5 | 4.4 | 1.0 | | |
| " | 5.8 | | 4.4 | 50 | 9,50 | 5.6 | 65.4 | 16.94 | 1.4 | 2.6 | 2.5 | | |
| 17 | 5.8 | | 4.4 | 50 | , 9.50 | 5.4 | 65.4 | 14.12 | 1.4 | 2.6 | 2.1 | | |
| 11 | 5.8 | - | 4.4 | 100 | 9.50 | 10.9 | 65.4 | 25.52 | 1.4 | 2.6 | 3.7 | | |
| " | 5.8 | 450 | 4.4 | 100 | 9.50 | 11.1 | 65.4 | | <u> </u> | 2.6 | <u> </u> | | |
| " | 7.0 | - | 5.1 | 100 . | 9.50 | 11.1 | 65.4 | 22.25 | 1.3 | 2.5 | 3.0 | | |
| | 3.3-7.0 | | 4.2-5.9 | 48-105 | | 5.3-11.7 | | 6.25-40.96 | | 2.4-5.8 | i i | | |
| Mean | 4.7 | 506 | 5.1 | 32.3 | 9.50 | 8.5 | 65.4 | 17.65 | 1.4 | 4.0 | 2.6 | | |
| S.D. | 1.1 | 220 | 0.6 | 24.7 | - | 2.8 | 0 | 10.94 | 0.2 | 1.0 | 1.8 | | |
| 16/3 | 3.6 | | 6.1 | 50 | 9.50 | 5.6 | 65.4 | 19.77 | 1.9 | 1.8 | 3.9 | | |
| 11 | 3.6 | | 6.1 | 50 | 9.50 | 5.5 | 65.4 | 16.59 | 1.9 | 1.8 | 3.7 | | |
| 11 | 3.3 | | 5.3 | 100 | 9.50 | 11.1 | 65.4 | 30.71 | 1.7 | 4.5 | 5.5 | | |
| | 3.3 | - 150 | 5.3 | 98 97 | 9.50 9.50 | 10.9 | 65.4 65.4 | 22.24 15.53 | 1.3 | 4.5 | 3.0 | | |
| | 3.5 | - 130 | 5.3 | 97 | 9.50 | 10.7 | 65.4 | 13.77 | 1.3 | 4.5 | 1.9 | | |
| 17/3 | 3.8 | - | 5.0 | 98 | 9.50 | 10.7 | 65.4 | 22.24 | 1.4 | 3.5 | 3.3. | | |
| 19/3 | 3.0 | 420 | 4.7 | 98 | 9.50 | 10.9 | 65.4 | 17.65 | 1.4 | 3.8 | 2.6 | | |
| " | 5.3 | 360 | 5.8 | 98 | 9.50 | 10.9 | 65.4 | 17.65 | 1.4 | 3.3 | 2.6 | | |
| Range | 3.0-5.3 | 150-420 | 4.7-6.1 | 30-100 | 9.50 | 5.5-11.7 | 65.4 | 13.77-30.71 | | 1.3-4.5 | | | |
| Mean | 1 | 277 | 5.4 | 87.3 | 9.50 | 9.7 | 65.4 | 19.42 | 1.5 | 3.6 | 3.2 | | |
| S.D. | 0.7 | 198 | 0.5 | 21.2 | | 2.4 | 0 | 4.94 | 0.3 | 1.1 | 1.1 | | |

TOXICITY OF TREATED SAMPLES AS A FUNCTION OF INTERFACIAL AREA

PRODUCED DURING FOAM FRACTIONATION

Influent characteristics:

Operating Conditions:

- Bleached kraft whole mill effluent
 pH adjusted to 7.0 8.0
 Flow = 0.3 m³/min
- Retention time = 40 min

- 2 stage system

| Interfacial Area (m /1) | No. of Samples Tested | MST of Treated Effluent (min) |
|-------------------------------|-----------------------------|-------------------------------------|
| . 0 | . 1 | 360 |
| 2.8 | 1 | 2900 |
| 2.8 | 1 | 3600 |
| 3.8 | 1 | 2200 |
| 4.0 | 1 | 1440 |
| 4.0 | 4 | 2200 |
| 4.0 | 8 | N.T. |
| 4.8 | . 1 | N.T. |
| 8.4 | 1 | N.T. |
| 14.6 | 1 | N.T. |
| 18.6 | 1 | N.T. |

APPENDIX XVII

EFFECT OF STAGING AT CONSTANT GAS-LIQUID INTERFACIAL AREA ON DETOXIFICATION

PERFORMANCE OF JET FOAM GENERATION SYSTEM

Operation

Liquid flow rate: 100 gal/min pH: 7 - 8 Retention time: 20 min/stage

Jet Aeration System

Type: 2" diameter jet c/w submersible pump Fluid velocity: 60 cm/sec through jet nozzle.

| | | | Т | | Form Ser | paration Sys | rem | | Gas-Liquid | Foam Char | acteristics | Toxicity | (LT50:mir |) of Efflu | ient |
|---------------------------|---|--|--|---------------------------|------------------|---|--|---|--|--|--|--|---|--|--|
| Stage | Sample No. | Type of Sample Taken | lst | No. of | | Total Air Load (ft ³ /min) | Retention Time (min) | G/L | Interfacial Area (m ² /1) | Flow Rate (ft ³ /min) | Toxicity (LT50:min) | Feed | After 1st Stage | Foam Separ 2nd Stage | |
| Single Stage System | 1 2 3 4 | Comp. Grab Grab Grab | Stage 1 1 1 1 | Stage - - - - | - - - | 7.4 7.4 11.3 11.3 | 20 20 20 20 20 | 0.7 0.7 1.1 1.1 | 5.3 5.3 7.1 7.1 | 10.7 11.3 15.4 18.2 | 15 15 17 20 r os samples f samples de | >480<1380 >480<1380 380 600 taken | 5760 Nontoxic 2900 Nontoxic 4 2 | - - - | - - - - |
| Two Stage System | 1 2 3 4 5 6 7 8 9 10 11 12 | Comp. Comp. Comp. Grab Comp. Grab Comp. Grab Comp. Grab Comp. Grab Comp. Grab Comp. Grab | 1 1 1 1 1 1 1 1 1 1 1 1 | | | 9.2 11.3 11.3 11.3 11.3 11.3 11.3 11.3 11 | 40 40 40 40 40 40 40 40 40 40 40 | 0.9 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1.1 1 | 5.5 7.1 7.1 7.1 7.1 7.1 7.1 7.1 7.1 7.1 7.8 7.8 | Detox 3.3 12.6 13.8 13.8 13.0 13.1 12.6 13.8 12.4 11.9 13.3 12.4 14.1 | 15 30 30 17 17 17 15 15 15 15 17 17 18 | >480<1380 >480<1380 2000 >480<1380 400 >480<1380 >480<1380 >480<1380 >480<1380 >480<1380 1380 420 1440 420 360 | 3160 Nontoxic Nontoxic 4300 Nontoxic 4300 Nontoxic 5000 Nontoxic Nontoxic 2880 Nontoxic Nontoxic Nontoxic | Nontoxic Nontoxic Nontoxic 4760 Nontoxic Nontoxic Nontoxic Nontoxic Nontoxic Nontoxic Nontoxic Nontoxic Nontoxic Nontoxic Nontoxic Nontoxic 2880 | - |
| | 14 | Grab | 1 | 1 | | 12.7 | 40 | 1.2 | 7.0 | No. | er of samples of samples de xification s | etoxified | 14 8 57% | 14 12 86% | - - - |
| Three Stage System | 1 2 3 | Comp. | 1 2 3 3 3 | 1 1 3 3 | 1 1 3 3 | 9.2 10.7 10.6 10.6 | 60 60 60 60 | 0.9 1.0 1.0 | 7.6 7.6 | 7.9 9.2 13.6 13.0 | 10 15 20 20 | >480< 960 600 >480< 960 420 | 5760 | Nontoxic Nontoxic Nontoxic Nontoxic | Nontoxic Nontoxic Nontoxic Nontoxic |
| Th St Sy | 4 | Comp. | | _! | | | | | | No. | er of sample of samples d exification s | etoxified | 4 3 50% | 3 3 100% | 3 3 100% |

APPENDIX XVIII

FOAM BREAKING PERFORMANCE BY A TURBINE SYSTEM

Operation:

Type : 3 blade 30 cm diameter vaned disc Power : $1/3\ hp$

Rotation speed: 1800 rpm Tip Velocity : 3600 cm/sec

| Day of | | | nfluent acteristics | | n Character | istics | Foam |
|-----------|----------|------------|------------------------------------|------------------------|---------------------------|-----------------------|------------------------|
| Operation | Sampling | рH | Foam tendency ^Σ t | Foam flow | Foam liquid content | Foam stability | Breaking Efficiency |
| | (hrs) | | (min) | (ft ³ /min) | (%: v/v) | (^E s:min) | (%) |
| 1 | 5 | 7.2 | 6.0 | 2.22 | 2.56 | 5.6 | 100 |
| 2 | 1 2 | 8.0 | 4.5 4.8 | 10.45 | 2.43 | 3.7 | 100 |
| | . 3 | 8.0 | 4.8 | 10.98 11.26 | 1.70 1.52 | 3.7 4.6 | 100 |
| | Average | 8.0 | 4.7 | 10.91 | 1.88 | 4.0 | 100 |
| 3 | 1 | 8.0 | 5.4 | 12.78 | 1.52 | 4.5 | 100 |
| | 2 | 7.0 | 6.1 | 12.50 | 1.33 | 5.3 | 100 |
| | Average | 8.0 | 5.8 | 12.64 | 1.43 | 4.8 | 100 🔻 |
| 3 | 4 5 | 7.2 | 5.1 5.6 | 13.91 13.24 | 1.32 | 4.5 | 100 |
| | Average | 7.2 | 5.4 | 13.59 | 1.34 | 5.1 4.8 | 100 |
| 4 | 1 | 8.0 | | 12.11 | 1.43 | - | 100 |
| · | 2 | 8.0 | - | 12.99 | 1.06 | _ | 100 |
| | 3 | 8.0 | - | 12.80 | 0.82 | _ | 100 |
| | 4 | 8.0 | - | 11.58 | 0.67 | - | 100 |
| | 5 6 | 8.0 | _ | 10.59 11.75 | 1.20 0.90 | _ | 100 |
| | Average | 8.0 | | 12.00 | 1.01 | | 100 |
| 5 | 1 | 8.0 | - | 15.07 | 2.6 | _ | 100 |
| | 2 | 8.0 | - | 15.36 | 2.75 | _ | 100 |
| | 3 | 8.0 | - | 17.44 | 3.29 | - | 100 |
| | 4 | 8.0 | - | 19.13 | 3.36 | - | 100 |
| | 5 6 | 8.0 8.0 | - | 17.47 | 3.04 | - | 100 |
| | Average | 8.0 | | 18.32 17.13 | 3.04 2.92 | <u>-</u> | 100 |
| 6 | 3* | 7.2 | 5.6 | 18.04 | 2.04 | 5.1 | 100 |
| 7 | 1 | 8.0 | | 13.45 | 0.75 | | 100 |
| ř | 2 | 8.0 | _ | 16.45 | 0.67 | _ | 100 |
| | 3 | 8.0 | - | 16.34 | 0.67 | - | -100 |
| | 4 | 8.0 | - | 17.65 | 1.00 | - | 100 |
| | 5 | 8.0 | - | 23.62 | 0.86 | | 100 |
| 0 | Average | 8.0 | | 17.51 | 0.79 | - | 100 |
| 8 | 1 2 | 8.0 | _ | 18.04 18.89 | 1.36 1.32 | - | 100 100 |
| | 3 | 8.0 | - | 17.23 | 1.28 | _ | 100 |
| | 5 | 8.0 | _ | 22.31 | 2.53 | _ | 100 |
| | 6 | 8.0 | <u> </u> | 25.14 | 1.51 | | 100 |
| | Average | 8.0 | - | 18.00 | 1.32 | - | 100 |
| 10 | 6 | 8.0 | 5.7 | 21.00 | 1.5 | 5.3 | 100 |
| 14 | 4 | 8.0 | 6.2 | 21.04 | 1.26 | 5.6 | 100 |
| 16 | _3 | 7.2 | 5.5 | _ | 0.57 | 5.1 | 100 |
| 22 | 2 | 7.3 | 6.0 | 14.47 | 1.51 | 5.6 | 100 |
| 26 | 4 | 8.0 | 5.6 | 23.76 | 1.06 | 5.1 | 100 |
| 30 | 4 | 8.0 | 6.2 | 20.72 | 1.06 | 5.4 | 100 |
| 35 | 2 | 8.0 | 6.6 | 16.31 | 0.62 | 3.1 | 100_ |
| 40 | 3 | 8.0 | 6.6 | 16.31 | 0.62 | 5.6 | 100 |

APPENDIX XIX-a

SIZING OF SCREENING AND PUMPING EQUIPMENT

A pumping station basically consists of a travelling screen submerged in an effluent collection chamber to separate the undigested wood chips from the effluent and a pumping system capable of delivering 17,000 gal/min of effluent.

A. EFFLUENT COLLECTION CHAMBER

Basis:

To accomodate approximately 50,000 gal of effluent with a 3 min retention time.

Selection of Equipment:

Concrete tank of diminseion $1 \times w \times d = 100' \times 10' \times 8'$.

Capital Cost: \$70,000

Installed Cost: $\frac{\text{Capital Cost}}{60\%} = \frac{\$70,000}{0.6} = \$117,000$

B. TRAVELLING SCREEN

Basis:

To separate the wood chips and knots from the effluent.

Selection:

0.5' opening, 10 ft/min velocity, 10' x 8' travelling screen Installation:

5' submergence in effluent collection chamber.

Capital Cost: \$50,000 complete with motor

Installed Cost: $\frac{\text{Capital Cost}}{60\%} = \frac{\$50,000}{0.6} = \$83,000$

C. PUMPS

Basis: 17,000 gal/min flow rate

Maximum Head = 25 ft

Four pumps, each rated at 5000 gal/min

Electricity = 1¢/kwh

Estimation of Power Requirement

Work =
$$\frac{5000 \text{ gal/min}}{7.4 \text{ gal/ft}^3} \times 62.4 \frac{1b}{\text{ft}^3} \times 25 \text{ ft} = 1.1 \times 10^6 \frac{\text{ft-1b}}{\text{min}}$$

At 70% efficiency,

Estimated BHp =
$$\frac{\text{work}}{33000 \times 0.7}$$
 = $\frac{1.1 \times 10^6}{23.1 \times 10^3}$ = 47.6

Hp required = Estimatd BPH x Safety Factor

$$= 47.6 \times 1.3 = 61.9$$

Selection: Four 5000 gal/min pump

Power = 65 hp/pump, 260 hp total

Type = Single stage, dry pit, vertical turbine.

Capital Cost: \$150,000 asuming that cost installed is 60% of Capital.

Installed Cost:
$$\frac{\text{Capital Cost}}{60\%} = \frac{\$150,000}{0.6} = \$250,000$$

Power Cost/day = HP required x 0.745 $\frac{\text{kwh}}{\text{HP}}$ x 24 hr x $\frac{1c}{\text{kwh}}$

$$= 4 \times 50 \times 0.745 \times 1c = $35.76$$

D. SUMMARY

Total Cost Requirement of Screening and Pumping Facility

Installed Cost: \$450,000

Total HP: 260

Power Consumption: \$35.76/day.

APPENDIX XIX-b

ph CONTROL SYSTEM

At present, the pH of the final combined effluent in a kraft mill is most commonly controlled by a two-stage process. Initially, lime mud is added to the acid sewer to increase the pH to approximately 3.0. At pH greater than 3.0, neutralization by lime mud becomes ineffective. Instead, slaked lime or calcium hydroxide is added to the acid sewer in such a way that the pH of the combined mill effluent will be approximately 5 to 6. To increase the pH to 7.0, a condition where detoxification by foam separation is most effective, addition of caustic solution will be required. This can be done in the first stage of the foam generation tank.

A. Caustic Storage Tank

Duty: To store 7 days supply of 25% caustic at a rate of 846 gal/day (129).

Selection: 7000 gal glass lined storage tank with cover.

B. Caustic Feed Pump

Duty: To pump 0.6 gal/min of caustic against 5 ft of head.

Selection: 3 gal/min non-corrosive pump.

C. pH Controller

Duty: To control pH at 7.0.

Selection: Uniloc pH system complete with control elements.

D. Summary

Total Cost Requirement of pH Control System

Capital Cost: \$150,000

Installed Cost: \$200,000

APPENDIX XIX-c

SIZING OF FOAM SEPARATION SYSTEM

A. FOAM GENERATION TANK

Basis: 3-stage channel shaped system semi-circular at both ends.

Cover to provide installation of foam breaker.

Each stage with central baffle.

Estimation of Foam Generation Tank

Retention time = 1 hr

Liquid volume = $(17,000 \times 60)$ gal = 1.02 M gal.

Gassed Volume = $1.02 \times 1.2 \text{ M gal} = 1.23 \text{ M gal}$

$$=\frac{1.23 \times 10^6}{7.48}$$
 ft³ = 136,500 ft³

Volume of each stage = $45,500 \text{ ft}^3$

Liquid depth = 20 ft

Foam height = 3 ft

Free board = 2 ft

Overall dimension $(1 \times w \times d) = 150 \times 86.5 \times 20$

Tha layout of the system is shown in Figure 48.

Construction: - Common wall construction is most applicable.

- Valves are installed to control the gravity flow between each stage.
- Walkway above common wall should be installed for servicing of pumps.

Assuming construction cost at \$65/yd³ capacity

Installed Cost: $\frac{136,500}{27}$ x \$65 = \$330,000.

B. JET AERATOR

Basis: Size of jet aerator = 1" diameter gas-liquid interface = $20 \text{ m}^2/1$ G/L = 6
Air loading = $50 \text{ ft}^3/\text{min per jet}$

Estimation of Jet Aeration Systems:

Total aeration requirement = $G/L \times liquid flow rate$ = $6 \times \frac{17000 \text{ gal/min}}{7.48 \text{ gal/ft}^3}$ = $13600 \text{ ft}^3/\text{min}$

Aeration required/stage = $\frac{13600}{3}$ ft³/min = 4545 ft³/min Number of jet aerator units required = 91 units.

Selection:

Commercial jet aeration systems can be built with 24 1-in diameter units on a common header. Four jet aerator systems each with 24 jet units are selected and installed in each stage.

INSTALLATION:

Installed at the bottom of the basin, as shown in Figure 52 at 17-ft submergence. Each system is connected to a recirculation pump and air blower.

Capital Cost: \$200,000 complete with piping and supports.

Installed Cost: $\frac{\text{Capital Cost}}{60\%} = \frac{\$200,000}{0.6} = \$350,000$

B. JET AERATOR

Basis: Size of jet aerator = 1" diameter gas-liquid interface = $20 \text{ m}^2/1$ G/L = 6

Estimation of Jet Aeration Systems:

air loading = $50 \text{ ft}^3/\text{min per jet}$

To produce bubbles of 1 mm diameter, a minimum liquid submergence of 15' and air to power ratio of >1 is required.

Total aeration requirement = $G/L \times 1$ iquid flow rate = $6 \times \frac{1700 \text{ gal/min}}{7.48 \text{ gal/ft}^3}$ = $13600 \text{ ft}^3/\text{min}$

Aeration required/stage = $\frac{13600}{3}$ ft³/min = 4545 ft³/min Number of jet aerator units required = 91 units.

Selection:

Commercial jet aeration systems can be built with 24 1-in diameter units on a common header. Four jet aerator systems, each with 24 jet units are selected.

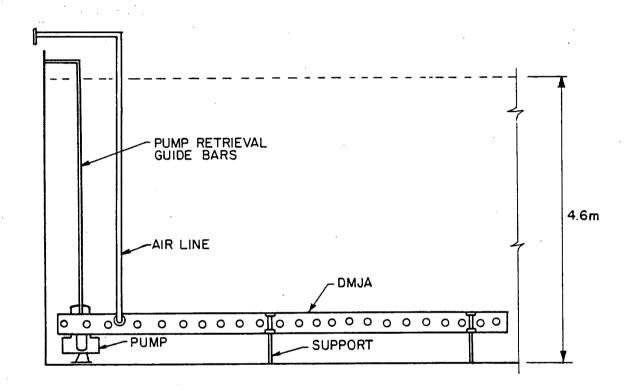
INSTALLATION:

Installed at the bottom of the basin, as shown in Figure 52 at 17-ft submergence. Each system is connected to a recirculation pump and air blower.

Capital Cost: \$200,000 complete with piping and supports.

Installed Cost: $\frac{\text{Capital Cost}}{60\%} = \frac{\$200,000}{0.6} = \$350,000$

Figure 52
INSTALLATION OF JET SYSTEM IN FOAM SEPARATION TANK



C. RECIRCULATION PUMP

Basis: Liquid velocity of 50 ft/sec through the jet is required to produce 1 mm bubble diameter and promote gas-liquid contact time.

Estimation of Pumping Requirement

Cross sectional area of 1" jet unit = $\pi \times (\frac{0.5^2}{12})$ ft² = 0.01 ft² Since each jet aeration system consists of 24, 1" jets, total cross sectional area = 0.24 ft².

For each jet aerator system, the pumping rate required to achieve 50 ft/sec velocity = cross sectional area x liquid velocity = $0.24 \times 50 \text{ ft}^3/\text{sec} = 12 \text{ ft}^3/\text{sec} = 720 \text{ ft}^3/\text{min}$ = $720 \times 7.48 \text{ gal/min} = 5385 \text{ gal/min}$.

A 5500 gal/min pump is used, with liquid submergence of 17' and 70% efficiency.

Estimated BHp = $\frac{\sqrt[3]{20 \times 62.4 \times 17}}{33000 \times 0.7}$ = 33

HP required = Estimated BHP x Safety Factor (1.3)

 $= 33 \times 1.3 \text{ hp} = 42.9 \text{ hp}.$

Selection: Submersible centrifugal pump rated at 45 hp, 5500 gal/min

No. of pumps: 12, 1 standby

Total HP = 540

Capital Cost: \$120,000

Installed Cost: $\frac{\text{Capital Cost}}{60\%} = \frac{\$ 40,000}{0.6} = \$200,000$

Power cost/day = $45 \times 12 \times 0.745 \times 24 \times 1c$

= \$96.55.

D. BLOWER CAPACITY

Basis: Aeration requirement/stage = 4545 ft³/min
Estimation of Blower Capacity:

Pressure drop of liquid head = $\frac{17 \text{ ft}}{33 \text{ ft}}$ x 14.7 psi = 7.6 psi

Pressure drop of air header, blower piping, branch

connection and air supply lines = 1 psi 1 psi

Pressure drop across jet aerator = 0 psi 0 psi

Total 8.6 psi.

A 10 psi blower is required, at an efficiency of 70% $BHP = \frac{\text{psi x (ft}^3/\text{min) x 144}}{33000 \text{ x 0.7}} = \frac{10 \text{ x 4545 x 144}}{23100} = 283.$ Total HP requirement = 283 x 3 = 849

Selection: Centrifugal type blower rated at 10 psi 300 hp, $4500 \text{ ft}^3/\text{min air flow}$.

No. of blowers = 3, 1 standby

Total HP = 900.

Capital Cost: \$150,000

Installed Cost: $\frac{\text{Capital Cost}}{0.6} = \frac{\$150,000}{0.6} = \$250,000$ Power cost/day = 900 x 0.745 x 24 x 1c = \$160.92.

E. SUMMARY

Total Cost Requirement of Foam Generator

The total cost installed and power requirement are shown as follows:

| Foam Generating Element | Horsepower | Installed Cost |
|-------------------------|------------|----------------|
| Jet Aerator | - | \$350,000 |
| Pump | 540 | 120,000 |
| Blower | 900 | 250,000 |
| Total | 1440 | \$ 720,000 |

APPENDIX XIX-d

SIZING OF FOAM DISPOSAL SYSTEM

A. FOAM BREAKER

Basis: Influent conversion to foam = 1.2%

Liquid content = 1.5%

Foam flow rate = $1800 \text{ ft}^3/\text{min}$

Foam breaker = 2 ft diameter, 1800 rpm, 3-blade vaned disc turbine Estimation of Foam Breaking Capacity

Foam breaking capacity of a 3 blade turbine is given (128) by:

$$F = (2.6 \times 10^{-3} N + 7.7 \times 10^{-2} D - 4.7) \frac{m^3}{min}$$

where N = rotation speed, rpm

D = diameter of turbine, cm

F =
$$(2.6 \times 10^{-3} \times 1800 + 7.7 \times 10^{-2} \times 31-4.7) \times 35.3 \times \frac{\text{ft}^3}{\text{min}}$$

= $173 \text{ ft}^3/\text{min}$.

Total No. of foam breakers required = $\frac{1800}{173}$ = 10

For safety measures, 12 will be installed.

The power of each unit is given by (128):

P = F x (51.7 x
$$10^{-17}$$
 N³D⁵ + 51.2) Watts
= 173 x (51.7 x 10^{-17} x 1800^3 x 2^5 + 51.2) x $\frac{1}{745}$ HP
= 16.7 HP

Selection: 3 blade vaned disc turbine 2'diameter rated at 20 hp, 1800 rpm

Total HP = 240

Capital Cost = \$110,000

Installed Cost =
$$\frac{\text{Capital Cost}}{0.6} = \frac{\$110,000}{0.6} = \$180,000$$

Power/day = $240 \times 0.745 \times 24 \times 1c = 42.9

B. FOAM TREATMENT BY AERATED LAGOON

Basis: Collapsed foam flow = 200 gal/min

 BOD_5 reduced from 400 mg/1 to 50 mg/1

Selection: Volume of 3-day aerated lagoon = $200 \times 1440 \times 3 = 0.86 \text{ M gal}$

 $\frac{BOD_5 \text{ destroyed}}{hr} = 200 \frac{gal}{min} \times 60 \text{ min } \times 350 \text{ mg/l } \times 60 \text{ min } \times 350 \text{ mg/l} \times 100 \text{ min}$

3.8 $1/ga1 \times 2.205 \times 10^{-6} \text{ 1b/mg} = 35.5 \text{ 1b}$

Oxygen transfer of surface aerator = 1 1b/hp-hr

Horsepower = $\frac{35.5}{1}$ = 35.5, a 45 Hp unit is chosen.

Installed Cost: \$300,000 (1)

Power cost/day = $45 \times 0.745 \times 24 \times 1c = 8.04

C. SUMMARY

Total Cost Requirement of Foam Disposal System

Installed Cost: \$480,000

Total HP: 405.

Power Consumption: \$72.4/day.

APPENDIX XX

LIST OF PUBLICATIONS

- 1. Zajic, J.E., and K.S. Ng (1969). Biochemical Uranium Leaching. Dev. in Ind. Microbiol., 11: 413.
- 2. Ng, K.S., J.E. Zajic, and D.F. Manchester (1972). Effect of SO₂ Removal on Biodegradability of Arbiso Black Liquor. Proc. of 7th Can. Poll. Res. Sym.
- 3. Ng, K.S., J.C. Mueller and C.C. Walden (1973). Detoxification of Kraft Mill Effluents by Foam Separation. Pulp Paper Mag. Can. 74(5): T263.
- 4. Ng, K.S., J.C. Mueller and C.C. Walden (1974). Process Parameters of Foam Detoxification for Kraft Effluents. Pulp Paper Mag. Can. 75(7): T263.
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- 6. Ng, K.S., J.C. Mueller and C.C. Walden (1976). Foam Separation For Detoxification of Bleached Kraft Mill Effluents. J. Water Poll. Cont. Fed. 48(3): 458.
- 7. Mueller, J.C., and K.S. Ng (1976). Foam Separation—A Novel Technique for Detoxification of Kraft Effluents. Prog. Water Tech. 8(2/3): 259.
- 8. Ng, K.S., and P. Temoin (1977). Design Considerations of Foam Separation Process for Detoxifying Kraft Effluents. Pulp Paper Mag. Can. 78(2): T29.
- 9. Ng, K.S., J.C. Mueller and C.C. Walden (1977). Foam Breaking-A Key process in Detoxification of Kraft Mill Effluents by Foam Separation. Can. J. of Chem. Eng. <u>55</u>; 439.
- 10. Ng, K.S. and L. Gutierrez (1977). Mechanical Foam Breakers-A Means for Foam Control in Sewage and Industrial Waste Treatment. J. Water Poll. Cont. Fed. (in press).
- 11. Ng, K.S., J.C. Mueller and C.C. Walden (1977). Ozone Treatment of Kraft Mill Wastes. J. Water Poll. Cont. Fed. (in press).
- 12. Ng, K.S., L. Gutierrez and J.C. Mueller (1977). Toxicity Removal By Foam Separation-Pilot Plant Assessment of Major Operation Equipment and Detoxification Reliability. (Presented at PNPCA Conference, Portland, Oregon).

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- 1. Zajic, J.E., and K.S. Ng. (1969). Biochemical Uranium Leaching. Dev. in Industrial Microbiol., 11:413.
- Ng, K.S., J.E. Zajic, D.F. Manchester and Y.K. Ng. (1972). Effect of SO₂ Removal on Biodegradability of Arbiso Black Liquor. Proc. of 7th Can. Poll. Res. Sym.
- Ng, K.S., J.C. Mueller and C.C. Walden. (1973). Detoxification of Kraft Mill Effluents by Foam Separation. Pulp Paper Mag. Can. 74(5):T187.
- 4. Ng, K.S., J.C. Mueller and C.C. Walden. (1974). Process Parameters of Foam Detoxification for Kraft Effluents. Pulp Paper Mag. Can. 75(7):T263.
- 5. Ng, K.S. and J.C. Mueller. (1975). Foam Separation A Technique for Water Pollution Abatement. Water and Sewage Works (June, 1975):48.
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- 9. Ng, K.S. J.C. Mueller and C.C. Walden. (1977). Foam Breaking A key process in foam separation process. Can. J. for Chem. Eng. 55:439.
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- 12. Ng, K. S. and L. Gutierrez. (1977). Toxicity Removal by Foam Separation Pilot plant assessment of major operating equipment and detoxification reliability. (accepted for presentation at the 1977 PNWPCA conference, Portland, Oregon).