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NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC., 260 MADISON AVENUE, NEW YORK, N.Y. 10016

# PULP AND PAPER MILL IN-PLANT AND CLOSED CYCLE TECHNOLOGIES - A REVIEW OF OPERATING EXPERIENCE, CURRENT STATUS, AND RESEARCH NEEDS

TECHNICAL BULLETIN NO. 557

OCTOBER 1988

**NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.**
**260 MADISON AVE. NEW YORK, N.Y. 10016 (212) 532-9000**

October 31, 1988

**Dr. Isaiah Gellman**
President
**(212) 532 9000**

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# PULP AND PAPER MILL IN-PLANT AND CLOSED CYCLE TECHNOLOGIES - A REVIEW OF OPERATING EXPERIENCE, CURRENT STATUS, AND RESEARCH NEEDS

Over the last two decades, the pulp and paper industry has made significant gains in its efforts to reduce fresh water usage and minimize effluent discharges. These accomplishments have been made by developing and implementing a number of new technologies which (a) enable more efficient use of fresh water and (b) have the potential to reduce chemical losses to the environment. These technologies are generally referred to as in-plant control or closed cycle technologies.

This technical bulletin is a review of various in-plant and closed cycle technologies applicable to the kraft pulping industry. Among the technologies examined in this report are (a) water reuse, (b) spill management and process control technologies applicable to pulp mills, bleach plants and paper mills, and (c) add-on technologies such as the Rapson-Reeve closed cycle process, the Billerud-Uddeholm and other resin processes, activated carbon adsorption, chemical coagulation, ultrafiltration, and reverse osmosis. The objective of this review was to document the current status of various in-plant and closed cycle technologies and to identify and list candidate technologies for possible future research funding. Consequently, in describing various technologies emphasis has been placed on (a) identifying operating problems and (b) listing research needs which are associated with the implementation of these technologies.

The work reported here was carried out by NCASI staff as part of NCASI's responsibilities as the Project Manager for an R&D program funded by Louisiana-Pacific Corporation and Simpson Paper Company. The program itself was undertaken by the two companies as a condition to the two mills' 301(m) effluent discharge permits issued for the Samoa and Fairhaven, California mills in 1987. The technical bulletin was written by Ashok K. Jain, who is a Regional

Manager at the NCASI Southern Regional Center. Guidance in preparing the reports that formed the basis of this technical bulletin was provided by Dr. C. Edward Taylor of Louisiana-Pacific Corporation, Quintin A. Narum of Simpson Paper Company, and William J. Gillespie of our New York office.

Your Comments on this technical bulletin are solicited and should be addressed to Ashok K. Jain at (904) 377-4708 or to this office.

Very truly yours,

Isaiah Gellman

Isaiah Gellman
President

IG:mh
Attach.

# TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

TABLE OF CONTENTS (Cont'd)

# PULP AND PAPER MILL IN-PLANT AND CLOSED CYCLE TECHNOLOGIES - A REVIEW OF OPERATING EXPERIENCE, CURRENT STATUS, AND RESEARCH NEEDS

## I INTRODUCTION AND BACKGROUND

In 1987 Louisiana Pacific Corporation's bleached kraft pulp mill located at Samoa, CA and Simpson Paper Company's bleached kraft pulp mill located at Fairhaven, CA were granted NPDES permits in accordance with Section 301(m) of the Clean Water Act. These permits required the mills to implement a research and development (R&D) program "to study applicable wastewater treatment systems, with resources initially targeted at the development of closed cycle and in-plant control technologies." It was also stipulated in the two mills' 301(m) permits that the research programs should be associated with, but not limited to, the kraft process, and must be demonstrated to be of value to the pulp and paper mill industry.

The permits specified that the R&D program should be carried out in two phases. The first phase activities were identified as literature review, technology assessment, and identification and ranking of candidate technologies for future research. During the second phase, actual research on the high priority technologies would be carried out by approved contractors.

In December, 1987 NCASI was approved as the Project Manager for the R&D program by the two companies and the regulatory agencies overseeing this program.

This technical bulletin has been prepared from the reports that were submitted by NCASI as Project Manager for the R&D program. It reviews various in-plant and closed cycle technologies applicable to the kraft industry, assesses the current state of knowledge in this area, and presents information on the major problems encountered with implementing some of the technologies. A list of areas of research that are likely to be pursued under the R&D program is also included.

## II STUDY METHODOLOGY

In order to conduct this study the following four tasks were carried out:

(1) Literature search

(2) Review of NCASI files and data bases

(3) Mill visitation

(4) Industry contacts.

The activities carried out under each of the above tasks are summarized below.

A. Literature Search

The literature search primarily consisted of an on-line computer search utilizing PAPERCHEM, from the Institute of Paper Chemistry, and NTIS (National Technical Information Service). The abstracts of the articles of interest identified from those searched were organized and used to obtain the original papers to the extent possible.

B. Review of NCASI Files and Data Bases

NCASI files were examined extensively to obtain information not identified in the literature searches. This effort yielded substantial unpublished information on operating experiences and member company activities.

In addition to searching NCASI files, NCASI data bases were also examined and analyzed to identify exemplary mills in their respective subcategories for mill visitation, under the in-plant control technology assessment program.

C. Mill Visitation

On the basis of information obtained from the NCASI data bases and staff knowledge of environmental pollution control activities at various mills, over 10 pulp mills were selected for visitation. In selecting these mills, it was recognized that there is considerable overlap between closed cycle and in-plant control technologies. Consequently, the mills were closed if they had implemented an identified closed cycle process, were operating at low water usage rates, or had implemented a control technology that could enhance our understanding of the two technologies being examined. Because of the many common components of the closed cycle and in-process control technologies, mill visits by NCASI staff could not be identified as being specifically related to one or the other technology.

Each visit typically lasted one day. During the visit the NCASI staff member(s) met with the environmental manager, technical managers and their staff, and mill operating personnel to discuss their experiences with the closed cycle or in-plant control technology of interest at that location.

D. Industry Contacts

Following the mill visitation, a number of investigators were contacted for any new information and to obtain a better understanding of the issues of concern to the industry.

At the conclusion of these tasks technology assessment reports for in-plant and closed cycle technologies were prepared (1,2).

## III IN-PLANT AND CLOSED CYCLE CONTROL TECHNOLOGIES EXAMINED IN THIS STUDY

During the last two decades, as a result of increasing concerns for the environmental impact of industrial effluent discharges and the increasing marginal cost of effluent treatment, there has been increasing emphasis on water conservation and reuse in the pulp and paper industry. The technologies associated with water reuse and conservation or recovery of certain substances which are normally sewered are classified as "closed cycle" or "in-plant" control technologies.

In this report the following in-plant and closed cycle control technologies have been examined:

(1) Pulp mill and power plant in-plant control technologies

(2) In-plant control technologies related to spill prevention and management

(3) Bleach plant in-plant control technologies

(4) Paper mill in-plant control technologies

(5) Rapson-Reeve process

(6) Billerud-Uddeholm and other resin processes

(7) Activated carbon adsorption

(8) Chemical coagulation

(9) Ultrafiltration

(10) Reverse osmosis

In the sections that follow, the status of a number of in-plant and closed cycle control technologies applied to various areas of pulp and paper mills have been reviewed, and research needs associated with these technologies have been identified.

# IV PULPING, CHEMICAL RECOVERY, AND POWER PLANT IN-PLANT CONTROL TECHNOLOGIES

## A. Improved Brownstock Washing

(1) Introduction - In the kraft process, cooked pulp from the digester, referred to as brownstock, is washed to recover to the greatest extent possible cooking chemicals and organic materials. The efficiency of pulp washing is generally estimated by measuring the amount of sodium remaining in the pulp after washing and is expressed as pounds of salt cake ($Na_2SO_4$) lost per ton of pulp production. Salt cake losses, however, do not provide information on organics losses measured as BOD or TOC.

Although brownstock washing can recover 95 to 98 percent of the dry solids, the remaining 2 to 5 percent carried with the washed pulp can contribute significantly toward mill saltcake and BOD losses. In an NCASI report (3) washer soda and BOD losses were found to range from 16-188 lb/ADT and 11->35 lb/ADT, respectively. Since most of the soda, BOD and color losses measured at the washer have the potential to find their way into effluents, considerable research effort has been directed at addressing this subject.

(2) Factors Affecting Brownstock Washer Losses - The early studies of brownstock washing systems were conducted by Norden (4), who established a mathematical model for studying multi-stage counter-current washing of pulp on drum washers.

NCASI has conducted several studies aimed at developing an understanding of factors that affect BOD, saltcake, and color losses from brownstock washers (3,5,6,7,8). These studies have shown that BOD, color, and sodium wash out of pulp at different rates and possibly by different mechanisms. Miner (4) reported that significantly greater color and BOD can be extracted at elevated pH, whereas higher pH decreases soda release. The latter observation was also confirmed by Crotogino et al. (9). Oglesby (7) suggested that both diffusion and desorption effects must be considered in brownstock washing. Miner and Wiegand (10) reported that for a hardwood mill, every pound of BOD or TOC removed from the pulp entering the bleach plant would reduce approximately 0.9 pound of BOD and 0.8 pound of TOC from the bleach plant effluent.

(3) Brownstock Washing Equipment - The most widely used equipment for brownstock washing is the rotary vacuum washer. In general, several drum washers are used to wash pulp in a countercurrent manner to make optimum use of the wash water. Older systems typically used three washing stages. In many cases now, four or five washers are used in series to improve brownstock washing efficiency.

In addition to traditional vacuum drum filters, a number of types of new pulp-washing equipment are currently being used (9). Tait (11) described a pressurized drum washer suitable for washing brownstock. These systems do not require a vacuum leg, and are reported to achieve higher washing efficiencies than conventional vacuum drum washers.

Coffey (12) and Crotogino (9) have reported on horizontal belt washers which resemble the Fourdrinier section on a paper machine. A dilute suspension of pulp flows onto a travelling screen from a headbox, forming a pulp mat. Liquid is removed from the underside of the screen, and wash water is applied to the top side of the pulp mat. The reported advantages of these systems include reduced defoamer usage, containment of TRS containing vent gases, retention of heat, and lower power consumption.

Kamyr diffusion washers and Kamyr pressure diffusion washers (9) are widely used in combination with continuous digesters. In these systems, wash liquor is introduced into the pulp through distributors and is forced to go through the pulp to the screens where it is extracted. These washers wash pulp primarily by displacing more concentrated liquor with wash water/liquor containing lower solids.

In addition to the above, vacuum drum and screw-type wash presses are being used for pulp washing (9,13). These presses have pulp outlet consistencies as high as 40 percent, giving high washing efficiencies.

In operating a brownstock washing system one has to strike a balance between enhanced chemical recovery to reduce the cost of subsequent bleaching and/or waste treatment and the added cost of concentration of recovered chemicals for burning in the recovery furnace. The installed cost for pulp washing equipment is rather high, and the selection of equipment depends upon a variety of factors such as comparable cost versus performance, specific needs, available space, and environmental constraints.

## B. Condensate Segregation and Reuse

In the kraft process, condensation of vapors from digesters and evaporators provides significant volumes of condensate. Table 1 shows the range of condensate volumes generated from various processes (14,15).

TABLE 1 PROCESS CONDENSATE VOLUMES FROM KRAFT PULPING

| SOURCE | CONDENSATE VOLUME, GALLON/ADT |
|---|---|
| Batch Digester Blowheat Condensate | 210 - 340 |
| Turpentine Decanter Underflow | 30 - 100 |
| Evaporator Condensate | 1500 - 2100 |
| Continuous Digester Flash Steam | 100 |

These condensates contain significant quantities of BOD in the form of methanol, ethanol, acetone, terpenes, and other organics, and odorous reduced sulfur compounds (14,16,17,18). If sewered, these condensates contribute 2-30 lb/ADT of BOD to the mill waste treatment system, and increase discharge effluent rate substantially. Consequently, a number of technologies have been implemented that enable partial or total reuse of condensate streams. Some of these technologies are reviewed in this section.

(1) Condensate Segregation - Analyses of condensate streams have shown that contaminants are not uniformly distributed in various streams. Particularly in evaporator condensates, which contribute to one-half or more of total condensate BOD, about 80 percent of BOD and 98 percent of reduced sulfur compounds are contained in 40 percent of evaporator condensate volume (14). Segregating dirty condensates from the clean condensates enables the use of clean condensate in pulp washing and in the causticizing area, thus reducing effluent volumes. One mill is reported to use clean condensates for boiler feedwater (19).

A number of mills have installed vapor recompression evaporators (VCE), thus making available more clean condensate streams for recycle within the process (20,21,22).

Chandra (23) described two batch digester blow heat pre-evaporation systems that substantially reduce the amount of steam required for black liquor evaporation and concentrate most of the BOD in a small stream, thus making available more clean condensate for reuse in the process.

(2) Steam Stripping of Condensates - Dirty condensates contribute significantly to effluent BOD, and contain reduced sulfur compounds that cause odor around the waste treatment system (18). They also contribute to toxicity of untreated effluents (24). Because of their odor potential, these condensates are unsuitable for use in the brownstock washing and causticizing areas, consequently, a number of mills steam strip these condensates to remove TRS and BOD (25,26,27,28,29,30,31). A properly designed condensate steam stripping system with pH adjustment can remove almost all total reduced sulfur compounds and a large fraction of BOD from the feed stream. The older steam stripping systems installed in the pulp and paper industry required substantial quantities of steam. The newer systems, however, are generally integrated with multiple effect evaporators and require less energy to operate. Beder and Madrid described a system that combined VCE and steam distillation of foul condensates at a mill with a continuous digester (32). The VCE concentrated over 50 percent of BOD found in evaporator in less than 4 percent of total volume. The reported methanol and BOD removal efficiencies of the distillation column were 98 percent and 90 percent, respectively.

The stripped condensates are generally returned for brownstock washing or are used in the causticizing area, thus causing a net reduction in fresh water usage.

## C. Closed Screen Rooms

Pulp leaving the brownstock washer is screened and washed to remove impurities from the pulp prior to further processing. In mills with open screen rooms, the wash water used in the washing and screening operation is sewered. This allows the purging of a large fraction of BOD and soda brought forward with the pulp, thus minimizing chemical demand in the bleaching area. Open screen rooms, however, result in a discharge of 5000-10,000 gallons/ADT of effluents. Consequently, the industry trend is toward building closed screen rooms. Closed screen rooms are operated so that all the discharges are returned to the brownstock washer, thus eliminating that flow from the mill sewer. Closed screen rooms are essential for substantial mill closure and can reduce energy costs (33).

Foaming problems, especially associated with southern pine pulp, have in some instances necessitated increased defoamer use or installation of pressure screens (3). In addition, a closed screen room may increase chlorine requirement in bleached mills or acid requirements for pH adjustment before sizing in unbleached mills. Twitchell and Edwards have estimated that screen room closure may result in a four-fold increase in carryover to the bleach plant relative to an open screen room using fresh water (34).

## D. Non-Contact Cooling Water Segregation and Recycle

Segregation and reuse of non-contact cooling waters offers opportunities for substantial savings in fresh water usage at a pulp and paper mill.

The larger cooling water streams at a bleached mill include evaporator surface condenser cooling water, turbine condenser water, chlorine dioxide generator reboiler cooling water, lime kiln cooling water, turbine cooling water, lube oil cooling water, and the paper machine cooling water streams. According to Kramer et al. (35) the cooling water demands for a bleached mill could range from 14,400-24,000 gallons/ton, and in a closed system this volume could be reduced to 700-1000 gallons/ton. Massey (36) reported on a mill expansion in the South that incorporated an extensive water reuse program aimed at not increasing the fresh water supply to the mill. Successful implementation of this program required the installation of a cooling tower, needed for purging excess heat from the condensates during summer months, and 50 percent larger surface condensers so that they could accommodate the higher temperature cooling water. This program, along with a program of white water reuse on showers, resulted in a net reduction in water usage from 19,200 gallons/ton to 9,8000 gallons/ton.

Narum and Moeller (37) described the water conservation program at an integrated pulp mill near Anderson, California. This program included uncontaminated cooling water collection and reuse, with the return of the excess to the fresh water reservoir.

Most of the mills visited during the mill visitation phase of this investigation reported that they practiced some degree of cooling water segregation and recycle (38).

## V IN-PLANT CONTROL TECHNOLOGIES FOR SPILL PREVENTION AND MANAGEMENT

The programs of process stream spill prevention and management are intended to (a) minimize the loss of process materials which have economic value, and (b) prevent significant losses of process chemicals from interfering with smooth operation of waste treatment systems. Most of these programs have the following components:

(1) Monitoring of selected sewer streams to identify the occurrence of a spill.

(2) Sending spill information to the operating personnel so that corrective actions can be taken.

(3) Collection of streams containing the spilled material for recycle to the process or controlled discharge at a controlled rate.

This section summarizes information on various in-plant process stream spill collection and management programs, discusses control strategies that have been examined in operating a spill management system, and identifies information needs in this area.

### A. Mill Programs of Spill Management

NCASI Technical Bulletin No. 341 describes spill management programs at four mills (39). The first mill utilizes an 850,000 gallon spill tank and a strong waste storage pond in its spill management program. The spill tank has been designed to collect spills from liquor tanks, transfer pump leakage throughout the black liquor system starting with the filtrate from the first stage of the brown stock washer, the evaporator boilout storage tank, and the steam stripper feed tank. Conductivity meters are used to decide whether or not a particular stream is directed to the spill collection tank. A strong waste storage tank is employed to provide extra liquor storage capacity during recovery furnace operating problems.

It was reported that the system had operated successfully for four years with no NPDES BOD violations. The only problem encountered with the system was the failure of the conductivity detector to detect a soap spill.

The second mill installed an elaborate spill collection and management system to recover chemicals and to protect its Unox wastewater system from surges in influent concentrations. This system, shown in Figure 1, utilizes nine sumps, and two 700,000 gallon spill tanks, one for lean spills and the other for strong spills. Conductivity monitors are used to route spills to either the lean or the rich spill storage tanks based on a conductivity set point.

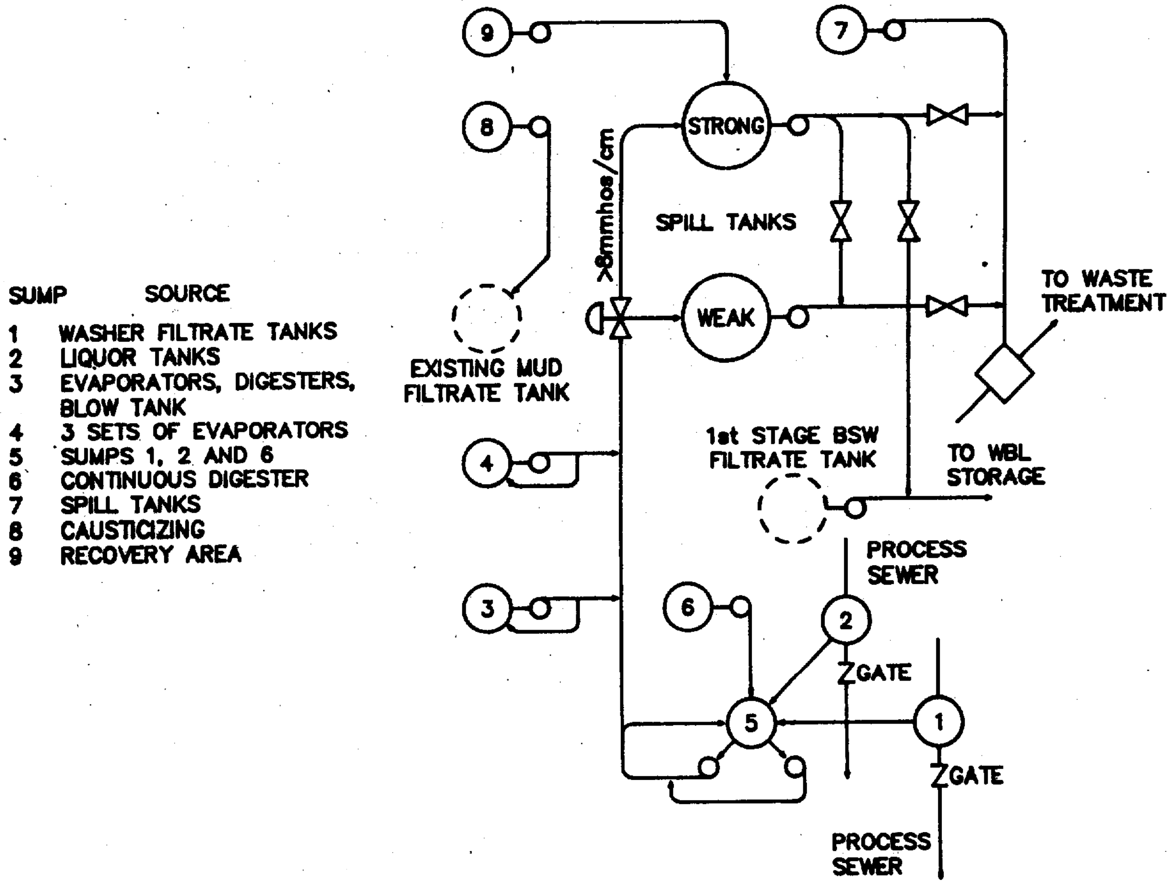



FIGURE 1 SCHEMATIC OF SPILL CONTROL AND RECOVERY SYSTEM AT A 1000 TPD KRAFT MILL

The third mill, which did not have a secondary treatment system, installed a spill collection system to minimize organic losses. This system has been designed to collect spills from the pulping and washing areas and route them to one of two spill tanks. Conductivity monitors are used to monitor spills.

The fourth mill, which discharged to a POTW, designed its spill collection system to prevent shock loads to the POTW. Figure 2 is a schematic of this system which consists of containment structures to capture spills, pumps and piping to return spills to the process, conductivity monitors for monitoring the system and notifying operators in the event of a spill, and a diversion structure and retention pond to capture nonrecoverable spills for controlled discharge to the sewer.

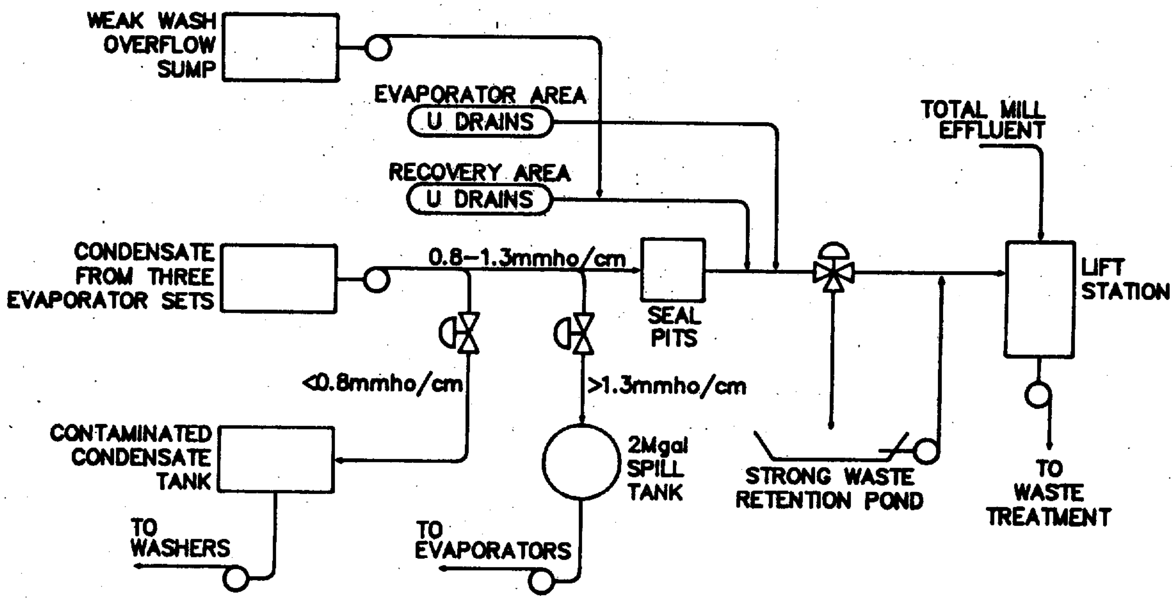



FIGURE 2 SCHEMATIC OF SPILL CONTROL SYSTEM OF AN UNBLEACHED KRAFT MILL

Gay (40) described a mill program to control intermittent process losses. Sumps for spill collection and recovery have been installed in the recovery furnace area and the evaporator area. Conductivity probes are used to monitor these sumps and direct their flow to a black liquor pond for recovery. In addition to the in-plant sumps, a spill pond has been built to capture for controlled release those spills that escape from the mill.

Baker and Ethridge (41) described a program for monitoring saltcake losses from a kraft pulp mill with the objective of minimizing such losses. Balsbaugh Series 1210 conductivity monitors are used to monitor a number of sumps and sewers, and provide an alarm to the operator when the conductivity exceeds a set point. The system also records the period during which a particular stream being monitored exceeds the set point. The system has been successful in substantially reducing process chemical losses.

At an NCASI Special Technical Session, one mill described its spill collection system (42). In this system water that collects in U-drains within the digester basement, brownstock basement, evaporator basement (boilouts, leaks), liquor storage tank areas, and recovery boiler basement is pumped to a spill collection tank. Additionally, rejects from the 14 percent black liquor filter ahead of the weak liquor storage enter this tank. Colored water from the spill collection tank is used for dilution at the secondary deknotter ahead of the brownstock washers. In this way spill liquor is reintroduced into the recovery cycle. The pulp mill and utilities department coordinate the use of this spill liquor in order to maintain the tank at a low operating level but not overdilute the black liquor.

## B. Other Spill Management Programs

Eriksson (43) described the Scandinavian program being carried out under the auspices of Nordmiljo 80. This program considered both dissolved and suspended matter, unlike the programs in this country which have focused on dissolved solids only. Consequently, a major effort of this program was directed toward monitoring the optical properties of various waste streams. Secondly, the Scandinavian program relies on process modeling to set control limits to avoid overreaction to planned production process changes.

Kramer et al. (35) described spill collection and management programs for a closed cycle bleached kraft pulp mill based on SSVL reports (44) and results of their visits of a number of mills in Europe and South Africa (35,44). They recommended separate spill collection systems for collecting black liquor spills and causticizing area spills. The black liquor spill collection system, shown in Figure 3, directs all U-drains in the recovery, evaporator, digester, and brownstock washer areas to sumps for recovery if the conductivity exceeds a set value. Dump tanks are provided for emergency dumping of pulp or chemicals, and a drum filter is used to remove fiber from the recovered weak black liquor.

In the causticizing area spill collection system, shown in Figure 4, all overflows from the clarifier and storage tanks are returned to the process. Accumulated solids are pumped periodically to the mud mixer and mud washer.

## C. Development of Spill Control and Management Strategies

In order to design a spill collection and management system, one has to quantify the nature and frequency of intermittent process losses. This would involve identifying those areas which have the most losses, and a determination of the magnitude of those losses. Once this information is available, a suitable system can be designed. Modeling and time series analyses may be useful in the above activity. NCASI Technical Bulletin No. 341 discusses various spill control and management strategies, and considerations in equipment selection (39).

FIGURE 3 BLACK LIQUOR SPILL COLLECTION SYSTEM

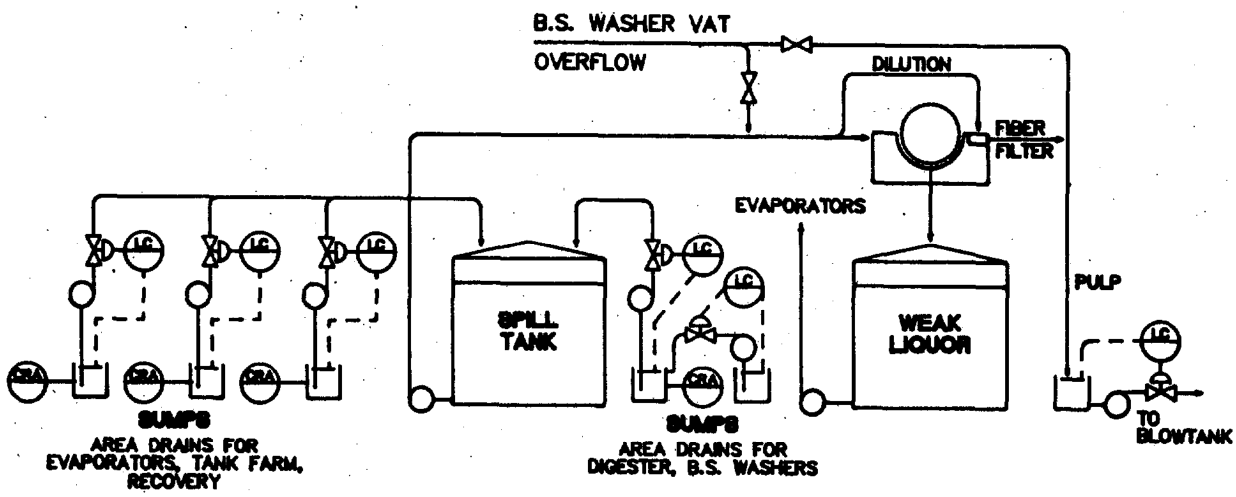
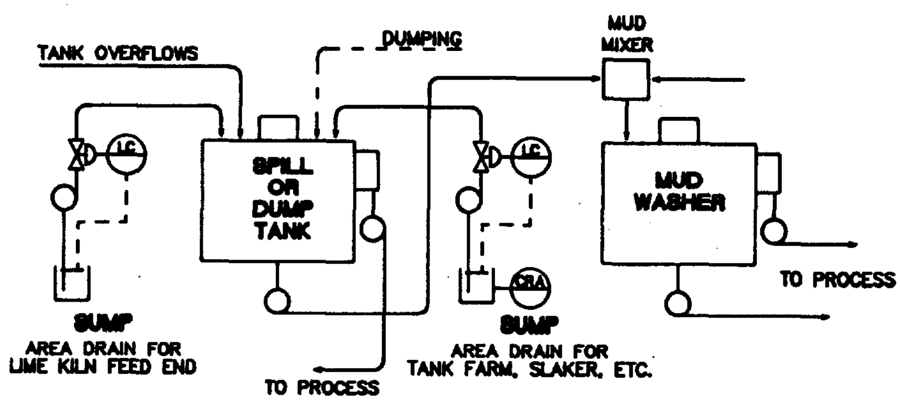



FIGURE 4 CAUSTICIZING AREA SPILL COLLECTION SYSTEM



## D. Limitations of Spill Collection Systems

The major limitation in implementing a successful spill collection and management program is the availability of excess capacity for evaporation, recovery, and steam generation. Since most of the recovered streams are fairly dilute, their recovery imposes an increased load on evaporation and steam generation. Additionally, since the recovered organic material is sent to the recovery furnace, additional recovery furnace capacity is also required.

# VI BLEACH PLANT IN-PLANT CONTROL TECHNOLOGIES

Bleach plants use large quantities of water. A survey by Gilmont showed that multi-stage bleach plants used as much as 50,000 gallons of fresh water per ton of pulp (45). Bleach plant effluents contribute almost all of the chlorinated organics, up to 85 percent of the color, and 50 percent of the BOD generated at a mill (46,47, 48). Bleach plants also consume large quantities of chemicals, plus energy, which are needed to heat various process streams. Consequently, over the years a considerable amount of research has been directed at examining and modifying bleaching technology to minimize its environmental impact. This research can be divided into two broad categories. The first category includes efforts that are aimed at modifying equipment and recycling streams so as to reduce effluent volumes and minimize fresh water usage. The second category includes changes in the pulping and bleaching chemicals to enable greater recycle of effluents, and reducing the application of chlorine to minimize the formation of chlorinated organics.

This section describes the status of various bleaching technologies, their current status, and industry experience with their implementation related to their impact on effluent characteristics.

## A. Bleach Plant Modifications Aimed at Minimizing Effluent Volumes

(1) Countercurrent Washing - Historically, in multi-stage bleaching the filtrate from each bleaching stage was sewered and fresh makeup water was used in each stage. Under these conditions up to 50,000 gallons of fresh water were used to produce a ton of pulp. In order to reduce the volume of water used in bleach plants, countercurrent washing systems have been installed in a number of bleach plants. Countercurrent washing may be direct, split-flow, and jump-stage (48). In countercurrent washing flows are managed in a way such that there is a net flow of filtrate from the final bleaching stage to the earlier stages, thus reducing the need for fresh water. Bleach plants with countercurrent washing typically operate at 8,000 to 10,000 gallons of water/ton, although some are known to operate at 4000 to 5000 gallons/ton. Filtrate recirculation was reported to reduce the chlorinated organic content of effluents (49).

The major hindrance to implementing countercurrent washing in bleach plants has been the impact of filtrate recycle on equipment corrosion. When filtrate streams are recycled within a bleach plant, this results in higher stream temperatures, buildup of chlorides, and lowering of pH of many streams. To withstand these conditions, bleach plants with countercurrent washing require much more corrosion resistant materials of construction such as titanium, Hastalloy, and series L stainless steels.

Countercurrent washing increases bleaching chemical demand as a result of buildup of organics in various streams, and requires adjustments to the process to accommodate elevated temperatures in various streams. Other problems such as increased foaming with the recycle of E stage filtrate, and pH control problems have also been reported (48,50).

(2) Use of Machine White Water in Bleach Plants - Since bleach plants are a large net user of fresh water, any substitution of the fresh water with recycle water from other sources will result in a net reduction in the volume of effluent from the manufacturing facility. At a number of mills, the bleach screen room and paper mill white water are used for diluting pulp entering the bleach plant from the high density storage chest, and for diluting the pulp leaving the final bleach plant washer. A number of mills visited during this investigation reported that they used machine white water for various bleach plant showers.

(3) Recycle of Bleach Plant Filtrate to the Pulp Mill - Only the Great Lakes Forest Products Company mill at Thunder Bay, Ontario has tried the recycle of bleach plant C and E stage filtrate to the pulp mill. This experience was, however, not very successful, and the mill has abandoned this practice. Details of experiences at this location are included in the "Closed Cycle Technologies Draft Report" (1).

B. Changes in Bleaching Technology Aimed at Minimizing Environmental Impact

This is the most active area of research within the pulp and paper industry. A number of newly developed or proposed new bleaching technologies and their potential benefits in terms of their environmental impact are described below.

(1) High $ClO_2$ Substitution in the C Stage - A number of investigators have examined the impact of increased substitution of chlorine with chlorine dioxide on bleach plant effluents. Their studies show that substantial substitution of chlorine with chlorine dioxide reduces effluent color, BOD, COD, chlorinated organics, and toxicity (47,51,52,53,54,55,56,57). Rapson has identified several other benefits of high chlorine dioxide substitution (52). A number of mills, including some visited during this investigation, practice $ClO_2$ substitutions as high as 70 percent in the first stage.

(2) Oxygen Delignification - In oxygen delignification, pulp is treated with molecular oxygen at elevated pressure under alkaline conditions. The delignified pulp is washed and sent to the bleach plant for further bleaching, and the alkaline filtrate from the oxygen stage is used for brownstock washing. The major advantage of oxygen delignification is that the lignin content of the pulp entering the chlorination stage is much lower, and consequently, the pollution load from the bleach plant is significantly reduced.

Carpenter et al. reported that applying oxygen delignification to a hardwood kraft pulp (reducing the kappa no. from 18 to 9-10) and returning the entire oxygen stage filtrate to the recovery furnace would reduce bleach plant color by 75 percent, COD by 35 percent, and BOD by 52 percent (58). Similar reductions of conventional pollutants and significant reductions in bleach plant organic chlorides releases have been reported for several full scale installations (59,60,61,62,63,64,65,66).

The first full scale oxygen delignification system was installed at the SAPPI facility in South Africa. Currently there are over 44 oxygen delignification systems worldwide (60). Most of these systems are high-consistency processes, although medium-consistency process installations are increasing in numbers.

According to Reeve, high consistency oxygen delignification has not gained wider acceptance in North America because of high capital costs and concern about the effect of oxygen on pulp strength (67). Additionally, installation of an oxygen delignification system directly impacts the chemical recovery and causticizing areas. In a new fiber line with oxygen bleaching, the total additional solids load to the recovery furnace increases by approximately 4 percent for softwoods and 3 percent for hardwoods. Solids increases up to 10 percent have been reported at older mills which installed oxygen delignification (68).

The heating value of black liquor from oxygen delignification is slightly lower because part of the solids from the oxygen delignification stage are partially oxidized. Since oxygen delignification systems utilize oxidized white liquor for providing alkalinity in the oxygen stage, there is a net increase of 3 to 5 percent on the causticizing plant and lime kiln load (68).

The above identified problems, along with the high cost of oxygen delignification systems, generally make oxygen delignification attractive only at those existing installations where the mill is undergoing a major modernization which includes increasing the capacity of the chemical recovery system, the lime kiln, and the causticizing plant.

(3) Extended Delignification - Sjoblom et al. reported the results of mill trials with extended delignification (69). Mera and Chamberlin recently reported the results of their trials with the extended delignification process using the Rapid Displacement Heating (RDH) cooking system (70). Their study indicated that the

RDH system could be used to cook pulp to much lower kappa numbers than practiced in conventional kraft cooking, while maintaining pulp quality. Since this process reduces the amount of lignin entering the bleach plant, it is expected to reduce the pollutant load from the bleach plant also.

(4) Peroxide Bleaching - Peroxide bleaching using hydrogen peroxide and sodium peroxide has been practiced for many years. The major environmental benefit of peroxide bleaching lies in the reduced need for using chlorine or chlorine-containing bleaching chemicals, which are responsible for forming chlorinated organics.

Peroxides are used for bleaching mechanical, chemical-mechanical, and sulfite pulps, and as an intermediate step in sequence with chlorine containing bleaching chemicals in kraft bleaching. According to McDonough, peroxide bleaching can result in improved strength characteristics in high-yield pulps (71). Ruhanen and Dugal investigated the use of peroxide as the first bleaching stage for kraft pulp (72). Their studies showed a reduction in effluent toxicity, 90 percent reduction in effluent color, and 40 percent reduction in effluent BOD. They concluded, however, that the price of peroxide relative to chlorine as an oxidant was too high, and had to drop significantly to justify using peroxide for kraft pulp bleaching.

(5) Ozone Bleaching - Ozone bleaching has been a consideration for many years. Singh and Scott Paper Company were granted a Canadian patent in 1975 related to ozone bleaching (73). A number of subsequent patents have been granted on modifications to this process (74,75). Some of the modifications involve total elimination of chlorine or chlorine-containing chemicals from the bleaching sequence, and total recycle of bleach plant effluents. Liebergott et al. (76) reported the results of their kraft pulp bleaching studies using oxygen, ozone, hydrogen peroxide, and sodium hydrosulfite. Their studies showed substantial reductions in effluent color as compared to the conventional 5-stage CEDED sequence.

The major limitation of ozone bleaching is its lowering of pulp strength and the high cost of ozone manufacture (67).

(6) Nitrogen Dioxide Bleaching - Efforts to use nitrogen dioxide as a bleaching agent have been ongoing for over twenty years. Nitrogen dioxide and water form nitric acid, and nitric acid reacts with lignin in the presence of nitrogen dioxide. However, nitrogen dioxide is not a selective oxidant and can cause a significant decrease in pulp strength. Currently, a considerable amount of research is being conducted on the use of nitrogen dioxide for extended delignification (77). Recently a "Prenox" pilot plant was installed in Sweden with the objective of reducing kappa number to below 10 by $NO_2$ pretreatment prior to oxygen bleaching (78).

## VII PAPER MILL IN-PLANT CONTROL TECHNOLOGIES

The paper machine is the largest user of water at a pulp and paper manufacturing facility. Consequently, over the years numerous programs aimed at closing machine water systems by reducing fresh water input into paper machines have been proposed or implemented. This section presents a brief summary of pulp/paper machine water requirements, water recycle practices, and major problems encountered in implementing a high degree of paper mill closure.

### A. Pulp/Paper Machine Water Requirements

In a pulp/paper machine water is required for pulp dilution, showers for the Fourdrinier and press sections, sealing and cooling of vacuum pulps, and cooling in the drying section. The water use demands around a paper mill have been described in several NCASI publications (79,80,81,82). Pulp from the high density chest at approximately 15 percent consistency is first diluted to approximately 3 percent consistency for stock preparation and is then diluted to approximately 0.5 percent consistency at the paper machine headbox. Dilution water is also used for pulper makedown, elutriation of cleaners and screen rejects, and chemical solution makeup.

Shower waters are needed to operate a multitude of sprays and showers of different types that are used in a paper machine. The quality and quantity of water used in these sprays and showers vary considerably, and have to be considered in any white water reuse program.

There are 1300 to 1500 gallons of water/ton of pulp required in liquid ring vacuum pumps used to create the vacuum for drawing water from sheets and felts. The temperature of this water is critical, because as its temperature increases, the vapor pressure of the water increases, thus reducing the vacuum that the pump can create. Water is also used to seal, lubricate, and cool packings of pumps. The quantity of water used for this purpose, normally referred to as gland seal water, is substantially less than used for water ring pumps.

Heating and cooling waters are required for heat exchangers, mechanical cooling units, sweat dryers, hydraulic systems, brake drums, etc. The quantity and quality of water used in these systems vary depending upon the system and the final intended use of the water.

### B. Pulp/Paper Machine Water Conservation Through Equipment Modification and Recycling

The quantity of water used at a paper machine can be reduced either through equipment modification, which results in a reduced fresh water demand, or through recycle of white water either within the paper machine or to some other process. A number of investigators have reported on machine water conservation technologies and experiences (83,84,85,86,87,88,89,90).

(1) <u>Reduction in Water Use Through Equipment Modification or Replacement</u> - The two most widely used examples of this are the replacement of conventional pumps with pumps with mechanical seals, and using high pressure low flow rate showers in place of low pressure high flow rate showers. In some applications, indirect heat exchangers are also used in place of direct heating or cooling. Both are, however, very expensive alternatives.

(2) <u>Reduction in Water Consumption Through Reuse Within the Paper Mill</u> - The reduction in water consumption through reuse within the paper mill is achieved through segregation, recycling after treatment, and blending.

Segregation generally involves separating streams of higher quality (lower temperature, less contamination) from lower quality (hotter temperature, more contamination) streams so that the higher quality streams can be utilized at those locations where higher quality is needed. Installations of systems for separating seal waters and/or cooling waters from contaminated streams containing fiber and/or dissolved solids are examples of stream segregation within a paper machine. At a number of locations the segregated vacuum seal water is recycled in a closed loop with cooling towers (90).

Treatment of machine white water by removing fibers and suspended solids and reusing the treated water at a location where the quality needs are consistent with the quality of the supplied water have been the methods most widely used for substituting fresh water with recycle white water on paper machines. Reports on white water recycle abound in the pulp and paper industry (79,80,81,82, 83,85,92,93,94,95,96,97). Major examples of water reuse in the paper mill include: (1) recycle of white water as the main source of dilution water use outside of the headbox loop, (2) use of filtered white water in most showers, (3) use of temperature controlled filtered white water as vacuum pump seal water, and (4) return of contaminated white water streams to process uses nearer their origin, thus avoiding unnecessary cleaning of streams in saveal ls.

In many instances contaminated streams are blended with less contaminated streams, or hot, clean streams are blended with cooler streams to match stream quality with needs.

(3) <u>Reduction in Water Consumption Through Reuse Outside the Paper Mill</u> - At some integrated mills a reduction in fresh water consumption is achieved by recycling machine white water to other parts of the mill. This is an important aspect of operating an integrated mill at low water usage. At an integrated mill, pulp is received from the high density chest at 12-15 percent consistency, and it leaves the paper machine at approximately 40 percent consistency. Consequently, for each ton of fiber converted into paper, 1000 to

1400 gallons of water are separated from fibers and must be discharged from the paper mill. In addition to this, any fresh water used anywhere in the paper machine must also be sewered for water balance. Paper mill excess white water flow rates of 4000 to 6000 gallons/ton are achieved at mills which practice high levels of recycle and reuse.

Lapp, Ayers and Parr reported that at Escanaba a part of the primary clarified paper machine effluent was sent to the raw water treatment plant for further treatment and use as process water (92). Narum and Moeller reported that at the Simpson Paper Company mill at Shasta, surplus white water was sent to the bleach plant (37). At several mills visited during this study, it was noted that machine white water was being used in the bleach plant and the pulp mill (98).

## C. <u>Problems Encountered in Recycling and/or Reusing White Water</u>

Among the problems that have been identified with a high degree of paper mill closure are: (1) increase in white water solids, (2) increased corrosion, (3) nozzle plugging, (4) increased deposits formation, (5) biological growth, (6) elevated white water temperature, and (7) product quality impacts.

(1) <u>Increase in White Water Solids</u> - As a result of paper machine closure, the dissolved and suspended solids content of the white water increases. This can result in poorer drainage and increased drainage aid demand (97).

(2) <u>Increased Corrosion</u> - In studies conducted to examine the impact of water recycle on corrosion rates of mild steel, it was observed that no single water quality criterion adequately defined uniform corrosion rate. Instead, strongest correlations were observed between decreased uniform corrosion rates and increased fresh water usage, and increased uniform corrosion rates and increased conductivity (82). Lightsey et al. reported an increased corrosivity of carbon steel in white water with higher white water recycle rates (99,100). Increased pitting and crevice corrosion have also been observed at some locations (82).

(3) <u>Nozzle Plugging</u> - The primary operating problem encountered with white water recycle is shower nozzle plugging. Nozzle plugging is most affected by the quantity and size of suspended solids. This problem can be minimized by using filtration devices that are suitable for the particular application, selecting appropriate nozzle orifices and operating pressures, blending fresh water with white water, designing systems to keep velocities high so that solids do not settle, and having an effective maintenance program (101,102).

(4) <u>Increased Deposits Formation</u> - Increased white water recycle increases the potential for scale formation, as well as deposits of pitch and slime. These deposits can plug filters, screens, wires, and forming fabrics, and can affect product quality (103). Mills

with high hardness water encounter calcium and magnesium carbonate scales. Barium sulfate scales have also been encountered at some locations. Rosinous pitch buildup is usually associated with liquor carryover and improper use of sizing (104).

The problems of deposits formation and their control are very site specific. A number of additives are used to minimize scale formation.

(5) Biological Growth - As a result of recycling, the nutrient concentration of white water increases. This leads to a greater potential for biological growth. Although recycling can elevate the temperature of white water around the machine to levels above 125°F, which will inhibit biological activity, in other parts of the white water loop temperatures are not that high, and this can result in increased growth of thermophilic bacteria (79,96,105,106).

The problem of biological growth, in general, is very site specific, and suitable solutions have to be found for each situation.

(6) Elevated White Water Temperatures - As noted earlier, increased recycle results in elevated white water temperature which affects scaling, corrosion rate, and biological growth. Elevated vacuum pump seal water temperature reduces the maximum vacuum that the pumps are able to generate, thus adversely affecting their performance.

(7) Product Quality - Questions have been raised regarding the impact of extensive white water recycle on paper properties such as strength, opacity, and brightness (107,108,109). Some mills have reported problems with internal sizing as a result of closing white water systems, while others have reported improved sizing (105).

## VIII RAPSON-REEVE CLOSED-CYCLE PROCESS

### A. Basic Concept of the Rapson-Reeve Process

The Rapson-Reeve process is based upon recycling the bleach plant filtrates to the pulp mill, thus eliminating discharges from the bleach plant. The organics in the filtrates are burned in the recovery furnace, and the sodium chloride introduced into the process is removed through the Salt Recovery Process (SRP).

The concept of the Rapson-Reeve process and its details have been published in a number of articles (110,111,112,113).

### B. Implementation of Rapson-Reeve Process at Great Lakes Forest Products Limited Mill at Thunder Bay, Ontario

The Rapson-Reeve process was applied in a full scale installation at Great Lakes Forest Products Limited's new bleached kraft mill, referred to as Mill B, in Thunder Bay, Ontario, Canada. The new Mill B was an addition to an existing manufacturing complex that, among other operations, included a bleached kraft pulp mill identified as Mill A and a newsprint mill. The mill was started in December 1976. The details of the process implemented at the Thunder Bay mill are described elsewhere (114,115,116). Figure 5 is a simplified flow diagram of Mill B.

The pulp mill at Mill B is equipped with a Kamyr continuous digester, two-stage diffusion washer, pressure screens, and a decker. The washed, thickened pulp enters a five-stage (DC)EDED bleach plant.

Figure 6 is a schematic of the bleach plant at Mill B. The bleach plant has been designed to operate with full countercurrent washing up to the first extraction stage. Machine white water is used on the last washer. On the first stage washer, the first two showers use $D_1$ filtrate and the last two showers use $E_1$ filtrate.

During closed cycle operation excess $E_1$ filtrate is used to dilute the concentrated white liquor from the Salt Recovery Process after salt has been removed from the liquor, and it is used for brown stock washing. The D/C filtrate is neutralized and used as shower water for the brown decker, and in the lime kiln scrubber. The use of D/C filtrate in the lime kiln is aimed at purging calcium from the system which can otherwise cause a serious scaling problem.

As a result of the recycle of bleach plant filtrates, significant quantities of sodium chloride are introduced in the chemical recovery cycle. The sodium chloride is removed from the white liquor using the Salt Recovery Process shown in Figure 7. This process is based upon the evaporation of white liquor and separation of crystallized chemicals in two stages.

White liquor from the recausticizing plant, containing NaOH, $Na_2S$, $Na_2CO_3$, $Na_2SO_4$, and 2-3 percent NaCl, is introduced into the evaporator where it is concentrated to 20-30 percent NaOH + $Na_2S$. Anhydrous $Na_2CO_3$ and burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) crystallize and are separated from the white liquor in cyclones. The clarified white liquor is further concentrated to 36-42 weight percent NaOH + $Na_2S$. NaCl, anhydrous $Na_2SO_4$ and burkeite crystallize and are separated from the concentrated white liquor in a second cyclone. The recovered salt is cleaned and used in the ERCO R-3 chlorine dioxide generator. The anhydrous sodium carbonate and burkeite separated in the first cyclone are added to the salt free white liquor prior to the liquor's introduction into the digester for cooking.

## C. Operating Experience at Thunder Bay

As anticipated, a number of operating problems were encountered with the mill at start-up. Many of these problems resulted in minor modifications to the process. Even after all the modifications to the process were completed, the mill was never able to achieve total recycle of bleach plant effluents. Typically, 50 percent recycle of

FIGURE 5 MILL B SIMPLIFIED FLOW DIAGRAM

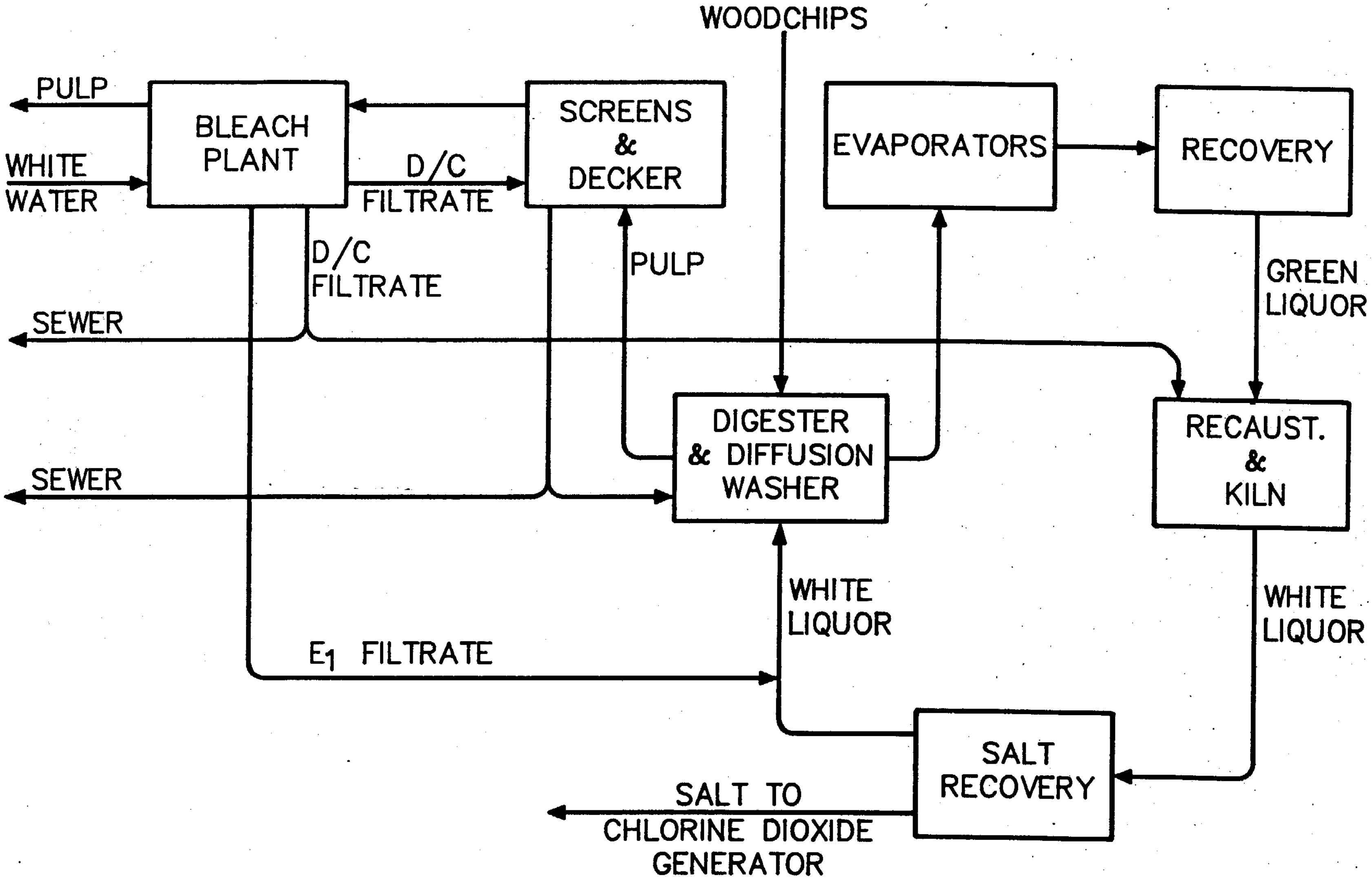


FIGURE 6 MILL B BLEACH PLANT FLOW DIAGRAM

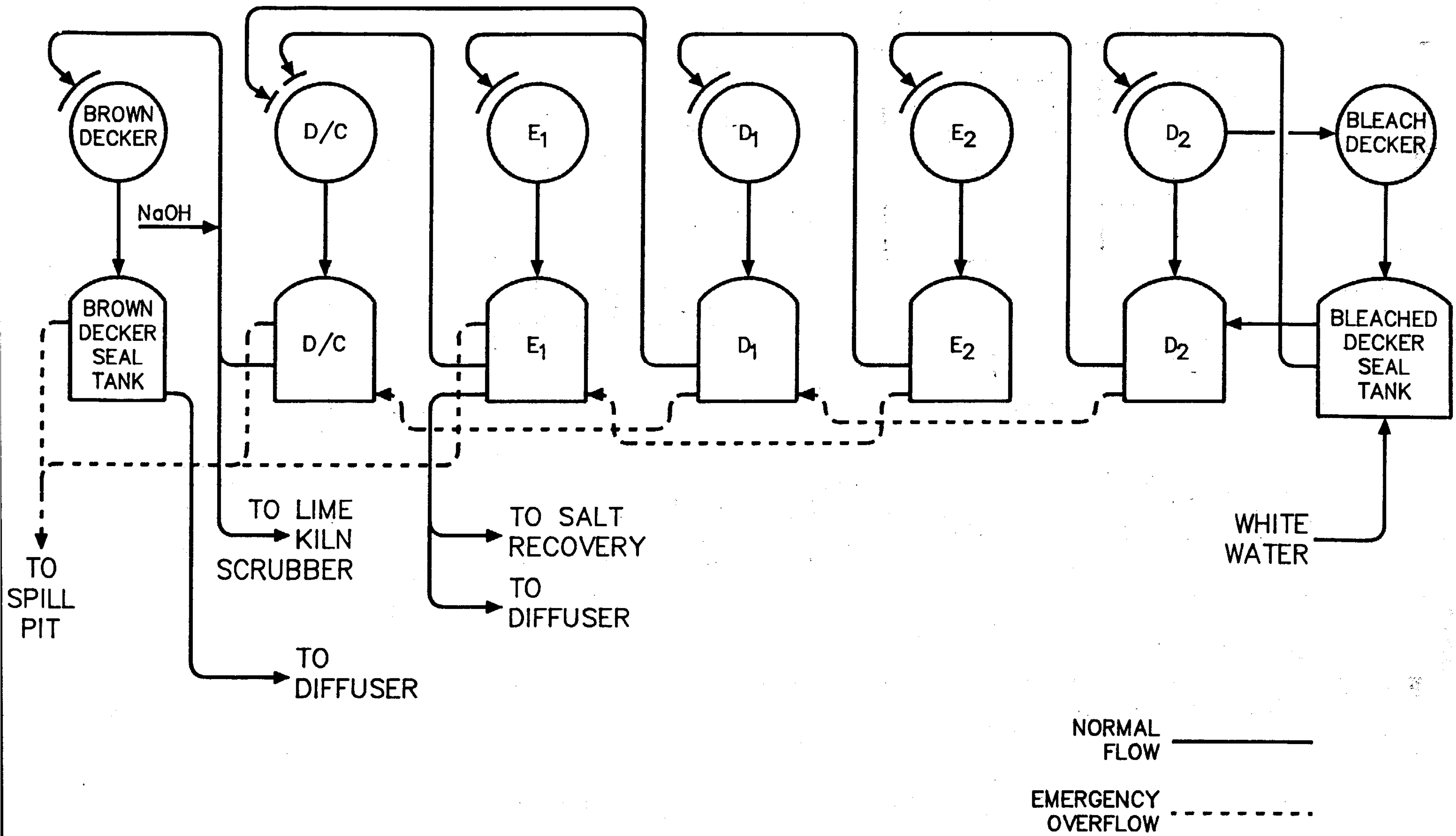
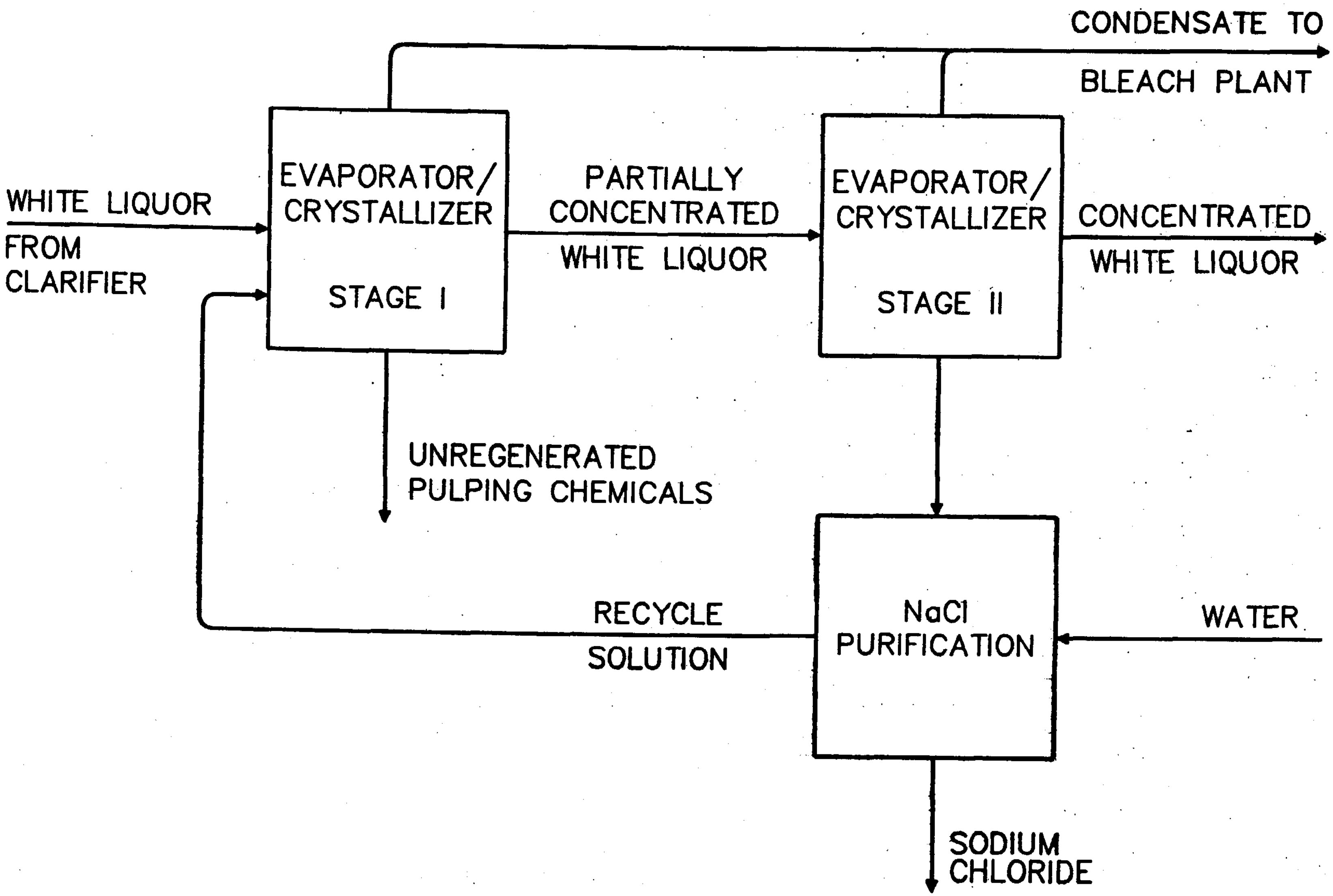


**FIGURE 7 SALT RECOVERY PLANT SCHEMATIC**



excess bleach plant filtrates was achieved for periods lasting 7 to 10 days. As a result of periodic sewering of the entire bleach plant excess filtrates, the mill never observed a significant accumulation of potassium in its recycle stream, which would be expected in a closed cycle mill (117). A description of some of the operating problems encountered at Thunder Bay is provided below.

(1) <u>Materials of Construction Failure/Corrosion</u> - A major consideration in designing this mill was the concern for corrosion in the entire mill because of the introduction of chlorides from the bleach plant into the pulping and chemical recovery cycle. Consequently, considerable attention was paid to the selection of suitable materials of construction. However, within the first two years of operation severe corrosion of the recovery furnace superheater caused tube failure, and closed cycle operation was discontinued for six months in order to change tubes. The system was restarted with a lower level of recycle of bleach plant filtrates to minimize chloride buildup in the system. According to the mill operating staff, the recovery furnace and evaporator tube life were one quarter of that observed at Mill A on the same site. Serious corrosion has also been observed in the SRP evaporators and many other parts of the closed cycle mill.

(2) <u>Bleach Plant Operations</u> - During initial operation, serious problems were encountered with pH control and flow balances. These problems were corrected. However, due to the concern for buildup of recycle chemicals in bleach plant filtrate streams, a continuous bleed of bleach plant filtrates was maintained.

The most severe problem with bleach plant operation was encountered when the mill switched its pulping practice from softwoods only to alternating between softwoods and hardwoods every 5 to 10 days. It was observed that during Aspen pulping, pitch would build up in the system to the extent that an acceptable quality market pulp could not be produced. During hardwood pulping serious problems were also encountered with the Salt Recovery Process due to the plugging of E-filtrate lines and scaling/solids precipitation in the first two evaporators of the salt recovery plant.

(3) <u>Chemical Recovery Area</u> - During closed cycle operation, the high sodium chloride content of the liquor reduced the smelt melting temperature which caused problems with bed maintenance.

Closed cycle operation reduced the heating value of the black liquor by approximately 6 percent, from an average of 14057 kJ/kg of oven-dry solids for the "A" kraft mill liquor, to 13122 kJ/kg of oven-dry solids for Mill B, when cooking the same pulp. This problem was further compounded by a lower solids content in the black liquor to the recovery furnace which was caused by a poorer pickup of black liquor on the cascade evaporator tubes.

The above problems with the liquor are likely to have a significant impact on TRS and $SO_2$ emissions from the recovery furnace. The Thunder Bay mill is subject to TRS and $SO_2$ emission standards that are based upon ambient impacts, and are not as restrictive as the new recovery furnace emission standards in the United States.

(4) Causticizing Area - During closed cycle operation significant operating problems were encountered in the causticizing area. Lime settling was very poor, requiring 2 to 3 times more settling time than in Mill A. There was more dusting in the kiln, resulting in more fines, which created the problem of blinding of the precoat filter. Lime reactivity was also lower. Although it may be argued that some of the operating problems of the kiln may not be directly attributed to the closed cycle operation, the operating staff emphasized that these problems were much worse during closed cycle operations.

## D. Current Status of Rapson-Reeve Process at Thunder Bay

The Great Lakes Forest Products mill decided to abandon the closed cycle process in 1988, and at the time of our visit in mid-1988 the mill staff was in the process of designing a secondary waste treatment system. In a recent Ontario Ministry of the Environment report it was stated that the Rapson-Reeve Process was not considered to be a demonstrated technology (118).

## E. Cost of Effluent Treatment Using the Rapson-Reeve Process

Based on 1979 data the cost of operating the Rapson-Reeve closed cycle system (assuming 0.80 US dollar/Canadian dollar) was estimated to be $5.99/air dried ton of pulp. This cost included the costs of steam production and consumption, bleach chemical consumption, salt production, defoamer use, treated water consumption, operating cost of salt recovery process plant, and increased cost of high $ClO_2$ substitution. These costs do not include the cost of installation of the Rapson-Reeve system, nor do these costs include the higher equipment replacement cost as compared to a conventional mill due to the reduced life of equipment caused by increased corrosion.

## F. Research Needs

A review of the earlier section dealing with operating experience with the Rapson-Reeve Process at the Thunder Bay mill suggests the following needs for research in order to enhance the possibility of implementing this technology at a future greenfield mill:

(1) Examine methods to eliminate the buildup of pitch during hardwood pulping.

(2) Evaluate materials of construction for their ability to withstand high levels of chlorides expected in a closed cycle mill.

(3) Examine the applicability of the Rapson Reeve Process to mills that use much less chlorine and chlorine dioxide than was used at the Thunder Bay mill. Low chlorine and chlorine dioxide use may be achieved through oxygen delignification, extended delignification, or some other means.

## IX BILLERUD-UDDEHOLM AND OTHER RESIN PROCESSES

### A. General Information

Resins remove desired chemicals from solutions either through ion exchange or sorption. Over the last twenty years a number of investigators have conducted studies or proposed the use of resins for removing color and organics from water and effluent streams. Although their methods vary in detail, the basic resin treatment technology is the same. In most cases resin treatment starts with effluent pretreatment to remove large particles and to optimize the effluent pH to make it suitable for resin treatment. The effluent then passes through a resin column where color and other organics are removed. The column is used until its removal capacity drops below a certain specified level, at which point the column is taken out of service and put in a regeneration mode. During regeneration, a very small stream at a pH very different from that of the waste stream being treated removes the material collected on the resin, and the resin is regenerated. The concentrated stream of the pollutants recovered during resin regeneration is recycled to the process.

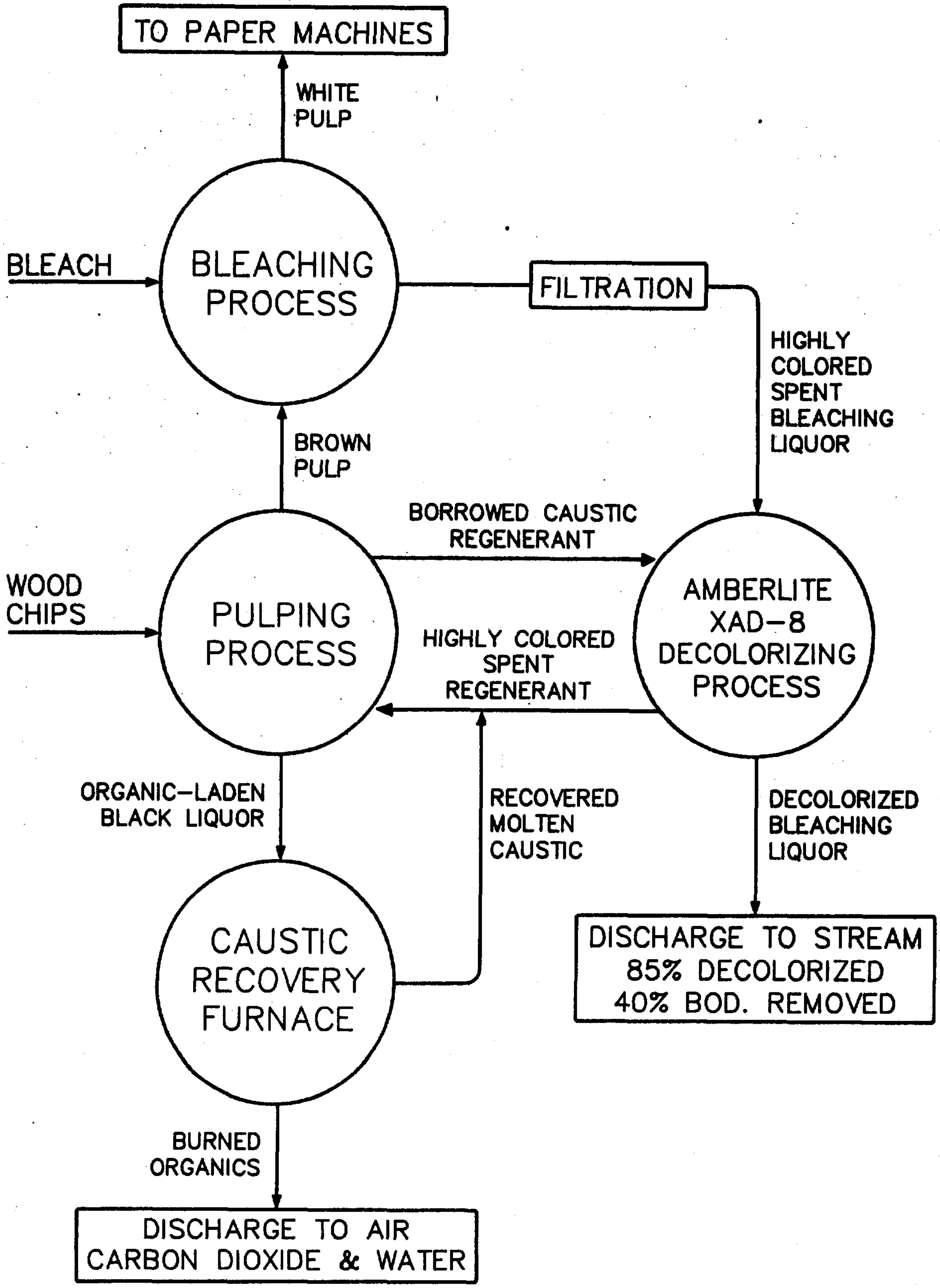
### B. Application of Resin Processes in the Pulp and Paper Industry

A number of investigators have reported on the effectiveness of resins for removing color from bleach plant effluents (119,120, 121,122,123). Several reports have reviewed the status of resin technologies for bleach plant effluent color control (124,125,126). According to these reports three resin processes (Rohm and Haas Process, Dow Process, and Billerud-Uddeholm Process) have either been piloted or implemented on a full scale. These processes are discussed below.

(1) Rohm and Haas Process for Effluent Color Reduction - The Rohm and Haas Process utilized a highly cross-linked hydrophilic, porous polymer named Amberlite XAD-8. The resin contained no ion exchange groups, and color removal resulted from adsorption of organics on the resin. Figure 8 is a flow diagram of the Rohm and Haas Process.

In a paper published in 1974, Rock (127) reported 70 to 95 percent removal of color, and BOD and COD removals of 33 percent and 43 percent for a combined caustic extract/chlorination effluent stream using this process. The efficiency of the resin was highest at a pH of ≤2.5, and the resin was regenerated with white liquor. No results were provided on the efficiency of the resin to remove chlorinated organics.

**FIGURE 8    ROHM AND HAAS PROCESS FLOW DIAGRAM**



Wilson found XAD-8 to be best suited for combined bleach plant effluent (128). Additional conclusions from this study were: (1) any alkaline solution (including caustic extract) could be used to regenerate resin; (2) caustic extract could be used for regeneration several times before disposal; and (3) use of a countercurrent contactor was valuable only for frequent bed regenerations.

The reported disadvantages of this process are its low pH requirements and the potential for chloride build-up in the pulping process water as a result of recycle of the spent reagent to the chemical recovery process.

(2) Dow Process for Effluent Color Reduction - In 1975 Chamberlin, et al. (129) reported on the use of a new resin (XD-8704) manufactured by Dow Chemical. Their results showed 82 percent removal of color in a combined bleach plant effluent. The resin was reported to be effective over a pH range of 2 to 9. Figure 9 is a flow diagram of the Dow Process outlined by Chamberlin. The resin was regenerated by treatment with weak wash and chlorination stage extract.

The Dow Chemical Company later employed a new family of resins (XF-4283L) at a mini-pilot plant of the process, as operated at a 650 ton per day bleached kraft softwood plant (130). Caustic extract effluent was passed through sand filters, a charcoal bed, and then applied to resin columns. After breakthrough, weak wash, which could be recycled several times, was used for resin regeneration. After three hours, at a flow rate of 7.5 bed volumes per hour, color was reduced by 85, 92, and 84 percent at pHs of 7.0, 5.4, and 4.0, respectively.

(3) Billerud-Uddeholm Process - The Billerud-Uddeholm Process utilizes a weak anionic resin capable of both ion exchange and adsorption for removing color and organics from the first caustic stage effluent. A schematic of the pilot plant, which was described in 1976 (131), is shown in Figure 10. In the pilot plant the effluent was first filtered/screened to remove suspended solids. The filtered effluent passed through two beds of resin to remove color and certain organic compounds. When the resin was saturated with pollutants, it was regenerated with an alkaline stream such as caustic or oxidized white liquor which was sent to the evaporator. Following regeneration, the resin was reactivated by passing spent acid from the chlorine dioxide generator or C stage effluent. The resin was then reused for treating $E_1$ filtrate.

It was reported (131,132,133,134) that the process accomplished the following:

(a) An average color reduction of 90 percent, COD reduction of 80 percent, and BOD reduction of 50 percent.

(b) Almost complete elimination of chlorinated phenols and guaiacols.

FIGURE 9 DOW PROCESS FLOW DIAGRAM

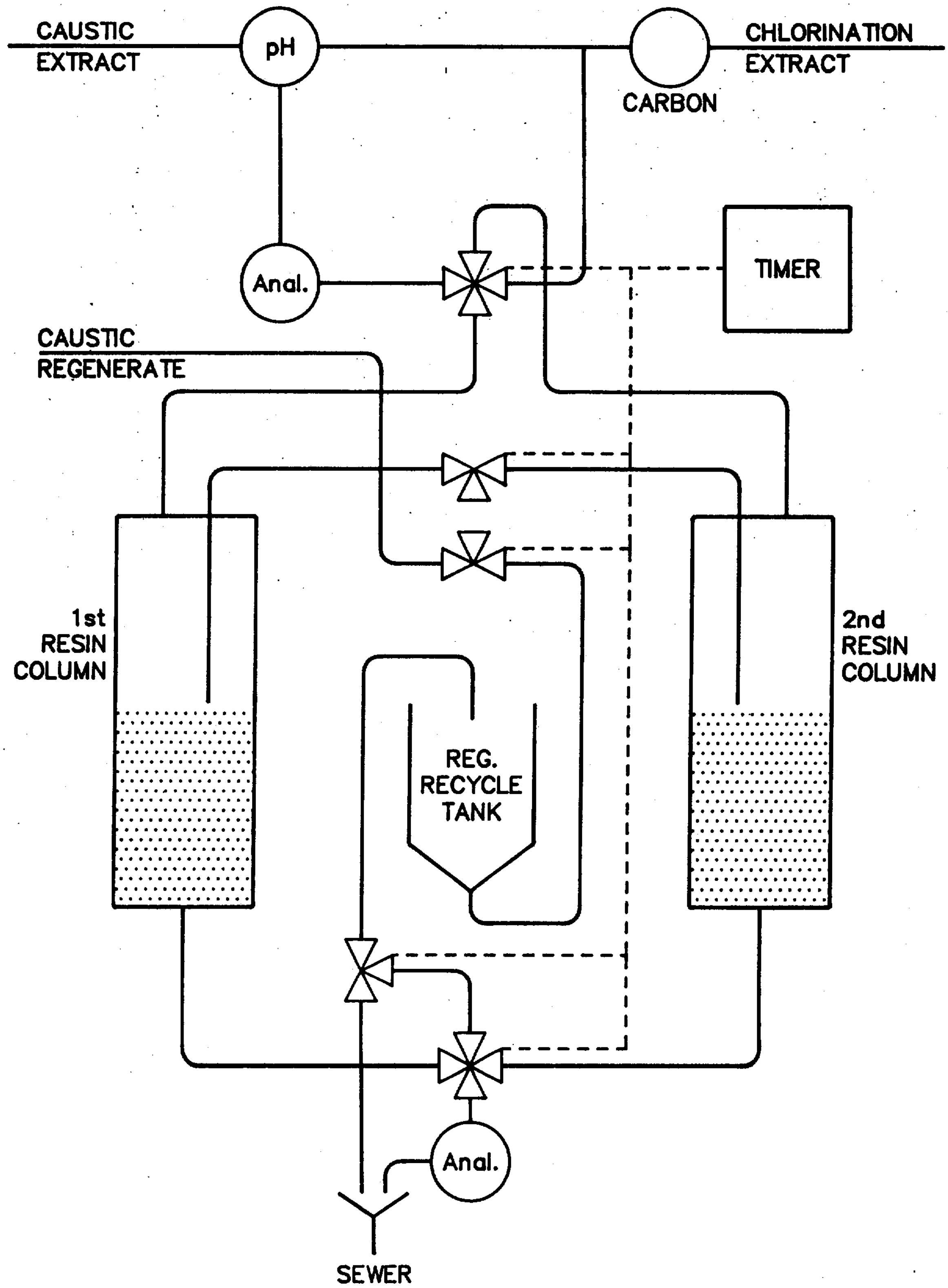
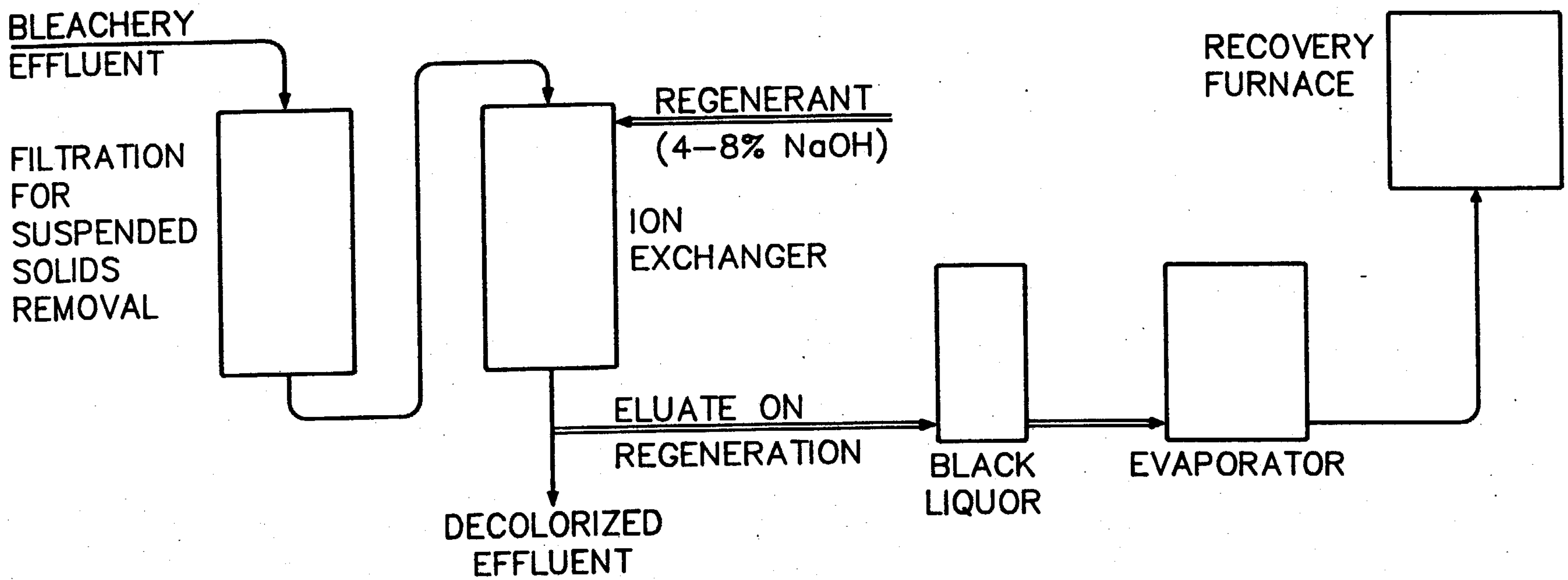


FIGURE 10 BILLERUD UDDEHOLM PROCESS PILOT PLANT FLOW DIAGRAM



(c) Almost complete elimination of effluent toxicity.

(d) Some removal of trace metals.

The process did not remove resin and fatty acids, and no significant buildup of chlorides was observed in the white liquor. It was theorized that since the process did not recycle inorganic chlorides, the small amount of chlorine recycled with organic chlorides was being purged from the system as HCl in the presence of significant concentrations of $SO_2$ in recovery furnace gases. The life of the resin was reported to range from 1 year to 3 years.

A major problem with this process has been the short resin life and the variability in the performance of the resin from different batches. According to persons knowledgeable about the process, at times an entire new batch of resin exhibits such poor removal efficiencies that it has to be abandoned and replaced by another (135). In 1980 a full scale plant was installed at a 300 tons per day Billerud-Uddeholm bleached kraft mill in Skoghall, Sweden (136,137). The plant was designed to treat the entire C and $E_1$ stage effluents. The concept of the bleach plant was essentially the same as the pilot plant, except that in place of fixed beds of resin, the resin beds were moved from stage to stage. After a long and troublesome start, the system operated with some success for some time. However, due to problems encountered with low resin life and poor removal efficiencies, in 1987 the mill decided to abandon this process and install a secondary treatment system (138).

### C. Cost of Effluent Treatment Using Resins

In 1980 Lindberg and Lund (133) estimated the annual operating cost excluding depreciation and capital recovery of treating C and E effluents from a 300 ton/day CEHDED bleach plant at $3.50/ton of production, assuming a 2 year resin life. The equipment and installation costs were estimated at $13,000/ton of production/day. In 1981 actual operating and labor cost excluding depreciation and capital recovery for this system was reported by Börjeson and Lindberg (136) as ranging between $7.75 and $10.25/ton of production. As noted above, this process was abandoned in 1987 due to short resin life and higher than expected operating costs.

## X ACTIVATED CARBON ADSORPTION

### A. General Information

Activated carbon has been used for removing organics from water and wastewater streams for many years. According to Timpe et al. (139) activated carbon is characterized by an extremely large surface area per unit mass (450-1800 $m^2/g$), and has very high capacity for surface adsorption of organic molecules of relatively low water solubility. The higher molecular weight organic compounds are generally more amenable to activated carbon adsorption than are low molecular weight compounds. Colloidal organic compounds cannot penetrate the pores of activated carbon and are not effectively removed. Strongly polar organic compounds such as amino acids, hydroxyl acids, sulfates, and sugars are refractory to carbon treatment. Activated carbon is also not generally effective in adsorbing inorganic electrolytes from solutions.

The effectiveness of activated carbon in removing certain dissolved and colloidal materials by adsorption results primarily from its extremely high surface area per unit mass. However, other factors such as pore size distribution and surface chemistry of the carbon play an important role in determining the overall effectiveness of activated carbon.

Activated carbon treatment systems typically consist of one or more columns of activated carbon, through which the effluent is passed following some pretreatment. Certain organics are adsorbed on the carbon and the cleaned stream is available for reuse or disposal. After some use, the adsorption capacity of the system is exhausted and the carbon column is either regenerated or disposed of. Most larger scale systems are based upon carbon regeneration.

## B. Activated Carbon Application in the Pulp and Paper Industry

Several investigators have examined the feasibility of using activated carbon to remove color from pulp mill effluents. Timpe et al. published a number of reports on their laboratory and pilot plant studies on the use of activated carbon for treating effluents from an unbleached kraft pulp mill (140,141). Their studies showed that a microlime treatment for color precipitation followed by adsorption on granulated activated carbon could produce effluent containing 100 units of color and 100 mg/L of total organic carbon, suitable for reuse in the unbleached kraft mill. They also reported that activated carbon treatment removed all of the foaming tendency of the effluent.

In a later study, Lang et al. investigated the effectiveness of activated carbon in treating E stage filtrate from a bleached kraft mill (142). The study showed greater than 90 percent removal of color when effluent pH was adjusted to 5 prior to carbon adsorption. The spent carbon could be regenerated several times with caustic before thermal regeneration was necessary.

NCASI conducted a number of studies on carbon treatment of bleach plant effluents (143,144,145). The studies showed that molecular weight distribution of color bodies played an important role in treatment efficiency.

In 1980 Carpenter conducted laboratory studies to examine the effectiveness of the addition of powdered activated carbon to an activated sludge treatment system of pulp mill effluents (146). The study showed only modest removal of color at carbon dosages up to 1,000 mg/L.

In studies conducted by Chen (147), it was reported that a shorter contact time of 35 minutes required up to 230 pounds of activated carbon per 1,000 gallons of effluent to remove 80 percent of the color.

In a recent paper, Sierka and Bryant (148) examined the effectiveness of two commercially available powdered activated carbons in removing total organic carbon, total organic chlorides, and organic chlorides with an apparent molecular weight less than 1000 (TOX <1000 AMW). Their interest in TOX <1000 AMW emanated from an as yet unpublished study by Bryant (149) which showed a significant correlation between TOX <1000 AMW and both acute and chronic toxicities.

The study showed that one of the powdered activated carbons (F-300) removed 52, 79 and 62 percent of TOX <1000 AMW from combined sewer, caustic extract, and C stage filtrate streams, respectively. The study did not address the question of carbon regeneration and treatment of adsorbed material.

C. <u>Cost of Effluent Treatment Using Carbon Adsorption</u>

In a report submitted to the State of North Carolina (150), the cost of installing an activated carbon system at a mill to treat its entire secondary effluent to reduce its color by 80 percent was estimated to be $117,000,000 (1987 costs), and the annual operating cost including depreciation and capital recovery for the system was estimated to be $42,574,000 (1987 costs). This gives an installation cost of $3,343/1000 gallons of effluent flow/day and an operating cost of $3.43/1000 gallons of effluent treated. The flow rate and characteristics of the effluent to be treated are shown in <u>Table 2</u>.

The activated carbon color removal system design in the above system consisted of a pH adjustment and control tank to lower effluent pH to 5.5, sand filtration equipment to remove suspended solids, carbon adsorption columns with 30 minute retention at average flow to remove color, and final pH adjustment. Caustic would be used to wash color bodies from the used activated carbon, which would be regenerated and reused. The regenerant solution would be concentrated in a separate evaporator and incinerated in a rotary incinerator. The major assumptions in preparing this report were:

(1) Sand filtration was capable of reducing effluent TSS to less than 5 mg/L.

(2) The activated carbon thermal reactivation process and the concentrated stream evaporation/incineration process would work.

(3) It would be possible to obtain an operating permit for the incinerator.

## TABLE 2 DESIGN BASIS FOR EFFLUENT TREATMENT SYSTEMS

### EFFLUENT CHARACTERISTICS

Flow - 35 MGD Average
55 MGD Peak

Color - 357,000 lb/day Average
- 535,000 lb/day Maximum

pH - 7.3 Average
- 6.5 to 8.3 Range

TSS - 40 mg/L Average
140 mg/L Maximum

Temperature - 90°F Average
- 65 to 110°F Range

### D. Operating Problems and Research Needs

The major problems that have been identified with activated carbon systems are:

(1) Frequent plugging of carbon beds with suspended solids.

(2) Biological growth in carbon columns and gassing off, resulting in carbon bed wash-out.

(3) Absence of a suitable technology for treating the concentrate from carbon regeneration at bleached kraft mills.

Any research program which is aimed at advancing the application of this technology to pulp and paper mill effluent treatment would have to address the above problems.

## XI CHEMICAL COAGULATION

Chemical coagulants are known to destabilize large organic molecules such as color dissolved in water, resulting in the formation of flocs. The resulting flocs can be separated from water by allowing them to settle in a quiescent zone or by air flotation. Lime, alum, ferric chloride, and polyelectrolytes have been utilized for pulp and paper mill effluent treatment.

### A. Lime Treatment

(1) Application of Lime Treatment in the Pulp and Paper Industry - NCASI conducted a number of studies aimed at utilizing lime for

treating pulp mill effluents (151,152). These studies led to the development and patenting by NCASI of the "massive lime" process (153). This process was implemented at the Springhill, Louisiana mill of International Paper Company for a period of less than two years, and has been described in several articles (154,155,156,157). At Springhill, all the lime produced at the mill was slaked with the highly colored E stage filtrate. Slaked lime at a rate of 20,000 mg/L of lime was applied to the remaining colored effluent. The sludge was allowed to settle in a primary clarifier and was sent to the green liquor clarifier for chemical recovery. The clarifier effluent was recarbonated with $CO_2$ to recover the soluble lime as calcium carbonate. The study showed 90 to 95 percent removal of color and 50 to 75 percent removal of total organic carbon from the treated filtrate streams. The major shortcomings of the process were its high lime use and recycle of chlorides to the chemical recovery system which can cause severe equipment corrosion.

The problems identified with the "massive lime" treatment led to the development of "minimum lime" treatment, which utilized lower concentrations of lime than used in the "massive lime" scheme. This process was implemented at three different mills. The experiences at these mills have been reported in detail (158,159,160,161,162, 163,164,165). All of these systems were capable of removing 75 to 90 percent of color from the streams to which they were applied. None of these systems is currently in operation. The major problem encountered with all these systems was the inability to adequately remove moisture from the lime sludges that were obtained.

(2) <u>Cost of Effluent Lime Treatment</u> - Watanabe et al. (166) stated that in 1983 the operating cost of a lime treatment system in Japan designed to treat bleach plant effluents was $8.31/1000 gallons of bleach plant effluent treated (assuming 130 yens/dollar). No equipment and installation costs were provided, and the operating costs did not include depreciation and capital recovery.

In a report submitted to the State of North Carolina (167), the cost of installing a lime color removal system at a mill to treat its entire secondary effluent to reduce its color by 80 percent was estimated to be $55,500,000 (1987 costs), and the annual operating cost including depreciation and capital recovery for the system was estimated to be $23,177,000 (1987 costs). The flow rate and characteristics of the effluent to be treated are shown in <u>Table 2</u>. This gives an installation cost of $1,586/1000 gallons of effluent flow/day, and an operating cost of $1.86/1000 gallons of effluent treated.

The lime color removal system design for the above system utilized a reaction basin with 15 minute residence tim to add lime to the effluent, dual flocculating clarifiers with a 3 hour retention time, a carbonation basin to adjust the pH to 10.5 to convert calcium hydroxide to calcium carbonate, dual clarifiers/calcium carbonate settling tanks for separating and removing calcium carbonate from the effluent and a pH adjustment basin to adjust the effluent pH to 7.0 prior to final discharge. The sludge from the clarifiers would be dewatered and sent to a separate lime kiln where it will be burned to recover lime for use in the process. The major assumptions in preparing this report were:

(1) The increase in dissolved solids resulting from implementing this technology would not have to be controlled.

(2) pH adjustment of the effluent would not precipitate colloidal sulfur.

(3) It would be possible to obtain permits for the lime kiln needed to recover the lime.

B. <u>Alum Treatment</u>

(1) <u>Application of Alum Treatment in the Pulp and Paper Industry</u> - A system which treated pulp mill effluent with alum was implemented at Gulf States Paper Corporation in Tuscaloosa, Alabama in 1974. The system, described in several articles (168,169,170,171), was designed to treat the secondary treated effluent from the mill, while recovering the alum. Though the system removed 90 percent of color, its operation was intermittent due to severe problems with sludge thickening and alum recovery and reuse. The mill is no longer in operation.

Several other investigators have reported on their studies aimed at color removal utilizing alum (124,172), and full scale installations are reported to be operating in the USSR (173,174, 175). Smetanin et al. (176) described a lignin and organics removal system for treatment of treated pulp mill effluent at the Baikalsk mill in the USSR. The system consists of alum treatment, separation of alum sludge at a consistency of 0.25 percent, polymer addition and air flotation of the sludge to a consistency of 4.5 percent, concentration of the sludge to 15 percent consistency, and, finally, burning of the sludge in rotary kiln dryers. During a visit to this mill in August 1988, it was learned that alum was not being recovered and that ash from the rotary kiln sludge dryer was being disposed of in a pond (177).

(2) <u>Cost of Effluent Alum Treatment</u> - In a report submitted to the State of North Carolina (178), the cost of installing an alum treatment system at a mill to treat its entire secondary effluent to reduce its color by 80 percent was estimated to be $43,900,000 (1987 costs), and the annual operating cost including depreciation and capital recovery for the system was estimated to be $17,939,000 (1987 costs). The flow rate and characteristics of the effluent to be treated are shown in <u>Table 2</u>. This gives an installation cost of $1254/1000 gallons of effluent flow/day, and an annual operating cost of $1.44/1000 gallons of effluent treated.

The proposed alum treatment system design consisted of a pH adjustment and alum addition basin with 2 minute retention, dual reactor clarifiers for forming and settling alum floc, and a pH adjustment basin prior to final effluent discharge. The alum floc at about 0.5 percent consistency would be pumped from the clarifier to a dissolved air flotation unit to thicken it to 5 percent consistency. This would be further thickened to 25 percent consistency in a screw press. The dewatered sludge would be dried in a flash drying system and incinerated in a fluidized bed incinerator for alum recovery. The major assumptions in preparing this report were:

(1) The increase in dissolved solids resulting from implementing this technology would not have to be controlled.

(2) The disposal of alum sludge would not require landfill lining.

(3) It would be possible to obtain a permit to operate the incinerator.

C. <u>Ferric Chloride and Ferric Sulfate</u>

Ferric chloride alone, and in combination with other chemicals, has been examined for effluent color removal. Studies conducted by Smith and Christman in 1969 showed that approximately 90 percent of color could be removed with ferric chloride under acid conditions (179).

Olthof and Eckenfelder conducted laboratory studies that showed that as compared to lime, lower dosages of ferric chloride and alum are needed to achieve approximately 90 percent color removal (180).

Dugal et al. conducted laboratory studies on the effectiveness of combined lime and ferric chloride treatment in removing color (181). Their study showed that multivalent ions were effective in removing almost all the color bodies, whereas lime treatment was most effective in removing color bodies with a molecular weight greater than 400.

The major shortcoming of all these studies is their failure to address the question of sludge thickening and ultimate disposal of the sludge in a cost effective and environmentally sound manner.

D. <u>Organic Polymer Treatment</u>

(1) <u>Application of Polymer Treatment in the Pulp and Paper Industry</u> - Abstracts of papers published by Kamanomido, Shimirra, and Noda (182,183,184) suggest that the authors have had success in removing color from semichemical pulp mill effluents by treating them with ammonia-epichlorohydrin condensation polymer, aniline-formaldehyde condensation polymer, and polythioureas.

In 1976 NASA was granted a patent for removing color from unbleached kraft pulp mill effluent streams (185). In this process the effluent was treated with quaternary ammonium compounds and activated carbon to remove color and other adsorbable substances. The quaternary ammonium compounds were recovered by going through a process that used methanol and required three filtration steps.

Activated carbon was produced in the process by pyrolyzing the cellulosic material, and lignin solids were recovered separately.

In a study funded by the Tennessee Valley Authority, Roberts reported that in jar tests a cationic surfactant removed greater than 95 percent of color from caustic extract and secondary waste treatment effluent (186). They examined the effect of surfactant doses, pH, mixing, and coaddition of alum on color removal. They proposed a pilot plant using a surfactant and dissolved air flotation. No attempt was made to address the question of the disposal of the separated material.

In a recent paper Garcia-Heras and Melé (187) examined the effectiveness of removing bleach plant effluent color by flocculation with ferric chloride, lime, and acrylamide copolymers. Their paper included Table 3 which compared the results of color removal with Ca(II), Al(III) and Fe(III). Garcia-Heras and Melé found that ferric chloride at a pH of 4.5 was the most effective coagulant for a combined bleach plant C stage and E stage effluent. However, the zone settling velocity for the floc was small at high color removal efficiencies. The settling velocity could be increased significantly by adding a copolymer of acrylamide with an acrylic ester of ternary amine (trade name Praestol K 225 FL).

Charles Ackel reported on a process for coagulating color from a treated mill effluent patented by Stone Container Corporation. This process utilizes an organic polyelectrolyte coagulant followed by air flotation (188,189,190). The process was reported to be capable of greater than 95 percent color removal, and a sludge consistency as high as 6 percent was achieved. It was also reported that the sludge generated from the process could be treated for partial coagulant recovery and then mixed with weak black liquor for further evaporation and burning in the recovery furnace.

The Stone Container process has been in operation at an unbleached kraft and semichemical mill in Hodge, Louisiana since mid-1985. The system removes 90 percent of color, and 50 percent of BOD, COD, and TOC. A similar system has recently been installed by Stone Container Corporation at a second mill which produces 1800 TPD of pulp, including 200 TPD of bleached pulp. Approximately 50 percent of the total mill effluent will be treated for color removal.

At both of the mills that have installed the Stone Container process, the sludge is returned to the process for burning in the recovery furnace. However, as noted above, the first mill does not practice any bleaching. At the second mill, which bleaches only 200 tons/day out of a total production of 1800 tons/day, only 50 percent of the effluent is treated. Consequently, the operating experiences at these mills would not address the broader question of the potential impact of chloride buildup in the liquor cycle on mill operation when chloride-containing sludge from a fully bleached mill is returned to the recovery system.

TABLE 3 COLOR REMOVAL BY COAGULATION WITH Fe(III), Al(III) AND Ca(II)

| CATION | WASTEWATER | COAGULANT | pH OF COAGULATION | COAGULANT DOSES | PERCENT COLOR REMOVAL | PERCENT COD REMOVAL | PERCENT TOC REMOVAL | PERCENT BOD REMOVAL |
|---|---|---|---|---|---|---|---|---|
| | Caustic Extraction (CE) | Lime | Natural | Massive 10-20 $kg/m^3$ | 90-96 | | 80 | 20-50 |
| Ca | CE | Lime | 12 | 1000 $g/m^3$ | 82 | | 69 | 23 |
| | Bleaching | Lime | 12 | | 80 | 40 | | |
| | Total Factory | Lime | 12 | 1000 $g/m^3$ | 80-89 | | | |
| | CE | Al Chloride | 5 | 7 mole $Al/m^3$ | 95-99 | | | |
| | | Al Chloride | 4-5 | 3.3 mole $Al/m^3$ | 96 | | 85 | |
| Al | Bleaching | Al Sulfate | | | 95 | 40 | | |
| | Factory | Al Sulfate | 5 | | 81-93 | | 50-60 | 22-25 |
| | CE (diluted 10%) | Ferric Chloride | 3.3 | 0.7 mole $Fe/m^3$ | 90-99 | | | |
| Fe(III) | Bleaching | Ferric Chloride | 4-5 | | 85-98 | | | |
| | CE | Ferric Chloride | 3.4 | 3.6 mole $Fe/m^3$ | 97 | | 86 | |

**TABLE 3** (Cont'd) **COLOR REMOVAL BY COAGULATION WITH Fe(III), Al(III) AND Ca(II)**

| CATION | WASTEWATER | COAGULANT | pH OF COAGULATION | COAGULANT DOSES (*)$g/m^3$ | PERCENT COLOR REMOVAL | PERCENT COD REMOVAL | PERCENT TOC REMOVAL | PERCENT BOD REMOVAL |
|---|---|---|---|---|---|---|---|---|
| Mutual Cooperation Between Fe(III), Al, and Ca | CE | $Mg^{++}$ and Lime | 12 | $Mg^{++}$ = 300*<br>Lime = 2500* | 95 | | | |
| | | | | Lime = 1000*<br>Fe = 3 mole/$m^3$ | 95 | | 81 | 36 |
| Synergy | CE | Lime and $Cl_3Fe$ | 11-12 | Lime = 18000*<br>Fe = 3 mole/$m^3$ | 95 | | 88 | 47 |
| | Bleaching | Ca/$Mg^{++}$ and Aluminum Sulfate | 11 | $(SO_4)_3Al_2$ = 100*<br>$SO_4Mg$ = 100-150*<br>$Ca(OH)_2$ | | 62 | | |
| | CE | Fly Ash of Coal with Fe, Al, and Ca | 4.6-5 | $Ca^{++}$ = 20 mole/$m^3$<br>Fe = 3 mole/$m^3$<br>Al = 28 mole/$m^3$ | 94 | 74 | | |
| | Bleaching | Fly Ash of Coal with Fe, Al, and Ca | 5 | | 98 | 88 | | |
| | Factory | Fly Ash | | | | | 80 | 60 |

TABLE 3 (Cont'd) COLOR REMOVAL BY COAGULATION WITH Fe(III), Al(III) AND Ca(II)

| CATION | WASTEWATER | COAGULANT | pH OF COAGULATION | COAGULANT DOSES (*)$g/m^3$ | PERCENT COLOR REMOVAL | PERCENT COD REMOVAL | PERCENT TOC REMOVAL | PERCENT BOD REMOVAL |
|---|---|---|---|---|---|---|---|---|
| Mutual Cooperation Between Fe(III), Al, and Ca Synergy (cont'd) | CE | Sludges from Integrated Kraft Mill with Fe, Al, and Ca | 3<br>7 | Ca = 11 $mole/m^3$<br>Fe = 0.6 $mole/m^3$<br>Al = 0.7 $mole/m^3$ | 75 | | | |
| | | Fly Ash Plus Sulfite Spent Liquor Plus Al(III) Plus Fe(III) | | | 90 | 70 | | |

(2) Cost of Effluent Treatment Using Polymers - In a report submitted to the State of North Carolina (191), the cost of installing a polyamine system at a mill to treat its entire secondary effluent to reduce its color by 80 percent was estimated to be \$24,700,000 (1987 costs), and the annual operating cost including depreciation and capital recovery for the system was estimated to be \$21,936,000 (1987 costs). The flow rate and characteristics of the effluent to be treated are shown in Table 2. This gives an installation cost of \$706/1000 gallons of effluent flow/day, and an operating cost of \$1.77/1000 gallons of effluent flow.

The design of the above polymer system consisted of polymer addition ahead of the primary clarifier and settling and removal of the color bodies in the existing clarifier. The separated sludge would be thickened from 1-2½ percent solids to 4-5 percent solids on rotary screen thickeners, and then sent to belt presses to increase their solids content to approximately 20 percent. The 20 percent solids sludge would be dried to 45 percent solids in a rotary sludge dryer and hauled to a landfill. The major assumptions in preparing this report were:

(1) There would be no increase in effluent color during storage and biological treatment.

(2) The existing primary clarifier would be capable of handling the additional sludge.

(3) It would be possible to obtain a permit to operate the sludge incinerator.

## XII ULTRAFILTRATION

### A. General Information

Ultrafiltration is a membrane process in which physical separation is achieved by applying pressure to the fluids being cleaned. The selectivity of an ultrafiltration membrane depends upon its pore size, which can be regulated during manufacture.

Ultrafiltration is usually carried out in the 10-150 psi pressure range, and by proper selection of the membrane the molecular weight separation range can be varied from around 1000 to 1,000,000.

Ultrafiltration systems are available in four common configurations: (1) tubular, (2) hollow fiber, (3) flat sheet, and (4) spiral wound. In the tubular configuration, the ultrafiltration membrane is applied to a porous tube for strength. In the hollow fiber configuration, the membrane is applied to the inside walls of a porous fiber. In the flat sheet configuration, the membrane is connected to a rigid plate, and plates are stacked into a cartridge with void spaces alternately containing feed and permeate. In the spiral wound configuration, a fabric spacer is enveloped in two membranes with three sides sealed and the fourth side connected to the permeate collection tube. The feed is applied on the outside of the membrane.

## B. Application of Ultrafiltration to Pulp and Paper Industry Streams

A number of investigators have reported on the use of ultrafiltration membranes for treating various pulp and paper mill streams (192,193,194,195,196,197). In recent studies, carried out in laboratories and pilot plants, it has been demonstrated that properly selected polysulfone membranes can reduce color by 80 to 90 percent, COD by approximately 70 percent, and BOD by approximately 25 percent. Table 4 presents the data reported by Lundahl and Mansson (198) on ultrafiltration of E stage filtrate at a Swedish mill pulping softwood. It was also reported that for concentrating the E stage effluent to 7 to 8 percent of the original volume, the flux rate was approximately 3 $m^3/m^2$ day (72 $gal/ft^2$ day).

The data reported by Lundahl (Table 4), and by other investigators (199,200), clearly show that ultrafiltration membranes do not reject chloride ions, and the chloride content of ultrafiltration concentrates is relatively low. These studies have also shown that ultrafiltration removes a significant fraction of resin and fatty acid, but does not remove low molecular weight chlorinated phenolics, and causes no significant reduction in the toxicity of the E stage filtrate. It has been reported that two pulp mills in Japan have installed ultrafiltration plants for effluent COD control. One of these mills treats the E filtrate from its hardwood production line, which constitutes approximately 1/3 of its total bleached pulp production, in the ultrafiltration plant and returns the concentrate to the evaporator for further concentration and burning (166). The other mill is a large manufacturing complex which includes facilities for producing bleached kraft pulp, semi-bleached kraft pulp, unbleached kraft pulp, TMP, groundwood pulp, and deinked waste paper. This mill treats the E stage filtrate from the bleached kraft pulp mill in an ultrafiltration plant. The concentrate is recycled to multiple effect evaporators.

It was recently reported that ASEA Oil and Gas has developed a new Cross-Rotational (CROT) Membrane Filter which has shown high flux rates and 70 percent removal of TOCl in pilot trials. A full scale trial at a mill in Sweden with an O(C+D)(EO)DED bleach plant is scheduled for 1988.

TABLE 4 ULTRAFILTRATION AT IGGESUNDS AFTER 2000 HR OF CONTINUOUS OPERATION

| | E-STAGE FILTRATE | ULTRA-FILTRATION CONCENTRATE | ULTRA-FILTRATION FILTRATE | PERCENT REDUCTION |
|---|---|---|---|---|
| Volume, $m^3$ | 12 | 0.6 | 11.6 | 95 |
| Color, kg/ton of pulp | 150 | 130 | 20 | 87 |
| $BOD_7$, kg/ton | 5.6 | 1.3 | 4.3 | 25 |
| COD, kg/ton | 44 | 27 | 14 | 70 |
| Total organic carbon, kg/ton | 14 | 9.7 | 4.4 | 70 |
| Total organic solids, kg/ton | 30 | 19 | 11 | 65 |
| Total inorganic solids, kg/ton | 43 | 7 | 36 | 20 |
| Organic chlorine, kg/ton | 2.3 | 2.0 | 0.3 | 87 |
| Inorganic chlorine, kg/ton | 13.4 | 0.5 | 12.9 | 4 |
| Acute toxicity, %[a] | 17 | -- | 35 | ≈50 |

[a]Percent mixed with water to have $LD_{50}$ in 96 hr.

## C. Cost of Effluent Treatment Using Ultrafiltration

Lundahl and Mansson (1969) described an ultrafiltration system for treating the $E_1$ stage filtrate from a bleach plant using ultrafiltration. Their estimated total cost in 1979 was $5.50/ton or $2.08/1000 gallons of treated effluent.

On the basis of a pilot plant study, Dorica (199) estimated the cost of an ultrafiltration system for treating the $E_1$ stage effluent from a 890 odt/day bleach plant. His 1986 estimated equipment and installation costs (assuming 0.80 US dollar/Canadian dollar) for an $E_1$ stage flow of $2.4 \times 10^6$ gallons/day were $5,920,000, and the operating costs excluding depreciation and capital recovery were $497,000/yr (Canadian, 1983). These translate into an installation cost of $2,467/1000 gallons of flow/day, and operating cost of $0.58/1000 gallons treated.

Watanabe et al. (166) stated a 1983 operating cost for an ultrafiltration system in Japan designed to treat $E_1$ stage effluent of $3.37/1000 gallons of effluent treated (assuming 130 yens/dollar). No equipment and installation costs were provided, and the operating costs did not include depreciation and capital recovery.

In a report submitted to the State of North Carolina (201), the cost of installing an ultrafiltration system at a mill to treat its entire secondary effluent to reduce its color by 80 percent was estimated to be $204,000,000 (1987 costs), and the annual operating cost including depreciation and capital recovery for the system was estimated to be $64,726,000 (1987 costs). The flow rate and characteristics of the effluent to be treated are shown in Table 2. This gives an installation cost of $5828/1000 gallons of effluent flow/day, and an operating cost of $5.20/1000 gallons of effluent flow.

The proposed ultrafiltration system design in the above report consisted of sand filters for suspended solids removal, fifty ultrafiltration modules, each rated at 750,000 gallons/day, for color removal, and a cooling tower for cooling the effluent prior to its discharge. Five percent solutions of caustic and citric acid would be used to clean the membranes. The concentrate from the ultrafiltration system would be concentrated in a six stage falling film evaporator to 50 percent solids, and would be incinerated in a refractory-lined rotary kiln controlled with a wet electrostatic precipitator to remove sulfur oxides and halogens. The major assumptions made in preparing this report were:

(1) It would be possible to operate a large and complex ultrafiltration plant.

(2) Sand filtration was capable of reducing TSS to less than 5 mg/L.

(3) Utilities to operate the system would be available.

(4) A construction permit for building the incinerator could be obtained.

D. Operating Problems and Research Needs

The major technical problems that have been identified with the ultrafiltration process are:

(1) Low initial flux rates and gradual decline in flux rates with time of operation.

(2) Effect of burning ultrafiltration concentrate on chloride buildup in the chemical system, and its impact on the recovery process, particularly at those facilities that do not have high $SO_2$ emissions and, consequently, cannot purge chlorides as HCl from recovery furnaces.

(3) Absence of technologies for final disposal of the ultrafiltration concentrate if burning in the recovery furnace is not feasible.

(4) Inadequate information on the nature of membrane deposits, and procedures for cleaning membranes to restore their initial flux rates.

These problems need to be addressed in future research programs if ultrafiltration is to be applied for effluent treatment in the pulp and paper industry.

## XIII REVERSE OSMOSIS

### A. General Discussion

Reverse osmosis is a high pressure membrane process in which dissolved solids are separated from water by applying a pressure higher than osmotic pressure. When pressure is applied to the feed stream, water permeates through the membrane from the zone of high dissolved solids concentration to the zone of low solids concentration, giving clean water.

Reverse osmosis systems are generally operated at pressures in the range of 150-1500 psi, and this technology is widely used for desalinating or demineralizing water, especially high dissolved solids streams.

The design configuration of reverse osmosis systems is similar to that for ultrafiltration (Section XII-A), only the reverse osmosis membranes are different. Reverse osmosis membranes are made of a variety of materials including cellulose, acetate, aromatic polyamide, poly-ether/amine, polyethylenimine cross-linked with toluene 2,4-disocyanate, zirconium oxide, and polyacrylic acid (202,203). The section of the membrane material of construction mainly depends upon its chemical resistance, rejection properties, and strength.

### B. Application of Reverse Osmosis in the Pulp and Paper Industry

A number of studies have been conducted on the use of reverse osmosis in the pulp and paper industry. Early studies conducted by Ammerlaun and Wiley (204), Beder and Gillespie (205), Bansal, Duby and Wiley (206), and Wiley et al. (207) examined the feasibility of using reverse osmosis to treat pulp and paper mill process and waste streams. Following extensive laboratory and pilot plant studies (208,209,210,211), a full scale reverse osmosis system was installed at an NSSC corrugating medium mill (212,213,214). The spiral tube type membranes, manufactured by the Union Oil Product Company, reduced color by 99 percent and operated at a flux rate of 5.1 gal/ft$^2$/day. The concentrate from the system was returned to the white water pit for reuse, and the permeate was used for pump and agitator shaft seals. The system has since been abandoned due to the unavailability of suitable membranes and operating changes at the mill.

Pilot plant evaluations of reverse osmosis and freeze drying techniques for treating effluents from three different pulp mills were carried out by Wiley et al. (215). Their study demonstrates the technical feasibility of applying these technologies, although significant operating problems were encountered. The study did not address the question of the ultimate disposal of the concentrate.

## C. Cost of Effluent Treatment Using Reverse Osmosis

A number of investigators have reported on costs associated with reverse osmosis treatment of effluents from pulp and paper mills. For the NSSC mill effluent treatment system described above in Section X-B the operating cost of the system in 1976 dollars was reported to be $10.73 per 1000 gallons of purified water.

In 1978, Wiley et al. (215) examined the possibility of treating bleach plant effluents with reverse osmosis followed by freeze concentration of the concentrated material from the reverse osmosis process. For the three bleach plants they examined, the operating cost (excluding depreciation and capital recovery) ranged from $20.00 to $30.00 per ton of bleached pulp, and the capital costs were about $30,000 per daily ton of bleached pulp.

Dorica et al. (200) described a bleach plant effluent treatment ultrafiltration/reverse osmosis process based on color removal by ultrafiltration, chloride removal by reverse osmosis, and chloride removal from the concentrates by diafiltration. Diafiltration of the ultrafiltration concentrate required the dilution of the concentrate with a chloride free or low-chlorine stream and reconcentration of this stream using an ultrafiltration membrane which does not reject the $Cl^-$ ions. During diafiltration reverse osmosis process concentrates were treated with a more "open" membrane than that used in the reverse osmosis to separate $Cl^-$ from the concentrates. Their 1985 fixed investment costs (assuming $0.80 US dollar/Canadian dollar) were estimated to be $38,000 and $27,000 per daily ton of pulp production for treating bleach plant effluents from a C/DEHDED and a $(D_{40}C_{60})$EDED bleach plant, respectively. The direct operating costs for the C/DEHDED and the $(D_{40}C_{60})$EDED plans were $10.08 and $12.90 per oven dried ton of pulp.

## D. Operating Problems and Research Needs

Among the major operating problems that have been identified with reverse osmosis systems are:

(1) Membrane fouling resulting in flux reduction.

(2) Membrane degradation due to chemical reactions with chlorine.

These problems would need to be addressed in any research program that is aimed at advancing the application of this technology in the pulp and paper industry.

## XIV RECOMMENDED AREAS FOR RESEARCH TO BE CARRIED OUT UNDER THE R&D PROGRAM

As indicated earlier, the major objective of writing the two technology assessment reports (1,2) was to prepare a list of research areas suitable for funding under the R&D program. This section outlines and prioritizes NCASI's recommendations for research under the R&D program. These recommendations were published in a separate report (216).

The recommendations for research outlined in this section are broad in their scope and are based on information needs. Consequently, each of the research areas recommended in this report could include a number of research topics. The above approach has been taken with the objective of giving considerable latitude to potential investigators in their research proposals instead of requiring them to submit proposals directed at addressing narrowly defined research topics.

The following is a prioritized list of recommended areas of research, their rationales, and some of the possible research topics that could be investigated in the recommended research areas.

1. <u>TITLE</u>: Develop technologies for treating lignin, chlorinated organics, and inorganic chloride containing concentrated streams from various closed cycle technologies.

<u>Background</u>:

A number of closed cycle technologies such as ultrafiltration, polymer treatment, resin treatment and activated carbon treatment produce concentrated effluent streams that may contain high concentrations of lignin and chlorinated organics and some inorganic chlorides. These streams have to be treated either through recycling within the process or in a separate system. At present the only demonstrated technology for treating these concentrated streams is through concentration in multiple-effect evaporators followed by burning in the recovery furnace. A potentially serious adverse impact of burning these concentrated streams in the recovery furnace is the increased chloride level in various process streams. The elevated chloride levels cause equipment corrosion, affect recovery furnace operations through changes in smelt viscosity, and can result in increased hydrochloric emissions from the recovery furnace. The problem of equipment corrosion is likely to be more serious at those facilities where corrosion resistant materials of construction have not been used. Because of these concerns very few facilities are likely to implement those closed cycle technologies that require the burning of concentrated streams in the recovery furnace. Consequently, if technologies are developed that can effectively and economically treat the concentrated streams from closed cycle processes, this would significantly increase the possibility of implementing a number of closed cycle technologies at existing bleached kraft mills.

<u>Possible Research Topics and Their Justifications</u>:

(a) Examine/develop technologies for thermal destruction of concentrated streams from closed cycle processes in a device other than the kraft recovery furnace.

Thermal destruction in devices such as rotary kilns or fluidized bed combustors has gained considerable acceptance in the field of hazardous waste incineration. It may be appropriate to examine one or more of these technologies for their suitability to destroy color and chlorinated organics in the concentrated streams from various closed cycle processes.

(b) Examine/develop technologies for chemical treatment of concentrated streams from the closed cycle process.

Chemical treatment of waste streams to eliminate their hazardous components is widely used in many industries. It may be appropriate to develop a chemical treatment method capable of treating the concentrated streams from various closed cycle processes by converting organic chlorides to inorganic chlorides and destroying the color. The chemically treated material can subsequently be treated in the biological treatment system.

(c) Examine other treatment technologies such as gamma radiation or supercritical oxidation for breaking down chlorinated organics in the concentrated streams from closed cycle technologies and for reducing color and other organics.

Gamma radiation has been proposed for chlorinated organic destruction. Supercritical oxidation has been proposed for treating streams containing organics. It may be possible to apply these or other technologies for treating concentrated streams from closed cycle processes.

2. <u>TITLE</u>: Evaluate/develop biological treatment technologies for removing color and chlorinated organics from selected bleach plant effluent streams and concentrated streams from closed cycle processes.

<u>Rationale</u>:

Certain fungi have been found to reduce effluent color. Several investigators have reported on the use of enzymes or specially developed bacteria for treating effluent streams. The use of a biological process to treat selected bleach plant effluent streams or concentrated streams from closed cycle processes for color and/or chlorinated organics reduction would be a natural extension of the whole mill effluent biological treatment technology which is used widely in the pulp and paper industry.

3. TITLE: Conduct research aimed at examining the feasibility of implementing the Rapson-Reeve process at mills that practice oxygen delignification, extended delignification, or some other technology that uses less chlorine or chlorine derivatives in the plant than was the case at the Thunder Bay mill.

Rationale:

One of the major problems encountered at the Thunder Bay mill was high equipment corrosion caused by chlorides in various recycle streams. A mill which practices oxygen delignification, extended delignification, or some other technology that requires less chlorine/ton of pulp than is used at the Thunder Bay pulp mill will have a lower chloride content in the recycle stream. The operating advantages and feasibility of implementing the Rapson-Reeve process at a mill that uses much less chlorine should be examined.

Possible Research Topics:

Develop a chemical recovery cycle model for the Rapson-Reeve process and use it to simulate the impact of changes in the pulping and bleaching technologies on the process. The process parameters that could be examined may include chlorides, pitch buildup, and recovery furnace emissions.

4. TITLE: Conduct research aimed at mitigating the adverse impact of pitch buildup on the Rapson-Reeve closed cycle operation.

Rationale:

Problems associated with the buildup of pitch during hardwood pulping were a major reason for abandoning the Rapson-Reeve closed cycle operation at Thunder Bay. This problem will have to be addressed if a closed cycle mill is designed in the future. During mill visits, one mill reported that it used soap from softwood pulping for dispersing pitch. Other similar process changes may be capable of minimizing the operating problems resulting from pitch buildup in process streams. Consequently, research in this area would prove beneficial to future implementation of this and other closed cycle technologies.

5. <u>TITLE</u>: Examine/develop new technologies for pulping and bleaching that eliminate or significantly reduce the use of chlorine and chlorine derivatives in the bleach plant.

<u>Rationale</u>:

A major hindrance to closed operation of a bleached mill is the use of chlorine or chlorine containing oxidants in the bleach plant which results in a chloride buildup in the system. If technologies that eliminate or substantially reduce chlorine and chlorine derivative usage in the bleach plant are developed, they will enhance the feasibility of achieving greater levels of closure at a bleached mill.

6. <u>TITLE</u>: Develop a treatment technology that utilizes polymers to reduce color and chlorinated organics from selected effluent streams and is capable of recovering the polymer.

<u>Rationale</u>:

Two mills are currently known to be using polymers for removing effluent color. These treatment technologies are currently being applied to total mill effluents where the recovered material is burned in the recovery furnace, and polymers are not recovered. Because of the high cost associated with treating large volumes of low concentration streams, it would be desirable to examine polymers for their effectiveness in reducing color, chlorinated organics and toxicity from selected bleach plant streams. Successful application of this technology would mean that only a few streams would have to be treated, thus substantially reducing its cost.

<u>Possible Research Topics</u>:

Evaluate various polymers for their ability to reduce color, chlorinated organics and toxicity of selected process streams, and examine/develop the technology for solids separation and disposal, and chemical recovery. The study should address the toxicity of the polymer itself and the consequences of its loss during routine operation, process upsets, or as a result of an accidental spill.

7. <u>TITLE</u>: Conduct studies aimed at developing technology for suspended solids removal from selected streams.

<u>Rationale</u>:

A number of effluent treatment technologies such as ultrafiltration, reverse osmosis, activated carbon treatment, and resin treatment require that a low level of suspended solids be present in the stream being treated. To achieve this these streams have to undergo a pretreatment step requiring suspended solids removal. Although a number of suspended solids removal systems are currently available, they are not always able to meet the needs of the advanced treatment processes listed above. Consequently, the development of an effective technology for suspended solids removal would enhance the feasibility of successfully implementing the above identified technologies at pulp mills.

8. <u>TITLE</u>: Develop/examine chemical recovery technologies other than kraft recovery furnaces for handling incremental amounts of black liquor recovered as a result of improved brownstock washing, chemical loss prevention, and/or oxygen delignification.

<u>Rationale</u>:

A large number of pulp mills are recovery furnace capacity limited. Consequently, pollution control programs such as improved brownstock washing, spill collection and recovery, and/or oxygen delignification, which result in an increase in the amount of organics that have to be burned, are not feasible at such facilities.

The development of a technology capable of burning the incremental amount of organics resulting from in-plant control programs would address the needs of recovery furnace limited facilities and is likely to have a direct impact on environmental programs that minimize the sewering of chemicals. The technologies that could possibly be examined may include pyrolysis, gasification, and fluidized bed combustion. In examining the potential technologies, the investigators should examine the impacts of these technologies on chemical recovery and energy balance, and should address the environmental significance in terms of discharges to air, water and solid waste.

9. <u>TITLE</u>: Examine pulp washing process modifications other than equipment change that could improve pulp washing and thus reduce the amount of chemicals that is ultimately sewered in the bleach plant or from the paper machine.

<u>Rationale</u>:

More than 95 percent of all the cooking chemicals used in kraft pulping are recovered through brownstock washing. However, most of the small fraction of cooking chemicals that leave the pulp mill with brownstock are separated from fibers in the bleaching or papermaking operations and are sewered. As described in the report on in-plant control technologies (1), a number of new equipment are being designed and installed to improve brownstock washing. However, as an alternative to installing new equipment, it may be feasible to make changes in the operating conditions in a brownstock washer through process modifications that improve brownstock washing, thus reducing waste loads from bleach plants and paper mills. The reduced loads from papermaking and bleaching operations will improve effluent quality and may have an impact on effluent toxicity.

It has been suggested that brownstock washing could be substantially improved through elevated wash temperature, chemical assistance or pH control. Very limited work has, however, been done in this area, and the potential impacts of these process modifications on the rest of the mill have not been identified. Consequently, it would be desirable to conduct studies to examine the feasibility of improved brownstock washing through process modifications such as chemical assistance, pH control, and elevated wash water temperature.

Possible Research Topics:

Examine the feasibility of improved brownstock washing through chemical assistance, pH control, or elevated wash water temperatures.

10. TITLE: Develop technology for recycling alum from the processes that use alum for effluent treatment.

Rationale:

Alum has been proposed and is currently used for effluent color and organics treatment. Although the alum treatment technology has always been proposed as being capable of alum recovery, this has not been possible. Most recently the Baikalsk mill in the USSR is not recovering alum from the ash, thus creating a solid waste disposal problem. The development of a technology to recover and recycle alum would significantly enhance the possibility of full scale installation of the alum treatment process.

11. TITLE: Evaluate new resins to examine their ability to reduce color, TOCl and toxicity of selected bleach plant effluent streams.

Rationale:

The major reason for abandoning the resin processes as applied to bleach plant effluents has been the unpredictable and short resin life. If new resins capable of better performance become available, it would be appropriate to examine their effectiveness in reducing color, chlorinated organics, and toxicities of bleach plant effluents.

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