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PULP MILL PROCESS CLOSURE: A REVIEW OF GLOBAL TECHNOLOGY DEVELOPMENTS AND MILL EXPERIENCES IN THE 1990s

TECHNICAL BULLETIN NO. 860
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PRESIDENT'S NOTE

The impact of effluent discharges continues to be an important issue for the pulp manufacturing industry. Since the mid-1980s regulation of chlorinated compound discharges has shifted the focus from effluent treatment to prevention at manufacturing sources. Compliance with such requirements has been achieved almost exclusively by process modifications designed to minimize waste generation. Looking forward, it is apparent that mills will continue to be called upon to reduce their environmental emissions and discharges. In many cases such reductions may only be achieved through additional pollution prevention measures, so-called manufacturing "process closure."

In 1988, NCASI published a review of pulp and paper mill in-plant and closed cycle technologies. Since then, many important technologies have been developed and implemented. Zero effluent operation is now a reality for a few bleached chemi-thermomechanical pulp (BCTMP) pulp mills. In kraft pulp manufacturing, important developments include widespread adoption of new cooking techniques, oxygen delignification, closed screening, improved process control, new bleaching methods, and systems that minimize pulping liquor losses. Advances in delignification and bleaching prompted some companies to pursue bleach plant closure and many of these have been successful in eliminating of a portion of their bleaching wastewaters.

Much of the technology development associated with kraft mill bleach plant closure has focused on mitigating undesirable consequences such as scale deposits, corrosion, loss of bleaching efficiency, increased evaporative loads, reduced production capacity, and loss of operational flexibility. These issues have caused many companies to reconsider the role of process closure in minimizing effluent impacts. For many mills, the optimal solution has been found to be a high degree of closure coupled with external biological treatment of the remaining process effluent. Example mills include SCA Östrand, M-Real Husum, Södra Cell Mörrum and Värö, and Metsä-Botnia Rauma. There are no bleach plants at papergrade bleached kraft mills that are known to operate effluent-free on a continuous basis.

This document is intended to be a source of information on process closure technologies to assist mills as they seek to understand the options available to them to minimize wastewater loads, and to address the inquiries of customers, employees, and the public. It characterizes the important commercial technology developments that came of age principally during the 1990s.

Ronald A. Yeske

May 2003

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Mot du président

L'impact du rejet des effluents liquides demeure toujours un enjeu important pour l'industrie de fabrication de la pâte. La réglementation du milieu des années 1980 portant sur les rejets de composés chlorés a réorienté les efforts qui étaient dédiés jusque là au traitement des effluents, pour les diriger vers la prévention à la source dans les activités de fabrication. La conformité à cette réglementation a été obtenue presque exclusivement grâce aux modifications apportées aux procédés dans le but de réduire la production de déchets. Il semble bien que cette tendance se poursuivra dans le futur et que les fabriques seront appelées à réduire leurs émissions et rejets dans l'environnement. Dans plusieurs cas, de telles réductions ne pourront être réalisées que par des mesures additionnelles de prévention de la pollution, ce qu'on appelle les « procédés en circuit fermé ».”

En 1988, NCASI publiait une revue des technologies en circuit fermé dans les fabriques de pâtes et papiers. Depuis, plusieurs technologies majeures ont été développées et implantées. Les opérations qui génèrent zéro effluent sont maintenant une réalité pour quelques fabriques de pâte chimico-thermomécanique blanchie (PCTMB). Pour ce qui est des opérations de fabrication de pâte kraft, on constate d'importants développements tels que l'adoption de nouvelles techniques de cuisson (largement utilisées), la délignification à l'oxygène, le tamisage en circuit fermé, l'amélioration du contrôle de procédé, les nouvelles méthodes de blanchiment et les systèmes qui minimisent les pertes de liqueur. Les avancées technologiques en matière de délignification et de blanchiment ont poussé certaines compagnies à poursuivre les efforts pour obtenir un procédé en circuit fermé dans les usines de blanchiment et plusieurs d'entre elles ont réussi à éliminer une portion de leurs effluents de blanchiment.

La plupart des travaux associés aux procédés en circuit fermé dans les usines de blanchiment de pâte kraft se sont concentrés sur la mitigation des conséquences indésirables telles que les dépôts de tartre, la corrosion, la perte d'efficacité de blanchiment, l'augmentation des charges dans le système d'évaporation de liqueur usée, la réduction de la capacité de production et la perte de flexibilité opérationnelle. À cause de ces enjeux, plusieurs compagnies ont été forcées de reconsidérer le rôle du procédé en circuit fermé pour minimiser l'impact des effluents. Pour plusieurs fabriques, la solution optimale résidait en un procédé en circuit presque fermé combiné à un traitement biologique externe des effluents de procédés restants. Parmi les exemples de fabriques mentionnons SCA Östrand, M-Real Husum, Södra Cell Mörrum et Värö et Metsä-Botnia Rauma. Il n'existe pas d'usines de blanchiment dans les fabriques de papier kraft blanchi qui opèrent sans effluent sur une base continue.

Ce document se veut une source d'information sur les technologies en circuit fermé qui permet d'aider les fabriques dans leur recherche des options qui sont à leur disposition afin de minimiser les charges en eaux usées et de répondre aux interrogations des clients, des employés et du public. Il contient une description des développements de technologies commerciales qui ont vu le jour dans les années 1990.

Ronald A. Yeske

mai 2003

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ABSTRACT

This report provides a summary of the pollution prevention and effluent minimization (so-called "process closure") technologies developed and implemented during the 1990s whose impacts have been to reduce the generation and discharge of waste materials from pulp manufacturing operations. It focuses primarily on bleached kraft pulp mills, but includes information on mechanical and sulfite pulping processes. The report includes a description of important technologies and a review of operating experiences of mills that typify the state of the art in one or more areas of process closure. The most notable developments have been the widespread adoption of extended and oxygen delignification, the use of modern washing and screening technologies, and the development and implementation of chlorine alternative bleaching systems. Recovery of a portion of bleaching filtrates at several mills is another significant development, although the substantial costs and impacts on operations attributable to such closure have kept this from becoming mainstream technology. Reducing mill process liquor spills and leaks through improved management and control systems is often noted as a key cost-effective component in minimizing pulp mill wastewater loads.

KEYWORDS

bleaching, delignification, effluent minimization, mill experiences, process closure, pulp mills, recovery, research programs, technologies, treatment, wastewater, zero discharge

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 796 (October 1999). *Study of water quality and recycle and reuse practices at low- and zero-discharge recycled paperboard mills.*

Technical Bulletin No. 733 (June 1997). *Experience at recycled paperboard and containerboard mills operating at or near zero discharge.*

Technical Bulletin No. 609 (May 1991). *In-plant and closed cycle technologies R&D program - First year research reports - Add-on control technologies.*

Technical Bulletin No. 608 (May 1991). *In-plant and closed cycle technologies R&D program - First year research reports -In-plant and process technologies.*

Technical Bulletin No. 557 (October 1988). *Pulp and paper mill in-plant and closed cycle technologies - A review of operating experience, current status, and research needs.*

Les procédés en circuit fermé dans les usines de pâte: une revue des principaux développements technologiques et de l'expérience des fabriques dans les années 1990

Bulletin technique no. 860
mai 2003

Résumé

Ce rapport contient un sommaire des technologies de prévention de la pollution et de minimisation des effluents (appelées procédés en circuit fermé) développées et implantées durant les années 1990 afin de réduire la génération et le rejet des déchets issus des opérations de fabrication de la pâte. Il traite principalement des fabriques de pâte kraft blanchie mais comporte également des informations sur les procédés mécanique et au bisulfite. Le rapport présente une description des technologies importantes et fait la revue de l'expérience de fabriques dont les opérations de pointe sont caractéristiques d'un ou plusieurs aspects des procédés en circuit fermé. Parmi les développements les plus notables mentionnons l'adoption répandue de la délignification poussée et de la délignification à l'oxygène, l'utilisation des technologies modernes de lavage et de tamisage et le développement et l'implantation de systèmes de blanchiment utilisant d'autres produits que le chlore. La récupération d'une portion des filtrats de blanchiment par plusieurs fabriques représente un développement significatif mais les coûts substantiels de même que les impacts sur les opérations constituent des obstacles à la popularité de cette technologie. La réduction des déversements et des fuites de liqueur de procédé grâce à une meilleure gestion et à des systèmes de contrôle est souvent présentée comme étant un des moyens les plus rentables pour diminuer les charges dans les eaux usées des fabriques de pâte.

Mots clés

blanchiment, délignification, minimisation des effluents, expérience des fabriques, procédé en circuit fermé, fabriques de pâte, récupération, programmes de recherche, technologies, traitement, eaux usées, zéro rejet

Autres publications de NCASI dans ce domaine

Bulletin technique no. 796 (octobre 1999). *Study of water quality and recycle and reuse practices at low- and zero-discharge recycled paperboard mills*.

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1.0 INTRODUCTION

The idea of eliminating process effluent discharges has long intrigued the wood pulp manufacturing industry. Freedom from the constraints associated with water supply and effluent disposal is an appealing concept. For the vast majority of pulp mills, zero-effluent discharge is currently impractical. Even so, great progress has been made in minimizing impacts associated with pulp mill effluents, much of it through the adoption of modern, efficient manufacturing technologies in areas such as delignification, pulp screening and washing, bleaching and process control. Development and implementation of such "process closure" technologies peaked in the 1990s, largely driven by the desire to limit the discharge of chlorinated organic compounds. In particular, a great deal of progress was made in developing new delignification and bleaching methods.

This report documents progress in the development and implementation of process closure technologies, i.e., those which effect or enable the reduction of waterborne wastes from pulp manufacturing facilities. Such technologies serve to divert wood components and other raw materials from liquid waste streams by prevention, reuse, or recovery. Ideally, the diverted materials exit as product or are converted to energy or useful chemicals that can be reused or sold. The report is focused primarily on the kraft pulp industry, but also includes significant developments in the mechanical and sulfite pulping sectors, where for example, in the last decade, three new mechanical pulp mills were built to achieve zero effluent in locations where water resources cannot support a discharge.

Interest in process closure was heightened by the discovery in 1985 that 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) was present in the wastewater treatment plant sludge from a publicly owned treatment works (POTW) that treated bleached kraft mill wastewaters. This discovery, which evolved into a broader concern over chlorinated organic matter formation resulting from chlorine bleaching, precipitated major changes in pulp bleaching practices worldwide. Regulations that effectively mandated the changes were adopted by many countries. In the U.S., EPA promulgated limits for TCDD, 2,3,7,8-tetrachlorodibenzofuran (TCDF), twelve chlorinated phenolic compounds, chloroform, and adsorbable organic halides (AOX), a measure of the amount of chlorine chemically bound to organic compounds. To comply with the new effluent limits, mills upgraded or replaced aging bleaching facilities and upgraded chlorine dioxide generation capability to enable so called "elemental chlorine-free" (ECF) bleaching. In addition, many mills installed extended and/or oxygen delignification systems. These investments produced significant reductions in chlorinated and other organic matter discharged from mills.

For some companies, these investments also provided the impetus and technological base to pursue virtual elimination of chlorinated organic matter from bleaching effluents and, for some, elimination of bleach plant effluents altogether. Examples include development and implementation of Union Camp Corporation's C-free ozone bleaching process (Nutt et al. 1993), and Champion International Corporation's BFR process for partial bleach plant closure (Maples et al. 1994). A few companies, most of them based in Scandinavia, chose to completely eliminate chlorine-based chemicals from bleaching at some of their manufacturing sites. This was motivated in part by the initial belief that effluents from such totally chlorine free (TCF) bleach plants could be routed to the recovery cycle more easily without the substantial input of chloride inherent in closure of ECF bleach plants. However, subsequent operating experience has shown that full closure of TCF bleach plants has proven to be difficult, and it has not fully realized its anticipated benefits in this regard.

It is paradoxical that improvements made to mills in the 1980s and 1990s to modernize bleach plants have, on the one hand, increased the likelihood that bleach plant effluent recovery may be achieved, while on the other, minimized the benefits to be realized from doing so. At many mills, amounts of dissolved chlorinated and other organic compounds have been reduced to fractions of their previous levels. Studies of toxic effects on aquatic organisms associated with treated effluents from today's bleach plants suggest that for most mills, further closure of the bleach plant may provide few benefits to the environment.

The Alliance for Environmental Technologies, AET, an industry organization founded to promote the environmental, economic, scientific, and technical benefits of chlorine dioxide in pulp bleaching, organized a panel of experts to debate the priorities for minimum effluent manufacturing in bleached kraft pulp mills. The panel dealt with several questions related to the desirability, technical feasibility, and impacts related to elimination of bleaching effluents. Using a modern ECF bleach plant as a baseline, the panel members concluded that elimination of bleaching effluents was not the highest environmental priority objective, and may in fact be undesirable if raw materials, energy, or other resource use increased to accomplish this objective. Elimination of bleaching effluents was not felt to have value in reducing environmental impacts, except in special situations where water quality standards cannot be met through effluent treatment. The panel felt that placing emphasis on, for example, reducing process liquor losses and eliminating effluents from wood processing areas would probably provide greater value in minimizing effluent impacts (Axegård et al. 1997).

Important business issues must also be factored into process closure decision making. Capital investments must be justified based on financial return and/or meeting clearly defined environmental objectives. Equipment and technology must be commercially viable and designed to withstand the pulp mill environment. Generally speaking, changes to a production process that result in lower production rate, reduced product quality, increased operating costs (raw materials, labor, maintenance, etc.), greater complexity or operational difficulty, or reduced reliability will not be adopted. These are very real business constraints that must be weighed against the anticipated benefits of any given project.

An important development in the 1990s was a general shift in how the industry thinks about and manages the whole array of environmental issues it faces. The traditional piecemeal approach evolved into a more holistic one that encompasses all aspects of the manufacturing spectrum, from the management and harvest of forest lands to the ultimate disposal of products. This shift is exemplified by the philosophy of “Minimum Impact Manufacturing,” part of a larger corporate “Vision for Environmental Balance” that was put forth by the Weyerhaeuser Company in 1995 (Erickson, Zacher, and DeCrease 1996). This vision was developed with input from four stakeholder groups and encompassed management of forestry resources and manufacturing enterprises in a manner that balanced the needs of shareholders, customers, employees, and communities. A similar corporate vision is that adopted by Stora Enso called Ecobalance (Broman and Lindberg 1996), a term used to define the objective of the company’s environmental quality work. Key components of the vision include sustainable forest management, efficient use of resources, full utilization of raw materials, low emissions with minimal biological impact, fiber recycling optimization for products and energy production, incorporation of transportation impacts in product life-cycle assessments, and supplier accountability. The value of these holistic approaches is that resources are focused on the highest priority issues, providing a more optimum system for realizing real progress toward economically and environmentally sustainable pulp mills.

While pollution prevention through process closure plays an important role in the industry’s environmental performance, so too does effluent treatment. The overwhelming majority of pulp and paper manufacturing facilities generate wastewaters that undergo primary treatment to remove settleable solids, followed by secondary treatment to remove biodegradable organic matter. These treatments remove most of the oxygen-depleting potential of effluents, virtually eliminate acute and chronic toxic responses to test organisms, and greatly improve the compatibility of effluents with receiving waters. Most effluent discharge permit limits are based on the performance of mills utilizing such treatment. The widespread adoption of biological treatment systems, first in the U.S. and more recently in Canada and Scandinavia, underscores the fact that this treatment process provides the greatest improvement in effluent quality with the least impact on manufacturing operations. Given the presence of secondary treatment at a facility, the incremental environmental benefits of process closure may be difficult to justify.

Some of the funding for this project came from the 301(m) program, a research and development program funded by Louisiana-Pacific Corporation and Simpson Paper Company. During its 15-year tenure, the 301(m) program spent over $2 million to fund various facets of research in the area of in-plant and closed cycle technologies. A number of universities and private companies participated in this research. The funding made it possible for many scientists to pursue research in the field of mill closure, and the reports and publications of the studies funded by this program have contributed to knowledge in this field. This report concludes this innovative and exciting research program.

2.0 TRENDS IN INDUSTRY WASTEWATER LOADS

Trends in U.S. pulp and paper industry water and wastewater loads for the period 1975 through 1995 are shown in Figures 2.1, 2.2, and 2.3. These survey data are median values across all sectors of the industry. The populations of mills participating in the surveys were not the same from year to year, but this would not be expected to impact median values in a significant way.

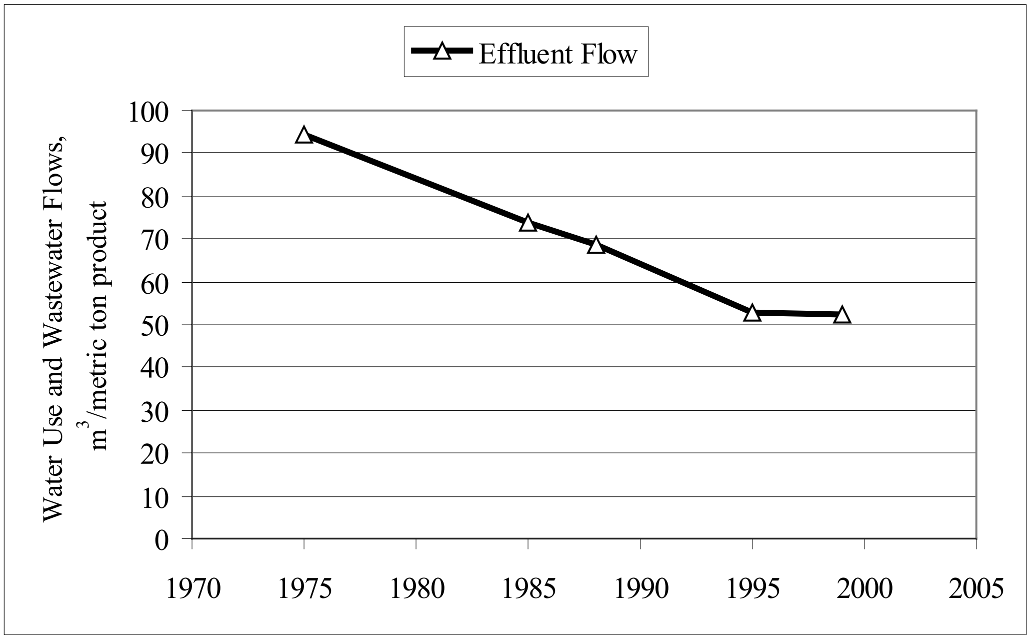


Figure 2.1 Wastewater Flow Trends for the U.S. Pulp and Paper Industry Based on Median Values

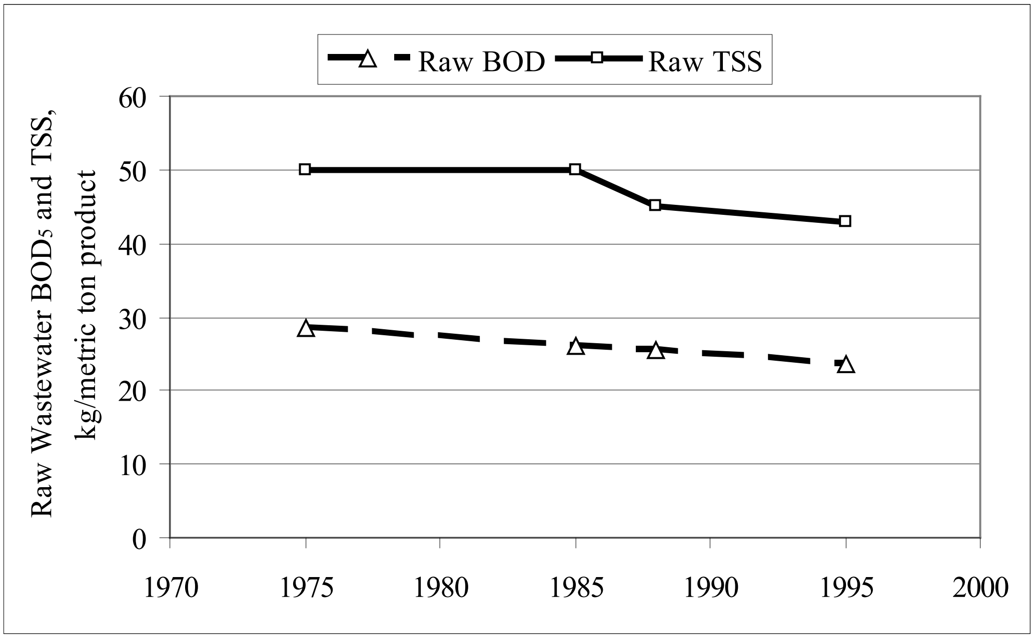


Figure 2.2 Untreated Wastewater BOD$_5$ and TSS Load Trends for the U.S. Pulp and Paper Industry Based on Median Values

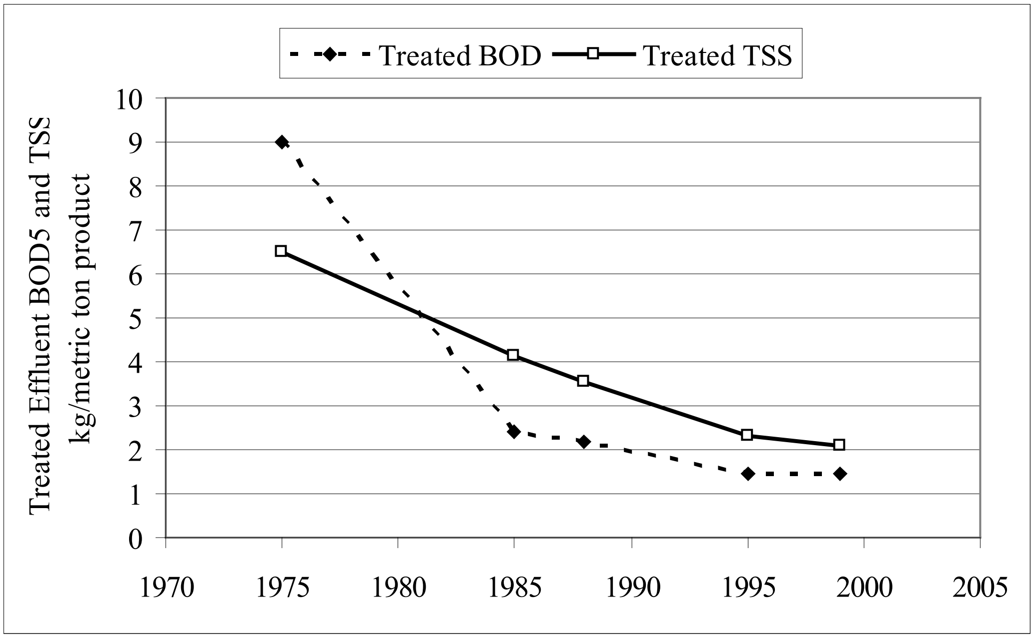


Figure 2.3 Treated Wastewater BOD$_5$ and TSS Load Trends for the U.S. Pulp and Paper Industry Based on Median Values, Direct Dischargers Only (no POTWs)

Water use and wastewater flow trends shown in Figure 2.1 reveal a steady decrease over the entire period. From 1988 to 1995, both parameters decreased by about 23%. Raw or untreated BOD_5 and TSS loads also declined. Reductions averaged 7.9 and 4.6%, respectively, for BOD_5 and TSS from 1988 to 1995. Treated effluent BOD_5 and TSS loads declined by about 34% in 1995 compared to 1988. Although the specific reasons for the decreases are not easily established, it is likely that process modifications are responsible for most of the gains achieved.

Effluent flow, BOD_5, and AOX data from bleached kraft pulp and paper mills in the U.S. are shown in Figures 2.4, 2.5, and 2.6, respectively. This sector was chosen to illustrate the reductions in these three parameters over the decade of the 1990s, primarily attributed to process modifications and resulting reductions in water use and effluent loads. The data shown in these figures were gathered by NCASI and AF&PA. Mills providing these data represent about half of U.S. bleached kraft mills.

From 1988 to 2000, flow was reduced by about 28% based on mean values, and 33% based on the median. The reduction in effluent BOD_5 was even larger, about 67% based on the mean and 58% based on the median. Reductions in final effluent BOD_5 may be due to treatment system optimization and/or process modifications (which lower BOD_5 loads). In some cases reductions in per ton discharges are the result of production rate increases that have been accomplished within existing discharge permit limits.

AOX reductions over the period from 1995 to 2000 were about 66% and 58% based on mean and median values, respectively. Figures for BOD_5 and AOX also show that over this period the ratios of mean to median declined, generally indicating that mills with higher discharge levels of these parameters achieved greater reductions. Essentially all of the AOX reduction is attributable to bleaching process modifications that enabled ECF operation.

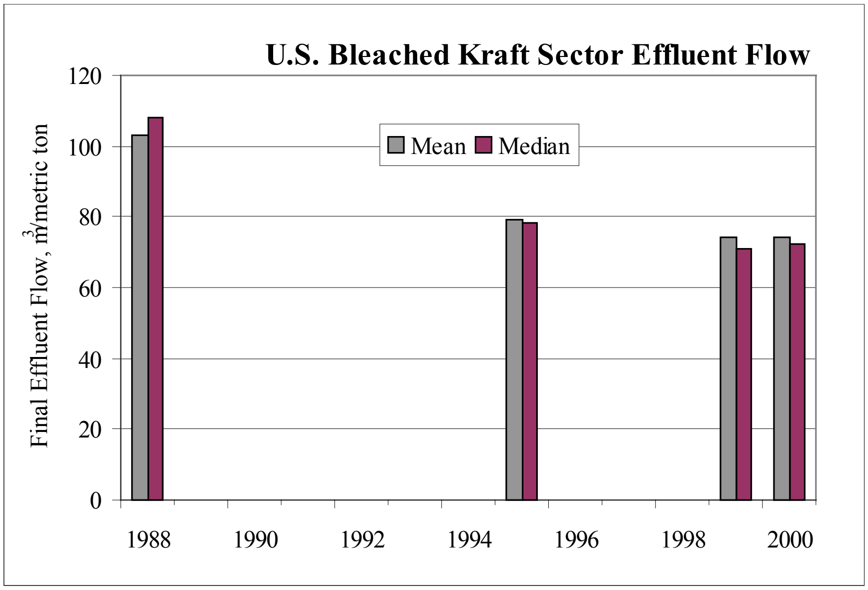


Figure 2.4 Final Effluent Flows for U.S. Bleached Kraft Pulp and Paper Mills (data are from mills representing about 50% of the sector)

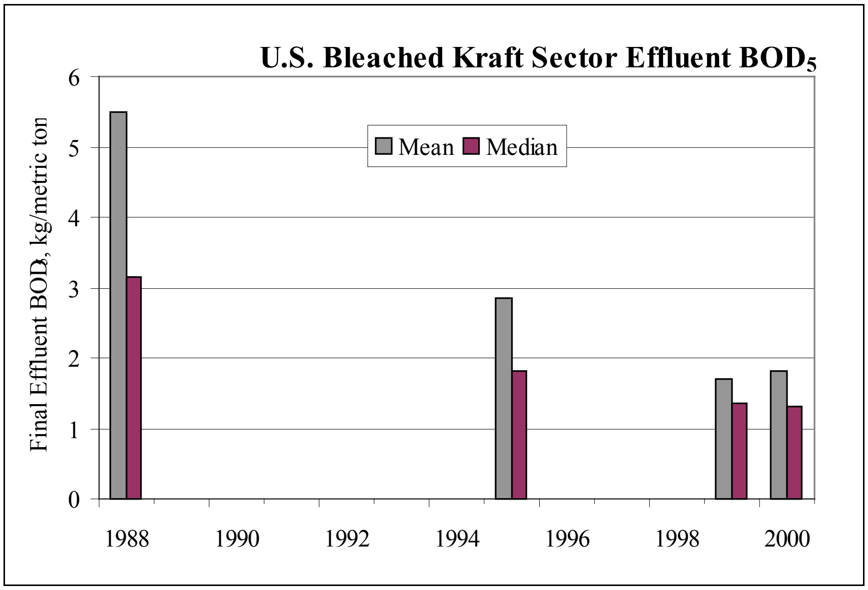


Figure 2.5 Final Effluent BOD_5 Loads for U.S. Bleached Kraft Pulp and Paper Mills (data are from mills representing about 50% of the sector)

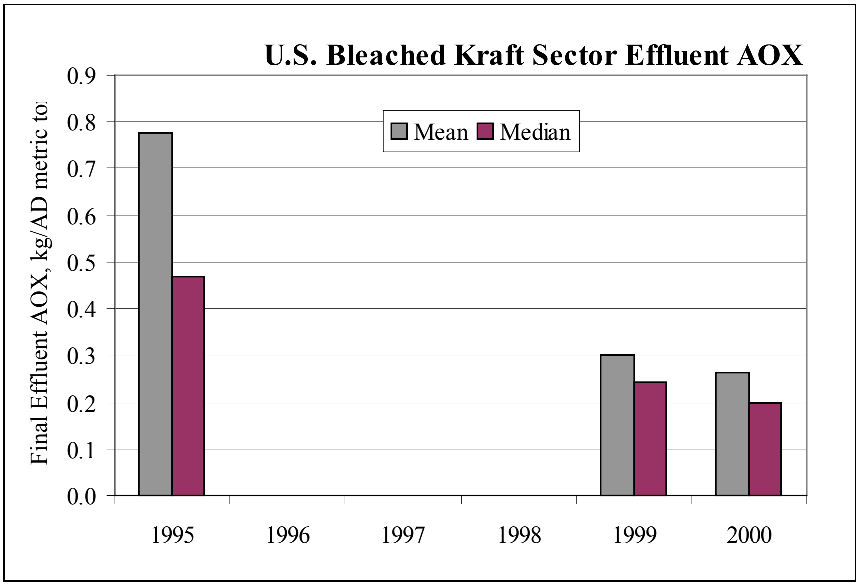


Figure 2.6 Final Effluent AOX Loads for U.S. Bleached Kraft Pulp and Paper Mills (data are from mills representing about 50% of the sector)

3.0 REVIEW OF PROCESS CLOSURE TECHNOLOGIES

The processing of wood into pulp suitable for paper and board manufacturing involves many steps. Trees must be cut into suitable lengths, stripped of their bark, and cut into chips. The chips are often washed and screened before being subjected to chemical and/or mechanical energy which reduces the wood to pulp fibers. The pulp is processed to remove physical and chemical impurities and to improve papermaking properties. Chemical pulp mills include recovery systems which recover and reconstitute pulping chemicals and generate steam and power by combusting the dissolved wood components. Wastes are generated at each step, and some of the waste material is discarded as process wastewater.

The goal of process closure with respect to effluent discharges is to minimize the amount of waste generated. This has been accomplished by using more efficient processes, using processes that do not require water, or recovering the waste materials. Modern technology and process designs have enabled mills to reduce or virtually eliminate wastewater discharges from many processing operations. This section reviews several of the important process closure technologies currently used, as well as some that have been proposed, as means of reducing wastewater and wastewater loads.

3.1 Historical Perspective – Lessons from Thunder Bay (Rapson-Reeve Process)

The idea of process closure is not new to the pulp and paper industry. Since the first prototype of the Tomlinson recovery furnace was installed in 1934, a technology that dramatically improved both the environmental and the economic viability of the kraft process, the industry has had a history of process closure resulting in progressively lower effluent discharge levels. A key development in the history of process closure in the pulp and paper industry occurred in 1967 when Rapson proposed a vision for bleached kraft pulp manufacturing that had the potential to greatly reduce, if not eliminate, effluent discharges (Rapson 1967). This vision was based on a collection of technologies, including increased use of chlorine dioxide for bleaching and a process for generating this chemical that could be fully integrated with the chemical requirements of the kraft pulping and bleaching processes. The primary basis for his proposal was a cost-effective alternative to biological effluent treatment. Rapson's proposed process, later modified and called the Rapson-Reeve Process, was adopted by the Great Lakes Paper Company in Thunder Bay, Ontario, for the design of a new bleached kraft mill at an existing mill site. A lack of sufficient real estate to install wastewater treatment facilities was noted as a major factor in the decision (Anon. 1977). The mill operated in a partially closed manner for several years before the concept was abandoned and a secondary treatment plant was installed. This pioneering effort clearly established the technical challenges that must be overcome to eliminate bleached kraft mill discharges. A brief review of this work is included here to illustrate these challenges, thereby providing a basis for understanding more recent process closure developments.

The original effluent-free mill concept was based on these ideas:

- Replace 70 to 80% of the chlorine in the chlorination stage with an equivalent amount of chlorine dioxide to allow all the bleaching stages to be operated at the same (higher) temperature without excessive damage to the pulp and to minimize chloride input to the recovery system.
- Use a new chlorine dioxide generating process to produce chlorine and chlorine dioxide in concentrated aqueous solutions.
- Use countercurrent washing in the bleach plant, utilizing wastewater from the wet end of the pulp dryer or paper machine to minimize the volume of filtrate to be recovered.

- Use a portion of the bleaching filtrate to wash the unbleached pulp, allowing the dissolved materials from bleaching to be recovered via evaporation and burning.
- Use the remainder of the bleaching filtrate to wash the lime mud and green liquor dregs and to dissolve the smelt from the recovery furnace.
- Treat the evaporator condensates with a small amount of chlorine dioxide to oxidize the foul-smelling compounds and use the oxidized condensates in place of fresh water on the wet end of the pulp dryer or paper machine.
- Remove sodium chloride from the liquor cycle by extracting it from the dust collected from the recovery furnace flue gas in the electrostatic precipitator. A portion of the extract would be used to generate chlorine dioxide for the bleach plant and the remainder would be discarded.
- Establish closed water systems for wood debarking, pulp screening, and cleaning.

Most of these ideas had already been demonstrated at mills. The installation of the new 'B' line at Thunder Bay was based on many of these ideas and included provisions to operate with minimal effluent:

- dry drum debarkers
- pressure (closed) primary knotters and screens
- use of pulp dryer vacuum pump seal water in the wet end of the dryer and use of excess white water on the final D stage bleach plant washer
- full countercurrent washing in the bleach plant
- a new salt removal process (SRP) based on evaporation of the white liquor in two stages to produce crystalline sodium chloride
- use of excess filtrate from the E1 washer to dilute concentrated white liquor and to wash the unbleached pulp
- use of excess D/C filtrate after neutralization with caustic or white liquor for brownstock washing and in the lime kiln scrubber, and subsequently for smelt dissolving
- high molybdenum alloy washer drums on three of the nine washers and extensive use of FRP piping and tanks to minimize potential problems due to corrosion
- 70% chlorine dioxide substitution for chlorine in the first stage (D70/C30) to minimize chloride load to the recovery system
- air doctors on pulp washers to minimize water infiltration
- an extensive spill collection and recovery system
- a stripping column to clean the foul condensates

The mill operated in this manner beginning in June 1977 when bleaching filtrate recovery began. Localized corrosion in certain sections of the recovery furnace superheater, discovered in July 1978, halted filtrate recovery until the corroded tube sections could be replaced in January 1979. This corrosion was attributed in part to molten slag caused by high chloride concentrations and non-uniform temperature distribution in the superheater. The tube replacement and other furnace changes enabled the furnace to run without corrosion problems thereafter. Filtrate recovery resumed and continued through 1982 (Reeve 1984). The bleach plant effluent volume was reduced to 16 m^3/ADt, representing about 70% reduction compared to a conventional open bleach plant of that era. Stripped foul condensates and condensate from the SRP were also discharged from the mill.

Although the process was technically successful, management ultimately elected to terminate recovery of bleaching filtrates and install a secondary treatment facility. Based on the experience at Thunder Bay, Reeve (1984) outlined the key provisions needed to achieve effluent-free operation:

- condensate stripping, cleaning, and management sufficient to make this a reliable water source for use on the final bleach plant washer
- use of condensate for bleaching chemical dilution and transport
- salt recovery employing minimal evaporation
- low net flow of bleaching filtrates to minimize black liquor evaporation
- an effective and reasonable cost bleaching process suitable for closed operation
- systems for removing minor wood components such as potassium, calcium, and pitch
- an effective spill management system

It is interesting to note that the issue of chloride control is only one of the seven needs outlined by Reeve. Much of the interest in and development of non-chlorine-based bleaching technology has been justified based on the presumption that such systems should be more easily closed than chlorine-based processes. While the requirement for chloride purging is certainly greatly reduced if chlorine-based chemicals are not used in bleaching, other requirements for effluent-free operation are not resolved by eliminating chlorine-based chemicals. Rapson (1982) summarized the situation:

> It is important, however, to understand that the main problems in making a mill effluent-free do not lie in the effect of salt on the equipment or on the pulp properties, or in the recovery of salt. Rather, significant problems are common to all bleaching processes, whether the chemicals contain chlorine or not. First and foremost, about a quarter of the water pollution of bleached kraft pulp mills comes from spills and washups, and these must be collected and recycled with all the accompanying problems. Second, if there is any acid stage in the sequence, as there is with ozone, it will be a “calcium trap” since calcium carbonate travels with the pulp in neutral or alkaline stages, but dissolves in any acid stage. If countercurrent washing is used, which is essential for decreasing the water and energy consumption in a conventional mill, the calcium is precipitated into the pulp in any previous alkaline stage and carried forward to be re-dissolved in the acid stage. Third, the flow of filtrate into and out of each washing stage must be precisely balanced to obtain the correct displacement ratio and purge for each stage. Fourth, the concentration of organic matter in each filtrate must be controlled carefully to minimize the consumption of oxidizing agent in subsequent stages through incomplete washing. These and other problems must be addressed in tightening any pulp washing system, regardless of the nature of the chemicals involved.

3.2 Wood Processing

Wood arrives at pulp mills as logs in long or short lengths, as chips produced at remote sites, and as chips and sawdust residuals from lumber and veneer mills. Some mills receive all their wood in chip (and/or sawdust) form, while other mills may receive chips, tree-length stems, and logs (roundwood). The increased use of sawmill residuals and chips generated at remote processing facilities are two trends that have reduced or eliminated wood processing operations and their associated water uses at many mill sites. Sawmills and many remote chip mills typically use dry debarking (ring and drum) systems.

Wood received as tree-length stems must first be cut into bolts on a slasher. Bark is removed in drum, cutterhead, ring, and hydraulic debarkers (Fuller 1983). Debarked logs are then sent to a chipper which cuts them into small pieces suitable for pulping.

Water use in wood preparation is highly mill-specific and depends on the type of process, weather conditions, and the availability of fresh water or suitable wastewater from other process areas. With regard to wood processing, water can be used for several purposes (Carter and Gleadow 1994):

- Logs are transported from storage piles to the woodroom and debarked wood blocks to groundwood mills via flumes. While being transported the logs are thawed and washed of ice, snow, and grit.
- Logs are thawed and/or washed to condition them before debarking. This is achieved by showers or by soaking in conditioning ponds. Paper machine white water is often used for this application.
- Wet debarking is performed in barking drums where the logs are bathed in water for thawing and washing. This creates a high level of BOD as the bark is crushed in the water. Paper machine white water is also often used for this application.
- Hydraulic debarking uses high pressure water to erode and separate the bark from the log. This process can produce very clean logs by reaching into crevices to remove bark and rot.
- Steam injection is used in drum debarkers to thaw logs to aid debarking. This practice produces a contaminated condensate.
- Debris collection and transport may use pans, sluices, or flumes (e.g., under conveyors). This type of process is normally used as a convenient extension of water-based systems where water is also used for debarking or transport.
- Wash down water is often employed to clean equipment or floors and to flush away a build-up of debris in trenches.

Wet processing of wood generates wastewaters contaminated with dissolved organics such as resin and fatty acids that exert an oxygen demand and may produce a response in effluent toxicity assays. Effluent process closure of wood processing areas involves minimizing or eliminating contact between the wood and process waters during transport, thawing, cleaning, and debarking operations.

Specific process closure techniques include use of dry transport devices such as belt and chain conveyors or portal cranes in place of log flumes, and use of ring or dry drum debarking devices in place of hydraulic and wet drum debarkers.

Information on wastewater loads from debarking was provided by the Finnish Ministry of Environment (Finnish BAT Report 1997). This document indicates that dry debarking significantly reduces but does not eliminate wastewater discharges from wood processing. The primary water use in dry debarking systems is for log washing. Wet bark is pressed in some mills to reduce moisture content prior to burning in a boiler. This practice increases the fuel value of the bark but generates a wastewater stream containing 20 to 60 kg COD/m^3 wood (European IPPC Bureau 2000). A summary of the ranges of flow, BOD_5, COD, and total phosphorus for wet and dry debarking is shown in Table 3.1.

Table 3.1 Wastewater Characteristics from Wet and Dry Debarking Operations

Debarking Technique	Effluent Volume m^3/m^3 wood	BOD_5 kg/m^3 wood	COD kg/m^3 wood	Total Phosphorus, g/m^3 wood
Wet debarking and bark pressing	0.6 to 2.0	0.9 to 2.6	4 to 6	5 to 7
Dry debarking and bark pressing	0.1 to 0.5	0.1 to 0.4	0.2 to 1.0	2 to 4

Source: Finnish BAT Report 1997

3.3 Brownstock Pulp Processing

Following cooking, kraft brownstock pulp is processed to remove a majority of the solid and liquid impurities that exit the digester. Such processing includes screening and washing and may also include refining, deknotting, and cleaning. In some older systems, in which screening is the final step, the pulp is thickened on a decker or other dewatering device prior to storage. In newer systems, screening is done prior to the final washer, which also serves to thicken the pulp.

Wastewaters may be generated in the brownstock processing area on a continuous basis and also intermittently due to upset conditions. Continuous discharges can occur as a result of screening and thickening operations, and any dissolved materials exiting the terminal washer with the pulp may be discharged in wastewaters from open processes downstream. Brownstock wastewaters contain spent pulping liquor chemicals and lignin and other wood components dissolved during the cook. Such wastewaters are highly alkaline and contribute BOD, COD, color, and conductivity. Deknotting and refining operations are typically closed operations with no continuous discharges.

Historically, screening systems utilized vibratory and gravity centrifugal screens open to the atmosphere. To control foaming problems, especially in mills with inadequate washing, large external dilution flows (known as “sweetener”) were often used prior to screening. Subsequent thickening of the pulp prior to storage would result in the generation of large volumes of dilute black liquor filtrate, most of which would be discharged as process wastewater because evaporation would be prohibitively expensive.

The use of modern pressure screens virtually eliminates foaming issues and the need for external dilution water. This technology enables screening to be done prior to the final stage of washing, so additional thickening is not necessary. Modern screen room designs effectively eliminate continuous wastewater discharges previously associated with screening operations and are effectively closed operations with respect to process wastewaters.

A closed brownstock fiberline refers to operation of the brownstock portion of a kraft mill (i.e., from chips entering the digester to stock leaving the last brownstock washer or last post-oxygen washer) without a continuous process wastewater discharge during normal operating conditions. In practice there typically is a small discharge due to, for example, pump seal water, drainage from knots and screenings, and minor leakage from piping and equipment. A key principle in such an operation is that any water entering the process must leave either with the unbleached pulp, as contaminated steam condensate, or with the weak black liquor being fed to the chemical recovery system. Closed fiberline operation requires that the volume of water entering the system be as small as possible to minimize capital equipment requirements for additional evaporator capacity and operating cost in the form of additional energy required to evaporate the excess water. Key components of the closed fiberline include sufficient brownstock washing capacity, closed screening, control of water inputs and effective process controls.

3.4 Liquor Loss Management

Pulping chemicals lost as waste must be replaced at some cost, and can impact the cost and performance of wastewater treatment and the characteristics of final effluent discharges. Consequently, all mills have incentives to minimize liquor losses to some degree. For example, weak white liquor from washing the lime mud, known as weak wash, is sewered in some mills because the volume of water used for washing exceeds the input requirements for smelt dissolving. Such losses may raise the pH of wastewaters and, in the case of green liquor, can consume oxygen vital to aerobic biological treatment system performance.

With respect to impacts on treatment plant performance and treated effluent quality, losses of black liquor are of much greater concern than losses of green or white liquors, due to the organic matter present in black liquor. The organic fraction of black liquor is composed of degraded lignin; carboxylic and hydroxy acids; wood sugars; extractives consisting of resin acids, fatty acids, and neutral compounds such as sterols; and a variety of other compounds. The composition of a black liquor is highly dependent on the wood species from which it was generated. The various types of compounds are removed to different degrees in biological treatment systems. For example, formic and acetic acids and wood sugars are readily biodegradable, exerting a BOD load on treatment systems. Lignin degradation compounds are not readily biodegraded; they pass through treatment into the effluent, contributing COD and color. Finally, the extractives are somewhat biodegradable but may produce toxic effects in treatment systems and final effluents.

Black liquor may be lost from the kraft mill at a variety of locations in the fiberline and recovery areas. Leakage from seals on pumps, agitators, and other rotating equipment occurs in almost all kraft mills. Certain events may generate wastewaters containing black liquor, including startups, shutdowns, and cleanings of storage and process vessels. Most black liquor evaporators do not have continuous losses, although carryover of liquor into evaporator condensates may occur, especially in older rising-film design units, units with poor mist eliminators, or units that are heavily loaded. Evaporator boilouts may result in losses of dilute black liquor. Boilouts are initiated every few days or weeks to remove water-soluble scales that reduce heat transfer performance. A boilout involves shutting off the liquor feed and purging the system with clean water or thin liquor while maintaining steam flow. As the product liquor becomes more dilute, the boilout liquor is diverted to a tank for later recovery. Some mills recover all of the boilout stream, while others divert the most dilute portions to the wastewater system. Factors which may influence specific practices at mills include value of the recovered chemicals and energy, treatment cost and capacity, evaporation cost and capacity, effluent discharge limitations, or other constraints. A review of mill spill management practices (Amendola, Vice, and McCubbin 1996) shows that, in the absence of such constraints and using assumptions to represent a typical ECF bleached kraft mill, recovery of dilute black liquor directly to the evaporators becomes uneconomic at concentrations below about 4% black liquor solids. However, recovery of black liquor is often practiced down to a concentration of 0.5% solids (McCubbin 2001a).

The recovery of tall oil and turpentine byproducts are activities with potential to generate potent wastewaters that can impact treatment performance and effluent quality. At many mills these byproduct recovery areas are isolated from the mill wastewater collection system so that any spills can be recovered. These materials contain high levels of BOD and COD and can be toxic to treatment plant biota and effluent bioassay test organisms. EPA included best management practices (BMPs) for spent pulping liquors, tall oil soaps, and turpentine in its Cluster Rule regulation promulgated in 1998 (USEPA 1998). Bleached chemical, soda, and stand-alone semi-chemical pulp mills are required to comply with the BMPs at this time. Inclusion of BMPs indicates an increasing focus on the importance of fiberline and recovery area wastewaters from chemical pulp mills.

Spill control can be one of the most cost-effective means by which a mill can reduce wastewater loads. It can be especially effective at minimizing color loads, since black liquor losses can represent a substantial contribution to color and conventional effluent treatments do not remove color efficiently. Managing liquor losses involves both behavioral and hardware systems. A review of mill spill management practices (Amendola, Vice, and McCubbin 1996) indicated that mills achieving the lowest levels of liquor loss emphasized preventive measures to avoid the need for spill recovery. McCubbin (2001a) indicated that conventional bleached kraft mills with untreated effluent COD of roughly 40 kg/ton would be considered to have good spill control. Mills with oxygen delignification would be expected to be about 10 kg COD/ton lower. However, many other factors could influence these values.

Training of mill operators and maintenance personnel is an important aspect of good spill control. Such training should focus on developing an awareness of the type and size of significant spills, key parameters, and how area operations affect effluent discharge. Equipment and procedures that can generate spills should be identified and explained, and corrective actions established. Operators should be able to understand monitoring data, diagnose causes, and take corrective actions. Routine review of spill incidents and actions at production meetings can facilitate effective feedback to operators.

Continuous real-time monitoring is another important aspect of spill control, including tank levels, overflow alarms, and monitoring of floor drainage. Specific conductance (conductivity) is the most widely used parameter due to the robust nature of conductivity sensors. However, this parameter is not specific to black liquor, so system design is important to minimize “false” alarms from non-black liquor streams. Overflows of foam from black liquor tanks can be effectively detected by temperature monitoring in the downleg.

To augment preventive measures, mills typically have spill recovery sump pumps in critical areas that are automatically activated when a stream monitoring parameter, usually conductivity, exceeds a set point value. Design of sumps should be appropriate for the size and type of spills likely to be encountered. The objective is to recover the spilled material and return it to the liquor system with minimal contamination. Water is a contaminant, as it must be subsequently removed from the recovered spill. Some mills isolate clean water streams (e.g., seal water) by running them into separate pipes laid on the bottom of floor drains (McCubbin 2001b).

3.5 Evaporator Condensate Reuse

Weak black liquor from brownstock washing is on the order of 15% dissolved solids (85% water) by weight. Prior to firing the liquor in a recovery furnace, it is concentrated to 60 to 85% dry solids. Thus, for each kilogram of black liquor solids (BLS), about five kilograms of water must be removed. The majority of this water removal is accomplished in multiple effect evaporator sets, each consisting of a series of vessels equipped with heat exchangers. Fresh steam enters the first effect, which operates above atmospheric pressure to evaporate water from the most concentrated liquor. The resulting water vapor (low pressure steam) passes to the next effect, which operates under a lower pressure, to evaporate additional water, and so on. The final effects of the evaporator train are under vacuum. Condensates are generated in each effect as the vapors transfer heat to the liquor. The initial vapors from boiling the weak black liquor, typically condensed in the final effects and surface condenser, contain most of the volatile components of the liquor.

The volumes of evaporator condensates generated are substantial. A mill with an evaporator load of 5 kg water/kg BLS and 1500 kg BLS/ADMTP would produce at least 7.5 m^3/ADMTP of evaporator condensates. Actual volumes generated may be substantially higher in evaporator sets equipped with barometric condensers, which can add from 2 to 45 m^3 cooling water per ADMTP (Blackwell et al.

1979). Modern evaporator systems use non-contact surface condensers to condense the final vapors. Additional condensate volumes are generated by vacuum pumps or steam ejectors used to provide vacuum.

Evaporator condensates contain the volatile low molecular weight compounds present in black liquor, including alcohols, ketones, terpenes, phenolics, organic acids, reduced sulfur compounds, and others. Methanol is the primary constituent, accounting for up to 95% of the total organic content of condensates. Methanol is easily biodegraded, each kilogram exerting about 1 kg BOD_5. The total BOD_5 load from condensates has been reported to be about 8 to 12 kg/ADMT pulp (Blackwell et al. 1979).

Evaporator condensates are typically segregated according to their level of contamination, with the goal of reusing the cleaner fractions and minimizing the volume requiring treatment. There are many different segregation schemes in use at mills. A simple scheme might involve collecting the most contaminated (foul) condensates from the sixth effect and final surface condenser in one stream, and all the remaining condensates in a second, larger, combined stream. The evaporator foul condensate stream would then typically be combined with other foul condensate streams from the digester area prior to treatment in a steam stripper or biological treatment plant to minimize the release of hazardous air pollutants (HAPs). The combined condensates and stripped foul condensates are often used as wash water on the final brownstock or post-oxygen washer, and sometimes for mud washing in the causticizing plant. In most mills, the available volume of condensates exceeds the total requirement of these two areas, and the excess becomes wastewater.

There are other process areas such as the bleach plant where there is a need for clean hot water. Because condensates are hot and have very low concentrations of metals, they are potentially attractive hot water sources, especially in peroxide-based bleach plants where transition metal ions have adverse impacts. Condensates also have very low hardness (calcium and magnesium) levels and may reduce scaling in mills with hard process water. Due to their COD and reduced sulfur compound content, additional treatment may be required before reuse in the bleach plant would be considered in many mills. However, Annola, Hynninen, and Henricson (1995) showed in laboratory studies that even highly contaminated condensates (COD of 6218 mg/L) had only minor effects on peroxide or ozone bleaching performance or pulp quality, and the bleached pulps were free from unpleasant odors.

Sodra Cell's Varo mill in Sweden reported on its operation of a second condensate stripper to clean evaporator condensates characterized as having an intermediate level of contamination, on the order of 2000 mg COD/L. The unit was installed with and is integrated into a new evaporator set. Performance was reported to be 90% removal of COD and greater than 95% removal of reduced sulfur compounds. The unit has enabled the mill to reuse all its condensates and eliminate fresh water use in the bleach plant during normal operation. Bleaching is done with a peroxide-based totally chlorine free (TCF) sequence. Benefits from lower peroxide use for bleaching and better pulp strength, presumably due to lower metals concentrations, were also cited (Emilsson, Håkansson, and Danielsson 1997).

Dubé et al. (2000) reported on the improvement in effluent toxicity response resulting from the use of a reverse osmosis (RO) treatment for "clean" (COD of 1067 mg/L) condensate from the fifth effect of the evaporators at the Irving Pulp & Paper mill in St. John, New Brunswick, Canada. The RO unit uses a three layer composite membrane and concentrates at least 88% of the BOD and COD in a volume representing 1% of the feed volume. The concentrate is burned in the bark boiler or with the black liquor in the recovery furnace. The treated condensate is used for brownstock washing. Mill effluent, which is not biologically treated, produced a much lower toxicity test response when the RO unit was operating. Other methods for cleaning condensates prior to reuse have been proposed, such as aerobic biological treatment using a high temperature membrane bioreactor (Bérubé and Hall 2000).

The primary advantages of reusing the condensate streams are potential reductions in energy, water use, and effluent flow. The chemical constituents in evaporator condensates are generally removed to a high degree in mill effluent treatment plants anyway, so unless the treatment plant is heavily loaded, few benefits are expected in treated effluent quality due to separate treatment of condensates. Combustion of the stripped condensate organics, primarily methanol, in a boiler or incinerator converts all of the carbon to carbon dioxide and water. Methanol has a fuel value of 21 MJ/kg, and this has the potential to offset a significant portion of the energy required for steam to strip the condensates. Biological treatment, either in a dedicated unit or in a mill's effluent treatment plant, will convert a portion of the organic carbon into biological solids, which require dewatering and disposal.

3.6 Kappa Reduction Technologies

Historically, bleached kraft softwood and hardwood pulps have been produced by cooking to kappa numbers of about 30 and 20, respectively, followed by bleaching in a four or five stage bleach plant. Cooking to lower kappa numbers was not widely practiced due to excessive loss of yield and pulp strength. The discovery of the presence of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzofuran in bleach plant effluents drove a major effort to develop and implement processes able to minimize the discharge of these compounds to the environment. A significant part of the effort was focused on reducing the lignin content (as measured by kappa number) of brownstock pulps so that less work remained to be done in the bleach plant. Kappa reduction prior to bleaching can be achieved by modifying cooking conditions and also by using oxygen delignification technology. The basic idea of all kappa reduction technologies is that more of the lignin is dissolved, captured, and combusted in the recovery furnace and less is discharged from the bleach plant.

Extended cooking (or extended delignification) refers to a variety of techniques used to modify the chemical and/or temperature conditions in kraft digesters so that delignification is continued to a kappa number of about 20 for softwoods and about 14 for hardwoods in ways that minimize yield and strength losses. Many mills with Kamyr continuous digesters have made modest equipment and control changes to enable the cook to be extended somewhat, but modifications to extend the cook in conventional batch digester systems are generally not practical. Extended cooking capability is the norm in new continuous and batch digester installations. A recent survey conducted for NCASI indicates that currently there are about 131 continuous and 32 batch digester systems with extended delignification capability worldwide, capable of producing about 124,469 and 30,726 ADt/d of pulp, respectively. Figure 3.1 shows the worldwide growth of extended delignification since its commercial introduction.

Oxygen delignification is used after cooking and washing to remove additional lignin prior to bleaching. It involves reacting the pulp with oxygen under alkaline conditions and then washing to recover the dissolved lignin. This technology is more selective than most extended delignification processes, but may require significant capital investment to implement. Based on a survey conducted for NCASI, it is estimated that there are at least 252 oxygen delignification installations in operation worldwide with capacity for producing an estimated 195,561 AD metric tons of pulp per day. The technology is used commercially on both softwood and hardwoods. Figure 3.2 shows the growth trend in this technology since the first installation in 1970.

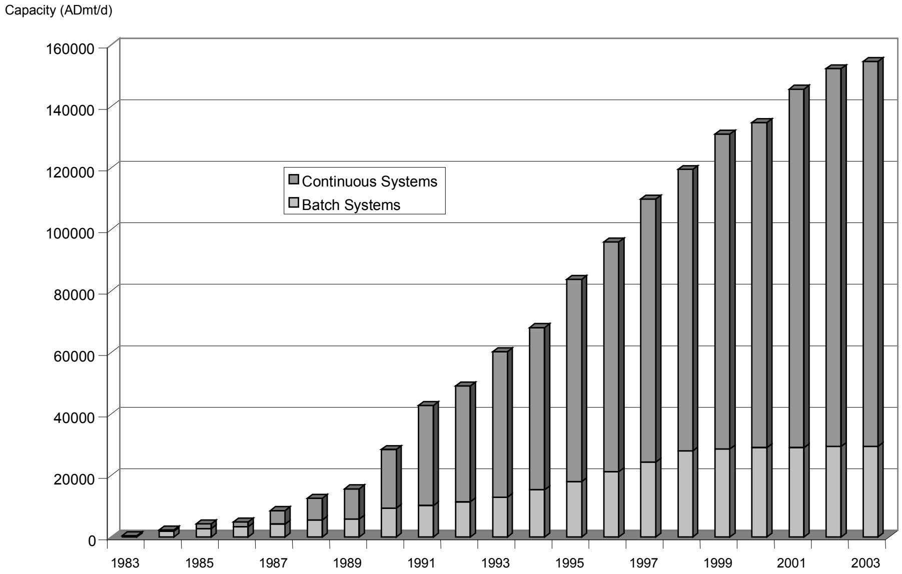


Figure 3.1 Worldwide Production Capacity of Pulp from Extended Delignification Processes

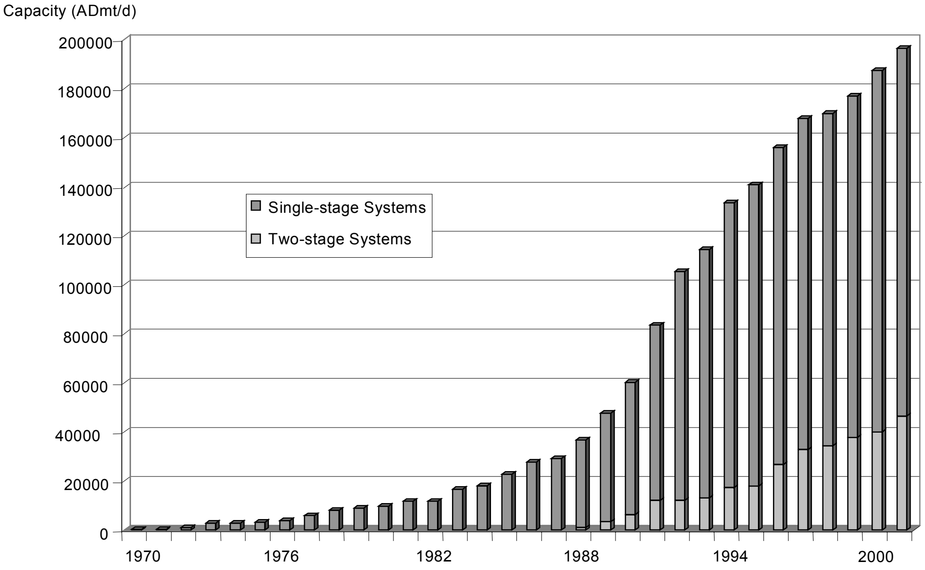


Figure 3.2 Worldwide Production Capacity of Oxygen Delignified Pulp

Some mills utilize both extended and oxygen delignification to achieve very low kappa number pulps prior to bleaching. Recently, strategies have been focused away from obtaining the most delignification possible in the digester and toward optimizing the fiberline as a whole based on economic, quality, and environmental factors. In these strategies, oxygen delignification plays a larger role because it can provide more selective lignin removal, i.e., with less yield loss, than extended delignification.

3.6.1 *Extended Cooking*

Prolonged delignification in conventional kraft cooking has generally resulted in lower pulp yields and strength because the reactions become less selective for lignin removal as the cook proceeds beyond a certain point. However, it has been demonstrated that the cook can be extended without impairing pulp quality by following certain principles (Berry 1993). Those principles, which maximize the selectivity of the pulping process, are:

- uniform application of alkali charge during the cooking process
- initial impregnation of chips with high sulfidity liquor
- removal of dissolved lignin, particularly during the residual (final) delignification phase
- lower and more uniform cooking temperature

These principles have been applied in various ways by suppliers of batch and continuous digesters. Each supplier is attempting to push delignification as far as possible by maximum use of these principles together with two other critical precepts: uniform chip thickness and thorough liquor impregnation (Berry 1993; Galloway et al. 1994).

While these principles allow mills to extend delignification to the maximum extent possible, they can also be applied in ways that do not target extremely low kappa numbers, but instead aim at producing pulp at a higher overall yield. More recent developments have focused on the latter goal (Headley 1996).

Extended cooking – continuous digesters

In continuous cooking systems, chips are heated with steam, impregnated with cooking liquor, and cooked to produce pulp which is subsequently washed in a linear continuous stream. A continuous digester usually comprises a single large digester vessel, although a separate impregnation vessel is also common. The main type of digester used for continuous cooking is based on the designs of the Kamyr Company and is often referred to as a Kamyr digester. Other types of digesters are available for cooking certain types of wood, such as mini-chips, sawdust, and non-wood fibers, but these do not tend to take advantage of extended cooking technology.

The original Kamyr Company was separated into two entities in the early 1990s. At this time, Kamyr Inc., based in the U.S.A., became part of the Finnish Ahlström Company, and Kamyr AB of Sweden became part of the Kværner Group. Since that time, there has been some degree of divergence in the designs offered by the two companies.

Modified continuous cooking applications for these digesters have been described in papers published on Kamyr MCC and EMCC processes (Dillner 1993a,1993b). Kværner has made further improvements with its ITC™ and BLI™ processes, and Ahlström with its Lo-Solids cooking designs.

Modified Continuous Cooking (MCC)

In a conventional continuous digester, all of the white liquor is added prior to the cooking zone and cooking is undertaken co-currently, with cooking liquor and chips traveling in the same direction through the cooking zone of the reactor. In the Modified Continuous Cooking (MCC) process (Backlund 1984), the white liquor addition is split into two parts, with part of the flow added to the co-current cooking zone as in a conventional digester and part added to a subsequent second countercurrent zone. The intent is to lower the initial concentration of alkali and keep it more uniform during cooking, thereby improving selectivity.

Extended Modified Continuous Cooking (EMCC)

The Extended Modified Continuous Cooking (EMCC) process takes the principles of the MCC cook a step further (Backlund 1984). In this process, the white liquor is split into three portions and the third fraction is added to the countercurrent washing zone in the bottom of the digester. This extends the delignification zone of the digester further and “flattens” the alkali profile, allowing the pulp to be delignified to a lower kappa number while maintaining selectivity.

Iso-Thermal Cooking (ITC)

The Kværner Iso-Thermal Cooking (ITC) process (Engström and Hjort 1995, 1996) is a continuation of the MCC and EMCC designs. In this process, the entire digester reactor vessel is used for delignification. The cooking temperature is kept constant and is somewhat lower than in other methods. Likewise, white liquor is added to all circulation loops in the countercurrent zone of the digester, giving a somewhat lower but very constant alkali profile. These improvements provide further reduction in the degree of degradation of the cellulose fibers.

Black Liquor Impregnation (BLI)

Black liquor Impregnation (BLI) addresses the point of having a higher sulfide ion concentration present during the initial part of the cooking process. In this process (Höglund, Pehu-Lehtonen, and Hjort 1994) spent cooking liquor, or black liquor, is recirculated from the digester extraction to the chip impregnation vessel ahead of the digester. This black liquor has a low residual alkali concentration and a relatively high sulfide ion concentration. This process requires that a new impregnation vessel be designed to accommodate the 40 minutes of retention time required.

Lo Solids Cooking

In the Ahlström Lo-Solids cooking approach (Marcoccia, Laakso, and McClain 1996), the objective is to minimize the concentration and amount of black liquor solids present in the bulk and final delignification phases of the kraft cook. As with other types of modified cooking, the intent is also to flatten the alkali profile throughout the cook. Wash filtrate is added to multiple circulation loops, and multiple points of liquor extraction are also used. Abbreviated versions of the process can be retrofitted into existing digesters, and installations have demonstrated improved digester plug flow and liquor circulation flows. A reduction in the “touchiness” of the digester level control has also been claimed.

Extended cooking – batch digesters

The second type of digester system used is known as the batch digester. In conventional batch systems, chips are sequentially loaded, cooked with white liquor, and discharged or “blown” to a blow tank. Normally, a batch digester system has several digester vessels discharging into a common blow tank. A cooking schedule is used to ensure that a constant flow of pulp is available from this tank to the rest of the fiberline.

Recent developments in batch cooking technology have incorporated the same basic principles for prolonging the cook without impairing pulp quality. Three systems are available, and all of them use similar concepts for extending the delignification of the pulp. These are known as the Beloit RDH process, the Sunds SuperBatch process, and the Voest-Alpine ENERBATCH process (Wizani, Eder, and Kubelka 1993). Advantages claimed for modified batch cooking systems include better delignification uniformity (less kappa number variation), improved energy efficiency, improved pulp yield, and improved strength delivery.

The RDH Process

The Rapid Displacement Heating (RDH) process from Beloit uses a series of steps involving the displacement of various temperatures of liquor with liquor of other temperatures (Andrews 1989). First, the digester is filled with chips and steam packed. The air in the digester is then displaced with warm black liquor. This liquor is displaced with hot black liquor and white liquor. Once this step is complete, the digester circulation is heated to get the chips up to cooking temperature, and they are then allowed to cook. Another displacement of the hot black liquor with washer filtrate is used to cool the pulp, which is then pumped to a pump-out tank. Displaced liquors are captured in accumulator tanks.

The initial fill with black liquor takes advantage of the low initial alkali and high initial sulfidity level principles. Maintaining lower cooking temperatures can be addressed through proper design of the system so that the digesters are large enough to cook at a lower temperature while allowing sufficient reaction time to achieve the desired degree of delignification.

The SuperBatch Process

The Superbatch process (Nordén, Reeves, and Dahl 1992) from Sunds Defibrator uses very similar sequencing to that of the RDH process and takes advantage of the same alkali, sulfidity, and temperature profile principles. The main differences are in the liquor displacement steps and the way these are performed. SuperBatch has two hot black liquor accumulators operating at different temperatures. There is also a hot white liquor accumulator that operates close to digester cooking temperature.

The Enerbatch Process

The Enerbatch process (Wizani, Eder, and Kubelka 1993) from Voest-Alpine also follows the same basic principles and gives the same basic advantages as the other two systems. There is significantly less operating experience available with the Enerbatch system compared to the other two competitors.

Split Sulfidity Liquors

The two principles of having a low initial alkaline concentration and high sulfide concentration in the early stages of the cook have led to the concept of producing white liquors of different sulfide concentrations. In this concept, white liquor would be treated using a process that would split it into two fractions:

- a high sulfidity (high HS- to OH- molar ratio) fraction which would be used for the initial application in the digester
- a low sulfidity (low HS- to OH- molar ratio) fraction which would be applied in the latter stages of the cook and could also be oxidized for use in an oxygen delignification stage or possibly even a bleach plant.

A variety of methods have been proposed for generating high and low sulfidity liquors and many have been tested in laboratory or pilot scale. Such processes include pressurized black liquor gasification (Stigsson 1996), green liquor hydrogen sulfide stripping using the Tampella process (Lange et al. 1975), green liquor crystallization by evaporation (Nevalainen 1996), green liquor crystallization by cooling (Ryham and Lindberg 1994), white liquor electrodialysis (Thompson et al. 1997), and recovery boiler smelt leaching (Herschmiller 1997).

3.6.2 *Anthraquinone*

In an effort to allow yield improvements in kraft pulping, many chemical additives have been tried (Courchene 1998). The objective of these efforts is to enhance the cooking process to give more pulp at a given kappa number, or to allow the mill to reduce the kappa number without affecting yield. Anthraquinone (AQ) is the most widely used and easily applied additive that enables cooking to lower kappa numbers. There is also increasing interest in polysulfide use, although by itself it does not enable kappa reduction. The yield benefits of anthraquinone and polysulfide when used together have been shown to be at least additive and possibly synergistic. It should be noted that AQ is not always used for kappa reduction. In many mills AQ is used to increase pulp production rates at a given kappa number.

Anthraquinone accelerates delignification reactions and stabilizes carbohydrate (cellulose and hemicellulose) end groups so that fiber dissolution is minimized. A typical dose of 0.06 to 0.08% AQ on OD wood would be expected to provide a drop of 4 to 6 kappa units for softwoods pulped with liquor at 25 to 30% sulfidity. AQ has been shown to be effective on both hardwoods and softwoods in a variety of chemical pulping processes, including kraft, soda, neutral sulfite, alkaline sulfite, and methanol. As of 1992, over 100 chemical pulp mills were using AQ (Blain 1993).

Katz (1993) discussed the application of anthraquinone in kraft processes as a means to improve the delignification capability of the kraft cook. Significant findings of laboratory experiments with AQ include:

- AQ can be used to reduce kappa number while maintaining yield.
- Viscosities of AQ pulps are equivalent to conventional kraft pulps.
- Despite the lower kappa number, pulp produced using AQ maintains the kraft strength properties.
- Yield gains with AQ are not lost in the bleach plant.
- AQ pulps appear to be easier to bleach and generate less AOX per ton than conventional kraft pulps at equivalent kappa numbers.

Liebergott and van Leirop (1981) presented laboratory work on the bleaching of hardwood soda-AQ, kraft, and kraft-AQ pulps using an ZDED sequence, comparing the results to those obtained for a conventional CEDED sequence. They concluded that pulping with AQ does not affect the bleachability of hardwood pulps. With the exception of a viscosity drop when bleaching with ozone, the strength properties of the fully bleached pulps showed no significant differences. The experiments also demonstrated that the yield improvement associated with AQ use was retained through bleaching.

3.6.3 *Oxygen Delignification*

Oxygen delignification is another technology that is used extensively to lower the residual lignin content (kappa number) of pulps prior to the bleach plant. Both extended cooking and oxygen delignification achieve their results by enabling more of the lignin to be dissolved and sent to the chemical recovery process via countercurrent pulp washing, rather than to the waste treatment plant via bleach plant filtrates. An oxygen delignification stage includes operations to mix and react oxygen with the pulp, separate waste steam and gases after the reaction, and wash the dissolved material from the pulp. Oxygen reacts at elevated temperatures (80 to 120°C) to make a portion of the residual lignin in the pulp soluble at a pH of 10 or greater. Oxidized white liquor or caustic (sodium hydroxide) are used as the alkali. There are two basic configurations of the process. In high consistency systems, pressed and fluffed brownstock pulp is introduced at a consistency of 17 to 27% into a reactor containing oxygen gas under pressure. The pulp falls through the oxygen atmosphere and forms a bed at the bottom of the vessel. Post-oxygen washer filtrate is pumped into the bottom of the reactor to convey the pulp slurry to a blow tank. The atmosphere in high consistency reactors must be continuously purged to prevent combustible gases from building up. This purge stream may be routed through a catalytic converter to destroy combustible matter and returned to the reactor, or it may be vented.

A majority of the oxygen delignification systems installed in recent years are medium consistency configurations typified by the flowsheet shown in Figure 3.3. These systems utilize high-shear mixing devices to disperse oxygen into the pulp at 10 to 12% consistency. The pulp is pumped through the mixer into an upflow tower reactor. Pulp exits the top of the reactor and is fed through a separator into a blow tank, allowing steam, residual oxygen, and gases produced by the reactions to be released via the blow tank vent.

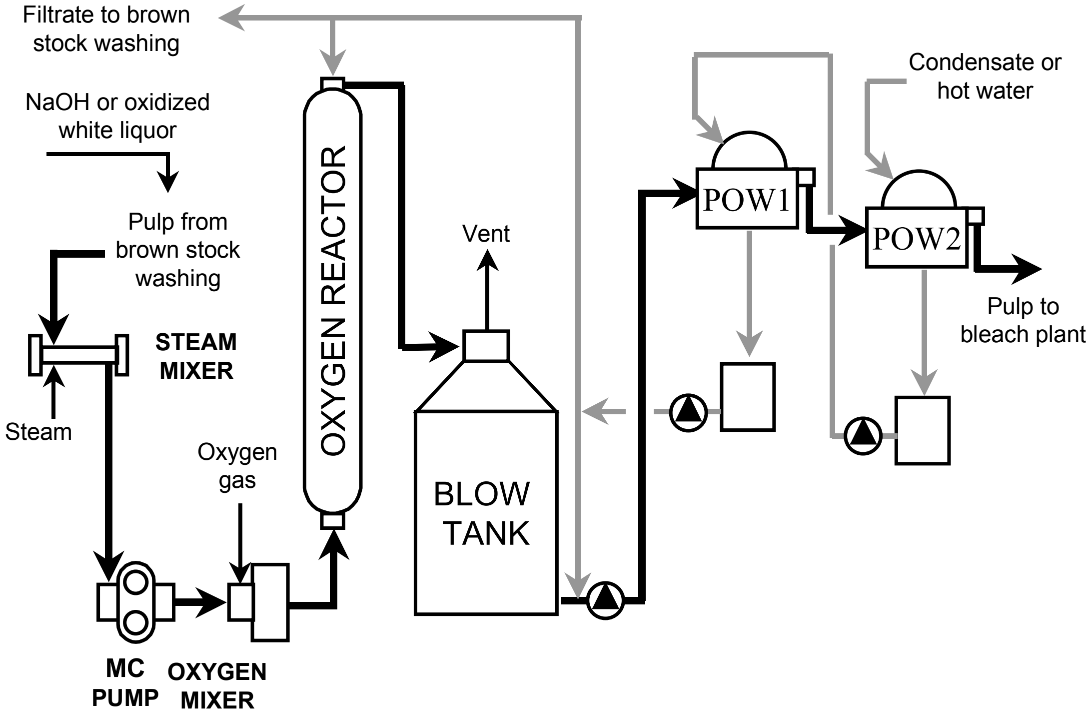


Figure 3.3 Flowsheet of a Medium Consistency Oxygen Delignification System

The pulp slurry is pumped to one or more pulp washers in series to separate the dissolved material from the pulp. Clean hot water and/or evaporator condensates are used to wash the pulp on the final stage of post-oxygen washing. Filtrate from each stage of washing is used to wash the pulp on the preceding stage. Excess filtrate from the first stage of washing after the oxygen delignification blow tank is used as shower water on the final stage of brownstock washing. Through countercurrent washing, the lignin and other organics removed during oxygen delignification, along with the spent alkali, become part of the black liquor solids sent to the chemical recovery system. Pulp exiting the final post-oxygen washer is often sent to a high density storage tank from which the first stage of the bleach plant is fed.

Oxygen delignification is a well-established technology. McDonough (1990) reviewed the fundamental principles associated with oxygen delignification; Tench and Harper (1987) and Lindström (1990) reviewed the design, operation, and performance of commercial units. The first oxygen delignification systems were high consistency single stage units. These saw limited implementation in Europe, North America, and South Africa. They are capable of achieving very high delignification results (70+%), but there has been a hesitancy to implement this technology due to the perception that it is complicated and that high consistency stock is difficult to handle.

It was not until improved medium consistency pumping and mixing technology became available in the 1980s that oxygen delignification systems operating in the 10 to 12% consistency range became available. At that point there was a tremendous surge in implementation as the technology was rapidly adopted (Johnson 1992). Delignification in single stages is usually limited to about 40 to 45% for softwoods and somewhat less for hardwoods, beyond which significant cellulose deterioration can occur. Single stage conventional oxygen delignification systems have been operated primarily to reduce the kappa number of pulp entering the bleach plant in order to reduce the chemical application required (McCubbin 1997).

The first two-stage medium consistency systems were probably introduced as a means to overcome equipment supply problems. Instead of supplying a single vessel with 60 minutes of retention time, the reactor was split into two smaller vessels which could be shop fabricated and transported to the site. It soon became apparent that an opportunity to vary the conditions in the two reactors existed, and that by doing so it was possible to extend the amount of delignification further without deteriorating the pulp. Newer oxygen delignification systems take advantage of this technology. The delignification achievable in these systems is often used to optimize the digester and oxygen stage kappa number targets in an effort to obtain the best overall yield possible, enabling a mill to reduce its wood cost per ton of product.

The Sunds OXYTRAC system (Bokström and Nordén 1998) is an example of a modern two-stage oxygen delignification process system. The first installation of this design was at SCA’s Östrand mill in Sweden. Very high delignification degrees, approximately 70%, have been achieved through optimization of the system. It is claimed that chemical consumption has been reduced and pulp quality improved with better selectivity than with the single-stage oxygen delignification this system replaced.

The OXYTRAC design utilizes two reactor stages. The first operates at high chemical charge and pressure (8 to 10 Bar) but at relatively low temperature (85ºC) and with a short retention (20 to 30 minutes). The high pressure is used to keep the concentration of dispersed oxygen high. The second reactor operates at lower chemical concentration and pressure but with higher temperature (100ºC) and a longer retention (60 minutes). Only direct steam to heat the stock is added between the reactors.

Other variations on the two-stage oxygen delignification include systems in which washing is carried out between the two oxygen reactors. Studies have shown that interstage washing improves the delignification power of the system (lower kappa out) and reduces the alkali charge required to maintain satisfactory pH levels due to the buffering characteristics of the lignin dissolved in the first stage (Allison and Wrathall 1998). It does not appear that dissolved solids carried over from the first reactor have any adverse impact on the selectivity of the system.

Two-stage systems with interstage washing are fairly rare, with only two of thirteen two-stage systems surveyed in a recent study using this approach (Carter et al. 1997). However, many newer two-stage systems have been designed and installed to allow for the possibility of adding an interstage washer at some time in the future.

A "mini" oxygen delignification stage (also called brownstock EO stage) is an option that has been implemented by some mills as a means of decreasing the kappa number entering the bleach plant. A mini oxygen delignification stage can provide approximately 25% additional delignification capacity in the fiberline. A typical arrangement, such as that installed in Pope and Talbot's mill near Nanaimo, British Columbia, involves the installation of a pressurized reactor tube between the last brownstock washer and the unbleached high density storage tower. A single stage of washing follows the high density tower, and this washer is "open" in that washer filtrate is used for tower dilution but is otherwise directed to the waste treatment plant.

3.6.4 *Kappa Number Reduction Impacts on Wastewater Loads*

Kappa number reduction technologies work in two important ways that impact bleach plant wastewater loads. First, they reduce the amounts of lignin that must be removed in the bleach plant. This translates directly into reductions in amounts of COD, BOD, and color in bleach plant wastewaters. The second important outcome of reducing kappa number in ECF bleach plants is that bleaching can be achieved using less chlorine dioxide in the first bleaching stage. It has been clearly established by many researchers (e.g., Axegård 1988; Earl and Reeve 1989; Lindström and Norden 1990) that the amount of AOX formed in bleaching is primarily determined by the amount of atomic chlorine applied to the pulp in the first bleaching stage.

The degree to which bleach plant wastewater loads are reduced through implementation of kappa reduction methods depends upon the kappa reduction achieved and the degree to which the dissolved organics are captured and sent to the recovery boiler. Good brownstock or post-oxygen washing and good process control are key elements of dissolved solids capture, and are discussed in other sections of this report.

In general, reductions in bleach plant BOD and COD loads achievable via kappa reduction techniques (assuming good capture efficiency) are proportional to the kappa reductions achieved. That is, an oxygen delignification system designed to achieve 50% delignification would be expected to reduce bleach plant wastewater BOD and COD loads by about 50%. Laboratory experimental results reported by Liebergott et al. (1991) serve to illustrate this point. The experiments included effects of kappa reduction using oxygen delignification on bleaching wastewater characteristics for two kraft pulps made from eastern and western Canadian wood species. The eastern (mixed spruce, balsam fir, and pine) pulp with a kappa number of 30 generated 52 kg COD/ODt in a D(EO)DED bleaching sequence. Single-stage oxygen delignification produced a pulp of kappa number 16.6 (45% delignification), which then generated 28 kg COD/ODt when bleached by this same sequence, a 46% reduction.

Color is another characteristic of bleaching wastewaters that would be expected to decrease by approximately the same percentage as the delignification achieved in extended or oxygen delignification, since most of the material that contributes to color is lignin-derived.

Reductions in AOX are primarily related to the total atomic chlorine charge applied to the first bleaching stage. Figure 3.4 shows example AOX discharges predicted using a commonly cited regression equation developed from published data from laboratory studies (NCASI 1993). The curves illustrate that as unbleached pulp kappa number decreases, predicted AOX generation also declines. Each curve represents a different kappa factor, which is the ratio of chlorine-based chemical applied (expressed as percent active chlorine equivalents on pulp) per unit of kappa in the unbleached pulp.

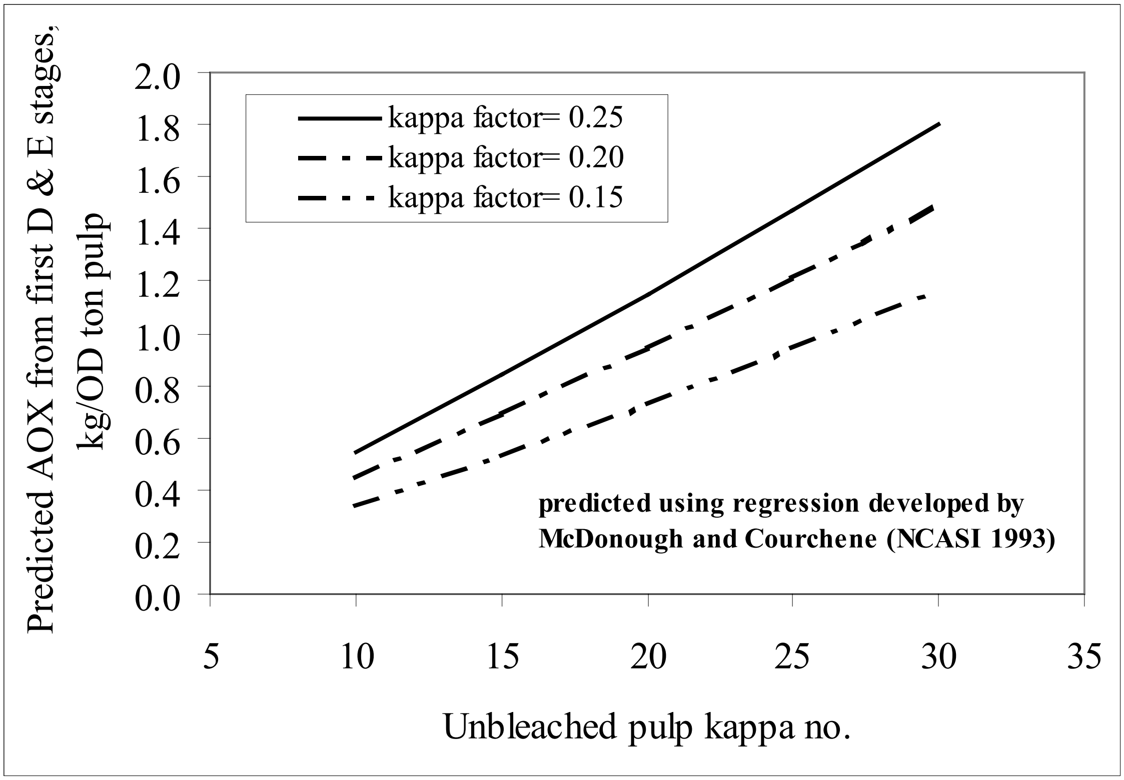


Figure 3.4 Generalized Relationships Between Kappa Number, Kappa Factor, and AOX Generation

3.7 Modern Bleaching Practices

3.7.1 *Bleaching Chemicals*

Chemical pulp bleaching involves the application of chemicals to remove the remaining lignin, to brighten the pulp, and to decolorize dirt and shives that contaminate the stock. Chlorine was found to be an inexpensive and highly effective delignifying chemical and it was used extensively since the early 1900s until recently. Chlorine modifies lignin so that it is easily extracted by subsequent treatment with caustic soda. A chlorination (C) stage followed by an alkaline extraction (E) stage can remove on the order of 90% of the lignin remaining in unbleached pulp. Consequently, these two stages together generate most of the BOD, COD, color, and chlorinated organic matter produced in a chlorine-based bleach plant. Further brightening of the pulp is accomplished using hypochlorite (H) and/or chlorine dioxide (D) in one or more stages following the E stage. In some bleach plants a second E stage is used between two D stages. Some representative bleaching sequences used prior to the 1980s include CEH (semi-bleached), CEHDH (~85% ISO brightness for integrated paper manufacturing), and CEDED (90% ISO brightness market pulp). Hypochlorite is not widely used today in kraft pulp bleaching due to concerns over chloroform generation.

In 1985, chlorine bleaching was implicated in the formation of the toxic and environmentally persistent compounds 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD), and 2,3,7,8-tetrachlorodibenzofuran (2378-TCDF). This finding, and the resulting broader concern about potential impacts of chlorinated organic compounds in general, drove most mills to greatly reduce chlorine use in the bleach plant, and ultimately to eliminate its use entirely. Statistics gathered by AET show that, on a worldwide basis, the amount of pulp bleached without chlorine has increased from 5.4% in 1990 to more than 75% in 2001. For the major pulp producing regions, the percentages for 2001 are: Scandinavia, 100%; Canada, 93%; U.S., 96%; and the rest of the world (Western Europe, Chile, Brazil, Southeast Asia, Africa, Australia, New Zealand, and Japan), 60%. In the U.S. chlorine is believed to be used for bleaching at fewer than five kraft mills. Chlorine use is expected to continue to decline worldwide (Alliance for Environmental Technology 2002).

Chlorine dioxide is the chemical most widely used to replace chlorine in bleach plants. Bleach plants that use chlorine dioxide as their only chlorine-containing chemical are known as elemental chlorine free, or ECF. Bleach plants that use no chlorine-containing chemicals are known as totally chlorine free, or TCF. As of 2001, the amount of pulp produced in ECF sequences was ten times the amount produced in TCF sequences. Scandinavia has the most TCF production, accounting for about one-third of total bleached kraft pulp tonnage in that region and about 58% of the world's TCF production. Recent trends suggest that worldwide growth in ECF is increasing, while TCF production has not increased substantially since 1995 (Alliance for Environmental Technology 2002).

ECF bleaching is practiced on both conventional and reduced kappa pulps. Example ECF bleaching sequences include OD(EOP)D, D(EO)DD, and DEDED. As is the case in chlorine bleaching, the first chlorine dioxide and alkaline extraction stages together account for some 90% of the lignin removal and wastewater COD, color, and chlorinated organic matter. However, the quantities of color and chlorine attached to organic matter are substantially lower in ECF sequences compared to chlorine-based sequences at the same incoming kappa number.

TCF sequences utilize ozone (Z), hydrogen peroxide (P), oxygen (O), peracetic acid (Paa), or some combination of these oxidants. Peroxide-based sequences include one or more chelation (Q) stages to control transition metals that decompose peroxide. In ozone stages, transition metals can promote carbohydrate degradation which lowers pulp strength. Ozone stages are operated at low pH (2 to 4), so metals control is typically achieved by acidification and washing to dissolve and purge the metals. All TCF bleached market kraft mills utilize some form of modified cooking and/or oxygen delignification to minimize the kappa number of the pulp entering the bleaching plant, usually to a value of 12 or less. An example sequence is one used at the Metsä-Botnia Rauma mill in Finland, OO(ZQ)(PO)ZQ(PO/PO). After the two oxygen delignification stages the pulp has a kappa number of 7 to 9 units (Gleadow 1999).

Debate over whether ECF or TCF bleaching was the best path forward for the industry began in the 1980s. Many advocacy groups asserted that use of any chlorine-containing chemicals is unacceptable due to formation of chlorinated organic compounds, and that effluent-free bleaching can best be accomplished with TCF sequences. Scientific assessments of ECF bleaching showed advantages with respect to cost, pulp yield, and pulp quality, and no difference in potential toxicity of ECF and TCF effluents. In 1997 the American Forest and Paper Association (AF&PA) commissioned a review of the technical literature related to product characteristics, environmental performance, and economics of ECF and TCF bleaching. EKONO, Inc., a technical consulting firm, reviewed and summarized technical literature published between 1992 and 1998. The following is paraphrased from the report's executive summary (EKONO 1998):

- With regard to pulp quality, broad generalizations were difficult to make because of pulp quality factors not related to bleaching.
- For softwood pulps, a 5 to 20% lower tear strength was noted for TCF pulps at a given brightness level. Differences were not noted for hardwood pulps.

- ECF bleaching filtrates contain chlorinated compounds not found in TCF filtrates. Polychlorinated compounds were not prevalent in ECF filtrates.
- COD levels were higher in TCF mills, but the COD may be more amenable to biological treatment. Resin and fatty acids were present in both types of wastewaters.
- TCF mills may have higher levels of nitrogen due to use of chelants. Conflicting data exist on the extent to which the nitrogen in chelants is biodegradable.
- No consistent differences were noted in the responses to bioassay tests of biologically treated ECF and TCF filtrates.
- Wood use in TCF fiberlines is generally higher by 1 to 5% owing to the higher yield loss from cooking to a lower kappa number, and possibly due to higher yield loss in the bleach plant itself.
- Studies of energy use show very little difference between TCF and ECF mills. Total energy usage based on product life-cycle analyses indicate that peroxide-based TCF sequences are the most energy efficient.
- Conversion of an existing bleach plant to TCF will probably occasion greater capital costs than conversion to ECF due to the need to produce a lower kappa pulp. Operating costs will also be higher due to increased wood requirements and somewhat higher bleaching chemical costs.

Many ECF sequences attempt to take full advantage of the power of oxygen-based (oxygen and peroxide) chemicals. This has led to the development of the pressurize peroxide (PO) stage which has been installed at a number of mills recently. Examples include UPM-Kymmene's Kaukas mill in Finland which uses a OD(EO)D(EP)D sequence for hardwood and a OD(EO)D(PO)D sequence for softwood; and the new bleach plant at the Sunila Oy mill in Finland which uses a D(EOP)(EOP)(DQ)(PO) sequence. Another example is the Stora Skoghall mill in Sweden which uses an O(OP)DQ(PO) bleaching sequence.

3.7.2 *Extraction Stage Modifications*

Modifications to the extraction stage can include addition of oxygen (EO), peroxide (EP), or both (EOP). Each of these can allow the overall application of chlorine dioxide in the bleach plant to be reduced somewhat. A reduction in chlorine dioxide of about 2 kg active chlorine per kg of oxygen added is typical. Since most of the lignin has been removed after the first two bleaching stages, and since oxygen can delignify but not brighten pulp, it is typically only used to fortify a first extraction stage. On the other hand, peroxide has been used to fortify both first and second extraction stages. Typical published results claim that about 2 to 3 kg active chlorine per kg of hydrogen peroxide can be saved in the (EO) stage through peroxide reinforcement versus 3 to 5 kg of active chlorine per metric ton in a second extraction stage. One to four kilograms of peroxide per metric ton of pulp can typically be charged in the (EOP) stage, and a maximum 2 kg/t in the (EP) stage (Fredström, Idner, and Hastings 1992).

In an (EO) stage, an upflow extraction tower or an upflow pre-retention tube installed ahead of a downflow extraction tower is needed to create the hydrostatic head required to keep oxygen dissolved in the pulp suspension. If this upflow tube or tower is pressurized by adding a control valve on the discharge, higher oxygen charges can be used. In an atmospheric tower, up to 4 kg of oxygen per metric ton can be charged, and for a pressurized reactor this figure may be closer to 6 kg/t (Fredström, Idner, and Hastings 1992).

Ultim-O is a variation in which the pulp is not washed after the first D stage, and the extraction stage is pressurized and operated at a temperature of greater than 95ºC. In laboratory bleaching experiments, this (DO)D bleaching sequence achieved about a 75% reduction in AOX compared to DOD (Cook 1991). This technique was developed as a means of minimizing AOX loads but is believed to be in very limited use commercially.

3.7.3 *Pressurized Hydrogen Peroxide Bleaching*

Hydrogen peroxide use in kraft mill bleach plants is now often undertaken in pressurized reactor vessels similar to those used in oxygen delignification systems. These vessels are used in both ECF bleaching sequences to reduce the charge of chlorine dioxide, and in TCF sequences to brighten the pulp. Higher temperatures and pressures than those achievable in atmospheric reactors increase efficiency of peroxide use and brightness capability. Many peroxide systems also utilize oxygen to boost performance. Pressurized peroxide stages may have one or two reactors in series. In a two reactor arrangement, the first stage will typically have a residence time of 5 to 30 minutes, in which 50 to 80% of the peroxide charge is consumed. The second stage will consume the remainder of the peroxide over a period of several hours, depending upon the temperature. Single stage pressurized peroxide stages are also designed for several hours of reaction time (Pikka et al. 1999).

A P_{HT} stage is an attempt to reduce the retention time requirement, and therefore the capital cost of these systems. P_{HT} stages operate at very high temperatures (110 to 150ºC) and pressures (5 to 25 bar). To achieve good delignification without pulp degradation, these processes require that peroxide stabilizers be added. Effective stabilizers include magnesium sulfate, silicates and poly-*a*-hydroxyacrylic acid (Devic, Pralus, and Suty 1998).

3.7.4 *Ozone Bleaching*

Ozone is an extremely powerful oxidizing agent and must be applied in a manner that minimizes cellulose degradation. In all cases, some basic preconditions for successful implementation, from a product quality and equipment cost point of view, apply. These include:

- Pulp fed to the ozone reactor must have a sufficiently low lignin content to allow full bleaching with a reasonable ozone application. This is required to eliminate excessive deterioration of the pulp fibers (preserve strength) and to limit capital and operating costs.
- Ozone bleaching on an industrial scale is carried out at either medium or high consistency under acidic conditions (pH <4). The pulp entering the ozone bleaching stage should be well washed and contain a low concentration of transition metal ions.
- In medium consistency (MC) ozone bleaching stages, the amount of ozone that can be applied in a single stage is limited by the gas volume that must be mixed into the stock. A practical limit is about 4 to 5 kg/ODt of pulp. A key component of the MC ozone stage is the mixer, which must ensure good contact between the ozone and the pulp fibers without excessive decomposition of the ozone. MC systems require ozone concentrations as high as possible (up to 14% in oxygen) and compressed to 0.6 to 1.0 MPa (90 to 150 psi).

High consistency (HC) reactors allow higher ozone application even at low ozone concentration and atmospheric pressure. The investment cost for a HC ozone stage is higher due to the need for an additional dewatering press, a fluffer (not being used in new installations), and a more complex reactor. These additional costs are partially offset by the ability of an HC ozone stage to utilize ozone at atmospheric pressure and at a somewhat lower concentration (6%) than MC systems.

Low and high consistency ozone bleaching methods were evaluated extensively in the 1960s and 1970s. There has been some renewed interest in low consistency ozone, which has been proposed as an alternative for replacing a low consistency first D stage.

3.7.5 *Peracetic Acid*

Peracetic and other peroxy acids have been shown to be effective as delignifying agents and to reinforce or replace chlorine dioxide or peroxide in brightening stages (Liebergott 1994). Peracetic acid (Paa) used in a peroxide-based TCF sequence can result in a brightness ceiling gain of about 2 points (from 86 to 88). It is used in some European mills and is reportedly being used on a trial basis in North America. Peroxy acids are unstable and must be manufactured on site. There is currently no distilled peracetic acid produced in North America.

3.7.6 *Chelating Agents*

It is common practice to use a chelating stage to remove metal ions prior to brightening mechanical pulps with hydrogen peroxide. An alkaline peroxide stage in a kraft mill bleach plant is almost always preceded by an acidic chelating stage that includes washing. Chelants tie up metal ions in solution, making them much less reactive. The most commonly used chelants are amino-carboxylates, especially diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA). Various chelating agents such as DTPA, Trilon ES9910, and Dequest 2060S were evaluated by Basta, Holtinger, and Hook (1991), but none of these performed better than EDTA. For alkaline peroxide delignification of kraft pulps, the optimum results were obtained when the pretreatment with EDTA was carried out at pH of 5 to 7, a temperature of 90°C, and an EDTA application of 0.2% on OD pulp (Basta, Holtinger, and Hook 1991). These conditions gave the optimum metal ion profile in the pulp for the subsequent hydrogen peroxide treatment. The desirable profile is a low concentration of transition metals, such as manganese, iron, and copper, and a relatively high concentration of the alkaline earth metals, such as magnesium (Galloway et al. 1994).

3.7.7 *Enzymes*

Enzymes are proteins produced by microorganisms to break down complex molecules for use by the cell. Enzymes known as xylanases that attack the hemicellulose xylan have been successfully used to reduce bleaching chemical use and increase the degree to which pulps can be brightened. Xylanases produced by different microbial strains may differ chemically, but all serve to degrade xylan. The removal of xylan from pulps is believed to enable residual lignin to be removed more easily in subsequent bleaching stages. Susceptibility of a pulp to xylanase treatment depends on the pulp and can be determined by measuring the amount of xylose released as a function of xylanase applied. In general, hardwood pulps are more susceptible than softwood pulps, and oxygen delignification increases susceptibility. Application rates may vary from 0.1 to 1.0 liter per ton of pulp (Tolan and Thibault 2000). Xylanases are applied to pulp after brownstock or post-oxygen washing, typically using a shower bar to disperse the enzyme solution evenly across the pulp mat on the final washing stage, and the pulp storage tower is used as a reactor. Enzymes are effective in a pH range of 4 to 9, so the pulp will typically require acidification prior to application (Farrell, Viikari, and Senior 1996). Reduction in chlorine dioxide application on the order of 15 to 30% and AOX reduction of 40% have been reported (Senior and Hamilton 1992; duManoir et al. 1991).

3.7.8 *Pulp Washing*

Pulp washers are designed to remove dissolved materials that can interfere with downstream bleaching stages. For example, dissolved organic matter carried from an extraction stage into a peroxide stage will increase the peroxide charge, and may limit the amount of brightening achieved.

Historically, the vacuum drum washer has been the mainstay of the industry for washing in both the fiberline and bleach plant. This style of washer is still the most prevalent, although several other types are used extensively, including pressure drum, wash press, dewatering press, diffuser, belt washer, and others. The style of washer is perhaps less important than the capacity of the units and the manner in which they are operated and maintained. A properly sized washer of modern design should provide good washing efficiency while minimizing wash water requirements.

3.8 Recovering Bleaching Wastewaters

Developments in delignification and bleaching technology have resulted in significant reductions in bleaching wastewater volumes and loads of dissolved organic matter, chlorinated compounds, and other constituents. Several companies have sought to achieve further reductions by routing the bleaching wastewaters to chemical recovery systems, primarily for the purpose of combusting the organic compounds in the recovery furnace. In addition to reducing wastewater loads, returning filtrates to the recovery cycle recovers chemicals and energy, potentially reducing the need for chemical makeup and increasing steam production.

Recovering bleaching wastewaters, known as filtrates, is not easy to accomplish, and the impacts can be profound. An essential prerequisite for filtrate recovery is volume reduction. The amount of water required in the fiberline and recovery systems of kraft mills is small relative to the volumes generated in most bleach plants. For this reason, recovery of a significant fraction of a bleach plant's wastewater requires that the volume be minimized. This can be accomplished by controlling clean water infiltration in the bleach plant and brownstock fiberline, and by maximizing reuse of filtrates within the bleach plant.

Water is critical to operating an effective bleach plant. In a conventional open bleach plant, all water entering the bleach plant is discharged as wastewater or exits with the pulp. A completely closed bleach plant would have no wastewater discharge – all excess filtrates would be used in the fiberline, kraft recovery system, or external recovery process. For kraft mills that bleach 100% of their pulp production, complete bleach plant closure on a full-time basis has not yet been demonstrated commercially. There are a few linerboard mills that bleach only 20% or so of their unbleached pulp production to make white top liner that have no bleaching effluent. However, these mills have unique circumstances with respect to washing and recovery system capacities that are not present in kraft mills that make only bleached pulps.

The attention paid to water conservation in recent years is reflected in the effluent flows from bleach plants representing three different generations. An example 1960s vintage bleach plant was shown to have on the order of 73 m^3/ADt, a 1980s design discharged some 31 m^3/ADt, and a 1990s bleach plant would be designed to discharge about 21 m^3/ADt (Carter and Gleadow 1994). Currently, open bleach plants are capable of achieving wastewater flows of less than 20 m^3/ADt by implementing demonstrated water conservation measures.

3.8.1 *Control of Water Infiltration*

Water which enters the stock or filtrate streams is generally known as "process" water. In addition, there are normally many "non-process" streams such as cooling water, seal water, and wash down hoses. These non-process streams normally leave via the process sewers and so contribute to the bleach effluent volume. Process water inputs may include:

- water with stock (mostly wash water from the final brownstock or post-oxygen delignification washing stage)
- water with bleaching chemicals

- condensate from steam used to heat pulp by direct injection
- pulp washing showers
- wire cleaning showers
- hydraulic and steam doctors for removing the pulp sheet from washer drums
- water inlets intended only for wash-up or starting an empty plant but left open inadvertently
- hose water added to washer vats in response to high vat consistency events
- leakage through valves in piping designed to supply fresh water at start-up or during unusual operating conditions
- seal water leakage into some centrifugal pumps and agitators
- dilution water added by operators to overcome the inability of specific equipment (e.g. agitators or screw conveyors) to operate as desired
- standpipe dilution for medium consistency (MC) pumps
- constant or excessive uncontrolled makeup to seal tanks to avoid process upsets

Non-process water uses may include:

- cooling water to hydraulic drives (often one on each washer drum)
- cooling to hydraulic supply units for diffusion washers
- cooling water for jackets on bearings
- hoses or other temporary cooling for faulty bearings
- seals on some types of washer drums
- packing or seals on shafts of pumps and agitators
- clean-up hoses

Some techniques for reducing fresh water inputs include:

- Operate wire cleaning showers intermittently. Fresh water at about the operating temperature of the washer is usually used for wire cleaning showers. These showers serve to clean the washer screen or deck of fiber and other solids that, over time, tend to plug the void spaces. To conserve water, many mills use the wire cleaning showers on an intermittent basis; for example, operating for one minute out of every ten.

- Use filtrates for wire cleaning showers. Hot filtrates, especially alkaline filtrates, are used in some mills in place of fresh water. Fiber removal may be required to prevent plugging of shower bars and spray nozzles. Modifying the shower system so that the shower bar and nozzles can be continuously or automatically purged may be an alternative to fiber removal.

- Replace hydraulic doctors with air or steam doctors. Doctors serve to separate the pulp mat from the washer drum surface. This can be effectively done using air or steam in place of fresh water. Also, the need for wire cleaning is decreased if an air doctor is used.

- Reduce water inputs with bleaching chemicals. For example, an ECF bleach plant using 3% chlorine dioxide at 10 g/L has an associated water input of 3.0 m^3/ODt. Increasing the solution concentration to 12 g/L would reduce water input to 2.5 m^3/ODt.

- Use filtrates for seal tank makeup. Makeup is needed to control the water level in tanks during conditions when outflows exceed inflows. Filtrates from a stage of similar chemistry can be used as makeup on an upstream stage in place of fresh water. For example, in a D(EO)DED bleach plant, D3 stage filtrate could serve as makeup to the D2 stage seal tank, and the D2 stage filtrate could serve as makeup to the D1 stage seal tank. In this scenario, fresh water would be used for makeup only on the D3 stage tank.

3.8.2 *Using Filtrates for Pulp Washing*

Using filtrates within the bleach plant to wash pulp is not a new idea, but the degree to which filtrates are being reused is greater than ever. Filtrates are always reused within a stage to the extent that dilution of pulp is required entering the stage, at the end of the reactor, and in the washer vat. Filtrates used for pulp washing are used in countercurrent fashion on washers upstream with respect to the direction of pulp flow. Generally, filtrates from the latter stages of a bleach plant may be reused in their entirety, whereas filtrates from the initial stages contain materials that interfere with bleaching and so are reused sparingly if at all for pulp washing. Filtrates are used on the stage immediately upstream (direct), on a stage of similar chemistry two or more stages upstream (jump stage), or a combination of both (jump stage split flow) (Histed and Nicolle 1973). Figure 3.5 shows how filtrates might be reused in an example D(EOP)DD sequence. Filtrate from the D3 stage is used on the D2 washer, and filtrate from the D2 stage on the EOP and D1 washers. Some of the EOP filtrate is used on the D1 washer and the balance of the alkaline filtrate is sewered. Acid filtrate from the D1 stage is sewered separately. Generally, the first extraction (in this example, EOP) stage filtrate is not used extensively on the D1 washer due to scaling and foaming concerns, although full direct countercurrent washing has been demonstrated successfully (Nutt et al. 1993).

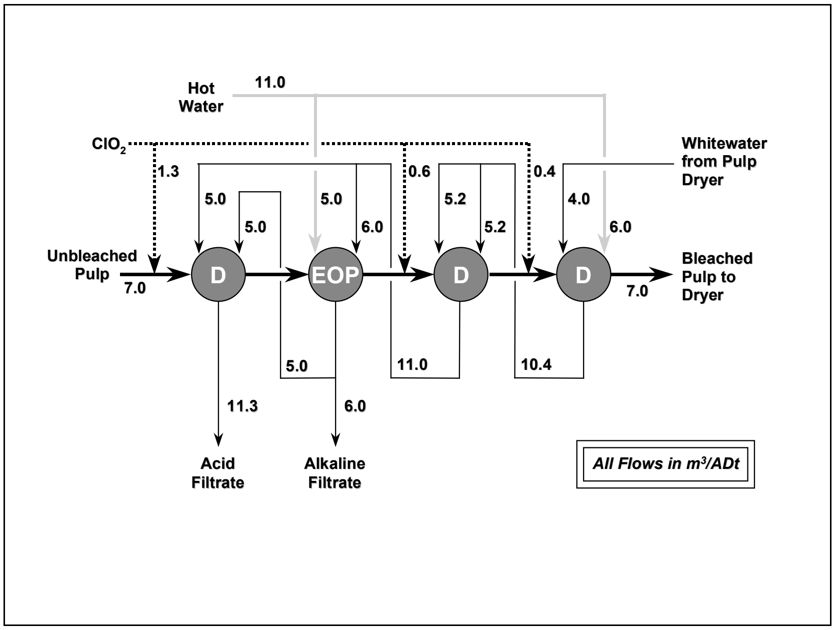


Figure 3.5 Example Filtrate Reuse Scheme in a Modern ECF Bleach Plant

3.8.3 *Filtrate Recovery Via the Fiberline*

The most common technique used to recover bleaching filtrates is to use the filtrates to wash the unbleached pulp in countercurrent fashion so that the dissolved materials in the filtrate become part of the black liquor. Recycling the bleaching filtrates to the fiberline takes advantage of existing washing and evaporation capacity to concentrate the dissolved organic matter. Several mills practice recovery of extraction stage filtrate by routing it to the post-oxygen washers. Filtrates recovered may be introduced into the wash line at a location where the concentration of dissolved material is most similar to that of the recovered stream, or at another convenient point.

Recovering filtrates in this manner may either increase the evaporative load, reduce washing effectiveness, or a combination of both, unless water conservation measures are implemented in the fiberline. The volume of filtrates that can be recovered via the fiberline is limited by the existing washing and evaporation capacities in a given mill. Using the example modern bleach plant of Figure 3.5, there is a total of about 17.3 m^3/ADt of excess filtrates. Assuming that the post-oxygen washer discharges pulp at 14% consistency, the total wash water usage in the fiberline is only about 10 m^3/ADt. Consequently, recycle of all the bleaching filtrates via the fiberline cannot be accomplished without additional measures to reduce filtrate flow rates or increase washing and evaporation capacities.

In addition to flow constraints, there are other issues that make bleaching filtrate recovery difficult. Recovery of acidic filtrates from acid wash, chlorine dioxide, and chelation stages to the alkaline fiberline must have some provision for purging alkaline earth metals that form scale deposits on equipment. Another consideration is some of the dissolved organic matter initially solubilized in the bleach plant being carried back into the first stage of bleaching through normal washing inefficiencies. These organics consume bleaching chemicals, reducing their efficiency and effectiveness, especially for ozone and peroxide.

There are two kraft linerboard mills in which a small proportion of the total production (20%) is bleached and all of the bleach filtrates are recycled to adjacent brownstock washing lines. The mills use peroxide-based TCF bleaching and recycle the Q stage wash water to adjacent brownstock fiberline washers. In these mills, the volume of bleaching filtrates recoverable is not limited by the water requirements for brownstock washing. Similarly in a third linerboard mill, in which 40% of the total production is bleached, part of the Q stage filtrate is evaporated separately and added to strong black liquor. These mills are discussed in more detail in Section 4.

3.8.4 *Filtrate Recovery to Causticizing*

Another potential location for introducing filtrates into the recovery system is the causticizing process. Some makeup water is used in this area because the smelt from the recovery boiler must be reconstituted into green liquor. Typically, water, often in the form of evaporator condensates, is made up to the lime mud washing system and the resulting weak white liquor, or weak wash, is used for smelt dissolving. One such approach, evaluated by Teder et al. (1990), involves neutralizing acidic bleaching filtrate with lime and using it in place of condensates or water for mud washing. This would enable the eventual destruction of the dissolved organics in the recovery furnace or lime kiln, and would take advantage of existing capabilities to purge metal ions present in the acid filtrate via dregs removal and mud losses.

The volume of acid filtrate that can be recovered is limited by the makeup water requirement in causticizing, a maximum of about 3 m^3/ADt. There may be process issues that further reduce the volume recoverable in this manner, such as impacts on dregs separation, lime mud settling and causticizing efficiency (Teder et al. 1990). The Aspa mill in Sweden experimented with using Q-stage filtrate in causticizing, but has abandoned the practice due to problems with fiber in their green liquor filter.

3.9 Managing Impacts of Closure

Process closure in general, and especially bleaching wastewater recovery, can lead to increased concentrations of so-called non-process elements (NPEs). If allowed to accumulate in mill process streams, NPEs can cause scale deposit formation, loss of bleaching capacity, increased evaporation load, increased recovery furnace downtime, and other problems. The degree to which filtrate recovery can be practiced is limited by the availability of means to effectively manage these and other impacts.

Raw materials, especially wood, water, and makeup chemicals, are important sources of NPEs. NPEs are often classified according to the kinds and locations of impacts they have. Chlorine (which exists almost exclusively as chloride ion in mill liquor streams) and potassium have adverse impacts on recovery furnace operation; calcium and barium can form scale deposits in the bleach plant and at locations where acidic bleaching filtrates are recovered; manganese, iron, and copper consume certain bleaching chemicals and the subsequent degradation products can cause pulp strength losses; and silicon and aluminum form scale deposits on heat transfer surfaces. A variety of technologies are available to manage the impacts of NPEs.

3.9.1 *Metals*

There are potentially significant impacts associated with certain transition metal ions, including Mn^{+2}, Fe^{+3}, and Cu^{+2}, that catalyze the decomposition of peroxide. In ozone bleaching Fe^{+3} and Cu^{+2} can result in substantial degradation of cellulose, presumably due to free radical species formed by reactions involving these ions (Chirat and Lachenal 1994). To limit the impact of transition metals in ozone and peroxide stages, provisions are made to sequester and/or remove these ions. Chelating agents, especially EDTA, are used in a Q stage just prior to a peroxide stage. The chelant's affinity for these ions affects their removal from the pulp and chemically isolates them in a dissolved state, and they are subsequently washed from the pulp and discharged with the Q stage filtrate.

In ozone bleaching, the transition metals are removed by treating the unbleached pulp with acid to a pH of about 2, followed by dewatering or washing to remove the dissolved metals ions. The acid treatment also provides the optimum pH for ozone treatment (van Lierop, Skothos, and Liebergott 1996). Transition metal ions do not appear to impact chlorine dioxide bleaching.

In addition to the transition metals, kraft pulps contain alkaline earth metals, especially calcium and barium. These metals originate in the wood and as lime mud particles in the white liquor. They remain chemically or physically bound to the pulp through the fiberline, dissolving in the first acidic stage of the bleach plant, typically the first D stage, Q stage, or Z stage. In a conventional open bleach plant, the acid filtrate discharge serves as a purge for metals. As closure is pursued, a purge of these metals must be maintained, as they will precipitate onto the pulp if acidic filtrate is recycled to the alkaline brownstock or post-oxygen washing systems. The precipitated metals would then be carried forward into the bleach plant where they would be re-dissolved. Eventually, the concentration in this loop would build until scale deposits formed, plugging washer drums and causing downtime to remove the offending material. This phenomenon has been referred to as an acid/base trap or, specifically, a metals trap. Closure of a bleach plant, whether ECF or TCF, cannot be accomplished without new provisions for purging or stabilizing metals from acidic filtrates.

Aluminum and silicon are two other elements that can create problems in a kraft mill. These elements combine with each other and various anions to create scale deposits on heat transfer surfaces, especially in the black liquor evaporators. Although they are not removed as efficiently as other metals such as manganese and iron, aluminum and silicon are co-precipitated as double or triple salts and removed with the green liquor dregs.

One approach to purging metals from the acid bleaching filtrate is to install an auxiliary system to remove the metal ions from the acid filtrate. Chemical precipitation and ion exchange have been evaluated as metal removal schemes. Precipitation of metal hydroxides and carbonates can be achieved by addition of sodium hydroxide and sodium carbonate, or by adding green liquor (Lindberg, Engdahl, and Puumalinen 1994). The BFR process developed by Champion International includes a treatment of acid filtrate such as chemical precipitation or ion exchange (Maples et al. 1994). The BFR installation at the bleached kraft mill in Canton, North Carolina, (currently owned by Blue Ridge Paper Products Inc.) utilizes ion exchange technology (Caron and Williams 1996). A portion of the filtrate from the first D (D1) stage is filtered to remove fiber and other solid particles, and fed to ion exchange beds. The beds are periodically regenerated with sodium chloride, producing a low volume brine wastewater containing primarily inert metal chlorides. The treated filtrate is reused as wash water, primarily on the D1 washer. In essence, the D1 washer and ion exchange system serve only to remove metals. Organic compounds entering the D1 stage and those dissolved during bleaching reactions are ultimately carried with the pulp into the EOP stage, from which the filtrate is recovered via the post-oxygen washers.

Another method for purging metals is to operate an acid wash stage with a low volume purge. Sulfuric or other acid is added to control the pH below a value of 4, and the pulp is washed or dewatered to limit metals carryover into the first bleaching stage. Some of the acid filtrate can be recycled to the fiberline, as long as an adequate purge stream is maintained. This purge will contain some organic compounds; however, some of the organics, especially high molecular weight lignin fragments, will tend to partition onto the pulp under acidic conditions (Joseph and White 1996). This scheme is practiced on the OZED bleaching line at the bleached kraft mill in Franklin, Virginia, currently owned by International Paper Company. The oxygen delignified pulp is treated with acid and dewatered prior to the ozone (Z) stage. A purge is maintained to control metals, and the Z and E stage filtrates are recovered via the post-oxygen washers.

Controlling aluminum and silicon is difficult because they are relatively soluble in alkaline liquors compared to other metals. Lowering inputs by utilizing makeup lime with low levels of these elements may be an effective control strategy. They are more soluble in white liquor than in green, so efficient dregs removal can minimize buildup of these elements. Addition of magnesium salts to green liquor can remove aluminum and silicon by precipitation of minerals and subsequent removal with the dregs (Wannenmacher et al. 1998).

Phosphorus is introduced into the mill primarily with the wood supply (Ulmgren and Rådeström 1997). The primary purges for phosphorus include the bleaching filtrates or unbleached pulp, grits, dregs, and lime mud losses. Recovery of bleaching filtrates can reduce or eliminate an important purge point for phosphorus. Its primary impact is that it can accumulate in the lime cycle as calcium phosphate, reducing the chemical availability of the lime and increasing lime requirements. Increased purging of lime mud has been suggested as a corrective action, although the increased fresh lime makeup could bring additional aluminum and silica into the liquor cycle (Ulmgren and Rådeström 1997).

3.9.2 *Dissolved Organic Matter*

Dissolved organic matter consumes bleaching chemicals. Closure of the bleaching process increases the concentrations of dissolved organics, so some increase in bleaching chemical usage is expected to occur. The source of the organic compounds is a key variable in determining the amount of bleaching chemicals consumed. It has been demonstrated that organics from cooking (black liquor) consume more chlorine or chlorine dioxide than solids generated in oxygen delignification, which in turn consume more chemicals than bleach plant extraction stage organics (Canovas and Maples 1995). Generally, organics generated in chlorine dioxide stages are well oxidized and consume only minor amounts of chlorine dioxide. Joseph and White (1996) reported that oxygen delignification stage dissolved organics consumed about twice as much ozone as organics from the extraction stage of an OZ(EO)D bleaching sequence, whereas Z stage organics consumed negligible amounts of ozone.

The primary means of mitigating the effect of organic matter on bleach chemical use is efficient washing, especially after oxygen delignification. In this regard, the performance of pulp washing equipment is the most important consideration.

3.9.3 *Pitch*

Organic compounds in the wood known as extractives, including resin and fatty acids, can result in pitch deposits on process equipment and in the product. Pitch is of particular concern in acid or neutral sulfite mills, as resinous material is not saponified as it is in most alkaline pulping systems. Traditional means of controlling pitch are through the use of dispersants, fixation agents and talc. Process closure at mills is likely to increase extractives concentrations, potentially increasing pitch accumulations. A process developed by Kemira Chemicals Oy to remove extractives from process filtrates utilizes polyethylene oxide flocculant and flotation separation. The process was first implemented at the Domsjö Fabriker sulfite mill in Sweden, enabling closure of its TCF bleach plant. The process appears to be effective on kraft mill filtrates as well, and removal of problem metals such as iron and calcium was demonstrated in tests. The resulting pitch-containing residue may be suitable for burning in a wood waste fired boiler (Rampotas, Terelius, and Jansson 1996).

3.9.4 *Chloride and Potassium*

The element chlorine enters a kraft mill as the chloride ion with the wood and makeup chemicals such as sodium hydroxide (caustic). Chloride is extremely soluble in the alkaline liquors of the kraft cycle, and will accumulate there. The typical chloride purge points in a mill include recovery boiler stack emissions, washing losses from brownstock or post-oxygen washing into the (open) bleach plant, and losses of green, white, and black liquor. Because process closure minimizes such losses, chloride and potassium concentrations will increase unless alternative purge means are provided. The concentration of chloride in mill liquors will be determined by the input and output rates. In a typical “inland” mill, the chloride concentration in the as-fired black liquor will be about 0.2 to 0.5% of dry solids. Concentrations are higher in mills that use caustic with high levels of sodium chloride contamination and for coastal mills that use seaborne logs. Chloride levels in coastal mill black liquors may range from 3 to 5% of dry solids (Tran, Barham, and Reeve 1989).

The primary impact of chloride in the liquor cycle is to modify the physical behavior of the condensed fume particles formed in the recovery furnace. Chloride, sodium, sulfur, and other inorganics are volatilized from burning liquor droplets and the smelt bed in the furnace. This fume condenses as a mixture of salts, accumulating on the boiler tube surfaces, reducing heat transfer and plugging the flue gas passages between the tubes. These accumulations are controlled by frequent soot blowing using steam jets. Most furnaces also require periodic cooling or washing the inside of the furnace with water, events that reduce black liquor burning and, at most mills, pulp production capacity. For many mills, managing chloride and potassium levels in the liquor cycle is an important part of operations.

Within the range of chloride concentrations in typical black liquors, increasing chloride concentration will lower the melting point of the condensed fume. The mixture will have a higher molten fraction for a given temperature, potentially making it stickier and increasing the accumulation rate on tube surfaces. If the fume is sticky as it passes through the generating bank of tubes, boiler plugging may proceed rapidly.

Potassium has much in common with chloride with respect to inputs and outputs, chemical behaviors in the liquor system, and impacts on chemical fume modification. These two elements are normally considered together in addressing recovery furnace impacts. Wood is the primary input vector for potassium. Concentrations in black liquor are typically in the range of 0.8 to 1.5% of dry solids in softwood mills, and 2 to 5% in hardwood mills (Tran, Barham, and Reeve 1989). Loss of pulping chemicals is the primary purge mechanism.

Another potential concern with chlorides in the liquor cycle is corrosion. This problem is commonly cited in discussions of recycling chloride-containing bleaching filtrates. H.A. Simons (now AMEC Forest Industry Consulting) and the Pulp and Paper Research Institute of Canada cooperated on a four year research program, “Engineering Modifications Towards the Closed-Cycle Bleached Kraft Pulp Mill,” from 1991 to 1995. One of the observations in the study was that chloride corrosion was not apparent if conditions remained highly alkaline, such as in brownstock washing and the liquor system. The areas of concern were corrosion under oxygen-rich gas phase environments such as may be encountered in high consistency oxygen delignification reactors (however, most installations are medium consistency in which all surfaces are wetted) and, additionally, equipment in the fiberline being subjected to acidic conditions due to, for example, acidification of the final stages of brownstock washing or use of acidic bleaching filtrates on pulp washers not designed for such conditions.

Recovery boiler corrosion is also a concern. One of the problems encountered during closed-cycle bleaching with the Rapson-Reeve arrangement at Great Lakes Paper (now Bowater) in Thunder Bay, Ontario, was that a portion of the recovery furnace superheater tubes suffered severe corrosion and required replacement within two years of startup. The corrosion was seen as a result of high chloride levels causing slagging of chemical deposits that normally protect the superheater tubes from chemical attack (Reeve et al. 1983). This contrasts with the experience of recovery furnace operation at mills in coastal locations in which the wood supply is floated in salt water, such as the Harmac and Powell River mills in Western Canada. Many of these mills operate at chloride levels up to two and a half times those which caused problems at the Thunder Bay mill. For example, the Powell River mill has operated at chloride levels up to four times those seen at Thunder Bay. However, a key difference was that the furnace at Thunder Bay was designed to operate with a superheated steam temperature of 900°F as compared to the west coast mills which operate at about 750°F. The higher steam temperature at Thunder Bay apparently reduced that thickness of the frozen smelt layer which serves to protect the tubes from chemical attack. Design factors that can impact the susceptibility of superheaters to fireside corrosion include location of the superheaters relative to the furnace nose, tube geometry and arrangement, the number and location of attemperators, tube metallurgy, and the direction of steam flow (La Fond, Verloop, and Walsh 1992).

ECF bleaching filtrates contain chloride, chlorate, and organically bound chlorine, virtually all of which exist as chloride ions in the liquor cycle. Amounts present in filtrates returned to the chemical recovery system are generally greater than amounts in wood and chemical makeup inputs, and thus their recovery represents a significant technical challenge in minimizing operating impacts. Also, closure of the bleach plant eliminates an exit point for chloride and potassium, namely brownstock or post-oxygen washing losses. In general, as mills reduce their liquor losses, chloride and potassium concentrations will increase unless inputs are reduced or additional means for purging these ions are implemented. The recovery of filtrates from TCF bleach plants may also require additional purge capacity, though not to the extent required for recovery of ECF filtrates.

There are a variety of options for managing chloride and potassium impacts. Coastal mills in British Columbia, Canada, are designed to cope with very high chloride levels due to seaborne wood inputs. In particular, the recovery furnaces at these mills are designed with larger superheater sections so that the upper furnace temperatures are somewhat lower than in units of more common inland designs. The lower temperatures reduce the potential for the condensed fume particles to accumulate in areas where the flue gas passages are narrow and easily plugged.

A few techniques are used by mills to control chloride and potassium levels in their liquor systems. These techniques are generally of limited capability, and so are not likely to be sufficient where recovery of ECF bleaching filtrates is contemplated or practiced. However, they may be very effective in counteracting the buildup of chloride and potassium due to progressive kraft cycle closure, and to mills recovering TCF bleaching filtrates. A relatively simple measure is to use only makeup chemicals, especially caustic, with very low chloride content. Another commonly used technique is to periodically purge some of the recovery furnace precipitator catch (the condensed fume from the furnace), which is enriched with chloride and potassium compounds. Normally, this chemical ash collected by the electrostatic precipitator (ESP) is returned to the black liquor just prior to firing. A periodic or fractional purge of this material may require some minor modifications to the ash collection system. The purged ash may be dissolved in water and discharged as a low volume brine wastewater. This technique is generally limited because the ash, while enriched in chloride and potassium, is mostly sodium sulfate, and any loss of sodium and sulfur represents a loss of pulping chemicals.

Higher chloride and potassium purge capacities can be achieved by separating the chloride and potassium from the ESP catch so that most of the sodium and sulfur is returned to the liquor cycle. The simplest process to accomplish this is to leach the chloride and potassium from the ESP catch, taking advantage of the higher solubility of sodium and potassium chlorides compared to sodium sulfate. The liquid phase is then sewered and the saltcake (sodium sulfate) is returned to the black liquor. This approach was proposed by Wright (1956), and has been used at mills in Canada and Brazil.

Higher chloride and potassium removals and saltcake recovery efficiencies can be achieved by completely dissolving the ESP catch and crystallizing the sodium sulfate by evaporation or cooling. The crystals are separated by filtration or centrifugation and returned to the black liquor. Two basic versions of this process have been developed. One type generates sodium sulfate decahydrate, Glauber’s salt, and the other generates anhydrous sodium sulfate. The process based on cooling involves acidifying the dissolved material to remove carbonates by purging carbon dioxide, and concentrating the solution by cooling crystallization. Glauber’s salt is returned to the black liquor and a concentrated chloride and potassium solution is purged. Tateishi et al. (1998) reported on the results of a four-month mill trial with such a system at a kraft mill in Japan. Fujisaki et al. (2001) reported on results for the seventh mill to adopt this patented technology, known as Potassium Removal Equipment. The system has met chloride and potassium removal efficiency targets of 90% and 75%, respectively, and has achieved 96.6% recovery of sodium sulfate.

Sterling Pulp Chemicals developed a process based on evaporative crystallization known as the Chloride Removal Process, or CRP. The first CRP unit was installed as part of the BFR technology demonstration facilities in Canton, North Carolina. CRP uses forced circulation evaporation to concentrate the dissolved ESP catch. Sodium sulfate crystallizes at saturation and is removed by filtration and returned to the black liquor. Chloride and potassium are purged as a low volume brine wastewater. Other CRP units have since been installed at mills to improve recovery boiler performance where no bleaching filtrate recovery is practiced. Eka Chemicals markets a similar process known as the Precipitator Dust Recovery (PDR) process. This process also relies on evaporative concentration of a solution of precipitator dust to generate sodium sulfate and, to the extent sodium carbonate is present, burkeite (a double salt of sodium sulfate and carbonate) solids for recovering and a brine rich in potassium and chloride that is purged (Minday et al. 1997).

Other processes for removing chloride and potassium from the ESP catch have been proposed and developed. An example is the Precipitator Dust Purification (PDP) process that was jointly developed by Paprican and ProSep Technologies, Inc. of Canada. This process utilizes ion exchange technology to generate a purged stream rich in NaCl and a recovered stream rich in Na_2CO_3 and Na_2SO_4. Precipitator dust is dissolved in water and filtered prior to the ion exchange step. Water is used to regenerate the ion exchange resin. Laboratory development studies using precipitator dust from two mills showed efficiencies of more than 95% for chloride removal and of at least 85% for sodium recovery. Potassium was not significantly removed. The recovered stream would be directed to the black liquor evaporators (Jemaa et al. 1999).

Another approach to chloride purging is to promote the formation of hydrogen chloride gas which will pass through the ESP where it can be scrubbed from the flue gas. Sulfur dioxide (SO_2) reacts with NaCl in the flue gas to give HCl gas. The reaction is:

$$2NaCl(s) + SO_2(g) + \frac{1}{2} O_2 + H_2O \rightarrow \quad 2HCl(g) + Na_2SO_4(s)$$

SO_2 concentrations generally limit the amount of NaCl converted to HCl, but mills that operate at high liquor sulfidity may have most of the chloride load in HCl form. A number of Scandanavian mills operate in this manner, utilizing scrubbers for SO_2 control. In these mills, the scrubber wastewater may serve as a significant chloride purge.

All of the technologies that rely on the recovery furnace partitioning of chloride and potassium are limited by the extent to which these elements are volatilized. The fraction volatilized is determined to a great extent by the temperature of the char bed in the furnace. Equilibrium calculations indicate that at a bed temperature of 950ºC, about 20% of the chlorine is emitted from the bed. At 1200º C the fraction increases to about 80% (Hupa et al. 1990). Furnaces that operate at higher temperatures would therefore present a greater fraction of the total chloride and potassium in the flue gas, enabling potentially higher purge capacities. However, dust formation also increases as temperature goes up (Janka, Backman, and Wallén 2001), increasing the amount of dust to be treated to achieve a given purge rate of these elements.

Treatment of the white or green liquors has been proposed as a means to purge large amounts of sodium chloride. The Rapson-Reeve process implemented at Thunder Bay utilized two-stage evaporation of the white liquor to produce sodium chloride crystals, a portion of which were subsequently used for chlorine dioxide generation. This system was capable of purging 60 to 120 kg NaCl/ADt from the liquor cycle (Shivgulam, Barham, and Rapson 1979).

3.9.5 *Chemical Makeup*

Recovery of bleaching filtrates changes the sodium and sulfur makeup requirements in a kraft mill. Sulfur recovered from sulfuric acid used in the first bleach stage, and caustic used in extraction and peroxide stages represent new inputs to the liquor cycle, and chloride and potassium removal systems may create new sodium and sulfur losses. Chemical losses via brownstock or post-oxygen washing would may also be reduced. Such changes may require new strategies for determining and controlling chemical makeup requirements. For example, Maples et al. (1994) indicated that use of oxidized white liquor for a portion of the alkali charge in the bleach plant extraction stages was indicated to balance kraft cycle sodium and sulfur inputs, based on computer simulations of bleach filtrate recovery scenarios for one mill.

3.9.6 *Process Control*

Recovery of bleaching filtrate requires attention to process control issues. For example, if filtrate recovery is needed on a full time basis, i.e., for purposes of permit compliance, then filtrate storage provisions would be needed for periods when the bleach plant production rate exceeds the rate of unbleached pulp production. In most mills a high density pulp storage tank is located in the process between the fiberline and bleach plant which allows each to operate independently over short periods of time, usually less than 12 hours. Where continuous closure of the bleach plant is required, a filtrate storage tank with a capacity corresponding to that provided by the pulp storage tank would be needed.

Good control of washer filtrate tanks is also important where high degrees of filtrate recovery are desired. Tanks must be of adequate volume to allow proper level control and to contain the filtrates in the event of upsets. Piping and valves must be sized properly, and flow and level controls must be tuned to minimize tank overflows. Careful consideration of the filtrate flow control scheme is important to ensure that filtrate recovery is achieved without jeopardizing washing and filtrate management in the fiberline.

3.9.7 *Recovery System Capacity*

Process closure at kraft mills is likely to increase amounts of water and solids that must be processed in the recovery cycle, and to decrease the heating value of the fired black liquor solids. Most mills are operated at the limit of their recovery system capacity, typically controlled by the recovery furnace, and any increase above this level due to process closure will require additional capacity or a reduction in production rate. Extending delignification generally increases both the inorganic and organic solids loads to the recovery boiler. The degree of increase in inorganic load is dependent on how much additional chemical is charged and the organic loading increase is dependent on the yield (or selectivity) of the additional delignification performed. The change in heating value and the actual increase in solids depend on the net result of these factors, and on the degree to which the additional lignin solids are oxidized (through oxygen delignification) or otherwise modified (due to pulping chemistry changes or the effect of pulping additives such as anthraquinone).

To illustrate the nature and extent of such impacts, Warnqvist (1996) and Warnqvist et al. (1995) reported on Scandinavian studies in which the impact of full closed-cycle operation for softwood bleached kraft mills was assessed through computer simulation. In those studies closed-cycle operation was reported in comparison to a base mill which cooked to kappa no. 30 and oxygen delignified to kappa no. 16 before bleaching. The closed-cycle case cooked to kappa no. 20 and oxygen delignified to kappa no. 10 with recovery of bleaching filtrates. Organic solids to recovery showed an increase of 11.1% in the closed-cycle case; inorganic solids increased by 25%; recovery heat release increased by 8%; heating value decreased by 4%. These results show some highly significant penalties for closed-cycle operation such as increased recovery boiler requirements.

An estimated change in fiber yield to bleaching of close to 100 kg/ADt (10% on pulp or around 5% on wood) is implicit in these results. This would indicate the low kappa closed-cycle case study may require 8 to 10% more wood. However, mills adopting low kappa pulping typically compensate for the yield penalty by installing one or more yield-improving process changes such as changing from one- to two-stage oxygen delignification (reported to increase yield by 1.5% on pulp), modified cooking (1 to 3% on wood), better chip screening and conditioning (1 to 3% on wood), and use of AQ (up to 1% on wood). The overall fiber yield (ton of pulp per ton of wood) is an important parameter both for recovery boiler sizing and operation and for wood resource demand.

Jaegel, Gleadow, and Bruce (1999) presented another treatment of this subject based on an energy use characterization and conservation study. The study described the yield and energy implications of moving from chlorine bleaching to TCF bleaching and to future closure of the bleach plant. Mass and energy balances were developed for the mill, using mill data to reconcile the important energy related parameters. Specific (per ton) steam and power use increased by 17.2 and 5.7%, and yield decreased from 40 to 38.5% in moving from chlorine to TCF bleaching (with partial bleach filtrate recycling). The principal cause for the increase in energy use per ton was an 18.4% reduction in production rate due largely to the lower kappa pulp required for TCF bleaching. The implementation of energy-intensive pollution control technologies such as steam stripping of condensates, separate burning of non-condensible gases, extended and oxygen delignification, and increased evaporation loads due to recovery of bleaching filtrates also increased energy use. Priorities for making the mill more energy efficient are focused on increasing production rate and yield by debottlenecking the digester and bleach plant.

Part of the detrimental effects of decreasing heating value and increasing solids from closure can be offset by increasing the solids content of the fired liquor, which decreases furnace gas volumes and allows for easier handling of lower heating value liquors. Other modifications can be made to existing recovery furnaces to overcome particular bottlenecks. These may involve firing and air system upgrades, fan upgrades, soot blower upgrades, and installation of additional heat exchange area (installation of screen tubes, replacement of economizer sections). Similarly, additional evaporation capacity might be realized by, for example, adding additional bodies to an existing evaporator set. If furnace capacity is limited by frequent plugging of the flue gas passages with condensed fume particles, control of chloride and potassium levels in the liquor cycle can increase the temperature at which the dust becomes sticky, allowing higher temperatures in the generating section before the onset of plugging. It should be noted that the costs for any of these modifications are not trivial.

3.10 External Treatment Technologies

Conceptually, the collection, concentration, and combustion of bleach effluent in a separate dedicated system is appealing. The existing chemical recovery processes are left undisturbed and this type of installation could be applied equally well in new or existing mills. The organic material that would otherwise go as wastewater to treatment would be eliminated through complete oxidation (to water and CO_2) in a combustion device designed for the purpose.

These “concentrate and burn” schemes have the added advantage that they would remove from the kraft recovery process not only chloride ions, but also potentially troublesome elements such as potassium, silicon, aluminum, manganese, calcium, and magnesium. These ions would be purged, primarily as inorganic salts, as part of the ash from the combustion device.

In spite of their appeal, such external treatment schemes are not commonly used. Their principal disadvantages are the added capital cost of the separate bleach plant filtrate processing system and the energy required to concentrate and combust the dissolved solids. An additional cost may be incurred for handling and disposing of the ash generated by the combustion device.

One proposed scheme (Myréen 1993) involves recovery of alkaline bleaching filtrates via the fiberline combined with external treatment of the acidic filtrates. Acidic filtrates are evaporated in a low temperature evaporator of the type used to desalinate seawater. The system uses vapor recompression to supply the heat, and the heat transfer elements are made of inexpensive plastic. A pilot unit with capacity of 2 m^3/hour was tested at a bleached kraft mill in Kuusaniemi, Finland. Results over more than one year indicate that the distillate is effectively free of chloride and non-volatile organics. Power consumption was estimated to be 10 kWh per m^3 of distillate produced.

Fouling of the unit with fibers was the only significant problem reported. A filter installed on the feed stream alleviated the problem.

The concentrate would be combusted in a separate incinerator specifically designed for the purpose. It would consist of a drum dryer and rotary kiln using sand to convey the dissolved solids. HCl gas would first be evolved by addition of sulfuric acid in the steam atmosphere of the dryer. The dechlorinated residue would become fixed to the sand, which passes through the kiln in which the organics are combusted.

3.10.1 *Concentration of Alkaline Filtrates*

For kraft mills, alkaline bleach filtrates are almost completely compatible with the kraft mill recovery cycle and there is little reason why these cannot be burned in the recovery boiler provided the boiler has sufficient capacity. The alkaline filtrate is, however, very dilute, even compared to weak black liquor, and if taken directly to the existing evaporator systems (i.e., not used as wash water in brownstock) it would increase the load on the evaporators significantly. Consequently, various technologies have been assessed to concentrate alkaline filtrates.

Ultrafiltration

One method that has been used to concentrate alkaline filtrate is ultrafiltration. In ultrafiltration systems, membrane filters are used to separate organics from the substrate. The concentrated organics can then be taken to the recovery cycle and the recovered permeate can be re-used as wash water in the bleach plant. The degree to which the organics partition into the concentrate depends upon the membrane type, operating pressure, and other variables.

As with any membrane filtration system, throughput is limited by the maximum flux rate of the membrane. In a kraft mill, treatment of all the alkaline filtrate would generally require many parallel membrane chambers. Commercial ultrafiltration plants treating bleach plant extraction stage filtrates have been operated at the Taio Paper Iyomishima and Nippon Paper Industries Iwankuni mills in Japan, and at the Modo Husum mill in Sweden. COD partitioning into the concentrate streams ranged from 40 to 82% (NCASI 1998).

Cooling towers for concentrating EO filtrate

A novel approach to the concentration of bleach plant effluents is to use evaporative cooling in cooling towers to remove water from the effluent. This method has been tried by SAPPI at its Ngodwana mill in South Africa with some success. The alkaline effluent did not exhibit any scaling or corrosion tendencies in the cooling tower system. The high pH of the alkaline effluent inhibited biological fouling activity. The energy for evaporation comes from the process heat rejected to the cooling stream (which is waste heat) (Böhmer 1992). Use of this method may require some consideration of the volatile organic compound (VOC) emissions from the cooling towers.

3.10.2 *Treatment of Acid Filtrate*

Acid filtrates present more potential problems when returned to the kraft recovery cycle because they contain significant quantities of acid-soluble, alkaline-insoluble material such as calcium and pitch which could precipitate as scale in the alkaline environment of the recovery cycle processes. In addition, acidic filtrates contain potassium and, in the case of ECF mills, chloride which can accumulate in the liquor systems and cause recovery boiler operational problems. Therefore, separate concentration and combustion of the acidic filtrate may be more desirable than for the alkaline filtrate. However, volumes of acid filtrate are typically greater than those of alkaline filtrates by a factor of two or more, generally resulting in higher treatment costs.

Several types of concentration schemes have been proposed for this purpose, including freeze crystallization, low temperature evaporation, and several propriety systems.

Freeze crystallization

Freeze crystallization is an adaptation of a technique used for concentrating fruit juice. The basic theory is that freezing technology is more efficient than evaporation technology because the latent heat for the solid-liquid phase transition (latent heat of fusion) is significantly less than that for the liquid-vapor phase transition (latent heat of vaporization).

The process was initially marketed by HPD (now part of U.S. Filter Corporation) for bleach effluent applications. An initial installation for Louisiana-Pacific's Chetwynd closed-cycle CTMP mill in British Columbia was unsuccessful, however, as severe problems with crystal growth were encountered. The process was decommissioned and a vapor-recompression evaporator system was installed to replace it. HPD is no longer marketing freeze crystallization for pulp mill installations.

Low temperature evaporation

Several systems are available for concentrating bleaching effluents without using a high energy steam source. Low temperature evaporators are finding application for recycling filtrates in TMP, paper, and board mills striving for zero effluent. Examples include Ahlstrom's waste heat powered ZEDIVAP installation at Enso-Gutseit, Kotka Mills, and the Hadwaco mechanical vapor recompression polymeric film evaporators employed for water desalination and effluent evaporation at the Saudi Arabian Paper Mill recycled liner plant in Dammam, Saudi Arabia. Conventional MVR evaporators supplied by Resource Conservation Corporation are used at the zero discharge CTMP mills in Meadow Lake, Saskatchewan, (Millar Western) and in Myrtleford, Australia (Australian Forest Industries).

Use of evaporators such as these has been proposed for recycle of bleaching effluent. They are particularly suitable for low solids content (0.5 to 2%) feed. Because the boiling point rise is low, blowers may be used for pressurizing the MVR units, or additional evaporation may be attached to the existing multiple evaporation set without compromising efficiency, and in effect using low grade waste heat.

A pilot low temperature evaporation plant (ZEDIVAP) has been installed at the Varkaus Pulp Mill in Finland. It is used to concentrate debarking effluent from a bark press. There are no reports of any bleached kraft mills pursuing closed-cycle operation that have installed low temperature evaporation for bleach effluent concentration. Use of low temperature evaporation (either direct or with mechanical vapor recompression) may be useful to augment spill recovery capacity in the evaporator area, should evaporator capacity limit filtrate recovery.

3.10.3 ***Treatment of Combined Acid and Alkaline Filtrates***

SAPPI Bleach Chemicals Recovery Process (BCRP)

The SAPPI Bleach Chemicals Recovery Process (BCRP) (Böhmer et al. 1991; Böhmer and Davies 1993), developed for installation at their Ngodwana, Republic of South Africa mill, takes the "concentrate and burn" option a step further. This mill does not have a surface water discharge, but rather disposes of its effluent by irrigation. Sodium and chloride in the effluent lower the quality of the soil over time. Conceptually, the BCRP process offers the ability to recover bleach plant chemicals. Although SAPPI found that this return was not large enough to justify the project in its own right, it did provide a better return than that for traditional effluent treatment technologies. The process design incorporates the following steps:

- concentrating the alkaline filtrate
- neutralizing the acidic filtrate with magnesium oxide
- concentrating the mixed filtrates in a 12-effect evaporator
- separating NaCl crystals and $CaSO_4$ solids from the concentrated $MgCl_2$ brine in an evaporative crystallizer
- incinerating the brine in a spray roaster
- scrubbing the roaster flue gas to recover HCl, which is used in chlorine dioxide manufacture
- leaching the ash from the roaster to recover magnesium oxide, which is reused to neutralize the acidic filtrate.

Initial design of the processes was undertaken and construction initiated at the Ngodwana mill in South Africa. Construction was abandoned when an alternative means to lower chloride content of irrigated effluent, the use of ozone in place of chlorine in the bleach plant, appeared promising. SAPPI subsequently installed ozone-based ECF bleaching at Ngodwana.

The SAPPI process relies on neutralization of acidic chlorine compounds in bleach effluent with magnesium. It would not appear that the process can be applied to ECF mills because the amounts of acidic chlorine compounds in ECF bleach plant acidic filtrates do not appear to be sufficient for the magnesium neutralization and recovery steps to work efficiently.

3.10.4 *Other Proposed Treatments*

Wet-air oxidation/supercritical water oxidation

Wet-air oxidation and supercritical water oxidation are technologies based on the principle of using unique combinations of temperature, pressure, flow and exposure to gaseous oxygen (or air) in a reactor to decompose contaminants in liquid form or as a slurry.

Wet-air oxidation has been commercially applied to paper machine sludge and soda pulping spent cooking liquors. However, its use is extremely limited in the industry and it has never been used to treat bleach plant effluents. Supercritical water oxidation is still under development and has not been proven in any commercial application.

Wet-air oxidation

In the wet-air oxidation process, liquids are pumped to reactor pressure by high pressure pumps, mixed with compressed air, passed through heat exchangers, and brought to oxidation temperature. The oxidation is exothermal and destroys complex structures or converts them to biodegradable forms. Depending upon the degree of oxidation required and the constituents of the waste stream, oxidation temperatures range from about 300 to 600°F and pressures range from 300 to 3000 psig. This process has been applied to a number of different inorganic and organic waste streams, including pulping liquors, paper mill sludge, and biological sludge. The oxidation products are carbon dioxide, water, and residual low molecular weight organic compounds such as acetic and formic acid. Generally, inorganic compounds are oxidized and precipitated out of solution as metal oxides and carbonates. The amount of ash produced is dependent on the oxidation temperature and the amount and type of inorganic compounds present in the original waste (Pradt 1972; Kubes, Lunn, and Keskin 1994). Wet-air oxidation is used commercially to oxidize paper mill sludge (Gosling, Lamparter, and Barna 1981; Ichinose 1983). It has also been used to treat spent pulping liquor at two pulp mills using the soda pulping process. At least one of these two mills has since been shut down.

Supercritical water oxidation

In the supercritical water oxidation process, organic materials in a mixture of water and oxygen are oxidized at temperatures and pressures above the critical point of water (705°F, 3190 psig). The organic material is converted almost entirely to carbon dioxide. Most heavy metals are removed as inert oxides in the ash. Destruction efficiencies for organic wastes are comparable to those attained by incineration technology. Supercritical water oxidation has been put forward as an attractive method for destroying pulp and paper mill sludge and other dilute waste streams without the need for costly dewatering equipment. Strategies for using supercritical water oxidation to treat bleach plant effluent have been proposed (Hauptmann, Garins, and Modell 1994) in which bleach plant effluent is concentrated using membrane technology (ultrafiltration for alkaline effluent, reverse osmosis for acidic effluent), added to primary and secondary sludge, then treated in a supercritical water oxidation process. These strategies have not been tested, either in the laboratory or in mill trials.

Biological treatment

Although the published literature contains a considerable amount of information on the biological treatment of whole mill effluent containing bleach plant filtrate, there are very few reports of biologically treating segregated bleach plant filtrates. Those reports that have been published on the biological treatment of segregated bleach plant filtrates concentrate on the use of anaerobic treatment to remove chlorinated organic compounds prior to aerobic treatment of whole mill effluent. They do not address reuse of treated filtrate in the mill.

Anaerobic treatment has been shown to be quite effective in dechlorinating compounds found in bleach plant effluents (Hakulinen and Salkinoja-Salonen 1981; Salkinoja-Salonen et al. 1983; Qiu and Ferguson 1987). The use of a high rate anaerobic reactor (Parker, Hall, and Farquahar 1991) and an anaerobic membrane bio-reactor (Onysko and Hall 1993) to remove organochlorine (measured as total AOX) from segregated kraft bleach plant effluent has also been reported. AOX removal efficiency was comparable (approximately 56%) for the two types of reactors. No other effluent characteristics were mentioned.

4.0 MILL APPLICATION OF PROCESS CLOSURE TECHNOLOGIES

A great many mills have adopted process technologies to minimize effluent loads. Here, the applications of technologies are presented in the context of individual mills. This section is organized by mill type because this primarily defines the technologies used and the degree to which effluent loads have been minimized.

4.1 Zero and Low Effluent Discharge Mechanical Pulp Mills

Compared to chemical pulp mills, mechanical pulp mills using the chemi-thermomechanical pulping (CTMP) process produce effluents with much higher levels of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) and that are much more toxic to aquatic organisms. Effluents from CTMP mills are also much higher in BOD, COD, and toxicity than effluents from mechanical pulp mills using older mechanical pulping processes such as thermomechanical pulping (TMP) and stone groundwood (SGW). There is a strong correlation between the load of pollutants in the effluent and the yield of pulp from wood because, unlike chemical pulping, mechanical pulping has no chemical recovery process and therefore any material dissolved out of the wood during the processing of mechanical pulp probably ends up in the effluent. If the pulp is brightened, the additional pollution load from the chemical brightening operation is roughly related to the amount of brightening chemicals used. The BOD and COD discharge ranges from various mechanical pulping processes are shown in Figure 4.1.

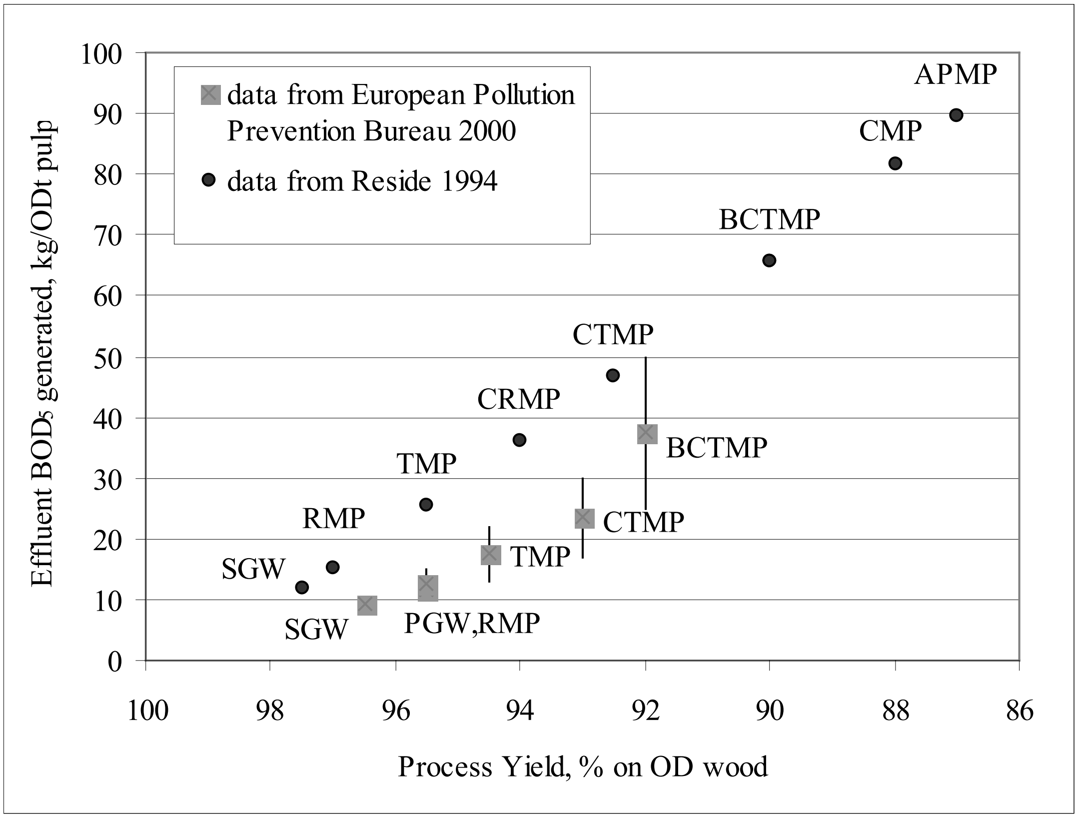


Figure 4.1 Wastewater BOD_5 Generation in Mechanical Pulping Processes (data are from European IPPC Bureau 2000 and Reside 1994; bars represent data ranges)

Most mechanical pulp mills employ primary and secondary biological effluent treatment to reduce the impact of their discharges on receiving waters. This treatment would normally include sedimentation to remove suspended solids followed by aerobic or anaerobic/aerobic biological treatment. Effluent treatment of this nature usually removes in excess of 95% of the BOD and produces a non-toxic effluent. The characteristics of the treated effluent will generally satisfy the regulatory requirements of most jurisdictions.

However, in recent years a number of new mechanical pulp mills have been built in areas where water supplies are limited or where receiving waters are not suitable for the introduction of treated effluents. In such situations, mills designed to operate with no effluent discharges may be the only alternative.

To achieve zero discharge status, contaminants must be removed from the effluent, producing clean water suitable for reuse in the process. Processes with potential applications include various concentration and separation processes such as freeze crystallization, evaporation, ultrafiltration, flotation, distillation, and reverse osmosis to separate contaminants from the water. These are commercial technologies, but their application to effluents from mechanical pulp mills was relatively unproven until the 1990s.

To date, two basic approaches have been tried to achieve zero discharge. In one approach, steam-driven evaporation is used to concentrate contaminants which are then incinerated. The other approach uses freeze crystallization as the primary technology, followed by evaporation. The processes are described in more detail herein. Currently, all zero discharge mills utilize evaporation as the primary separation method.

Two zero effluent bleached chemi-refiner mechanical pulp (BCTMP) mills started up in Canada in the early 1990s: Louisiana-Pacific Canada Ltd. (recently purchased by Tembec Ltd.), Chetwynd, British Columbia (June 1991); and Millar Western Pulp Ltd., Meadow Lake, Saskatchewan (February 1992). There are a number of other mechanical pulp mills that are using or have used evaporation technology to reduce or eliminate effluents, including AFI in Myrtleford, Australia; the StoraEnso CTMP mill at Fors, Sweden; Inpacel, at Arapoti, Brazil (operating as a TMP mill); and StoraEnso at Kotka, Finland (TMP). The Chetwynd mill was idled in April 2001 but its new owner plans to restart it in early 2003. AFI Myrtleford, Australia, was shut down in March 1999, and the Inpacel mill shut down its evaporator and smelter in April 1998.

4.1.1 *Millar Western Pulp (Meadow Lake) Ltd. – Meadow Lake, Saskatchewan, Canada*

The Millar Western Pulp (Meadow Lake) Ltd. mill has been the most successful zero effluent discharge market pulp mill operation to date. It is a totally chlorine-free, alkaline peroxide pulp/bleached chemi-thermomechanical pulp (APP/BCTMP) mill, with a current production capacity of 300,000 metric tons per year of market pulp made from 100% aspen. Pulp produced per mass of wood consumed by this high-yield mill ranges from 85 to 95%.

A groundbreaking wastewater treatment and recycling system implemented by Millar Western at the mill allows the manufacture of pulp with no discharge of liquid effluent, eliminating water pollution concerns for the mill.

Millar Western started construction of the mill in Meadow Lake in 1990, and began full operation in 1992. Despite the challenges associated with operating a pioneering effluent recycling system, the mill was producing at its original design capacity of 240,000 air-dried metric tons (ADt) per year within three months, the most rapid startup of any pulp mill built to that date (Millar Western 2003).

The original design of the project called for freshwater to flow to the pulp mill from a nearby lake, and for effluent to be discharged to a river following advanced biological treatment. The decision to implement a zero effluent discharge process was made for several reasons, including concerns regarding the availability of sufficient fresh makeup water and suitability of the intended effluent receiving water.

A typical BCTMP mill might have a freshwater intake and effluent discharge rate of approximately 19 cubic meters of water per air-dried ton of pulp (Reside 2001). Millar Western Meadow Lake's effluent recycling system achieves a freshwater intake rate of 2.5 m^3/ADt and eliminates effluent discharge.

Makeup freshwater treatment includes clarification, filtration, reverse osmosis, and zeolite softening. Process wastewater, which carries wood waste and chemicals, is sent to a flotation clarifier, where suspended solids are removed. It is then concentrated in a three-stage mechanical vapor recompression (MVR) evaporation system and steam-driven liquor concentrator. Strong liquor is combusted in a small recovery furnace. A portion of the smelt is recycled and the remainder is stored for future use in a lined landfill. Ninety percent of the distillate is reused directly in the pulp mill as freshwater makeup, with the remainder sent to a biological treatment pond and storage reservoir until needed as process water.

Mechanical vapor recompression evaporation instead of multiple effect evaporation was selected in part because lower shell-side temperatures (5°C differential) reduce scaling tendencies. Silica-containing scales are minimized by controlling chemical additions and are removed by caustic washing. Organic acid washing is used to remove carbonate scales. To date, silicate scaling has not been an issue and the evaporators operate at 90% of design capacity (Millar Western 2003).

The mill environmental discharges are water vapor, wood waste (pin chips, knots), grit (sand), and recovery boiler smelt (85 to 90% sodium carbonate). Raw water treatment wastes from the reverse osmosis unit (concentrate) and zeolite softeners (regeneration brine) are sent to the bio-polishing pond (and thus eventually end up in the smelt from the boiler).

The mill produces approximately 20% of the smelt that would be produced by a kraft mill of the same production capacity. Alternative technologies to recausticize the smelt, such as bipolar membrane electro-hydrolysis, were investigated. However, these were determined to be not cost-effective. In 1998, the mill ran a successful autocausticizing trial using a sodium borate base (Hoddenbagh et al. 2001). Work is ongoing to implement this technology. Currently, the mill recycles approximately 30% of the smelt as green liquor to replace caustic used in the pulping process (Millar Western 2003).

Freshwater is clarified and used to generate potable water and boiler feed water and to provide makeup water (2.2 to 2.7 m^3/ADt). Water recycling averages 9 m^3/ADt of pulp produced. From 1992 to 2002 mill production increased from 485 ADt/d to 875 ADt/d. Currently, makeup water from the lake averages 2.5 m^3/ADt and effluent treatment volume varies between 8 and 10 m^3/Adt, depending upon the grade of pulp being produced.

While evaporation plus incineration appears to be the technology of choice for zero effluent mechanical pulp mills, high capital costs are a concern. A concentration and combustion system like the one at Millar Western represents 15 to 18% of total direct capital, whereas a biological treatment system designed for an effluent flow of 12 to 15 m^3/ADt and consisting of two-stage activated sludge treatment with tertiary clarification would cost 5 to 6% of total direct capital (Gerbasi et al. 1993; AMEC Forest Industry Consulting files). Operating costs are also higher (Gerbasi et al. 1993), although they are reported to be competitive with those of conventional biological treatment for similar mills (Knorr and Fromson 1993; Reid and Lozier 1996).

Both Millar Western's Whitecourt and Meadow Lake mills are among the lowest cost BCTMP mills in the industry. To further reduce operating costs, the Meadow Lake mill is currently investigating the feasibility of a co-generation facility (hog boiler and condensing turbine) to utilize the mill's waste fiber sources to replace purchased electricity and natural gas.

Through implementation of its groundbreaking wastewater system, Millar Western has been able to minimize water use, eliminate environmental concerns associated with the discharge of effluent, and maintain a highly competitive cost structure (Millar Western 2003).

4.1.2 *Tembec (formerly Louisiana-Pacific) – Chetwynd, BC, Canada*

Louisiana-Pacific constructed a new BCTMP mill in Chetwynd, British Columbia, in the early 1990s. The factors which weighed in the decision to go zero discharge at Chetwynd included: a corporate vision for efficient resource use and to meet and exceed current and future environmental regulations; concerns over regulatory delays for permitting an effluent discharge; progress in CTMP technology which made operation at low water and effluent flows possible; anticipated demographic changes; and market trends. The zero discharge technologies Louisiana-Pacific considered included freeze crystallization, evaporation, conventional water treatment, and membrane technologies (Rogers and Arac 1997; Arac 1998).

The freeze crystallization process was selected for the Chetwynd mill because of its low energy requirement relative to evaporation (the heat of fusion for water is much lower than the heat of vaporization), lower scaling tendency, reduced corrosion, lower capital outlay, lower operating costs, and lower volatile organic compound emissions (Rogers and Arac 1997; Arac 1998). The technology is based on the principle that ice crystals can be formed in a controlled manner by the partial freezing of a waste stream. These crystals can be separated, washed, and subsequently melted to form clean water. This technology was developed for the food industry to produce such products as frozen concentrated orange juice.

The freeze crystallization system included pretreatment, water treatment, and evaporation systems. Effluent was pretreated in a dissolved air flotation clarifier and stored in a 95 million gallon effluent pond which provided significant buffer capacity.

The water treatment plant was comprised of the crystallizer, ice harvester, and effluent pre-cooler. The crystallizer concentrated the effluent solids from 2 to 10%. The effluent had a 3°C freezing point depression, and a 50% ice fraction was maintained for crystal growth in the circulating crystallizer.

The ice harvester resembled an inverted clarifier, in which ice was separated by density. Ice on the top of the ice column was washed, and a screw harvester and melter (integrated into the refrigeration system) returned clean water to a storage pond. The concentrated underflow was blown down to maintain 10% solids. The 10% liquor was concentrated to 50% solids in a two effect evaporator. The thickened liquor was sold or stored for future sale or use.

The mill started up and operated the system, successfully demonstrating that contaminant-free ice crystals could be formed. However, a number of difficulties were encountered and the plant could not operate at the rate and quality required. These difficulties included poor separation of ice from the mother liquor, problems with distribution in the harvester (which impacted ice washing), changes in the effluent properties due to anaerobic activity in the effluent storage pond, inadequate pretreatment (fiber and solids removal), inability to maintain design rates in the ammonia refrigeration plant, tube side scaling and plugging of the crystallizers, and insufficient crystal size.

The mill installed four vacuum drainage table filters with wash showers (which are similar to a belt washer or paper machine fourdrinier). This improved performance but did not provide the effluent processing capacity and quality needed. At that time, Millar Western Meadow Lake was successfully operating with an evaporation system, and this was seen as a lower risk option than proceeding with freeze system modifications (Rogers and Arac 1997; Arac 1998).

In converting to an evaporation-based system, the mill sought to reuse existing equipment. The crystallizer bodies were converted into mechanical vapor recompression (MVR) evaporators. Pre- and post-evaporator treatments were improved, a process stage to deactivate scale-forming (calcium) material was added, and a recovery boiler to combust concentrate was added. The evaporation system was successfully started up and operated from 1993 to 2001.

Excellent water quality was obtained from the evaporation system, as shown in Table 4.1. The power consumption was 18 to 22 kW hr/ton of water. In 1997 the MVR evaporators had some scaling issues, and were being taken out of service for 24 hours every 60 days for pressure cleaning. The multiple effect units were operating for eight months between high pressure cleanings. The concentrators operated for two months before being washed with clarified effluent. Recovery boiler (220 ton dry solids per day Babcock and Wilcox unit) operation was not limited by capacity or cleaning requirements.

In 1993 it was reported that Louisiana-Pacific had spent more than CAN$70 million on zero discharge technology.

Table 4.1 Water Quality at Chetwynd BCTMP Mill

	Pulp Mill	Freeze Crystallization		MVR	Mill Water Clarifier	
Parameter	Effluent	Harvester	Belt Filter	Evaporation	In	Out
Turbidity, FTU		200	40	0	125	20
Color, Pt-Co		150	250	0	250	30
Conductivity, µS/cm	12000-18000	500	800	20	700	800
Total solids, %	2-3			0		
Dissolved solids, %				0	0.1	
Suspended solids, %	5000-10000			0	80	
pH				7.6	7.5	6.5
Iron, mg/L				0.04	0.5	0.5

SOURCE: Arac 1998

Chetwynd Pulp Mill was operated by Millar Western from 1999 to 2001. The mill closed indefinitely in April 2001. In October 2002 the mill was purchased by Tembec, Ltd. which plans to restart the mill by January 2003 (Anon. 2002).

4.1.3 *Stora Enso – Fors, Sweden*

Stora Enso has a CTMP and paperboard mill at Fors in central Sweden. Production capacity is 150,000 tons per year of CTMP and 325,000 tons per year of paperboard. All CTMP is used in board manufacture, with the balance made up of purchased pulp. Paperboard has been produced since 1952.

In 1996 a CTMP plant with evaporation was added. The primary process effluent from the CTMP mill is evaporated in a seven effect Zedivap (Andritz-Ahstrom) evaporator. The evaporator has a capacity of 120 tons per hour. Effluent is fed at 0.9% total solids and discharged at 30 to 50% total solids. The condensates are reused for pulp washing in the CTMP process. The concentrate is shipped to a nearby kraft mill for recovery. The heating steam supply for the evaporator is regenerated from CTMP refiner waste heat.

Board machine wastewater is sent to effluent treatment consisting of primary (sedimentation), secondary (biological), and tertiary (chemical precipitation and filtration) stages before discharge. Wastewater flow in 2000 was 14 m^3/t (freshwater was 18.9 m^3/t).

Sludge is used as fuel, groundcover for landfills, or raw material for the production of absorbents (for cat litter and oil spills).

4.1.4 *Stora Enso Laminating Paper Oyj – Kotka Mill, Finland*

The five-stage multiple effect black liquor evaporator was expanded in 1994 with three stages of low temperature evaporation (Andritz Zedivap) and a condenser for mill-scale process water evaporation testing. The evaporator plant was installed as part of a wider initiative at the mill, which resulted in a 23% decrease in effluent discharge per ton of product between 1995 and 2001 (Stora Enso 2001; Andritz Ahlstrom 2001). Several expansion phases where carried out, including additions of heat transfer surface and a cooling tower to reach a sustained capacity of 1700 m^3/day. Initially, the new evaporator was used to concentrate TMP effluent to 5% solids (corresponding to 5 to 6 tons of COD per day). The concentrate was blended into the weak black liquor for combustion in the recovery furnace. Gradually decreasing capacity due to precipitation of calcium compounds (oxalate, silicate) on heat transfer surfaces required manual cleaning once a year. Since 2002 the three evaporator stages have been used for segregation of foul condensates from the kraft mill cooking plant in order to reduce toxic substances to the wastewater treatment plant, which includes anaerobic and activated sludge processes (Suur-Hamari 2003).

4.1.5 *Stora Enso Oyj, Fine Paper – Varkaus Mill, Finland*

Debarking effluent is concentrated by evaporation and added into the black liquor. The debarking plant, operated in two shifts, consists of three wet debarking drums. The plant has been operated with a closed water loop since 1996. A mechanical vapor recompression (MVR) evaporator (Andritz Zedivap) is fed 24 hr/day with 1000 m^3/d filtrate from the bark presses. All the condensate is fed into the debarking drums and is blended into the weak black liquor at 20% solids. The combusted COD varies between about 10 (summer) and 20 (winter) tons/day. The total energy consumption is 17 kwhr/m^3 of water evaporated. Scaling is controlled by adding alkali to the feed and manually cleaning the heat transfer surfaces once a year (Suur-Hamari 2003).

4.1.6 *Australian Forest Industries (formerly a division of Bowater Tissue Ltd.) – Myrtleford, Australia*

Australian Forest Industries operated a CTMP mill in Myrtleford, Australia. Both hardwood and softwood effluents were sent to an evaporator followed by a concentrator. The system capacity was 1.2 million liters per day. Effluent was concentrated from about 2% solids to 35% solids in the evaporator. The concentrator further reduced effluent volume, producing a 70% solids product which was stored in a secure landfill. One of the major reasons for installing the plant was to reduce the effluent load in an area of Australia which has saline soil conditions. The Murray River is used as a major irrigation source down stream of the mill, and any discharge of poor quality water aggravates the very bad saline conditions experienced by farmers in Australia.

More than 90% of the effluent was recovered as distilled water for reuse in the pulping process, primarily for pulp washing (Fosberg, Lloyd, and Kelland 1993). The pulp mill and effluent plant were shut down in March 1999. The company is considering using the effluent plant at another facility as an alternative to using the effluent for silvicultural irrigation.

4.1.7 *Inpacel Brasil (now part of International Paper Company)*

Inpacel operates a mechanical pulp mill and coated paper mill producing light and medium weight coated papers. Paper production started in 1918, and a new coated paper machine and TMP plant started producing base papers in 1992 and coated papers in 1994. The mechanical pulp mill, although configured to make CTMP, operates as a TMP mill with a capacity of 420 tons/day. The mill utilized an evaporate and burn system for the TMP effluent, including a six-effect falling film evaporator with a capacity of 180 tons per hour, for concentration to 40% solids. Concentrated effluent was burned in a smelter, and the smelt was causticized with lime (University of Toronto 1997). The evaporator and smelter were shut down in April 1998. Currently, TMP effluent is treated using primary clarifiers and a small aerated basin, followed by activated sludge treatment and a polishing lagoon.

4.1.8 *Norske Skog Paper Mills (Australia) Ltd. – Albury, Australia*

Norske Skog Paper Mills (Australia), formerly Australia Newsprint Mills (ANM), operates an integrated pulp and paper mill at Albury, Australia. Production is 210,000 tons per year of newsprint from TMP, recycled fiber, and 20,000 tons of recycled fiber pulp.

The Murray River provides the mill's water supply and formerly received its treated effluent. Cooling water (about 7 m^3/t) is reused several times and discharged back to the river. The Murray

River is Australia's most significant river and flows through three states (New South Wales, Victoria, and South Australia). Its water is used for agricultural irrigation and a variety of other purposes. In the early 1990s the state governments adopted a policy of phasing out all direct river discharges. The mill in Albury and three municipal sewage plants were the only remaining discharges on the river. In the early 1990s the mill successfully applied for permits to expand production by adding a recycled fiber plant. The mill investigated and implemented both process improvements to increase closure and irrigation of mill process effluent. Process changes included installing two dissolved air flotation clarifiers to close the white water circuit in the recycled pulp facility and paper machines, general water reduction and bleaching changes to reduce chelant and other chemical loads, and widespread reuse of treated wastewater.

Treatment of process effluent from the mill (about 12 m^3/ton) includes primary (clarification) secondary (biological), and tertiary (flocculation/filtration) stages. The effluent is then irrigated on a 350 hectare *Pinus radiata* plantation, established in 1993, adjacent to the mill. Sixty-six hectares of center pivot irrigated pasture have also been established. With evaporation (1487 mm/year) more than twice the annual rainfall (694 mm/year, mostly in the fall and winter), woodlots can use irrigated water for six to seven months of the year. The installation includes a 2200 million liter storage pond to store effluent and runoff during winter months, and over 70 km of irrigation piping and 1500 km of drip tube. There is a provision in the company's EPA license for treated effluent to be discharged to the river in wet summers when land based reuse would not be practical or environmentally desirable. Since 1996 (the scheme's commencement date) less than 8% of the mill's treated effluent has been discharged to the river (Environment Australia 2001; Coghill, Dahl, and Thurley 1995; Thurley, Niemczyk, and Turner 1997; NSWEPA 1995; Dahl 2003).

4.2 Low Effluent Sulfite Mills

Chemical pulping processes (kraft, soda, and sulfite) are inherently more complicated than mechanical pulping processes, as more wood and chemicals are needed per unit of product and chemical recovery systems are closely integrated with fiberline operations. This results in an increased input of trace impurities from wood and makeup chemicals, increased concentrations of such impurities due to high rates of recirculation, and increased potential for operational problems due to the wide range of temperatures, concentrations, and pHs encountered in the various unit operations. As a consequence, chemical pulp mills have greater challenges in process closure.

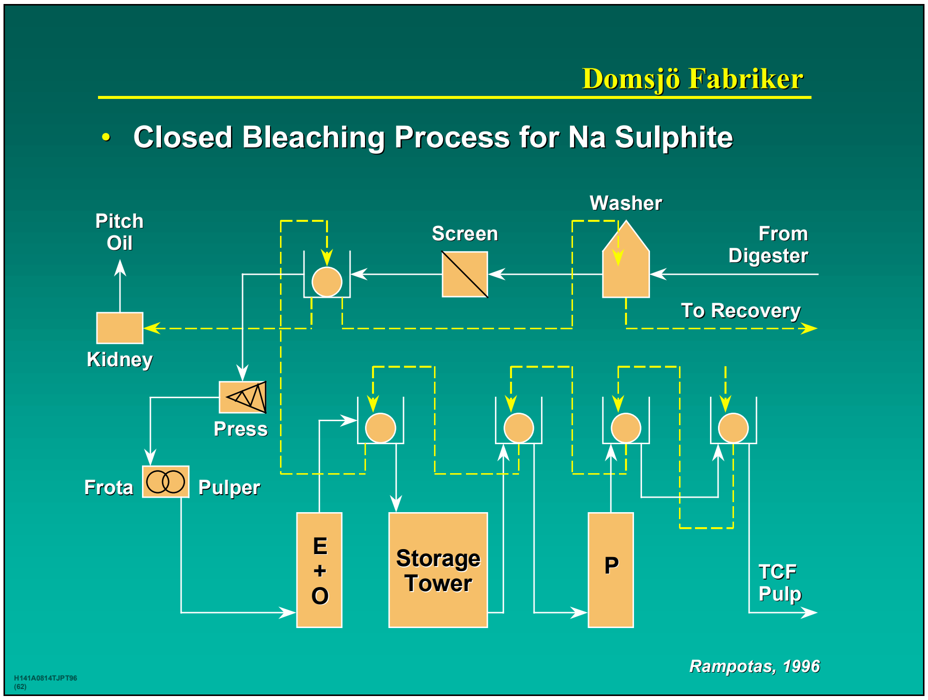
Three sulfite mills have been leaders in adopting closed-cycle technology.

4.2.1 *Domsjö Fabriker AB - Örnsköldsvik Sweden*

Domsjö has operated closed-loop TCF bleaching (EO-P) at its sulfite mill in Örnsköldsvik since 1985. The mill was previously owned by MoDo. Wood is pulped using an acid sulfite process followed by screening and washing. At first, the mill experienced pitch deposition problems when recycling alkaline bleach plant filtrate to the acidic washing system. This was solved initially through use of ultrafiltration and now more cost-effectively through chemical flocculation and removal in a dissolved air flotation unit.

In an acid sulfite (redstock) system, metal and scale forming materials (such as calcium) are dissolved in the liquor and washed from the pulp prior to bleaching. However, pitch and oily extractive materials are largely insoluble at low pH, carrying through to the bleach plant where they become dissolved in the alkaline bleaching filtrates. The primary limitation to recycle of bleaching filtrates is the deposition of this material when it is returned to the redstock system. In effect this is the converse of kraft pulping with bleach filtrate recycle, in which the extractives generally remain dissolved in the alkaline black liquor and the calcium and divalent metals contained in the acidic bleach filtrates form insoluble deposits when returned to the brownstock system.

MoDo and Kemira developed a combination of pulp and filtrate treatment techniques to act as a "kidney" for removal of the extractive material. A press is used as the final brownstock wash stage, which facilitates removal of finely suspended globular pitch material, followed by mechanical kneading and mixing with a frota-pulper. The filtrate is treated in a dissolved air flotation (DAF) unit, to which polyethylene oxide (PEO) is added as a flocculent. The PEO binds to pitch material to form a sludge, which is separated and burned. More than 90% of the extractives are removed in this manner. This PEO-assisted separation was developed and marketed by Kemira as the NetFloc process (Rampotas, Terelius, and Jansson 1996). The Domsjö mill's recycle scheme is depicted in Figure 4.2.


Domsjö Fabriker

- **Closed Bleaching Process for Na Sulphite**

Rampotas, 1996

Figure 4.2 Schematic of Closed Bleaching Process at Domsjö Fabriker Sulfite Mill (Rampotas, Terelius, and Jansson 1996)

A small aerobic/anaerobic treatment system is used to treat the evaporator condensates prior to discharge. In 1996 an activated sludge process was added, increasing BOD_7 removal to 99.7% and reducing suspended solids discharge by 90% (MoDo 1997). Over the last 20 years the mill has gone from "causing serious harm to the environment" to receiving awards from local authorities for its environmental achievements (MoDo 1998).

4.2.2 *Stora Enso – Nymölla, Sweden*

Stora Enso's Nymölla mill produces paper grade pulp and uncoated fine papers. The pulp production capacity is 325,000 ton per year (typical production is 165,000 ton/year of softwood from pine and spruce and 135,000 ton/year hardwood from mainly beech).

A magnesium bisulfite (magnefite) process is used for pulping. Liquor is recovered in the magnesium-based recovery process. Pulping is followed by delignification and bleaching using oxygen, peroxide, and sodium hydroxide. Because they cause plugging in the furnace, sodium and potassium cannot be recovered into the magnesium-based pulping liquor recovery.

In order to reduce effluent loads, particularly COD, and to aid in qualifying for the “White Swan” eco label, Nymölla installed an ultrafiltration (UF) plant for treating oxygen stage filtrates. The UF plant removes 50% of the COD into a small (2% of original flow), concentrated stream. The concentrate is combusted in the bark boiler. UF is effective at removing high molecular weight compounds that tend to be resistant to biodegradation, so the combination of UF and activated sludge treatment has resulted in efficient COD removal.

The UF plant started up in February 1995. At the time of installation, Nymölla had the world’s largest tubular membrane UF plant, representing more than 50% of total membrane area installed in Sweden.

Key operating and performance data are shown in Tables 4.2, 4.3, and 4.4. These tables show, respectively, wastewater stream characteristics, UF plant operating variables, and UF concentration factors (Wickstrom 1997). Table 4.2 shows COD loads into and out of biological treatment. The impact of the UF plant in removing material that is difficult to degrade biologically is apparent.

Table 4.2 Wastewater COD Loads for the Stora Enso Nymölla Mill

	Effluent load, kg COD/ton pulp	
Ultrafiltration plant running--->	Yes	No
Woodroom	15 - 20	15 - 20
Oxygen stages	40 - 45	80 - 85
Chelant stages	10	10
Peroxide stage	35	35
Evaporation, digesters, boilers	65 - 70	65 - 70
Paper mill	10	10
Biological plant feed	175 - 190	215 - 230
Biological plant reduction	125	130
Biological plant effluent	50 - 60	85 - 95

SOURCE: Wickstrom 1997

The membranes initially used (in pilot work) had a molecular cut-off of 4000 daltons; however, the hardwood line required development of a special membrane to limit fouling. Operating data are shown in Table 4.3.

The UF plant enabled the reduction of COD discharge from 45,000 ton/year to less than 15,000 ton/year. COD levels in 2000 were 40 kg per ton of pulp (12,900 ton COD per year); the permit limit is 20% above this. Wastewater flow is 69 m^3/ton of pulp.

The ultrafiltration system operation was reported to have increased production costs by 2%.

Table 4.3 Stora Enso Nymölla Mill Ultrafiltration Plant Operating Characteristics

Parameter	Production line Softwood	Hardwood
Membrane type	ES404	EM004
Feed flow, m^3/hr	220	155
Feed COD, g/L	11	12
Concentrate flow, m^3/hr	4,4	2,3
Concentrate DS, %	12	15
Stacks in service	5	5
Modules used / stack	152	72
Volume reduction factor	50	67
Temperature, °C	80	68
Module inlet pressure, kPa	690	880
Estimated power consumption, kW	280	600
Flux, L/(m^2*hr)	109	163
Membrane life time, months	>15	>15
Time between washing, hr	48	72

SOURCE: Wickstrom 1997

Table 4.4 Stora Enso Nymölla Mill Ultrafiltration Mass Flow Ratios

Parameter	Concentrate/Feed * 100 Softwood	Hardwood
Flow	2.0	1.5
COD	49 - 51	45 - 48
BOD	<15	<15
Sodium	<7	<5
Magnesium	~50	~50
Nitrogen compounds	~65	~65
Phosphorous compounds	~65	~65
Toxic compounds (Microtox)	>50	>50

SOURCE: Wickstrom 1997

4.2.3 *Lenzing AG – Austria*

Lenzing AB produces 135,000 OD tons/year of dissolving pulp from beech using a magnesium bisulfite cook and a TCF ((EOP)ZP) bleaching sequence. The pulp is converted to viscose fiber on site. Lenzing has been a pioneer in the application of oxygen and ozone in bleaching and the implementation of effluent-free bleaching. Its principal motivation in working towards process closure was to minimize the impact on the small receiving stream. The river is situated in one of Austria’s famous recreation areas (Krotscheck et al. 1995).

A chemical recovery system was installed in 1963 as a first step in closing up the mill. This was followed in 1973 with a spent liquor collection system and in 1983 with a extraction plant for removing acetic acid and furfural from evaporator condensates, enabling condensate reuse in the chemical recovery process for raw acid production. The acetic acid and furfural are purified and sold as commercial by-products of the process (Krotscheck et al. 1995).

In 1979 the bleaching sequence was converted from CEHH to EPHP, and then in 1984 to (EOP)HP. Medium consistency ozone stages were added to the small and large bleaching lines in 1990 and 1992, respectively. Meanwhile, in 1990, the first and most significant step was taken towards making the bleach plant effluent free with the installation of a separate concentrate and burn process for extraction stage filtrate. The EOP filtrate, containing about 2% dry solids, is concentrated to 52% dry solids in a multiple effect evaporation plant. The concentrated liquor is burned in a specially designed soda recovery furnace, recovering sodium carbonate as a smelt. The sodium carbonate is used for effluent neutralization, with consideration given to installing a causticizing plant and converting the sodium carbonate to NaOH using purchased lime. The by-product calcium carbonate would be used to neutralize effluent (Krotscheck et al. 1995).

A new sulfite recovery furnace was installed in 1992, and with it a magnesium sulfite decomposition plant. This plant thermally decomposes magnesium monosulfite ($MgSO_3$) to SO_2 at high concentration and MgO. The source of magnesium monosulfite is a side stream of red liquor from the recovery cycle. Generating SO_2 at a concentration high enough to bolster the free SO_2 of the sulfite cooking liquor reduced the amount of SO_2 required from sulfur burning and also considerably reduced the quantity of magnesium and sulfur (as $MgSO_3$) discharged with the recovery system effluent, a purge that was previously necessary to maintain the sulfur balance in the mill (Krotscheck et al. 1995).

Mill trials have been carried out in which the filtrates from the Z and P stages were used on the red liquor washers, confirming the feasibility of eliminating effluent from the bleach plant. The trials also confirmed previous laboratory studies that indicated higher bleaching chemical consumption due to COD carryover into the bleach plant. Several modifications to adjacent processes are required before closed-cycle operation of the bleach plant can be implemented on a permanent basis (Krotscheck et al. 1995).

Mill and laboratory trials in which filtrates from the P and Z stages are directly countercurrently recycled, with part of the Z stage being evaporated, were reported by Krotscheck et al. (1995). In the laboratory studies the dissolved organic material (DOM) originating in each bleaching stage was found to consume varying amounts of ozone, as shown in Table 4.5.

Table 4.5 Ozone Consumption for Filtrates of Different Origins

Filtrate origin	Specific O_3 consumption, kg O_3/kg DOC
EOP stage	0.33
Z stage	0.08
P stage	0.20

SOURCE: Krotscheck et al. 1995

The impact on ozone consumption during the trial is shown in Table 4.6. Carryover and carryback estimates are from simulations, and specific ozone consumptions are according to laboratory experiments (Krotscheck et al. 1995).

Table 4.6 Lenzing Countercurrent Washing Trial Results

Parameter	Unit	Value
Total O_3 consumption	kg/t	1.30
O_3 consumption by EOP carryover (EOP carryover: 0.30 kg DOC/t)	kg/t	0.10
O_3 consumption by Z carryback (Z carry-back: 1.90 kg DOC/t)	kg/t	0.15
O_3 consumption by P carryback (P carry-back: 0.70 kg DOC/t)	kg/t	0.14
O_3 left for pulp	kg/t	0.91
Specific delignification	1/(kg O_3/t)	1.45
Kappa before Z (measured)	-	2.09
Kappa after Z (calculated)	-	0.77
Kappa after Z (measured)	-	0.70

SOURCE: Krotscheck et al. 1995

Based on the study results, filtrate recycle was calculated to increase bleaching costs for Lenzing (in the early 1990s) by US$1.48/ton. The study authors' conclusions included the following comment: "It is apparent that bleach plant closure means additional chemical consumption. Before effluents are completely eliminated there is need for a thorough evaluation of the issue, whether the price paid for the 'benefit' of zero effluent is not too high." Attempts to contact the mill to determine the current status of the bleach plant were unsuccessful.

4.3 Low Effluent Kraft Pulp Mills

4.3.1 *Latest Generation Low Effluent Conventional Mills*

Johnson et al. (1996) discussed design and performance of the three newest kraft mills built in the Americas: Bahia Sul, Alabama Pine Pulp, and Alberta-Pacific. All three of these mills were designed for high economical and environmental performance utilizing high capacity, single line facilities employing modern technology for pulp production and effluent treatment. No recovery of bleaching wastewaters is practiced at any of these mills, yet their effluent quality is among the best in the world on a production-normalized basis.

Mill Descriptions

Bahia Sul Cellulose, S.A., has a capacity of 585,000 ADt/year of eucalyptus bleached kraft pulp. The pulp mill was commissioned in 1992 and a paper mill that produces about 230,000 ton/year of printing and writing papers started up in 1993. The mill is situated in a rural area in the state of Bahia, Brazil. The US$1.5 billion project included the mill, forestry facilities, a hospital, two schools, and two villages (Santos and Caldas 1996).

Wood is transported by truck to the mill site where is it debarked, chipped, and stored in open piles. Bark and fines are burned in a waste fuel boiler. Wood chips are screened by size and then fed into the single vessel continuous digester (MCC). Pulp is washed in an atmospheric double diffuser and parallel drum washers, followed by closed pressure screening and oxygen delignification to produce a pulp of kappa 10. Two double diffusers are used to wash the pulp after the oxygen stage. The four stage bleach plant (D(EOP)DP) utilizes upflow towers with single diffusion washers mounted on top.

The mill has spill control and recovery facilities to minimize effluent loads. Wastewater treatment facilities include condensate stripping, primary clarification, secondary treatment in an aerated stabilization basin, sludge thickening, and dewatering on belt presses.

Alabama Pine Pulp (APP) is a single-line bleached softwood kraft market pulp mill built on the site of the Perdue Hill, Alabama, pulp and paper complex which includes Alabama River Pulp, Alabama River Newsprint, and Alabama River Recycling. APP started operations in 1991 with a capacity of about 1300 ADMT/d. This facility takes advantage of shared utilities, including wastewater treatment, and an existing skilled workforce to keep its operating costs low (Johnson et al. 1996).

Screened southern pine wood chips are pulped in a two-vessel hydraulic continuous digester with EMCC capabilities. After the digester, brownstock pulp is washed in a pressure diffuser followed by closed screening and a decker. Oxygen delignification is a two-stage system followed by two pressure diffusion washers. Pulp enters the bleach plant at kappa 12.5 and is bleached in a four-stage diffusion bleach plant (D(EPO)D(D).

Wastewater from the entire Alabama River complex is treated through four primary clarifiers followed by equalization and cooling. Secondary treatment is accomplished in an oxygen activated sludge system, utilizing three enclosed aeration basins and five secondary clarifiers. Combined primary and secondary sludge is dewatered and either burned with bark in a power boiler, land spread, used as a beneficial by-product, or landfilled.

The Alberta-Pacific Forest Industries Inc. (Alberta-Pacific) mill is owned by Mitsubishi Corporation and Oji Paper Ltd. The project was initiated in 1988, but a prolonged environmental permitting process delayed the startup of the mill until September 1993. Alberta-Pacific produces bleached kraft softwood and hardwood (aspen) market pulp in a single line mill that is budgeted to produce 560,000 tons of pulp per year. The mill was designed to meet some of the strictest discharge limits in North America.

The Alberta-Pacific mill has a two-vessel hydraulic continuous digester operating with Lo-Solids technology. Spruce is cooked to kappa 23 and aspen to kappa 12. Brownstock washing includes an atmospheric diffusion washer followed by two pressure washers in parallel. The screen room is a closed design and is followed by a single vessel oxygen delignification stage and two displacement presses. The three-stage bleach plant was the first to be built exclusively for ECF operation. The sequence is the same for softwood and hardwood (WD(EPO)D). The bleach plant washers are rotary vacuum drums.

Alberta-Pacific is equipped with spill reclaim sumps and pumps to recover fiber and liquor spills, and has an extensive ongoing environmental training program to minimize wastewater loads. State-of-the-art treatment facilities include dual primary clarifiers, an equalization/cooling pond, two cooling towers, and an extended aeration activated sludge process comprised of two five-cell reactors and twin secondary clarifiers. Treated effluent passes through a foam control tower and is discharged into the Athabasca River through a submerged diffuser (Riebel 1998; White 2003). Further information is available on the internet at www.alpac.ca.

Fiberline and effluent performance data for these three modern mills are summarized in Tables 4.7 and 4.8, respectively.

Table 4.7 Fiberline Performance Data for Alabama Pine Pulp, Alberta-Pacific, and Bahia Sul Bleached Kraft Pulp Mills

Parameters	Alabama Pine Pulp	Alberta-Pacific		Bahia Sul
Wood species	so. pine	spruce	aspen	eucalypt
Digester				
Kappa number	22	23	12.7	16.5
Kappa std. deviation	1.5-2	-	0.6	1.2
Oxygen delignification				
Delignification, %	43	36	39	39
Kappa number	12.5	14.7	7.7	10
Kappa std. deviation	1-1.5	-	0.3	0.5
Washing loss, kg COD/Adt	8.5	7.5	<4.5	7.7
Bleaching				
Brightness, % ISO	90	>90	90.7	90.3
Viscosity in, dm^3/kg	770 (21[a])	-	1,025	958
Viscosity out, dm^3/kg	650 (15.5[a])	750 (20[a])	840 (25[a])	832
Viscosity loss, dm^3/kg	120 (5.5[a])	-	197	126
Final product				
Brightness, % ISO	89	90	90	89.7
Dirt, ppm	<3.0	<3.0	0.8	0.4

SOURCE: Johnson et al. 1996

[a] mill viscosity measurements in cP; viscosity as dm^3/kg is converted from cP

Table 4.8 Effluent Performance Data for Alabama Pine Pulp, Alberta-Pacific, and Bahia Sul Bleached Kraft Pulp Mills

Parameters	Alabama Pine Pulp	Alberta-Pacific	Bahia Sul
Flow, m^3/day	75,000	67,000	74,000
Primary clarifier, # x m^3	1 x 9,500	2 x 9,560	3 x 4,000
Bio-treatment process	Activated Sludge	Activated Sludge	Aerated Lagoon
Aeration basin, m^3	113,000	110,000	738,600
Secondary clarifier, # x m^3	2 x 13,000	2 x 12,720	-
Tertiary, m^3	26,000	-	-
Spill containment	to 1° clarifier	by area	by area
Emergency basin, m^3	14,000	104,000	74,000
Nutrients applied	NH_3 and H_3PO_4	NH_3 and H_3PO_4	N as urea
Cooling towers	3 cells	2 cells	-
Final effluent parameters			
BOD, kg/Adt	2.8[a]	0.25	0.3
COD, kg/Adt	2.3[a]	5.4	5.7
TSS, kg/Adt	7.9 [a]	1.8	0.3
AOX, kg/Adt	0.26[b]	0.1	0.15
Color, kg/Adt	60[a]	8.8	13.7
Temperature, °C	30[a]	30	30

SOURCE: Johnson et al. 1996

[a] combined effluent from multi-mill complex

[b] APP on ECF with ARP shut down

4.3.2 *Mills Practicing Recovery of Bleaching Filtrates – Linerboard Mills*

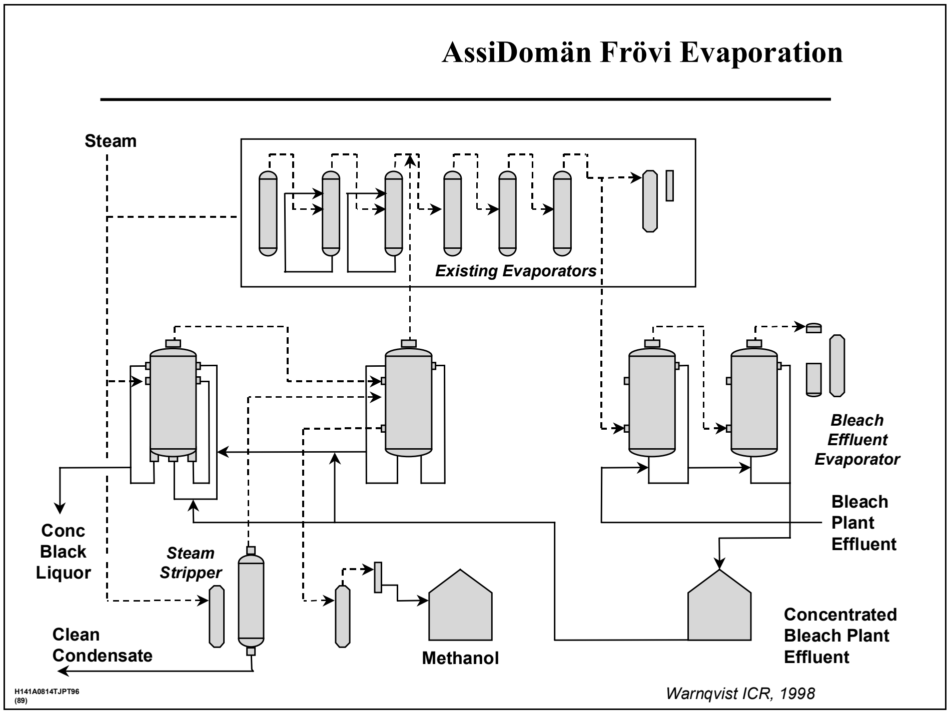
Linerboard is a multi-ply product that comprises the outer layers of corrugated boxboard. It is produced from unbleached softwood kraft pulps and from recovered fiber, primarily old corrugated containers (OCC). In applications where a bright surface for printing is desired, this may be achieved by application of opaque coatings or by making the outer ply from bleached pulp. Mills that make so-called “white-top” linerboard by the latter method usually have a small bleach plant capable of processing 20 to 40% of the unbleached pulp. The small capacity of such bleach plants relative to the total capacity of the brownstock system and chemical recovery facilities provides potentially favorable circumstances for recovering bleaching filtrates.

There are now three essentially closed-cycle bleach plants in operation in Sweden. In each of these, a small bleach plant was added to an existing brown paper and board mill in order to produce white-top liner. Alkaline filtrates from bleaching are recycled countercurrently to brownstock washing. The neutral or acidic filtrate is returned for washing brownstock on the unbleached portion of the production lines. The bleached pulp production represents only 20% of production in two of the mills, SCA Munksund and Kappa Kraftliner Piteå (formerly AssiDomän Lövholmen). In the third mill, AssiDomän Frövi, 40% of production is bleached.

AssiDomän Frövi – Sweden

AssiDomän has been a leading company in applying closed-cycle technologies. Research into the underlying process chemistry in areas such as scale formation in bleaching followed by successful and novel application of this knowledge in mills is a feature of its work.

AssiDomän Frövi is a linerboard mill which includes a zero-effluent TCF bleach plant that processes about 40% of the total pulp production to make top liner. The bleaching sequence is OO-Q1-Q2-PO where “ - ” denotes intermediate two-stage drum displacement (DD) washers. Half of the Q1 stage filtrate is fed countercurrently to the post-oxygen washer, and the other portion is separately pre-evaporated in two falling film units placed as effects seven and eight in the evaporation train, as shown in Figure 4.3. The concentrated bleaching effluent is mixed with the black liquor.



Warnqvist ICR, 1998

Figure 4.3 Integration of Bleach Effluent Evaporators into the Kraft Mill Black Liquor Evaporation Train at AssiDomän Frövi

Kappa Kraftliner (formerly AssiDomän) Piteå – Sweden

At Kappa Kraftliner Piteå, Sweden, a bleach plant for birch kraft pulp was started up in December 1995. Pulp of kappa number 17 to 19 is bleached in the TCF sequence OQ(PO) to 75 to 85% ISO brightness, depending on the pulp quality needed. Design capacity is 480 ADt/d, about 20% of total pulp production. Interstage washing is by wash presses. Even though the unbleached pulp has relatively high manganese content, it is possible to bleach to 85+% ISO brightness with good pulp strength properties. The (PO) and O filtrates are recycled and the Q stage filtrate is of sufficiently low volume (due to the wash presses) that it is completely included into the washing zone of the continuous digester of the parallel large, high kappa unbleached softwood fiber line. By these measures, no bleach plant effluent is discharged from the birch pulp mill.

Kappa Kraftliner Piteå also has the capability to produce sulfuric acid from waste sulfur emissions (Björklund, Valuer, and Lawler 1999). Increased closure of the kraft pulping process can result in an imbalance in the liquor cycle due to an increase in the S/Na ratio. A facility was installed which converts SO_2 in waste gas from the non-condensable gas (NCG) incinerator to sulfuric acid using a small contact sulfuric acid plant. This is believed to be the first application of its type in a kraft mill. The incinerator combusts strong gases from the evaporators and digester (dilute gases go to the recovery boiler). The internally produced acid is used to supply the needs of the tall oil acidulation plant, about 1 kg S/ADt pulp. This system provides control over the S/Na balance while reducing environmental emissions and makeup chemical requirements. The acid production plant experienced a period of problems with materials of construction but was recently reported to be working.

4.3.3 *Mills Practicing Recovery of Bleaching Filtrates – Bleached Papergrade Kraft Mills*

Blue Ridge Paper Products – Canton, North Carolina, U.S.A.

The bleached kraft mill in Canton, North Carolina, was originally built by Champion International Corporation in 1908. Champion divested the mill in early 1999 to an investor group operating under the name Blue Ridge Paper Products Inc. The mill is completely integrated, with pulp used to produce milk carton board and other specialty paper and board grades. The mill, situated in scenic western North Carolina near the Great Smoky Mountains, discharges into a small river. The impact of the mill's discharge on color in the Pigeon River has been a major point of contention with environmental activists in the region for decades.

In 1993, the mill completed a major capital project designed to assure compliance with state and federal water quality limits. The mill retained its conventional batch digesters but modernized the pulp processing and recovery areas. The project replaced two old pulp lines with a state-of-the-art 595 ADt/d softwood (pine) line including knotters, pressure screens, brownstock washers, medium consistency single-stage oxygen delignification, pulp storage, and a D(EOP)D bleach plant. The old softwood bleach plant was rebuilt and an oxygen delignification stage was added to produce 686 ADt/d of hardwood (mixed) kraft pulp. The bleaching sequence is D(EO)D. Two sets of black liquor evaporators were rebuilt and a condensate stripper was installed. A mill water distribution and cooling system was installed to reduce water use and effluent flow. The chlorine dioxide generator was expanded and the wastewater treatment plant was modified to maximize performance under greatly reduced hydraulic and organic loadings. These improvements enabled the mill to achieve a 30% decrease in flow and a 75% decrease in effluent color loading to the river (Stratton and Ferguson 1998).

Champion, purchased by International Paper Company in June 2000, developed and patented a process called Bleach Filtrate Recycle, or BFR, beginning in the late 1980s. Champion invested heavily in oxygen delignification and ECF bleaching technology at its bleached kraft mills, and developed the BFR process as a potential means to address future effluent compliance needs. The company elected to build and test the process full-scale at the Canton mill.

The BFR process was developed over a six year period using laboratory, simulation, and pilot studies to understand the impacts on bleaching, recovery cycle performance, washer scaling, product quality, and operating costs. The development used the documented experiences of the Rapson-Reeve closed-cycle process implementation at Great Lakes Forest Products (now Bowater) in Thunder Bay, Ontario, Canada, as a starting point. Issues raised and recommendations from the experiences at Thunder Bay that established the guidelines for BFR include:

- Chloride concentrations in the liquor cycle of the recovery process should be kept low.
- Salt (NaCl) removal should be accomplished with minimal evaporation.
- Net flow of bleach filtrate to the recovery cycle should be low to avoid additional evaporation requirements.
- Bleach chemical consumption due to higher levels of dissolved solids must be kept to a minimum.
- Minor wood components such as potassium, calcium, and pitch must be effectively removed.

The use of oxygen delignification, oxygen and peroxide fortified extraction stages, and chlorine dioxide bleaching provided a foundation for the process by minimizing both the recovery cycle chloride loading and the bleaching chemical penalty due to bleaching stage closure. Two add-on purge processes counteracted the buildup of nuisance materials, one to purge chloride from the recovery cycle and another to purge scale-forming minerals from the fiberline.

Chloride purging is accomplished by selective removal of sodium and potassium chloride from the recovery furnace electrostatic precipitator catch. The chloride removal process (CRP™), developed in conjunction with Sterling Pulp Chemicals Ltd., utilizes forced circulation evaporators to crystallize sodium sulfate (saltcake) from the dissolved precipitator catch. This saltcake is washed and returned to the black liquor, and the chloride-rich filtrate is purged. A schematic of the CRP is shown in Figure 4.4.

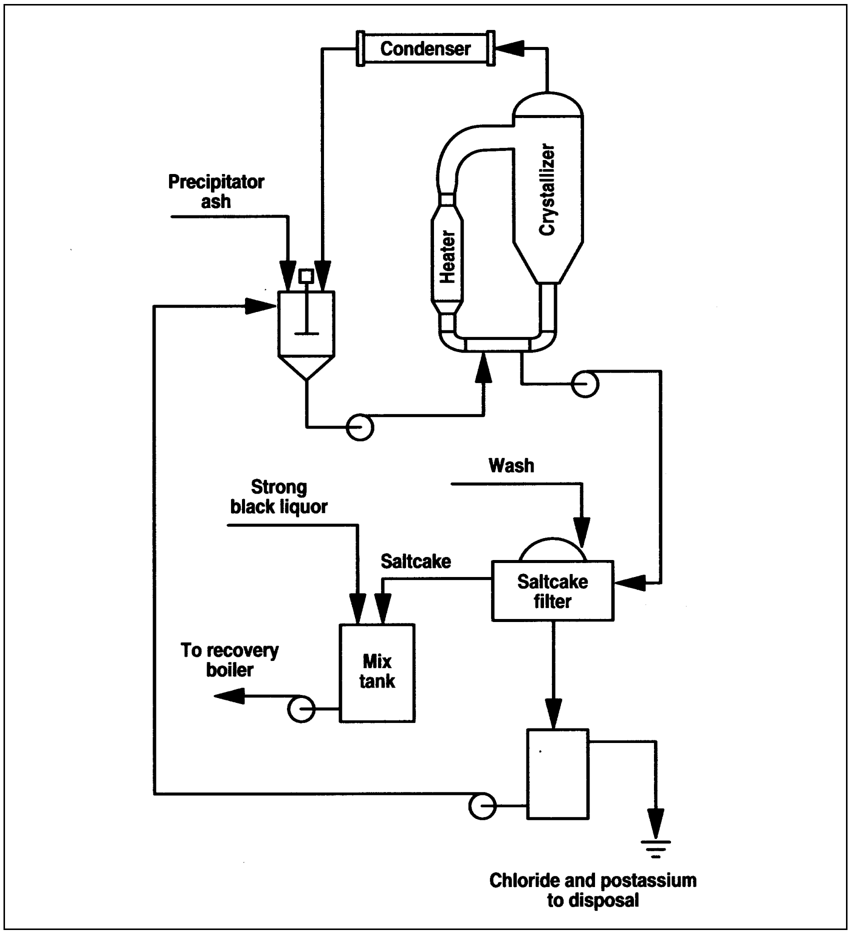


Figure 4.4 Schematic of CRP™ Chloride Removal Process (Maples et al. 1994)

The second process, called MRP for metals removal process, provides a purge of dissolved alkaline earth compounds from the first D stage (D1) filtrate. A portion of the filtrate is filtered to remove fibers, fines, and other particles, and is then passed through ion exchange units to exchange sodium ions for calcium and other multivalent cations. The "softened" filtrate is subsequently reused on the prebleach and D1 stage washers, and the exchangers are periodically regenerated with sodium chloride. Spent regenerant containing calcium and other ions is sewered. This arrangement closes the D1 stage to a high degree with respect to dissolved organic matter, while providing an effective purge of scale-forming minerals. The dissolved organic matter in the D1 filtrate passes into the EOP stage, from which filtrate is recycled into the post-oxygen washing system.

Canton was selected to demonstrate this technology because of the recent mill modernization and ongoing concerns about receiving stream water quality. Provisions to recover D1 and EOP filtrates from the new softwood bleach plant were installed, including piping, controls, and an MRP. The CRP was installed to treat all of the precipitator catch from both recovery furnaces to maximize chloride purging capability. Also, specific water conservation measures were implemented which avoided the need to increase black liquor evaporation capacity. These included:

- installation of cyclone separators on the pressure drum washer blower air lines (after the liquid ring compressor), preventing entrained seal water from entering the washer
- replacement of the screen room decker water doctor with an air doctor
- replacement of hot water used for brownstock washer wire cleaning with filtered EOP stage filtrate (this was not successfully implemented due to problems with the fiber filtration equipment).

Startup of the BFR process began in August 1995 with the CRP. Softwood EOP filtrate recycling was initiated in March 1996, and closure of the D1 stage began later that year. CRP was a robust and reliable operation, whereas MRP proved to be more challenging for the mill to operate and maintain. Ultimately, the mill has periodically achieved sustained closure of the D1 and EOP stages on the order of 80% by volume, with hydraulic capacity of the washers being the primary constraint to further closure. As of 1998, chloride levels in the liquor system were similar to pre-BFR values and potassium had been reduced by about 50%, from 10 to 5 g/l.

The mill started to recover a portion of the EO stage filtrate from the hardwood bleach plant in September 1998. There is no MRP on the hardwood line, so D1 stage closure is currently not an option.

The Canton mill has one of the strictest effluent color limits for a bleached kraft mill, amounting to about 17 kg/ton of pulp produced. The modernization project, BFR, and other color reduction measures have brought about a reduction of almost 90% in final effluent color since 1988. In spite of this remarkable achievement, the company continues to evaluate further color reduction measures as required by its effluent discharge permit.

The cost of BFR demonstration facilities at Canton were on the order of US$22 million for facilities expected to achieve full closure of the D1 and EOP bleaching stages on the 595 ton/day softwood fiberline (Ferguson 1996). Canton was particularly well suited to BFR process implementation because it had recently been modernized with evaporator, recovery, brownstock washing, and bleaching modifications including oxygen delignification and 100% substitution bleaching. Specific concerns that were addressed for Canton included the impact of the direct contact (cyclone) evaporators on dust loading to the ESPs (at Canton they intercepted 15 to 20% of the available ash) and black liquor carryover with the dust. Pilot trials by Sterling indicated that satisfactory saltcake precipitation in the CRP could be achieved with some black liquor organic solids present, and foaming in the crystallizers is controlled through addition of a defoaming agent.

A preliminary capital estimate (+/- 25%) for additional facilities to enable closure of the hardwood bleach plant to a degree similar to the softwood line was US$25 million (1994 basis). This included a hardwood line MRP plant, piping modifications, expansion of the CRP, additional white liquor oxidation capacity, and expansion of black liquor evaporators (Blue Ridge Paper 1999).

International Paper Company – Franklin, Virginia, U.S.A.

The integrated bleached kraft mill formerly owned by Union Camp Corporation is situated on a very small river. In fact, the mill must store its effluent for much of the year, discharging only during the winter months when stream flows are highest. The mill and its former owner were leaders in developing and adopting new pulping and bleaching technologies. The mill was one of the first in the U.S. to adopt high consistency oxygen delignification in 1981, and pioneered fully countercurrent washing in the bleach plant to minimize effluent flow (Nutt et al. 1993).

In the late 1980s, Union Camp undertook an extensive technical project to develop a commercially viable ozone delignification stage to replace the chlorination stages on Franklin's softwood bleaching lines. Through laboratory experiments, simulations, and pilot studies, the company developed the design for a full-scale high consistency (>35%) ozone bleaching reactor. Union Camp also conducted significant research in order to be able to model, track, and characterize both elemental and compound flows within the brown fiberline (Joseph and White 1996). The models predicted the effect of heat, pH, flow, lignin precipitation, and ion adsorption/desorption, as well as product concentrations of various components on each stream and unit operation of the plant. This allowed various purge strategies and processing options to be evaluated before installation. The models tracked flow, fiber, temperature, COD, cations (Na, K, Si, Fe, Mg, Mn, and Cu), chelant and chelated cations (DTPA, Fe, Mg, Ca, Mn, Cu), anions (Cl, CO_3, C_2O_4, SO_3, and SO_4), suspended solids (calcium oxalate, carbonate, and sulfate), and dissolved organics formed in the digester, oxygen, ozone, and extraction stages.

The technology was chosen for the new 'F' line at the Franklin mill, a 900 ADt/d (metric) softwood (pine) line which was built to replace two old chlorine-based bleach plants. The installed sequence was OZ(EO)D but currently operates as OZED. One of the major reasons for selecting the ozone stage was the ability to recover filtrates from the Z and E stages without significantly increasing chloride loading to recovery. The basic arrangement of Franklin's C-Free fiberline is shown in Figure 4.5.

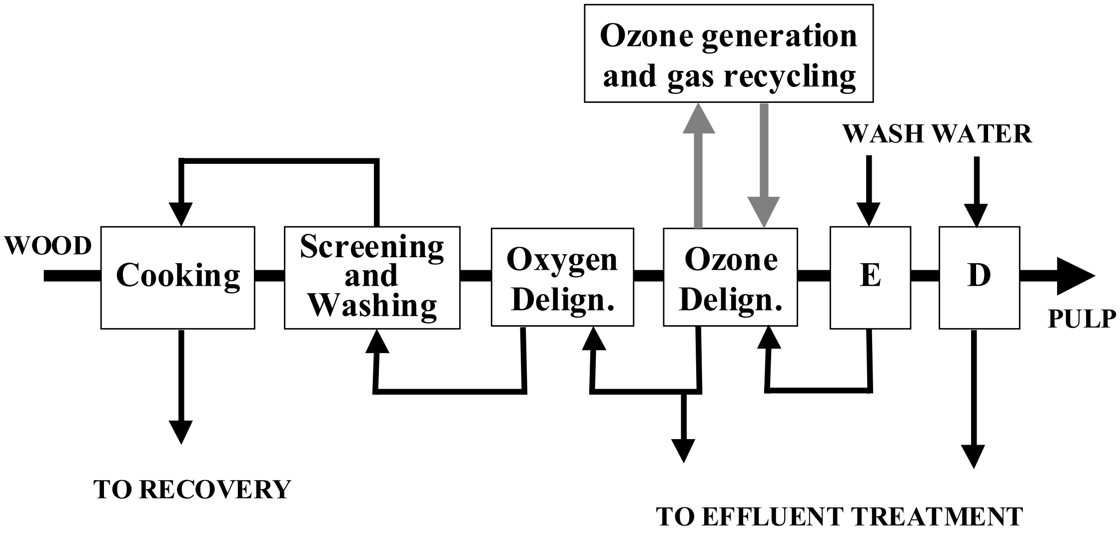


Figure 4.5 C-Free Fiberline ('F' line) Installation at International Paper Company's Franklin, Virginia, Mill

In this sequence, which started up in September 1992, both the O and Z stages operate at high consistency and an 84.5 GE brightness pulp is produced (the mill is fully integrated and does not require higher brightness levels). Filtrates from the O, Z, and E stages are returned to recovery via countercurrent washing, with a partial bleed of 2.1 m^3/ADt of the Z filtrate to prevent scaling. A calcium concentration of less than 500 mg/L is desired. The final D stage (7.3 m^3/ADt) filtrate is discharged to the waste treatment plant. The mill can run up to 88 GE brightness. Pulp properties are favorable to produce the same paper grades as those formerly produced with the CEDED bleached pulp. Environmental performance of the new bleach plant, per air-dried metric ton of pulp produced, was reported to be 9.4 m^3 flow, 0.05 kg AOX, 4.4 kg BOD_5, 11 kg COD, and 3.1 kg color. Figure 4.6 shows the filtrate recycling and recovery scheme and reported effluent flows (Griggs 1997).

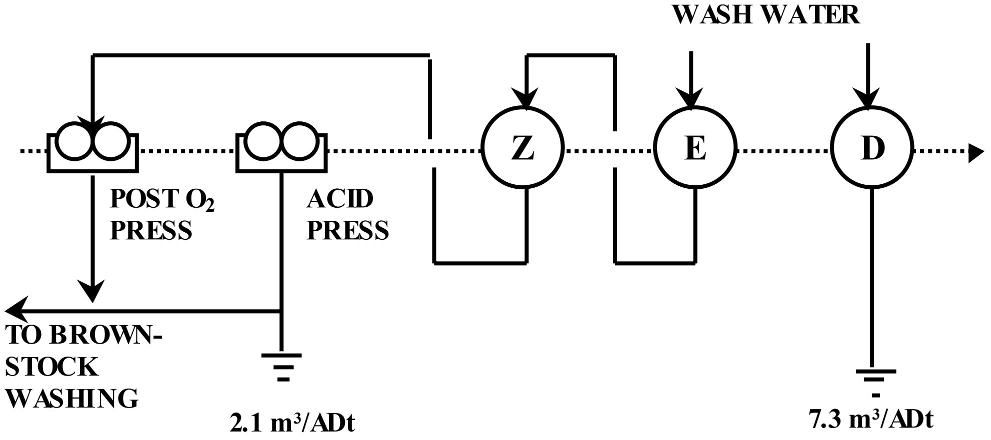


Figure 4.6 Filtrate Recycle Scheme at Franklin's 'F' line

C-Free technology has been installed at a number of mills worldwide, including SCA (Östrand, Sweden), Sappi (Ngodwana, Republic of South Africa), and Stora Enso North America (Wisconsin Rapids, Wisconsin, U.S.A.).

Samoa Pacific Cellulose – Samoa, California, U.S.A.

The Samoa Pacific kraft mill is on the Samoa peninsula in northern California, a short distance across the bay from the seaport town of Eureka. The mill, formerly owned by Louisiana-Pacific Corporation, was exempted from the Clean Water Act requirement that bleached kraft mills install external effluent treatment. As a provision of its discharge permit, this ocean-discharging mill was required to co-fund (with a neighboring mill) a study of in-plant and closed-cycle technologies. Louisiana-Pacific sold the mill to an investor group in February 2001. It currently operates under the name Samoa Pacific Cellulose, LLC.

Samoa produces both bleached and unbleached market pulp. It is the only bleached kraft mill in North America producing TCF market pulp. Mill production is 650 ADt/d made from predominantly softwood sawmill residues (25% redwood, 50% Douglas fir, and 25% mixed conifers). Samoa has a conventional continuous digester (built in 1965 with a 700 t/d capacity) and uses soluble AQ to achieve a softwood kappa of 16 for bleached pulp. The brownstock is washed in three vacuum washers, followed by closed screening (installed in 1987) and medium consistency single-stage oxygen delignification to produce a pulp of kappa 8 to 10. Post-oxygen washing consists of a pressure washer (CB filter) followed by a vacuum washer. The bleach plant uses towers originally designed for a CEHDED sequence, and beginning in 1994 ran using a Q(EOP)PPP sequence. Since 1997, the mill has utilized evaporator condensates for bleach plant washing and has recycled bleaching filtrates via the brownstock system.

With no external treatment facilities, the Samoa mill relies exclusively on pollution prevention, including an extensive liquor spill collection and recovery system, and steam stripping of condensates to comply with applicable effluent regulations. The non-direct contact evaporator design recovery furnace, installed in 1990, is capable of meeting all mill steam and electric power generation demands. A foul condensate stripper, started up in 1994, reduced the mill COD discharge by half. The mill has an advanced NCG collection system with co-firing of NCGs in the lime kiln and a dedicated incinerator, and the ability to transfer load without venting, should either combustion source fail. A green liquor filter (Ahlstrom X-Filter) and new pre-coat dregs filter were added in 1996 to provide enhanced lime burning, causticizing operation, and purging of non-process metals (Ledbetter et al. 1997).

The only bleach plant effluent discharged is from the chelation stage, and this was determined (during an EPA-sponsored testing program) to be 6.76 m^3/ADt. This is among the lowest bleach effluent flows for a kraft mill bleach plant. The study indicated that the bleach plant generated BOD_5 of 2.9 kg/ADt, COD of 8.9 kg/ADt, color of 4.2 kg/ADt, and TSS of 0.395 kg/ADt, among the lowest loadings for the six mills selected for the EPA study (USEPA 1996).

In 2001, a pressurized peroxide bleaching tower was installed and the sequence was modified to OQQPQ(PO), enabling 88% ISO brightness pulp to be made at reasonable production rates and chemical usage. Peroxide stage filtrates continue to be returned to brownstock washing. Evaporator condensates are used for pulp washing. The mill does not combust or landfill any process solid wastes. Wood rejects are sold to a local utility for power generation and causticizing wastes are sold for beneficial use as soil amendments.

Extensive effluent toxicity and air emission characterization has also been carried out at Samoa Pacific. In a 1995 study on hazardous air pollutants (HAPs), the mill was found to be significantly better than industry averages for non-chlorinated HAPs, despite concerns that the intensive bleach filtrate recycle would lead to greater HAP generation. The mill was in compliance with all Cluster Rule BAT guidelines (Jaegel 1997).

Difficulties with low effluent operations have included an episode of the recovery furnace generating bank tube pluggage as well as lime mud filtration and capacity difficulties. The pluggage event was caused by higher temperatures in the furnace due to the burning of gas, which is used as supplemental fuel during occasional hardwood pulping runs. This caused higher temperatures that led to plugging. Modifications to operating procedures to avoid high flue gas temperatures in the generating section have prevented any recurrence, and the mill has since had great success running hardwood. It is thought that the causticizing difficulties were due to recycle of bleaching filtrates containing high levels of magnesium sulfate when running hardwood. Mud was purged to restore lime availability and magnesium addition levels are now more closely controlled.

The Samoa mill is committed to producing TCF bleached market pulp and is also working to eliminate bleaching effluent through filtrate recycle. An important aspect for the mill is energy use. A study describing the energy implications of moving towards closed-cycle TCF operation was conducted with support from the U.S. Department of Energy's $NICE^3$ (National Industrial

Competitiveness through Energy, Environment and Economics) program. The study utilized process simulation to evaluate several operating cases including a reference case of chlorine bleaching without filtrate recovery, TCF bleaching with partial filtrate recovery, and TCF with recovery of all bleach plant filtrates (Jaegel, Gleadow, and Bruce 1999).

The study determined that, on a production weighted basis, thermal and electrical energy use at Samoa is higher than at new mills, but is comparable to mills of a similar age. Compared to a reference case of chlorine-based fully bleached pulp, TCF production resulted in increased energy use of about 21% for steam and 5.5% for electricity per ton of production. TCF with full bleach plant closure was estimated to further increase energy use modestly.

The principal causes for the increases in electrical and steam demand were a reduction in production rate from 630 to 532 ADt/d and a decrease in overall pulp to wood yield from 40 to 38.5% resulting from conversion to TCF operation. Energy use also increased with the retrofit of energy intensive pollution prevention technologies such as steam stripping of condensates, separate incineration of non-condensable gases, extended delignification in the digester, and increased evaporation loads due to bleach filtrate recycling.

A campaign was started to identify and eliminate a significant amount of energy use through waste heat reuse and elimination of tramp water streams going to evaporation.

Water use and effluent flows were also predicted as part of the study. Specific water use for the entire mill for the chlorine bleaching case is 110 m^3/ADt, is unchanged with TCF due to decreased production rate, and is 104 m^3/ADt with full bleach recycle.

Aspa Bruk – Smurfit Munksjö, Sweden

Aspa produces 170,000 ADt/yr of softwood kraft pulp. In 2000, approximately 20,000 ADt of this was unbleached, 80,000 ADt was ECF bleached, and 70,000 ADt was TCF bleached. The mill is located on the shore of Lake Vattern, Sweden's second largest lake and a source of drinking water for about 200,000 people. Aspa does not have secondary treatment and has sought to reduce effluent discharges through progressive process closure. The mill reduced AOX discharges from 8 kg/ADt in 1974 to 1.5 kg/ADt in 1989. The mill had to report its method to reduce this to below 0.5 kg/ADt (as TOCl, a precursor to the AOX test) by July 1990. Aspa pioneered the use of a pressurized EOP stage in 1988 and ran trials on the Lignox OQ(EP)D(EP)D process in 1989, which resulted in an AOX of 0.3 kg/ADt. In response to market indications that a TCF product, albeit at lower brightness, may be acceptable, Aspa used a Q(EP)Q(EP) sequence to make 70% (1990), 78% (1991), and 83% (1992) ISO brightness pulps.

In 1995 Aspa decided to increase production and upgrade the mill to meet stricter effluent limits. A permit for the modifications was obtained in December 1996. The investments include:

- new, improved NCG system (1996)
- PO stage in the bleach plant (1996)
- new lime mud filter (1996)
- new white liquor (pressurized disc) filter (1997)
- new green liquor (cassette) filter (1997)
- modifications to the digester, including a new pressurized diffusion washer (1998)
- modifications to the recovery boiler, including a new superheater and electrostatic precipitator (1998)

- modifications to the evaporation plant, including a new concentrator (1998)
- modifications to the screen room (1998)
- new slaker in the causticizing plant (1998)
- modifications to the turpentine system (1999)
- new two-vessel oxygen delignification stage, including a new pressurized diffusion washer and a new compact press washer (2001)
- new bleaching sequence for ECF pulp (2001)
- two more compact presses installed in the bleach plant (2002).

These improvements have enabled the mill to produce fully bleached ECF and TCF pulps. Currently, the TCF sequence is O-Q-PO, and the ECF sequence is O-Q-PO-D-D. The new ECF sequence has lowered the AOX load in the effluent from approximately 0.4 to 0.1 kg/ton of pulp. In 2000 the mill had a 20 ton/day effluent COD limit, and this figure will be reduced to 10 ton/day by 2006.

Aspa has been recycling all its alkaline filtrates to brownstock washing since 1993, and has been experimenting with using some of the Q stage filtrate in causticizing. The points of filtrate addition include lime mud dilution, mud washing, and the smelt dissolving tank. Warnqvist et al. (1995) reported that Q stage recycle increased the levels of calcium in the white liquor, but no scaling problems were observed in the digester or evaporators. No information or observations on VOC emissions from the kiln have been reported. Increased levels of Mg and Mn were precipitated with green liquor dregs, consistent with Q stage recycle, but there were no changes in the Na/K balance (Björk 1994; Wahlberg 1995). Q stage recycle to causticizing has been discontinued due to fiber problems in the green liquor filter.

Aspa's concept of bleach plant closure currently includes "open" Q and D stages. Aspa expects that its investments in process improvements, especially prolonged delignification in the oxygen stage, improved washing with the new compact presses, and closure of the PO stage, will make it possible to reach its ultimate COD limit of 10 kg/ton.

M-Real Sverige AB – Husum, Sweden

Husum has a yearly production of 650,000 ADt pulp, of which 350,000 ADt/yr is softwood and 300,000 ADt/yr is hardwood from birch. The mill can make up to 690,000 ton/yr according to its environmental permits. The integrated paper mill has permission to produce 600,000 ADt/yr of paper. Husum is registered for ISO 14001 for environmental system assurance. It has been undergoing upgrading and expansion in recent years.

Husum has looked toward in-plant process changes to meet effluent standards in lieu of external treatment of effluents. MoDo (the mill's former owner) made a press announcement in 1994 that the Husum mill would be the first totally effluent free bleached kraft mill. However, with a subsequent change in senior management focus within MoDo, its plans had been relaxed somewhat to focus more on production and increasing revenue. MoDo launched the first office paper from an "effluent free bleaching plant" with its MoDo Balans in late 1994 (Anon. 1994), which it produces from pulps made at both the Domsjö sulfite mill and the Husum kraft mill.

In 1981, a trial was made in which E1 filtrate from the softwood line was used as wash liquor on the hardwood line. Filtrate was not returned to the softwood line due to concerns about corrosion in the oxygen delignification stage. The recycle resulted in an increase of about 1 kg/ADt pulp for chloride input to the recovery system. The chloride content of the white liquor had increased from 1.2 to 2.7

g/L when the trial was discontinued. The expected chloride concentration based on simulation was 3.3 g/L. The only other major source of chloride was the wood supply, and major purge points were with the pulp and through an HCl scrubber stage in the recovery boiler scrubber. There were no major drawbacks during the trial, though ClO_2 consumption increased slightly (1 to 2 kg/ADt). It was determined that the maximum level of chloride in white liquor to avoid difficulties in the largest recovery boiler is 6 g/L, and 10 g/L for the two smaller boilers (Galloway et al. 1994).

From 1983 to 1985, EOP stage effluent was recycled from the softwood bleach line (which had been rebuilt as a (D/C)(EOP)DED sequence with two wash filters after the EOP stage). This was stopped due to concerns about corrosion of a new brownstock washer.

Following pilot testing of ultrafiltration technology in 1986, full-scale operation with ultrafiltration (UF) was carried out in 1988. In the full-scale operation, 40% of the EOP stage effluent was treated. Due to the double washer configuration, total EOP effluent flow was only 4 m^3/ADt. Four UF units were installed at Husum, each of one meter membrane diameter and 37 stacked cells per filter (for a total area of 50 m^2 per filter). Three of the filters were installed in parallel for primary treatment and one for further concentration in a secondary (cascaded) position. The permeate went to sewer and the concentrate was returned to the weak black liquor system. Long-term operating observations included a flux rate of 210 L/m^2/hr, a volume reduction factor (VRF) (feed:concentrate) of 15, trans-membrane pressure of 200 to 300 kPa (a low pressure was important to minimize fouling), and a washing frequency of two to three times a week (both acid and alkaline washing were used). By 1991, the substitution of chlorine dioxide for chlorine had increased from 15% to 100% and this was accompanied by decreases in effluent pollutant loadings. The elimination of chlorine lowered the range of molecular weights of the EOP effluent organics, causing the efficiency of the UF treatment to decrease (e.g., VRF dropped from 15 to 9 and the removal efficiency for AOX and COD decreased) and operating costs to increase. Ultrafiltration was stopped altogether in 1992.

TCF was then developed for the hardwood mill, with oxygen delignification installed in 1990 and ozone bleaching in May 1993. This enabled the mill to recover a larger portion of the bleach plant effluent, with a close up trial starting in the fall of 1993. During 1993, bleach plant effluent was reduced from 60 to 20 m^3/ADt through filtrate reuse.

Initial trials with closure of the entire TCF bleach plant were held in the fall of 1993 and spring of 1994 for two to three days each. Further investments were made to improve control of the water balance, including the installation of a 2500 m^3 filtrate tank (the same size as the post-oxygen pulp storage tower). The investment cost from 1993 to 1996 for "closed-loop bleaching" at Husum was SEK 170 million (US$25 million) (Ahlenius et al. 1996).

Direct countercurrent filtrate recirculation is used in the hardwood bleach plant, with fresh caustic used in the EO and P stages. As of 1996 the first two stages of bleaching were closed, with filtrate from the last two bleaching stages sewered during regular hardwood production. Approximately 25% of the time, the line is run completely countercurrently, with no filtrate sent to sewer. The hardwood line averages 5 m^3/t effluent on a monthly basis (Ahlenius et al. 1996).

Recycle of the bleaching filtrates to brownstock resulted in increased bleaching chemical consumption. Use of 3 to 5 kg ClO_2/ADt in the sequence has helped to decrease kappa number variations and achieve final product brightness at a lower cost than was possible with ozone and peroxide only. The introduction of additional chloride into the recovery system was expected to be manageable (Ahlenius et al. 1996).

Recovery boiler precipitator dust is removed for soda-sulfur balance control. With closed-cycle operations there are scaling problems, which have resulted in reduced productivity. The scaling problems are addressed through intensive mechanical cleaning.

The mill has also experimented with closed-cycle ECF and TCF softwood production, including recovery of filtrates from the alkaline stages and one of the two D stages. Husum can attain a softwood bleach plant effluent flow of 8 m^3/ADt. A measurable decrease in COD has been observed and pulp quality has been maintained (Ahlenius et al. 1996).

MoDo's environmental report in 1996 indicated that the mill was having some difficulties closing the softwood line, particularly with control of deposits, and by 1998 their environmental report did not mention process closure activities or its trademarked grade, MoDo Balans. The key question of whether to install a biological effluent treatment plant was expected to be resolved via a decision of the Environmental Court. Pilot trials had shown that the reduction in emissions from biological treatment would not lead to any reduction in environmental impact, and instead showed a greater impact on fish exposed to biologically treated water (MoDo 1996; MoDo 1998).

A decision from the Environmental Court in November 2000 stated that a biological treatment plant should be in operation by the end of 2004. The engineering for the plant has started and construction work is scheduled to begin in spring 2003 (Uhlin 2003).

SCA Pulp AB – Östrand, Sweden

SCA started up a new TCF bleach plant in May 1995 at their Östrand mill. The line cooks softwood in a conventional digester retrofitted for iso-thermal cooking (ITC) to 23 kappa followed by a blowline pressure diffuser, additional washing, two stage medium consistency oxygen delignification, and a bleaching sequence of Q(OP)(ZQ)(PO) with high consistency ozone bleaching (Annergren, Boman, and Sandström 1996). The pre-bleaching kappa number target is approximately 12. The chip supply to the digester was improved at the time the new fiberline equipment was installed. The mill has also pulped hardwoods but is not currently doing so.

The mill design makes use of displacement wash presses in the bleach plant. The bleach plant has been designed to concentrate metal ions in one stream using chelating agents. Manganese has not been a problem with increased filtrate recycle, but calcium oxalate deposits have occurred at the wash presses (Annergren, Boman, and Sandström 1996). The bleach plant currently operates with an effluent discharge of about 7 m^3/ADt.

Typical product properties are 80 to 88% ISO brightness with strength and cleanliness similar to ECF pulp. A bleach plant stock cleaning system was included in the TCF upgrade to enable cleanliness levels to be maintained at lower brightness levels. In comparing the new TCF line to the mill's old ECF line, there was a 75% reduction in water use, AOX was eliminated, bioaccumulative substances were reduced by 99.2%, wood extractives by 72%, and COD by 49% (Tannik 1997). Effluent treatment facilities have been installed recently, and the mill is working to improve treatment performance with the expectation that its COD discharge will be less than 10 kg COD/ADt. This would represent a reduction of some 80% compared to the old ECF plant (Morin 2002).

Södra Cell – Mörrum, Sweden

Södra Cell is a major producer of market kraft pulp. It had 1999 sales of 1.233 million ADt of pulp produced at mills in Mörrum, Mönsterås, and Värö (Södra 1999). The pulp is sold mainly to paper mills in western Europe. More than two-thirds of production is used for manufacturing writing and printing paper; the remainder is used for board, tissue, and various specialty papers.

During the 1990s, Södra Cell made a concerted effort to communicate its goal of becoming 100% TCF at all three of its bleached kraft mills. 2001 represented the eighth year of exclusively TCF production at Värö and the seventh year at Mönsterås. Through various advertising campaigns, Södra has communicated its belief that long-term environmental protection will require the adoption of TCF bleaching technology (Eklund 1995). It sought to differentiate itself with its customers based on environmental performance. Södra acquired the ECF bleached kraft mill in Tofte and a BCTMP mill in Folla, Norway, in July 2000. In 2001, about 66% of its total bleached kraft market pulp was TCF (Södra 2001).

Mörrum produces both hardwood and softwood bleached pulp on two lines, with a total capacity of 415,000 ADt/yr. Mörrum manufactured 393,000 tons in 1998, of which 66% was produced using a peroxide-based TCF sequence. In 2001, about 42% of the 390,000 tons of pulp produced was TCF (Södra 2001).

Södra rebuilt its Mörrum mill for TCF and expanded production capacity by 44,000 ADt/a to 415,000 ADt/a at a cost of SEK 1,100 (US$150 million). The project included a new bark press and shredder, replacement of the existing digesters with new RDH batch digesters, a complete rebuild of both bleach lines (a Kvaerner PREPOX pressurized peroxide stage with two washes has been installed with a capacity of 850 t/d softwood or 1100 t/d hardwood), increased evaporation and recovery boiler capacity, a cooling tower for excess heat, a system for collecting and stripping volatile malodorous gases, and a new effluent treatment plant.

The fiberline includes oxygen delignification and a QP sequence using presses for washing. The mill also installed several large buffer tanks to facilitate close-up. Evaporator capacity has been increased to 2200 tBLS/d, up from 1800 (Obrien 1995).

Södra's 1998 environmental report (Södra 1998) characterizes progress in closing the bleach plants at Mörrum:

> During April 1998, a new peroxide stage was started on line 1 which means that Mörrums Bruk is now prepared for a changeover to exclusively TCF production when market criteria exist. Work with a closed process of the bleach plant effluents continued, albeit less extensively than originally planned. To achieve the pulp quality, added care has had to be observed with regard to how the effluent is recirculated in the bleach plant. Problems in the form of formation of incrusts in evaporation apparatus have also meant that a reduced volume of effluent could be recovered. Work continues on developing still further technology for closed processes in the bleach plants.
>
> At the beginning of the year, the mill had difficulties in meeting the target value for COD (45 tonnes/day). Extensive measures were implemented, including optimizing washing equipment, effluent-handling, recirculation of effluent, kappa number optimization and intensified daily monitoring. The work was successful and after having exceeded the target value during the first three months of the year, the target value was comfortably met.

Södra's 1999 environmental report (Södra 1999) indicates that the bleach plant could not be closed to a degree sufficient to meet the long-term COD target:

> The technical possibilities of reducing COD discharges have been overestimated. A balancing act has also been necessary for reasons of quality, as too strict closing of the bleach plant processes has a negative effect on the finished pulp. In addition, recirculation of the effluent from the bleach plants was limited due to problems with clogging in the evaporation plant. COD discharges can be reduced through biological treatment and an application for permission to build such a plant was submitted to the Environmental Court in

> August. With biological treatment it will be possible to achieve the long-term COD target of 15 kilos/tonne pulp maximum in 2002.

The new treatment plant and an old recovery furnace rebuilt as a waste fuel boiler were both brought into operation in 2002 (Carlsson 2003).

Södra Cell – Värö Bruk, Sweden

The Värö mill produces about 330,000 ADt of softwood pulp on one line. Värö has made only TCF pulp since 1994, using a sequence based on hydrogen peroxide. Värö installed increased evaporation capacity to boost capacity from 345 to 485 t/h of evaporation and solids from 68 to 75%. This involved a new first-effect concentrator and three new parallel effects designed to reduce scaling. It also purchased a 200 t/h integrated steam stripping plant, in which all condensates are stripped to enable as yet unspecified reuse within the mill (Danielsson and Håkansson 1996).

In 1998 the mill completed work on a new wood handling system, a two-stage oxygen delignification system, a pressurized peroxide stage, and pulp washing equipment (Södra 1998). To facilitate closure of the bleach plant, an internal treatment (Netfloc) plant was installed to chemically remove metals from the bleach plant effluent. Its design was based on results from pilot tests at the mill during 1997 in cooperation with Kemira. This system enabled the mill to recycle a portion of the Q stage filtrate, thereby reducing EDTA consumption. The plant was modified in 1999 and was reported to be working satisfactorily (Södra 1999; Södra 2001). However, final evaluation showed that the technology could not compete with external biological treatment. An effluent treatment plant was installed and began operation in 2002 (Carlsson 2003).

Stora Enso – Skoghall, Sweden

The Stora Enso paperboard mill at Skoghall completed a major investment program which included the April 1997 start-up of a new bleach plant for kraft pulp. This rebuild is an example of the application of Stora's Ecobalance philosophy to bleached kraft softwood pulp production. A bleach plant with a sequence O(PO)DQ(PO) (Figure 4.7) was found to be best with respect to the product (bleached board), effluent flow (reduced 80% compared with the old OD(EOP)DED sequence), COD (reduced 50%), and AOX (reduced 65%). The new bleach plant utilizes presses for washing and dewatering, and PO stage filtrate is returned to post-oxygen washing. Environmental and bleaching parameters for the old and new bleach plants are shown in Figures 4.8 and 4.9, respectively. This bleach plant's wastewater flow is less than 10 m^3/ADt and contains 4 to 5 kg COD/ADt and about 0.05 kg AOX/ADt (Savolainen, Norborg, and Lindberg 1998).

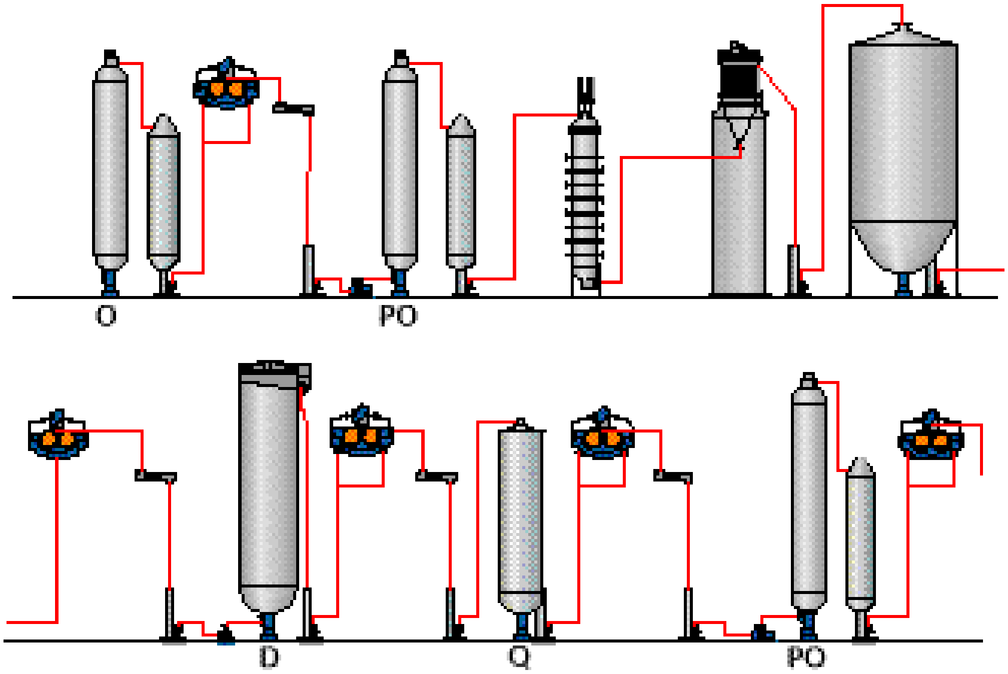
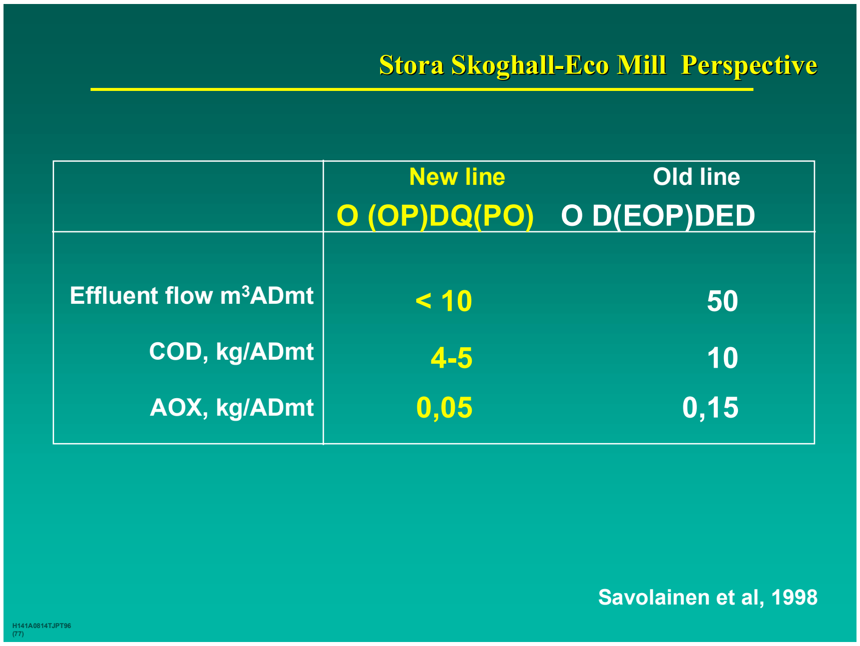


Figure 4.7 Schematic of Stora Skoghall Fiberline (Ernerfeldt, et al. 1999)



Stora Skoghall-Eco Mill Perspective

	New line O (OP)DQ(PO)	Old line O D(EOP)DED
Effluent flow m^3ADmt	< 10	50
COD, kg/ADmt	4-5	10
AOX, kg/ADmt	0,05	0,15

Savolainen et al, 1998

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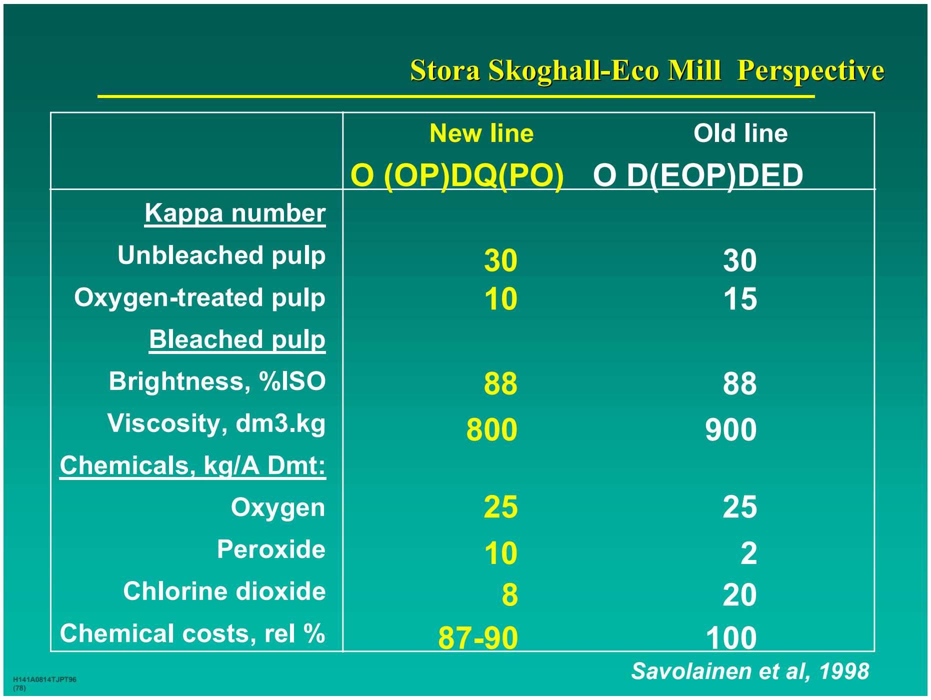
(77)

Figure 4.8 Stora Skoghall Effluent Parameters



Stora Skoghall-Eco Mill Perspective

	New line O (OP)DQ(PO)	Old line O D(EOP)DED
Kappa number		
Unbleached pulp	30	30
Oxygen-treated pulp	10	15
Bleached pulp		
Brightness, %ISO	88	88
Viscosity, dm3.kg	800	900
Chemicals, kg/A Dmt:		
Oxygen	25	25
Peroxide	10	2
Chlorine dioxide	8	20
Chemical costs, rel %	87-90	100

Savolainen et al, 1998

H141A0814TJPT96
(78)

Figure 4.9 Stora Skoghall Bleaching Parameters

Metsä-Botnia – Rauma, Finland

The Metsä-Botnia mill in Rauma, Finland (formerly known as Metsa-Rauma) is a 570,000 ADt/yr softwood pulp mill in southern Finland that began operations in 1996. The reported cost was FIM 3000 million (US$700 million). The mill was built specifically to produce TCF kraft pulp for use in integrated paper production and for sale as market pulp. The TCF sequence was expected to offer advantages both in the marketplace and in reducing bleach plant effluent flows.

Spruce and pine chips are cooked in ten SuperBatch digesters to kappa 20. Displacement presses are used for washing the brownstock. Two stage oxygen delignification followed by medium consistency ozone and pressurized peroxide comprise the bleaching operation. The capacity of the ozone plant is 6 kg/ADt. The mill was designed to produce both 85 ISO and 88 ISO bleached pulp grades.

Alkaline bleach plant filtrate is used for brownstock washing and the acidic filtrate is sewered. The bleach filtrate recycle arrangement is shown in Figure 4.10 (Gleadow 1999). As of 2001 the mill appears to have reached a limit with respect to further bleach plant closure, citing potential problems including excessive consumption of bleaching chemicals, scale deposit formation, and equipment corrosion, while noting that further closure would not reduce the mill's environmental impact. Total mill water use is 24 m^3/ton of pulp (Metsä-Botnia 2001). Mill effluent is co-treated with wastewater from the adjacent UPM-Kymmene paper mill in an activated sludge biological treatment plant.

The Rauma mill's original owners indicated that the investment and operating costs were lower with TCF than with ECF. The decision to use medium consistency ozone was based on a lower investment cost and the positive experiences of the Metsä-Botnia Kaskinen mill.

The mill features operation at high sulfidity, at times as high as 49%. The tall oil plant also initially acidulates with carbon dioxide to limit sulfur input to the tightly closed recovery cycle.

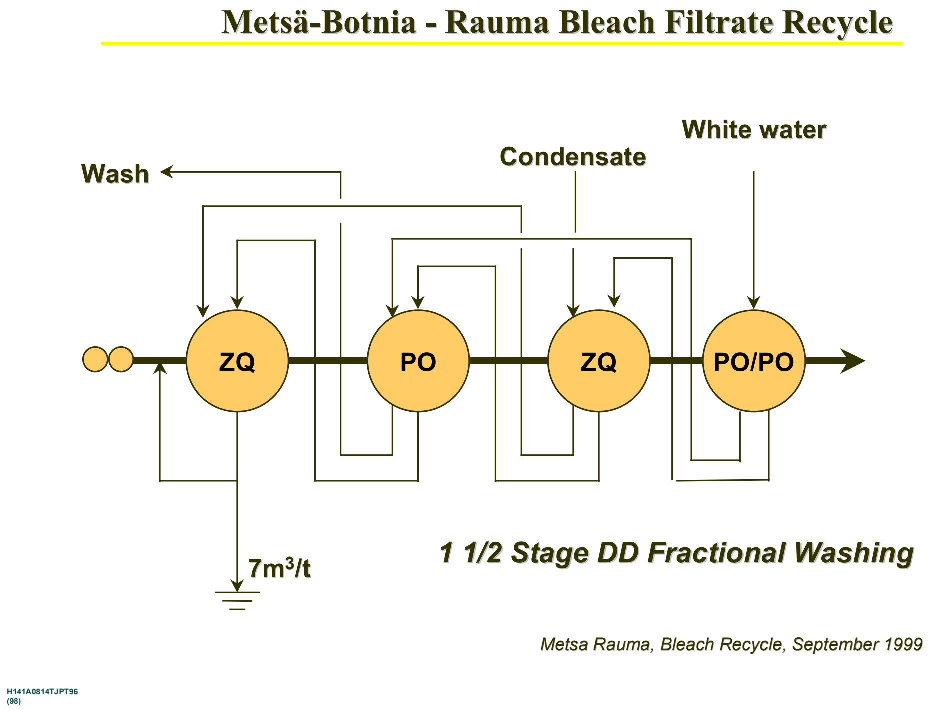


Figure 4.10 Filtrate Recycling Scheme at Metsä-Botnia - Rauma, Finland (Gleadow 1999)

The Rauma mill may be seen as the first of a new generation of mills built for TCF and water systems closure, analogous to the new generation ECF mills such as Alberta-Pacific in Canada and Bahia-Sul in Brazil. These mills offer or promise to offer exceptional environmental performance. The performance of the Rauma mill can be seen in its emissions and permit limits in Table 4.9.

Table 4.9 Metsä-Botnia Rauma Emissions and Permit Limits – 2000 and 2001

		Emissions[a]		Permit Limits[b]
	Annual Average 2000	Annual Average 2001	Max Month Average 2001	Monthly Average
Effluent Flow (m^3/t)	17	22	27	
TSS (t/d)	0.7	0.95	3.1	
BOD_7 (t/d)	1.6	0.86	4.4	3.3
COD_{Cr} (t/d)	9.8	9.8	22.3	45.0
AOX (t/d)	-	-	-	0.45
P (kg/d)	14	25	206	70.0
N (kg/d)	147	228	613	

SOURCE: 2001 Metsä-Botnia environmental report

Notes from source:

[a] Pulp mill has a joint effluent treatment plant with UPM-Rauma paper mill; emissions have been calculated at the verified reduction rate of the effluent treatment plant

[b] held jointly with UPM-Kymmene Rauma paper mill

UPM-Kymmene Wisaforest – Pietarsaari, Finland

Wisaforest was the first mill in Finland to implement both oxygen delignification (in 1988) and ozone (in 1993). Wisaforest's capacity as of 1999 was 580,000 tons per year bleached hardwood and softwood pulps, of which its TCF capacity is 280,000 t/year. The 1995 TCF production was approximately 100,000 tons, and was projected to be 115,000 t/year (30,000 t/year hardwood and 85,000 t/year softwood) in 1999. Wisaforest has two fiberlines; both are ECF- and TCF-capable. The ECF sequences make use of oxygen, ozone, peroxide, and chlorine dioxide for bleaching.

Fiberline 1, which was partially rebuilt in 1999, uses six conventional (160 m^3) and two Superbatch (300 m^3) digesters followed by two stage oxygen delignification. All digesters are currently operated conventionally, but the aim is to introduce Superbatch cooking in all vessels. The hardwood ECF post-digester kappa is 20 and post-oxygen kappa is 14. The hardwood TCF kappa is 18 to 20 post-digester and 11 post-oxygen. An acid (A) stage operated at pH 3.5 for six hours lowers the kappa to 8. Softwood ECF kappa is 32 to 34 and 15 to 18, following the digester and oxygen delignification, respectively. For softwood TCF operation, digester and post-oxygen kappa numbers are 22 and 11, respectively.

The ECF bleaching sequence is O(ZD)(O/EO)(ZD)EP. The chemical consumption for hardwood is 2 kg/t H_2SO_4, 5 kg/t ozone, 8 kg/t ClO_2, and 5 kg/t peroxide. Peroxide use for TCF is 15 to 20 kg/t. The TCF sequence is O(ZQ)(OP)ZP. Wisaforest has a full final D stage available but does not use it in the ECF sequence, as the final P stage gives good brightness and low reversion (yellowing). The oxygen and ozone stages are medium consistency, and Kvaerner supplied the ozone stages. Chemical consumption is approximately 6 kg/ADt ozone and 20 kg/ADt peroxide to obtain 88.5 ISO brightness on pine, and 6 kg/ADt ozone and 18 kg/ADt peroxide for 90 brightness on birch. Prior to conversion to the "ECF-lite" bleaching sequence (chlorine dioxide consumption was about 12 kg/t in the full ECF sequence), Wisaforest indicated that the bleaching cost for ECF pine and birch were, respectively, 94.8% and 93.5% of TCF costs. These costs include wood (yield), energy, chemical, and bleaching. Wisaforest's TCF pulps also have slightly poorer tear/tensile than their equivalent ECF pulps, and they make TCF as required to satisfy customer demand.

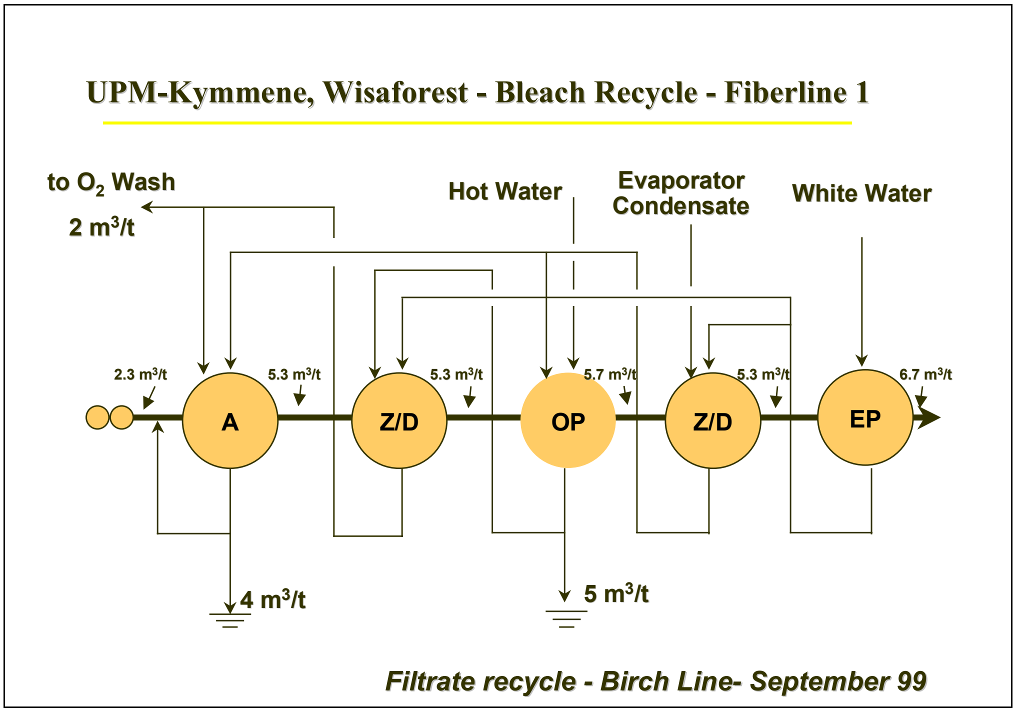
Fiberline 1 uses about 25 m^3/ADt of process water. This includes machine white water, evaporator condensate, and fresh, softened hot water. Fresh hot water use is about 4 to 6 m^3/ADt, and effluent flow is about 9 m^3/ADt.

Fiberline 2 has a liquor/vapor phase Kamyr continuous digester, with hot alkali extraction and two-stage oxygen delignification. Softwood kappa is 30 and 24 post-digester and post-oxygen, and the respective hardwood kappa values are 18 and 14. The ECF sequence is O(Z/D)(EOP)DP.

Fiberline 2 uses about 28 m^3/ADt of process water including hot water (10 to 15 m^3/ADt), machine white water, and evaporator condensate. The effluent flow is about 12 m^3/ADt. The mill is also working toward "closure" of air emissions with all "strong" odors and 85% of "weak" odors collected. The 1998 sulfur dioxide emissions were 0.14 kg/ADt pulp and the total reduced gaseous sulfur compound emissions were 0.24 kg/ADt. In 1998 treated AOX emissions were reported to be 0.21 kg/t.

Wisaforest has been progressively reducing its bleach filtrate effluent streams over the past several years, and process water use was about 25 m^3/ADt. The filtrate recycle arrangements used in 1999 are shown in Figures 4.11 and 4.12 (Gleadow 1999).

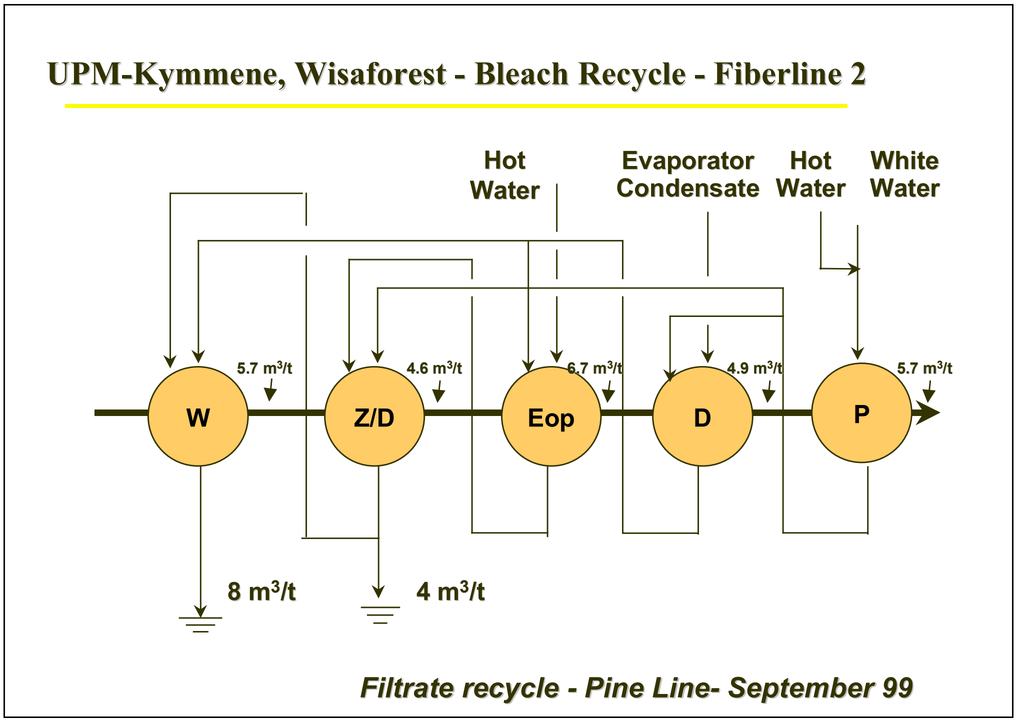
The mill indicated that it has "a comprehensive investment implementation going on in the Wisaforest pulp mill. The start up will be in the spring 2004.



UPM-Kymmene, Wisaforest - Bleach Recycle - Fiberline 1

Filtrate recycle - Birch Line- September 99

Figure 4.11 Bleach Filtrate Recycle Scheme at Wisaforest, Fiberline 1



UPM-Kymmene, Wisaforest - Bleach Recycle - Fiberline 2

Filtrate recycle - Pine Line- September 99

Figure 4.12 Bleach Filtrate Recycle Scheme at Wisaforest, Fiberline 2

5.0 MINIMUM IMPACT MILL RESEARCH PROGRAMS

A number of research programs focusing on minimum impact, sustainable, energy-efficient pulp and paper manufacturing were undertaken in the 1990s, some of which continue today. Many of these where funded at national levels, and typically involved national pulp and paper research institutes. Not all results from these programs are available in the general literature, as the pulp and paper research institutes primarily serve and support their member companies, and programs funded by national governments typically aim to give a competitive advantage to the home country.

5.1 Swedish Pulp and Paper Research Institute (STFI)

Closed-loop pulp and paper production is one of the five major research projects that the Swedish Pulp and Paper Research Institute (STFI) is conducting in 2000 to 2002. The others are impulse technology, mechanical pulp for surface stable printing papers, fiber as a building block, and optimal fiber utilization. A major research project at STFI spans several competence areas and has a number of sub-projects directed toward the project's goal.

STFI is situated in Stockholm, has approximately 230 employees (130 with degrees), and has been in operation for more than 50 years. Its annual budget is about 210 million SEK (US$23 million), and is derived from pulp and paper company members, governments, and foundations. STFI is the main contractor for the Ecocyclic Pulp Mill Research Program.

5.1.1 *The Ecocyclic Pulp Mill (KAM) Research Program*

The Ecocyclic Pulp Mill Research Program (or Kretsloppsanpassad massafabrik in Swedish, thus KAM) is financed by the Swedish Foundation for Environmental Research (MISTRA).

MISTRA was established in January 1994 with capital funding of SEK 2.5 billion, deriving from the former Employee (wage earner) Investment Funds. MISTRA's funds are held in the form of Swedish and foreign shares and securities. The capital in December 2000 had grown to 4.5 billion SEK (approx. US$500 million). Using a portion of the income earned, MISTRA funds a large number of research programs characterized by a strategic and environmental focus. MISTRA is the largest funding source for environmental research in Sweden. From 1994 to 2000, 800 million SEK (US$85 million) was disbursed. MISTRA's budget for activities in 1998 was SEK 300 million. Article 1 of MISTRA's statutes provides the basis for MISTRA's activities:

> The Foundation shall promote the development of strong research environments of the highest international class with importance for Sweden's future competitiveness. The research shall be of importance for finding solutions to important environmental problems and for a sustainable development of society. Opportunities for achieving industrial applications shall be taken advantage of.

The Ecocyclic Pulp Mill Research Program, officially titled "The Potential of Pulp and Paper Production as an Energy Producing and Truly Ecocyclic Process," has had two funding cycles to date: KAM1 from July 1996 to December 1999 and KAM2 from January 2000 to December 2002. Funding in these two cycles was 90 million SEK from MISTRA and business sector support of 18 million SEK (or a total of about US$11.5 million). MISTRA funding is normally obtained for programs of eight to ten years' duration, and is awarded in three yearly allocations. Although subject to review, it may be expected that the Ecocyclic Pulp Mill Research Program will receive an additional allocation.

The program descriptions herein are drawn from the MISTRA website (www.mistra-research.se, June 22, 1999), the Ecocyclic mill website (www.stfi.se/mistra/kamprog.htm), and review papers by the program director and administrator, Peter Axegård and Birgit Backlund (presented at the 1999 New Available Technologies Conference in Stockholm, June 1999). The illustrations are from the Ecocyclic Pulp Mill Research Program website and annual reports.

> The Potential of Pulp and Paper Production as an Energy Producing and Truly Ecocyclic Process. The aim of this programme is to solve problems relating to emissions and the energy potential of pulp mills. It is inspired by a well-founded vision: to create an entirely 'closed-cycle' system for the production of high-quality paper products which makes efficient use of the energy potential of the biomass.

Axegård and Backlund introduced the goals and main area of research in a 1999 review paper. In order to promote the development of the 2020 BKPM, MISTRA decided in 1996 to fund the Ecocyclic Pulp Mill. The aim of the program is to propose environmentally optimal solutions for greatly increased closure of the kraft pulp process, making efficient utilization of the energy potential of the biomass possible, and to establish extensive and successful research education in the field. The research is done at six Swedish colleges and universities within various disciplines, ensuring interdisciplinary research work, in close cooperation with STFI (Swedish Pulp and Paper Research Institute), the Swedish forestry industry, and its supplier companies. A total of about 60 researchers are engaged in the Program (Axegård and Backlund 1999).

The Program comprises the following projects:

- process chemistry
- separation processes
- Energy potential
- delignification
- material and energy balances
- process dynamics
- synthesis
- flow of mineral substances to and from the forest.

The "process chemistry" and "separation processes" projects focus on how to handle substances, which are disruptive to the process, and which are concentrated as the result of greater systems closure, to avoid problems such as scaling and chemical decomposition, increased energy consumption, and lower product quality. "Energy potential" studies the way in which energy flows can be optimally utilized. "Delignification" is aimed at increasing selective delignification in the cooking and oxygen stages. Success in this area significantly increases the potential for closing the remaining processes in the mill and increasing energy yield. "Process dynamics" studies dynamic processes in sub-processes and the system as a whole in a firmly closed feedback system. "Flow of mineral substances to and from the forest" studies the flow of minerals from forest soil to the pulp mill and the restrictions on returning minerals to forest soil. The new knowledge developed is linked by synthesis work covering the entire Program, which is carried out within the "synthesis," "material and energy balances," and "energy potential" projects. Within the synthesis work, consideration is given to outside factors as well as economy and product properties. In turn, the synthesis work provides feedback to the project work (Axegård and Backlund 1999).

The Ecocyclic Pulp Mill Research Program is helping coordinate and raise the visibility of Swedish closed-cycle research. The individual research projects are generally well conceived and executed, with technical publications and conference presentations on areas important in improving resource and energy efficiency. With a focus on education, there are also many younger professionals being trained in this area, and this will help ensure the longevity and application of the ideas being developed.

In addition to work involved in the overall program coordination and research synthesis, there are 33 projects identified for 2000 to 2002. These are in the areas (as above) of chemistry, separation processes, energy potential, delignification, material and energy balances, and flow of mineral substances to and from the forest (STFI 2002).

Chemistry projects include projects on complex formation between metal ions and fiber surfaces, inorganic precipitates in the bleach plant, process chemistry of trace elements, distribution of non-process elements between fiber and solution, interplay between “good and “bad” metal ions, and analysis of process-disturbing organic substances.

Separation process projects include electrodialysis, membrane bioreactor, crystallization and precipitation in acidic streams, separation of organic substances from alkaline streams, NPE (non-process elements) kidney before cooking, condensate purification, separation of residue products, separation of lignin from black liquor, and separation and use of sulfur-free lignin.

Energy potential projects include energy efficient closure, overall energy analysis, potential for generating a surplus of biomass fuel, and resources-efficient utilization of biomass fuel surplus.

Delignification projects include selective modified kraft delignification, high yield/extremely low sulfidity cooking, extended oxygen delignification, residual lignin characterization–bleachability, carbohydrate reactions during cooking and bleaching, and the importance of acid bleaching stages.

Material and energy balance projects include mass and energy balances, controllability analysis, and dynamic modeling.

Mineral balances include elemental flows from wood to solid by-products, reactivity of residual products, system analysis of recycling potential, and handling of waste products.

The reporting and research output, much of it in Swedish, is primarily focused on the Swedish industry. Through early 2002, there have been 70 published articles and reports, 84 oral presentations, posters, pre-prints, proceedings and internal reports, and 18 doctoral and licentiate dissertations. The research areas are comprehensive, and publications cover topics in pulping, bleaching, scaling and non-process element (i.e., barium, magnesium, calcium, manganese) behavior and control, energy balances and heat integration, separation and treatment processes including membrane processes, ion exchange, and mill process configurations.

STFI has produced a 250-page summary report of the first three years of research (KAM1). The reader is referred to this summary report and individual project reports and publications for more information. These are generally available for purchase from STFI, and are referenced on the project website (www.stfi.se/mistra/kamprog.htm).

STFI also has funding and involvement in other process closure “network” projects under a European Union initiative (the “COST” program) titled “Towards zero liquid effluent in papermaking.” This program ends in September 2002, and contact persons at STFI are Tom Lindström, Peter Axegård, and Lars Sjöström. A second EU project is “Separation methods for closed-loop technology in bleached kraft manufacture.” There is also a Nordic Industrial Fund study on “Keys to closing the bleaching loops." These projects are discussed under the activities of the Finnish Pulp and Paper Research Institute (KCL). STFI and KCL collaborate in areas of chemical pulp and mechanical pulp (STFI/KCL press release, 16 Feb 2000); the major driving force is the current globalization of the pulp and paper industry and its supplier industries, and synergistic and complementary effects are expected.

5.2 Finnish Pulp and Paper Research Institute (KCL)

KCL is an independent pulp and paper testing and research laboratory. It has a staff of 340 (150 professional staff). It was funded in 1999 by member subscriptions (45%), contract research (44%), and public funding from Finnish, Nordic, and European Union sources (11%). The basic (member) research is funded by four companies: the Metsäliitto-Group; Myllykoski (25% owned by Metsäliitto and a paper manufacturer); Stora Enso; and UPM-Kymmene. Unlike much of the world's research community, KCL had a stable funding base during the 1990s, and from 1994 to 1999 increased in staff from 300 to 340.

"Closure of water circulations" was one of the four process related priority research areas for KCL in 1999. A number of research projects in process closure were funded from both Finland (through TEKES – The National Technology as outlined in the next section) and the European Union. Two of these projects are highlighted here.

5.2.1 *Keys to Closing the Bleaching Loops*

This project ran from January 1, 1998, to December 31, 2000, with a budget of 9 million FIM (US$5 million) and was financed by the Nordic Industrial Fund. Participating organizations were KCL, STFI (Swedish Pulp and paper Research Institute), HUT (Helsinki University of Technology), AA (Abo Academia – a Swedish-speaking University in Turku/Abo, southern Finland), KTH (Royal Institute of Technology-Stockholm), and PFI (the Norwegian Forest Research Institute).

The aim was to explore the questions: Are there any disturbing substances attached to the fibers? What kinds of depolymerization products are formed? What happens to the extractives?

There were four main areas of research:

- fiber properties at KCL, STFI, and HUT
- depolymerization products at STFI, KTH, and KCL
- extractives at PFI, STFI, AA, and KCL
- research materials and simulation at KCL and STFI.

5.2.2 *Separation Methods for Closed-Loop Technology in Bleached Kraft Pulp Manufacture*

This project ran from December 1, 1996, to November 30, 1999, with a budget of 2 million Euros (US$2 million) and had partial funding (47%) from the European Union under the "FAIR" program (FAIR-CT96-1360).

Pulp production using closed-loop technology should be characterized as follows: despite the fact that large amount of material (mainly wood) is brought to the mill, no harmful substances are released from the mill either with the final product or as effluents. This project aims at strengthening the scientific and technological base needed for the development and use of necessary separation methods, "kidneys," to make closed-loop pulp production possible.

The Project is divided into four research tasks:

- reuse of condensates from black liquor evaporation
- handling of accumulating inorganic elements
- handling of accumulated organic substances
- process integration of separation methods

Reuse of black liquor evaporation condensates studies are being led by Klaus Niemelä at the Finnish Pulp and Paper Research Institute, and initial reporting suggested that the use of condensates (even the cleanest fraction) for washing after different bleaching stages carries a risk that odor will transfer into pulps or that some other undesired effects will occur. The effect of condensates on smell and other pulp properties (such as brightness, kappa number, and viscosity) has been investigated. The studies have been accompanied by detailed GC/MS analyses of the condensate impurities. The results show that at least the cleanest condensate fractions should be potentially useful at several bleaching stages without interfering with pulp properties or causing increased odor levels in pulps.

Handling of acidic and neutral bleach plant filtrates studies are being led by Per Tomani at Swedish Pulp and Paper Research Institute (per.tomani@stfi.se). Initial reporting indicated that a pilot-scale evaporator had been built and used for evaporating several ECF and TCF bleach filtrates from both hardwood and softwood bleaching processes. Before evaporation, the pH of the filtrates was adjusted to pH 6 to 10. Filtrates were investigated after concentration to a dissolved solids content of 2 to 25%. No scaling problems have occurred during the evaporations. NPE removal of the filtrates in a separate "kidney" based on chemical precipitation was studied before and after evaporation. Precipitation also occurs during the evaporation. According to the results, it is more beneficial to remove the NPEs after rather than before evaporation. In addition, separation properties of the precipitated material obtained during evaporation can be improved by applying the suggested "kidney."

The accumulation of organic substances studies are led by Michel Pichon at Centre Technique du Papier in France (michel.pichon@ctp.inpg.fr). Initial results showed that coagulation/flocculation or ultra/nanofiltration technologies can be considered as an available kidney to remove organic materials from alkaline bleach plant effluents. The use of mineral nanofiltration membranes for treating alkaline bleach filtrates is being tested at Orelis at a laboratory scale and then in a French kraft pulp mill. Operating conditions taking into account fouling and cleaning will be defined, and cost calculations will be made.

Torbjörn Jönsson at Swedish Pulp and Paper Research Institute (torbjorn.jonsson@stfi.se) is leading the activity to build a simulation model for TCF and ECF bleach plants. These were constructed in WinGEMS. These models were to be used to investigate high degree of closure, with and without integrated "kidneys" developed in the other projects (reuse of evaporator condensates and nanofiltration work).

Details on the individual projects above is from the Swedish Pulp and Paper Research Institute website (STFI 2) at www.stfi.se/documents/research/coopnet/euproj2.htm (December 2, 1999).

5.3 Finland – TEKES Supported Research

TEKES, the National Technology Agency, finances research and development (R&D) projects of companies and universities in Finland. Funds are awarded from the state budget via the Ministry of Trade and Industry. TEKES is the main financing organization for R&D in Finland. TEKES 2001 funding was 387 million Euros: 146 million for university and research institutes and 160 million for industrial R&D grants (81 million in R&D loans). A major mechanism for funding is through technology programs. Technology programs are used to promote development in specific sectors of technology or industry and to pass on results of the research work to businesses in an efficient way. During 2002, a total of about 45 extensive national technology programs were underway. In 2000, TEKES provided €157 million to finance technology programs. Each technology program has a steering group, a coordinator, and a responsible person at TEKES. The durations of the programs range from three to five years; their volumes range from €6 million to hundreds of millions of euros. TEKES usually finances about half of the costs of programs; the other half comes from participating companies. Finland has been using this funding model (technology programs) since the mid-1980s. Current technology programs in the forest sector are the value added wood chain, wood energy, and a third with some forest sector contribution, the process integration technology program. Little research scheduled in these programs relates directly to effluent minimization (www.tekes.fi).

Completed programs include the Water Management in Paper Making program (also known as CACTUS) which ran from 1996 to 2000 and focused on ways to reduce water consumption primarily in wood-containing papermaking, as detailed in Section 5.3.1, and the first phase of the Forest Cluster Research Program (or Wood Wisdom) that ran from 1998 to 2001 with €33 million of funding. The Forest Cluster Research Program was primarily concerned with "market-driven use of Finnish wood raw material in optimal wood and paper products." This included better production economics from forest to end product, including mechanical wood processing and pulp and paper production. The pulp and paper research of possible interest to process closure focused on selective bleaching, mass transfer (in pulping), and fiber engineering (property retention, modification and development, and fitness for purpose). Phase two of the Wood Wisdom program started in 2002 and focuses on the material science of wood.

5.3.1 *Water Management in Paper Making (1996 to 2000)*

The Water Management in Papermaking technology program was designed to create knowledge on control of raw materials, water, and energy that can be used at paper mills to achieve

- substantial reductions in raw water consumption
- at least present paper quality and runnability
- more effective utilization of chemicals
- efficient utilization of energy
- cleaner processes and better process management
- smaller environmental impacts on water, air, and soil.

The program was executed from 1996 to 2000. Research focused on wood-containing paper grades, and thus included paper machines, integrated mechanical pulp mills with debarking and chip preparation, and associated utilities such as effluent treatment and power/bark boilers. It did not specifically address chemical pulp mills.

The technology program covered the following research areas:

- characterization and analysis of circulating waters
- chemicals and their performance
- purification of circulating waters and their classification
- management of circulating water dynamics
- management of water and energy balances at paper mills
- final placement of concentrates.

The program consisted of about 50 research and industrial projects. The budget of the program was FIM 130 million (US$22 million), of which TEKES supplied FIM 70 million. Participants included the University of Jyväskylä, the Finnish Pulp and Paper Research Institute (KCL), Lappeenranta University of Technology, Tampere University of Technology, Helsinki University of Technology, VTT Automation, VTT Biotechnology and Food Research, VTT Chemical Technology, VTT Energy and Åbo Akademi. Companies supporting and participating were Ahlstrom Machinery Oy, Enso Oyj, Hadwaco Oy, Kemira Chemicals Oy, Metsä-Serla Oyj, Myllykoski Oy, Raisio Chemicals Oy, UPM-Kymmene Oyj, and Valmet Oyj.

Technical reporting was through seminars and publications. Because the program goals are to benefit Finnish industry, most material is in Finnish. The academic publication lists include 79 papers and publications and 24 theses, mostly in English. A program goal was to generate substantial knowledge on control of raw materials, water, and energy and to make this accessible. The project also maintains an “expert network” for water management in papermaking. Typically, six to eight experts are listed in the following areas: washing techniques of mechanical pulps; membrane filtration; evaporation techniques; oxidation techniques; enzyme technologies; final treatment of concentrates; process integration; wet end process technology; measurement techniques; and process chemistry.

The program’s final evaluation highlighted benefits in the increase in knowledge in the industry and in understanding problems associated with closures of water systems. It commented on the detail provided in specifying causal relations. It altered the knowledge base of companies that participated, proving some old assumptions wrong while supporting others. There was some comment that the academic nature of many of the publications has made interpretation of results difficult, and that some of the research was primarily continuation of existing themes. Most researchers saw that the best results were still to come, however the steering committee (influenced strongly by equipment manufacturers) decided to continue funding two projects which were concept studies for lean water papermaking processes (concentrating on pulp washing and concentration of wash filtrates) and development of the national design environment for papermaking processes (simulation products).

Selected summary research results, primarily drawn from the final project report (Edelmann 2001), are presented herein. They are in the areas of separation and treatment techniques, measurements, process chemistry, modeling and process simulation, and final utilization of concentrates.

Separation and treatment techniques

Projects in this area focused on the use of membrane processes as kidneys, the influence of pretreatment on membrane performance, and the influence of washing of mechanical pulps on extractive content (Ylhäisi 2001).

Ultrafiltration performed well on fiber, colloids, and solids; however, most of the COD and conductivity remain in the permeate. The ultrafiltered water costs about 2.5 FIM/m^3 and the flux is around 400 l/m^{2}h (60 to 70^{o}C). Nanofiltration technology is not yet commercial for papermaking applications and even in the best cases has a flux rate about one-third that of ultrafiltration. Nanofiltered water is suitable for universal reuse as it is, in principle, as clean as fresh water.

Extractives concentrate in white water circuits as effluent flows are reduced. Biological treatment removes a large part of the extractives, most of the lignins, and about 50% of the fatty acids. The sugars are also split up into smaller molar masses. Aerobic biological processes are sufficient for pretreatment for nanofiltration. With enzyme treatment, the filterability of the concentrate can be increased. Wet oxidation can also reduce the amount of extractives, but process costs are high. With ozonation the amounts of extractives can be reduced and all microbes removed, but it is also a fairly expensive process.

Measuring techniques

When the water use on paper machines is decreased, more advanced wet end control is required. Higher concentrations of detrimental substances cause unstable physico-chemical conditions, where even small variations, for example in pH or temperature, can disturb the chemical balance in the wet end and cause retention variations or deposition incidents. A fundamental knowledge of the detrimental substances, and their continuous monitoring, is important for understanding process disturbances and their control. Five projects developed techniques for laboratory analysis and on-line measurements in paper mills (Holmbom 2001)

In the project "Analytical techniques for paper machine process waters" at the University of Jyväskylä, several new laboratory techniques for characterization of dissolved and colloidal substances were tested. The objective was to develop routine and convenient tests to characterize detrimental substances (mainly carbohydrates and extractives), which will eventually cause runnability and paper quality problems. Process waters from TMP mills and paper mills were analyzed and characterized (in effect chemically "fingerprinted"). Molecular weight distributions (MWDs) of carbohydrates were made by high performance size-exclusion chromatography (HPSEC). Pitch components, such as resin and fatty acids, were analyzed by liquid chromatography-mass spectrometry (LC/MS) using electrospray ionization (ESI) and flow injection analysis (FIA) techniques. Characteristic molecular weight distribution curves of carbohydrates for each sample were obtained within 15 minutes. The FIA fingerprints presented all ionized compounds, including pitch components. In this case, the analysis time was only two minutes per sample. Both the FIA and HPSEC methods seem to have potential to be developed as on-line analytical techniques for determining detrimental substances in papermaking process waters (Knuutinen et al. 2001).

In a project at Åbo Akademi University, a commercial flow cytometry (FCM) instrument was tested for on-line measurement of colloidal particles in paper mill process waters. A system for automatic pre-treatment of water samples was developed. It was demonstrated that the FCM measuring system can work in paper mill conditions and is able to perform continuous measurement of colloidal particles of different types (Holmbom 2001).

In two projects, at KCL and VTT, capillary electrophoresis (CE) techniques were developed for on-line measurements in pulp and paper mills. In the VTT project, CE methods were developed for determination of 10 anions and 8 cations. The repeatability of the method was good. In the KCL project, a commercial CE instrument was modified to perform on-line measurements. In a follow-up joint KCL and VTT project, successful test runs were performed in a kraft pulp mill. (Holmbom 2001).

Attempts were made at VTT to develop a broadband impedance measurement technique for process water applications. However, already during the first year it was found that the technique was not very promising and the project was terminated. (Holmbom 2001).

Process chemistry

The objective of projects in this area is better understanding and management of chemical states in a paper machine when the water cycle is closed (Koivo 2001). These projects were completed:

Accumulation of detrimental substances in white water closure and their effect on paper quality was studied by the Laboratory of Paper Technology of HUT.

Modeling of dynamic chemical state of paper machine unit operations was studied at the Control Engineering Laboratory of HUT and VTT Chemical Technology. Modeling of chemical state concentrated on the chemistry of calcium carbonate and a multi-component model was created for it.

The results of modeling and simulation were applied to production processes. This was an important beginning in process chemistry modeling.

Effect of concentration of white water on the microbial growth in paper machine was studied by the Control Engineering Laboratory of HUT with VTT Biotechnology and Food Research. The results of laboratory experiments on microbial growth showed that closing the white water cycle might enhance the growth of some microbes and prohibit the growth of others. The prediction of effects on microbial flora in paper machines was found to be complicated. New advanced methods to quantify and identify the microbes, especially the harmful species, are needed for more thorough studies and modeling of the microbiology of a paper machine.

Minimization of fresh water consumption for the paper chemicals was studied at the Paper Technology Laboratory of LUT. Freshwater is usually used for the dilution and feed of papermaking wet end chemicals to ensure effective and stable performance of these chemicals. Water used for the dilution of chemicals can be 10 to 15% of the total machine consumption of fresh water, particularly if several wet end chemicals are used. Most water is used for dilution and feed of the retention aid and web sizing starch. Anionic substances act as detrimental impurities in the feed water of the cationic polyelectrolytes. They can greatly reduce the efficiency of the retention aids or even make them ineffective. The results showed that circulation water (clear filtrate) of many paper machines can be used as dilution water of cationic polyacrylamides (PAM) without any deterioration in the efficiency of these chemicals, as long as the amount of dilution water is low. If greater quantities of dilution water or dilution water with higher anionic concentrations are used, efficiency can be significantly reduced. The harmful effect is dependent on the dosage concentration and the charge density of polyelectrolyte. Low cationic polyacrylamide tolerates more impurities in dilution and feed water than medium cationic PAM without any loss of its efficiency. Closure of the water circuits in the papermaking process leads to the enrichment of anionic components in the circulation water, especially if mechanical pulp is used. This will have an effect on the feasibility of circulation water for the dilution of chemicals. Highly contaminated water can be treated for use through chemical pre-treatment with highly cationic polyelectrolyte (poly-DADMAC) before microfiltration. The quality of feed water required is dependent on the concentration and the charge density of polyelectrolyte, and lower quality dilution water can be used if the contact time between dilution and mixing into the furnish is short.

The dilution of AKD size with fine paper machine clear filtrate did not have any deterious effect on sizing. In fact, the sizing effect was better when clear filtrate was used. The solid material in clear filtrate breaks down the colloidal size droplets so the reaction between fiber and size occurs faster. However, clear filtrate without solid material can reduce the sizing effect of AKD size (Ryösö and Manner 2001).

Disturbances in closed water cycle papermaking. A pilot-scale device was used to study the build-up of detrimental substances from peroxide-bleached TMP under both acidic and neutral pH, corresponding to increasing levels of process closure. The time needed to stabilize closure depended on the papermaking chemistry and the pulps used.

In a neutral run with calcium carbonate as filler, TOC, cationic demand, and the concentration of lipophilic extractives in the white water increased until equilibrium was reached. When water usage decreased, chemical oxygen consumption of cycled water, concentrations of colloidal lignin, and charge increased. Mechanical pulp washing lowered the anionic trash content to less than half compared with the use of TMP filtrate. The influence of pulp washing was not as pronounced on pitch (lipophilic extractives) components as on anionic trash. In neutral run, the concentrations of lipophilic extractives (resin) in cycled water stabilized to the same process characteristic level, in spite of starting the run with filtrate or with clean water. During acidic simulation with alum, adsorption of lipophilic components onto pulp was greater than during neutral simulation with calcium carbonate. In neutral run, their concentrations were practically constant, independent of water usage. The wet end simulator can also be utilized in dynamic papermaking simulations studying pH control and the efficiency of chemicals for example fixing agents (Nyblom 2001).

Multi-staged strategy of pH control in the production of printing paper. The clearest, immediately usable results have been obtained in the development of multi-phase pH control strategy and modeling calcium carbonate behavior. The results have been utilized at UPM-Kymmene Kaipola and Keräyskuitu plants. The three-phase pH simulator developed in the project can be tailored to other mills. The utilization of results in the other projects is expected to occur over time (Ylén 2001).

Modeling and process simulation

Prior to the CACTUS program, process simulation was not widely used by pulp and paper operating companies in Finland. It was used primarily as a research and academic tool. Simulation can be useful to predict and resolve operating difficulties due to increased process closure. The modeling and process simulation projects had as a goal to develop “a comprehensive pulp and paper simulation environment” for research and development and “models and tools that could be used to analyze the impact of new technologies and process concepts on the use of energy and on the environmental load of an integrated paper mill,” and to “disseminate the use of developed simulation tools so that the use in the industry would continue after the end of the technology program.” The simulator developed by VTT Energy (Balans) was used as a basis for development, and unit operations useful for paper machines, heat recovery, TMP, and water and effluent treatment were developed. Unit operations have embedded typical pulp and paper operating characteristics, as well as specialized chemistry, for example, for the behavior of dissolved and colloidal material. The dissolved and colloidal material models use special reactors with sorption data. Balans has a link with Excel software, enabling easy visualization and reporting of modeled data. The simulator was used in the research program for several projects, including:

1. Modeling dissolved and colloidal material in papermaking (involved sampling and modeling of three papermachines and two TMP lines)
2. Development of a general mill model, particularly suitable for heat efficiency (pinch) studies, in which the impact of different combinations of new or existing technologies can be tested for their impact on energy use, process effects, and effluent flows
3. Development of a full energy and material balance model for a Best Available Technology (BAT) lightweight coated mill, including water treatment, effluent treatment, TMP and papermaking, debarking, and steam and power production; impacts of various water saving and process closure technologies including evaporation, ultrafiltration, and nanofiltration were assessed using this model
4. Looking at the impact of enzymatic treatments on selected process streams including a lipase reactor to treat the process waters coming from refining and pulp slurry

   Lipase enzyme breaks down mainly triglycerides in extractives. A pectinase reactor after bleaching was also evaluated. Pectinases are enzymes affecting various chemical bonds in pectins, cutting them to oligomers. Intact pectins cause significant cationic demand in papermaking. A mannanase reactor for the concentrated filtrates of a bleaching plant was also evaluated. Mannanase hydrolyzes glucomannan, causing viscosity in the filtrates which complicates evaporation or filtration.

At the end of 2000, 43 commercial licenses and several mill production lines had been modeled. Balans is in use in pulp and paper companies, chemical suppliers, and education institutes. It has also formed the basis for a dynamic simulator, the "Advanced Paper Mill Simulator," marketed by VTT Automation (Kaijaluoto 2001).

Final utilization of concentrates

Projects in this area looked at characterization of effluent and concentrates from TMP, CTMP, and debarking effluents, primarily using pilot tests in forced circulation evaporators. Viscosity modification of concentrated effluent using enzymes was evaluated and appears promising. Characterization of reject material from pilot membrane processes in the paper machine was also conducted. Different options for oxidation/combustion of concentrates were considered, for example, co-combustion with bark or at another facility (kraft mill), separate combustion (e.g., in a rotary kiln/smelter), wet oxidation, gasification and pyrolsis options, and the Conox process (thermal oxidation in pure oxygen atmosphere, 10 bar pressure). Separate studies also considered sludge drying using waste heat and drum and belt technology, to enable sludge currently landfilled to be combusted.

Some of the questions asked by operating companies were :

- Could the costs of separate treatment be acceptably low in some situations?
- Is the Conox process more competitive than the more traditional alternatives?
- Can the economics of the treatment process be improved by pretreatment or intermediate treatment?
- Is there any new competitive method for oxidizing concentrate?
- Are there any other approaches to resolving this problem?

The main steps in the separate treatment process are further concentration and combustion. Intermediate steps could be enzyme treatment or drying. Traditional concentration by evaporation can attain a dry solids level of 40 to 60%. By lowering the viscosity of the concentrate, e.g., with enzyme treatment, it should be possible to achieve even higher dry solids levels. Further concentration will nearly always be required if the concentrate is transported to another location for co-combustion.

An alternative low effluent TMP mill configuration was developed late in the project, in which bleaching effluent was separately treated from pulping and washing filtrates (not bought back to the TMP refining stage). This meant that pulping filtrates were essentially salt free. These salt free filtrates were also characterized, and if concentrated appear to be suitable for co-combustion in a bark boiler (McKeough 2001; Ylhäisi 2001).

5.4 Pulp and Paper Research Institute of Canada

The Pulp and Paper Research Institute of Canada (Paprican) is a not-for-profit research and educational institute that has been operating for more than 75 years. It has 31 member companies (dues-paying pulp and paper producing companies) and three associate members. A total of 340 scientists, engineers, and support staff work in three locations: research laboratories and pilot plant facilities in Pointe-Claire (Montreal), Quebec, and Vancouver, British Columbia; and a technology transfer center in Prince George, British Columbia. Its research program is planned in partnership with its members, and the current focus is to address critical technical needs in product quality and value, cost competitiveness, and environment. A feature of the environmental research is to "achieve a minimum-impact mill through progressive system closure, improved waste management, and understanding potential environmental impact." Paprican has a large, active research program in process closure, encompassing chemical and mechanical pulp mills and paper and board machines (www.paprican.ca, 16 August 2002).

Paprican's current research program in system closure dates from 1996, but had as a precursor work done in the early 1990s.

5.4.1 *Paprican – Simons Towards Closed-Cycle Kraft Program (1991 to 1995)*

In the late 1980s and early 1990s there were challenges to permitting of new kraft mills. These challenges led to the cancellation of the proposed Wesleyvale greenfield kraft mill in Tasmania, Australia, and delay in the Alberta-Pacific pulp mill project in northern Alberta, Canada. During this period H.A. Simons provided engineering for nine major kraft mill projects (including six greenfield mills) and assisted clients in working through permitting issues on a number of these.

In 1991 Paprican received funding support from the Canadian government for a program concerned with "Engineering Modifications Towards the Closed-Cycle Kraft Mill"; H.A. Simons and four operating companies received funding for a companion program "Towards Engineering Feasibility of the Closed-Cycle Kraft Mill."

Specific objectives of the Simons portion of the study included:

1. Develop and validate computer simulation models of kraft pulp mills, incorporating behavior relevant to reducing bleach plant effluent volumes, specifically components which may be difficult to remove from the recovery system, which contribute to scale formation, accelerate corrosion, and cause other operating problems.
2. Use simulations, and the information and expertise gained in developing them, to guide and assess laboratory and mill data gathered in this and the complementary Paprican research project.
3. Identify and provide technically plausible methods of reducing bleach plant effluent flows. This included impact on overall mill water, energy, and chemical balances; availability of suitable equipment; assessment of operability issues; and implications on capital and operating costs.

Multi-component simulation models based on extensive mill sampling and modeling of the four partner mills were developed. Three typical mill arrangements were chosen for closed-cycle design development; modeling, initial process design, and capital and operating cost estimates were prepared for these mill arrangements. Simons completed work under this program in early 1995.

Paprican conducted experiments in filtrate recycle to causticizing, brownstock washing (and characterization of interactions between fiber and non-process elements), corrosion issues, separation technologies, and a number of supporting literature reviews and process studies. They also supported the mill sampling program.

Simons also completed closed-cycle research (focused on eucalypt mills) for the Australian Government (Galloway et al. 1994) and the Pulp and Paper Research Organization of New Zealand (on mills operating with *pinus radiata*). At the end of the 1990s Simons partnered with Louisiana-Pacific in U.S. Department of Energy-supported work at the Samoa pulp mill (Jaegel, Gleadow, and Bruce 1999) in California.

Simons used the skill, knowledge, and tools developed in these research programs for subsequent process development and engineering, including work on the Champion (now Blue Ridge Paper) BFR demonstration at Canton, North Carolina, and other client installations which incorporate the ability to recycle bleaching filtrates.

Paprican went on to develop a wider-ranging research initiative in progressive system closure.

5.4.2 *Paprican Research In System Closure*

With the support of its member and allied companies as well as the Canadian and Québec governments, Paprican is currently leading the Canadian effort in system closure research. In late 1996, Paprican announced a program involving the expansion of the pilot plant facilities to develop systems closure technologies. The recently constructed pilot plant facilities include an expanded bleaching pilot plant, a new pilot paper machine, a new mechanical pulping pilot plant, and several separations pilot units for evaluating system closure concepts. Paprican's program in progressive system closure incorporates research, development, and mill implementation activities in the areas of water use reduction, improved prediction and design tools, dynamics and control, corrosion control, chemical separation and regeneration, removal and/or control of wood extractives, chemical additives, energy cost reduction, and management of solid and gaseous emissions. Paleologou et al. (2001) provide a good overview of Paprican's current activities in system closure. Voss (2000) also compiled research summaries of Paprican's environmental research.

Paprican has current activities in system closure for mechanical pulp mills, chemical pulp mills, and paper machines. Two benchmark criteria are applied to options investigated for system closure at Paprican. First, they should result in lower costs compared with current systems; second, they should help maintain or improve final product quality (Ramamurthy and Wearing 1998).

Kraft pulping process developments include improving oxygen delignification with peroxymonsulfate, use of laccase and other enzyme systems, development of efficient chelation and metal management strategies, integration of ozone stages in a low effluent fiberline, improvements in bleached pulp yield, ECF bleaching with reduced reliance on chlorine dioxide, and methods for hexenuronic acid removal (Voss 2000).

The recently rebuilt bleaching pilot plant includes washing with filtrate recovery and can run chlorine dioxide, peroxide, ozone, and single and double oxygen bleaching stages, complete with filtrate recycle (Paleologou et al. 2001).

Paprican has developed steady state and dynamic simulation capability including pulp washer control, modeling of bleaching chemical consumptions, and dynamic modeling of bleaching upset conditions.

Results from laboratory bleaching studies examining the effects of EO filtrate recycle on bleaching chemical consumption for a typical interior British Columbia softwood kraft mill are shown herein. This study examined the effects and differences of various mill filtrates and process streams (O_2, D0, EOP, condensate) as carryover on the D0 bleaching performance and estimated increases in chlorine dioxide consumption due to the carryover. Table 5.1 compares the estimated increases in the ClO_2 consumption caused by 10 kg COD carryover of each process stream (Paleologou et al. 2001).

Using a CADSIM Plus computer simulation of the fiberline of a member company mill, Paprican researchers estimated chlorine dioxide consumption on the basis of D0E brightness and compared the results with mill data obtained during EOP filtrate recycle trials. The components modeled in the simulation were water, fiber, dissolved inorganic and organic solids, and temperature. During the recycle trial, 100% of the contaminated hot water used in the second post-oxygen washer as wash water was replaced by EOP filtrate, representing about 47% of the alkaline (EOP) filtrate flow. Figure 5.1 shows the chlorine dioxide consumption for the pulp entering the D0 tower before and during the trial and compares these results to those obtained from the computer simulation. The simulation correctly predicted the observed increase in ClO_2 consumption. The increased demand for chlorine dioxide by the pulp entering the bleach plant was due both to the higher kappa number of the pulp and to the alkaline solids carried into the D0 stage as a result of filtrate recycle. For the base case, organic solids consumed 23.7% of the applied chlorine dioxide, whereas during EOP filtrate recycle this value rose to 27.5% (Paleologou et al. 2001).

Table 5.1 Estimated Increases in ClO_2 Demand for the D0 Stage at 10 kg COD/ton of Carryover

Source of Carryover	Calculated Increases in ClO_2 Demand: Based on D0E kappa number kg ClO_2/ton (in percentage)	Calculated Increases in ClO_2 Demand: Based on D0E brightness, kg ClO_2/ton (in percentage)
O_2 filtrate	2.3 (15%)	2.7 (19%)
D0 filtrate	0.37 (2.4%)	1.6 (11%)
EOP filtrate	1.4 (9.0%)	1.5 (10%)
Evaporator condensate	1.4 (9.0%)	1.6 (11%)

SOURCE: Paleologou et al. 2001

Paprican has also been developing technologies to help balance recovery chemical makeup. Three are now close to commercialization. They use ion exchange technology for chlorine dioxide generator acid purification (GAP), recovery boiler precipitator dust purification (PDP), and liquor splitting. Laboratory and pilot plant work using membrane technologies has also been conducted (Paleologou et al. 2001; Ramamurthy and Wearing 1998).

Paprican researchers developed a new approach for the removal of extractives from various pulp and paper streams. A commercial-scale continuous centrifuge with an inclined disc stack was employed to separate and remove a substantial fraction of the extractives from kraft mill streams such as oxidative extraction filtrates and weak black liquor (Paleologou et al. 2001; Allen and Lapointe 1995).

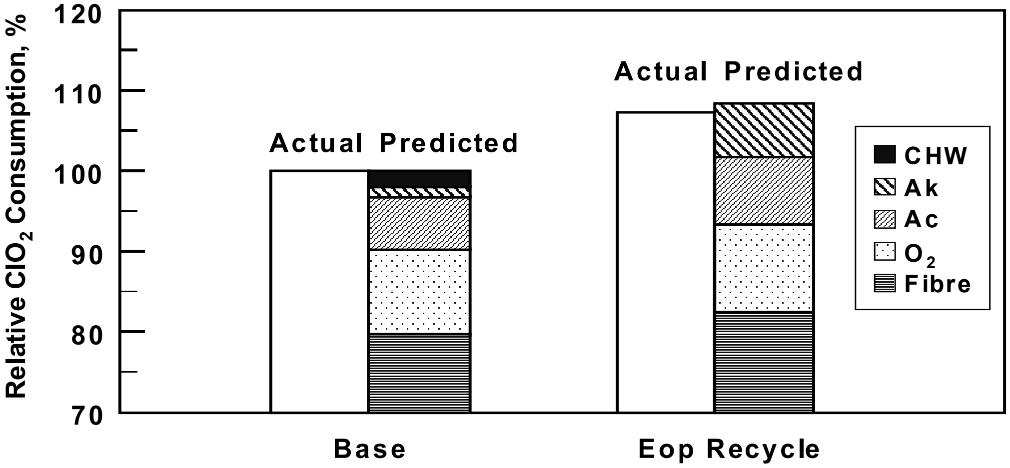


Figure 5.1 Chlorine Dioxide Consumption before and during EOP Filtrate Recycle Compared with Computer Simulation Results
[actual consumption for the base case was assigned the value 100%]
CHW = contaminated hot water organic solids; Ak = alkaline

Paper and board research includes:

- treatment and recovery options for paper machine additives, including pigmented coating materials; development of better retention and drainage aids, particularly for fine paper machines operating at high dissolved solids loadings
- development of techniques for suspended solids removal (a new process using sludge mat filtration for removal of effluent suspended solids was developed)
- steady state and dynamic models of fine paper machines to develop better control and understanding of the impacts of breaks, grade changes, and broke and white water management strategies.

Improvements in biological treatment (to facilitate recycle and reduce non-compliant emissions) have been made.

Paprican has also developed chemical analysis techniques, including an analytical technique for metals management incorporating ion chromatography, capillary electrophoresis, and inductively coupled plasma spectroscopy, combined with more rapid and efficient methods for solubilizing metals (Voss 2000).

Paprican's research has developed valuable insights into corrosion prevention strategies, particularly as process changes are made toward system closure, for both paper machine and kraft systems. Paprican has investigated and developed suitable microbial management strategies for paper machines operating under increased closure, resulting in increased white water nutrient levels.

Paprican has also been active in energy cost reduction, with some project overlap with system closure. The energy requirements of system closure technologies can be significant, but can be reduced with good process integration (e.g., use of waste heat for filtrate evaporation).

Paprican's significant investment in pilot plant facilities, membership support, and continuing partial funding from the Quebec and Canadian governments ensure that research and application in progressive system closure will continue to be a significant activity at Paprican.

5.5 U.S. Department of Energy – Agenda 2020

In 1994, the American Forest and Paper Association (AF&PA) formed a collaborative research partnership with the U.S. Department of Energy Office of Industrial Technologies (DOE OIT). This partnership, known as Agenda 2020, utilizes a competitive grants, peer-reviewed process and focuses on cost-shared research. Through Agenda 2020, a consortium of research institutions, industry, and national laboratories are developing new technologies, processes, and measurements to manufacture products more efficiently and cost-effectively while reducing environmental impacts of operations and maximizing efficient use and reuse of resources.

To meet these objectives, Agenda 2020 has identified six technology focus areas for collaborative research efforts. These six task groups represent a broad cross section of the forest products industry:

- sustainable forest management
- environmental performance
- energy performance
- improved capital effectiveness
- recycling
- sensors and control

Within each of these areas, research pathways to focus research in areas of critical importance have been developed (AF&PA 1999).

Technologies important for process closure are specifically referred to in two sections of the Agenda 2020 implementation plan: Pathway for Achieving Environmental Goals Relating to Process Alternatives Consistent with Pollution Prevention, and Pathway for Addressing Industry Capital Effectiveness Needs Related to System and Process Technologies. In this plan, each pathway comprises five sequential components: Agenda 2020 focus areas, areas of continuing research, future research directions, knowledge and tools, and results realized.

5.5.1 *Pollution Prevention*

In the Pathway for Achieving Environmental Goals Relating to Process Alternatives Consistent with Pollution Prevention, a 2020 focus area is on non-process elements. Continuing research includes technologies for treating effluent for reuse and methods for organic/inorganic separation. Future research directions include alternative pulping, bleaching and liquor processing technologies, and bleach effluent recycle technologies. Bleach effluent recycle technologies examples given are supercritical water oxidation, membranes, evaporation-crystallization, freeze crystallization, and precipitator management. The overall result to be realized is "improved understanding of fundamentals that allow early introduction of new, lower cost technologies and processes," with an end result of "improved global competitiveness by impacting the nature of technologies used to manufacture pulp and paper/wood products" (AF&PA 1999).

5.5.2 *Capital Effectiveness*

In the Pathway for Addressing Industry Capital Effectiveness Needs Related to System and Process Technologies, one of the topics for future research is minimum-impact manufacturing with a focus on reduced water usage and multimedia closure. The overall result from the capital effectiveness pathway, however, is stated as "improved global competitiveness by impacting the nature of technologies used to manufacture pulp and paper/wood products."

Most of the research projects supported under Agenda 2020 have an energy efficiency and industry competitiveness focus. A relatively small (less than 10%) focus of Agenda 2020 could be described as system closure/minimum effluent manufacturing. There is considerable overlap in other Agenda 2020 areas, including initiatives in black liquor gasification, improvements in energy efficiency, research into scale and corrosion issues, and basic process improvements in delignification (pulping and oxygen delignification) and bleaching.

Most of the research funded is from 1998 and is ongoing.

Control of the accumulation of non-process elements in pulp mills with bleach filtrate reuse – Oregon State University

In this study, the process behavior of metal ions in the brown and bleach fiberlines was investigated using a chemical equilibrium approach. This included sorption on pulp, formation of complexes with dissolved organic material, and formation and precipitation of inorganic materials (including silicates, sulfates, carbonates, phosphates, chlorides, hydroxides, and a number of double salts). Modeling data were verified and compared with laboratory and field (mill sampling) data. Data researched, collated, estimated, or otherwise developed include stability constants, equilibrium sorption constants, some kinetic sorption coefficients, and thermodynamic property and activity coefficients for components of interest (Frederick et al. 2000).

The model developed could be used for predicting the distribution of metal non-process elements in the aqueous streams of kraft pulp mills. It can predict the equilibrium absorption of metals on pulp fibers and the distribution of metals between wood pulp fibers and dissolved species in the presence or absence of metal binding organic liquids. In combination with advanced chemical equilibrium software (such as NAELS or OLI Systems Software, or ChemSage), it can also predict the absence of inorganic phase precipitates.

The model predicted formation of sodium salts within 10% for Na_2CO_3-Na_2SO_4-water and within 3% for Na_2CO_3-Na_2SO_4-NaOH-water.

For Ba, Ca, K, Mg, Mn, Na and Zn sorbed simultaneously in brownstock, the model predicted values 50 to 250% of observed values 90% of the time. The Non Aqueous Equilibrium Limited Solver (NAELS) developed at Oregon State University was used for mill process stream simulation. An interesting observation from this work was that the total number of divalent species present in the mill fiberline was much too great to be accommodated by sorption on the pulp and complexation with dissolved organic material. The authors conclude that this material is also in fine inorganic precipitates, which primarily partition into the pulp streams in brownstock washing.

Trace element solubility prediction for Ba and Mn in green liquor was within 25 to 110% of measured values. The model was 130-fold too low for Ca in green liquor and 30-fold too low for Ca in white liquor. Mn in green liquor was 50-fold too high, and in white liquor it was in the 50 to 120% range. Magnesium was predicted to be too low by a factor of about 1,000,000 in both green and white liquor (Frederick et al. 2000).

Area still to be addressed include:

- obtaining data to evaluate and improve the predictive capability for NPE data in pulp mill streams
- adding data on aluminum and silica, dissolved organic material from ECF bleaching
- looking at the effect of temperature on the stability of complexes of metals with soluble organic matter
- characterizing the acid-base behavior of the carboxylic acid and phenolic hydroxide groups on wood pulp fibers

Recycling of water in bleached kraft pulp mills using electrodialysis

Researchers at the Institute of Paper Science and Technology in Atlanta, Georgia, and Argonne National Laboratory in Argonne, Illinois, cooperated on a program to test the use of electrodialysis on acidic bleach filtrates as a possible filter (or kidney) to facilitate reuse of the filtrate through removal of deleterious materials.

Bleach plant acidic filtrates from three bleach plants (including Blue Ridge Paper in Canton, North Carolina) were run in a laboratory electrodialytic stack using commercial Neosepta™ membranes for 2.5 to 4.6 hour runs. Two ECF filtrates were run for 50 and 100 hours without evidence of membrane fouling.

Across a range of experiments, electrodialysis rejected: organic material 75 to 88%; manganese 85 to 98%; iron 15 to 70%; zinc 86 to 96%; aluminum 2 to 30%; strontium 92 to 98%; barium 55 to 98%; sodium 20 to 50%; magnesium 88 to 98%; potassium 55 to 75%; calcium 92 to 98%; sulfate 3 to 30%; phosphate about 1%; fluoride 12 to 55%; chloride 65 to 70%; and nitrate 40 to 80%.

Simple economics based on treating 3 m^3/t of acidic bleach filtrate in a 1000 tpd mill, and similar current density to that in the laboratory experiments give a membrane area of 810 m^2, a cost for the membrane stack of about US$500,000, and low electricity cost ($200/day) (Tsai et al. 1999). Typical acidic bleach plant flow is about 20 m^3/t, so considerable flow reduction measures would need to be implemented, and an engineered system would require much more equipment than the electrodialysis stack alone, possibly including fiber filters such as those used ahead of the ion exchange units at Canton.

A new freeze concentration process for minimum effluent process in bleached pulp – Tufts University

Qian and Botsaris (2001) revisited freeze crystallization as a means of recovering fresh water from bleach filtrates. They reported on laboratory-scale (25 and 120 liters) freeze crystallization experiments using super cooling and ultrasonic nucleation for crystal growth. Laboratory work used water, a synthetic 2.5 wt % glucose solution and mixed salt solution, and a glucose salt solution mixture (used to simulate combined acid and alkaline bleach effluent.) Planned work on ice crystal separation and washing was not conducted.

Estimated costs (half capital, half operating) were about $60 to $70/ADt for treating 5 m^3/t in a 600 t/d facility. The freeze train was made up of three crystallizers, so there was little further economy of scale if commercially applied (Qian and Botsaris 2001).

It would appear from the final project report that the researchers did not address the reasons for commercial failure of freeze crystallization at Louisiana-Pacific in Chetwynd as outlined in section 4.1.2.

5.5.3 *Select Agenda 2020 Projects of Possible Interest for Process Closure*

Many ongoing Agenda 2020-supported projects have potential application or use in looking at minimum impact mills.

Water Recycling/Removal Using Temperature-Sensitive Hydrogels – Auburn University

Auburn University researchers will study at least six different polymer-based hydrogels to determine if they can be used in the pulp and paper industry. For example, Auburn's polyhydrogel (N-isopropylacrylamide, PNIPA) absorbs a large quantity of water at 25°C but releases the water if the temperature is raised to 35°C. Larger molecules and solid particles are rejected by the small pores of the hydrogel and become concentrated in the exit stream. Since temperatures of in-process water streams and spent pulping liquor in pulping mills are typically 50 to 60°C and at a pH of 4 to 11, the promising hydrogels must be redesigned for use in these temperature and pH ranges. The research will focus on three pulp and paper processes:

1. white water clarification, during which a hydrogel will be used to remove organic and inorganic dissolved and colloidal materials present after deinking mixed paper; the purified water remaining can be reused in mill processes
2. oxygen delignification filtrate concentration, in which low levels of lignin and alkali present after the first stage of pulp bleaching are separated for different purposes, with the lignin-rich portion sent to the evaporator and the alkali-rich portion used in brownstock washing; their separation with a hydrogel will improve the performance and energy efficiency of using this filtrate
3. black liquor spill concentration, to collect black-liquor spills from various sources in the mill and to use a hydrogel to concentrate the lignin.

Non-process element removal (NPE) using functionalized monolayers on mesoporous supports, Pacific Northwest National Laboratory, Mobil Technology, Weyerhaeuser Technology Center

Electrically switched ion exchange (ESIX) for the separation of potassium and chloride to enhance water recycle opportunities in pulp mills, Pacific Northwest National Laboratory, University of Idaho, Weyerhaeuser Company, Parsons Corporation, Institute of Paper Science and Technology, National Council for Air and Stream Improvement, Inc. (NCASI)

Control of soluble scale fouling in high solids black liquor concentrators, Institute of Paper Science and Technology, Georgia Institute of Technology, Oak Ridge National Laboratory

Growth and property development of convection-pass deposits in recovery boilers, Sandia National Laboratory, Babcock & Wilcox, Institute of Paper Science and Technology, University of Toronto

Use of borate autocausticizing to supplement lime kiln and causticing capacities, Babcock & Wilcox, Fort James Corporation, International Paper Company, U.S. Borax, and Western Michigan University

Black liquor steam reforming/pulsed combustion, Manufacturing & Technology Conversion International, Inc. (MTCI), ThermoChem, Inc., Stone & Webster, Weyerhaeuser Company

There are additional projects of interest, for example in better understanding the recovery boiler (combustion, loading, and liquor properties), black liquor gasification, alternative pulping and bleaching chemical supply, liquor splitting, alternative pulping and bleach technologies (use of laccase for biobleaching, short sequence bleaching), and others.

6.0 SUMMARY

During the 1990s there was a great deal of activity devoted to developing and implementing technologies designed to reduce the wastewater loads from pulp mills. Much of this work was focused on lowering chlorinated organic matter levels in bleached kraft mill effluents; however, important process closure technologies were also implemented in sulfite and mechanical pulp mills.

Process closure methods include dry debarking, effective liquor spill control, closed screening and washing, condensate stripping, and other methods for minimizing loss of wood-derived organic matter. Extended and oxygen delignification can significantly reduce bleach plant effluent loads from kraft mills that have adopted either or both of these now widely practiced technologies. Several new mills were built in the 1990s, many of which were designed to be top performers both financially and environmentally. This was achieved primarily by the use of state-of-the-art process designs and equipment.

Bleach plants have seen the biggest change, with chlorine being replaced by chlorine dioxide, oxygen, peroxide, ozone, and other agents. Most mills adopted elemental chlorine free (ECF) bleaching where chlorine dioxide plays a critical role. A few mills have totally chlorine free (TCF) bleach plants. Reuse of filtrates within the bleach plant has enabled mills to reduce effluent volumes substantially.

These developments have in turn brought renewed interest in closed-cycle bleaching. A number of mills practice recovery of alkaline filtrates via the post-oxygen or brownstock washers. A handful of mills are recovering acidic bleaching filtrates, and at least two linerboard mills have small bleach plants for topliner production from which all of the filtrates are recycled to associated baseliner brownstock systems.

Much of the technology development associated with kraft mill bleach plant closure has focused on mitigating undesirable consequences such as scale deposits, corrosion, loss of bleaching efficiency, increased evaporative loads, reduced production capacity and loss of operational flexibility. These issues have caused many companies to reconsider the role of process closure in minimizing effluent impacts. In many cases, the optimal solution has been found to be a high degree of closure coupled with external biological treatment of the remaining process effluent. Examples include SCA Östrand, M-Real Husum, Södra Cell Mörrum and Värö, and Metsä-Botnia Rauma. There are no bleach plants at papergrade bleached kraft mills operating fully closed on a full time basis.

The 1990s also brought zero effluent bleached chemi-thermomechanical pulp (BCTMP) mills, the most notable example of which is the Millar Western mill in Meadow Lake, Saskatchewan, Canada. This mill incorporates water and chemical recovery systems involving physical and biological treatment, evaporation, concentration, and combustion of the concentrated organics. Distillates are reused in the pulp line.

A number of research programs with a focus on minimum impact and sustainable, energy efficient pulp and paper manufacturing were undertaken in the 1990s, some of which continue today. Many of these are funded at national levels, and typically involve national pulp and paper research institutes. Notable programs include Sweden's Ecocyclic Mill Research Program (KAM), U.S. Department of Energy's Agenda 2020, Finland's TEKES, and Progressive Systems Closure at the Pulp and Paper Research Institute of Canada.

REFERENCES

Ahlenius, L., Svensson, G., Liden, J., and Lindeberg, O. 1996. MoDo's experiences in closed loop bleaching. In *1996 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta, GA: Tappi Press.

Allen, L., and Lapointe, C. 1995. Centrifugal Cleaning of Pulp and Paper Process Liquids. U.S. Patent No. 5,468,396. November 21, 1995.

Alliance for Environmental Technology. 2002. Trends in world bleached chemical pulp production 1990-2000. http://aet.org/reports/market/index.html.

Allison, R.W., and Wrathall, S.H. 1998. Optimising two-stage oxygen delignification: Effects of interstage washing and metal ion control. In *Proceedings of the 1998 International Pulp Bleaching Conference.* Atlanta, GA: Tappi Press.

Amendola, G.A., Vice, K., and McCubbin, N. 1996. Design considerations for cost-effective kraft and sulfite pulping liquor spill control systems. In *1996 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta: Tappi Press.

American Forest and Paper Association (AF&PA). 1999. *Agenda 2020: The Path Forward: An Implementation Plan*. Washington, DC: American Forest and Paper Association.

Andrews, E. 1989. RDH kraft pulping to extend delignification, decrease effluent, and improve productivity and pulp properties. *Tappi Journal* 72(11):55-61.

Andritz Ahlstrom. 2001. Evaporation in Water Loop Closure. Kraft Mill Business Brochure 3, March 2001.

Annergren, G.E., Boman, M.G., and Sandström, P.E. 1996. Towards the closed cycle bleach plant. In *5th International Conference on Newly Available Techniques*, Stockholm, Sweden.

Annola, A.L., Hynninen, P., and Henricson, K. 1995. Effect of condensate use on bleaching. *Paperi Ja Puu* 77(3).

Anon. 1977. Effluent-free bleached kraft mill is pioneered at Great Lakes Paper. *Pulp & Paper* 51(3):94-99.

Anon. 1994. Newslines. *Pulp and Paper International* 36 (11): 17.

Anon. 2002. Tembec gets Chetwynd. *Pulp & Paper Canada* 103 (12):III.

Arac, C. 1998. Part 1 "Zero Liquid Effluent Discharge" at Louisiana-Pacific Canada's Chetwynd Pulp Mill. *CPPA PaperWeek.*

Axegård, P. 1988. Improvement of bleach plant effluent by cutting back on Cl_2. In *1988 International Pulp Bleaching Conference Proceedings*. Atlanta, GA: Tappi Press.

Axegård P. and Backlund, B. 1999. The ecocyclic pulp mill - A vision or future reality? In *SPCI '99 6th International Conference on New Available Technologies Proceedings*, Stockholm, Sweden.

Axegård, P., Carey, J., Folke, J., Gleadow, P., Gullichsen, J., Pryke, D., Reeve, D.W., Swan, B., and Uloth, V. 1997. Minimum-impact mills: Issues and challenges. In *1997 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta, GA: Tappi Press.

Backlund, E.A. 1984. Extended delignification of softwood kraft pulp in a continuous digester. *Tappi Journal*. 67(11).

Basta, J., Holtinger, L., and Hook, J. 1991. Controlling the profile of metals in the pulp before hydrogen peroxide treatment. In *Proceedings of the 6th International Symposium on Wood and Pulping Chemistry*, Melbourne, Australia.

Berry, R.M. 1993. Technological strategies for meeting the chlorine issue. In *Proceedings of the 2nd Market Pulp Conference: "Industry at the Cross Roads"*, Vancouver, BC.

Bérubé, P.R., and Hall, E.R. 2000. Removal of methanol from evaporator condensate using a high temperature membrane bioreactor: Determination of optimal operating temperature and system costs. *Pulp & Paper Canada* 101(3).

Björk, D. 1994. The closed-cycle mill – Impact on kraft recovery, mill experience (in Swedish); In *Swedish Recovery Boiler Conference Proceedings*, Stockholm, Sweden.

Björklund, P., Valuer, S., and Lawler, D. 1999. On-site sulphuric acid production at a kraft pulp mill. In *1999 6th International Conference on New Available Technologies Proceedings*, Stockholm, Sweden, June 1-4. p. 535-539.

Blackwell, B.R., MacKay, W.B., Murray, F.E., and Oldham, W.K. 1979. Review of kraft foul condensates, sources, quantities, chemical composition, and environmental effects. *Tappi Journal* 62(10).

Blain, T.J. 1993. Anthraquinone pulping: Fifteen years later. *Tappi Journal* 76(3):137.

Blue Ridge Paper Company. 1999. Canton Mill NPDES Permit Report. December 1999.

Böhmer, V.J. 1992. Recovery of water and chemicals from pulp bleach effluents. Master's thesis, Water Utilization, The University of Pretoria.

Böhmer, V.J., and Davies, C.J. 1993. The closed mill experience and opportunities. Paper presented at the 46th Annual Seminar of the Tappi Pacific Section, Seattle, WA, September 16-17.

Böhmer, V.J, Mitchell, D., van der Westhuizen. N, and Leske, A. 1991. A bleach-chemicals recovery process. In *Proceedings of the International Pulp Bleaching Conference.* SPCI, Stockholm, Sweden.

Bokström, M., and Nordén, S. 1998. Extended oxygen delignification. In *Proceedings of the 1998 International Pulp Bleaching Conference*, Helsinki, Finland.

Broman and Lindberg. 1996. Working toward ecobalance. In *1997 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta, GA: Tappi Press.

Canovas, R.V., and Maples, G.E. 1995. Bleach plant closure with the BFR™ process. In *1995 Non-chlorine Bleaching Conference Proceedings*.

Carlsson, E. 2003. Personal communication.

Caron, J.R., and Williams, L.D. 1996. Design and integration of the bleach filtrate recycle process. In *1996 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta, GA: Tappi Press.

Carter, D.N, and Gleadow, P.L. 1994. In *Water Use Reduction in the Pulp and Paper Industry 1994*. Montreal: Canadian Pulp and Paper Association.

Carter, D.N., McKenzie, D.G., Johnson, A.P., and Idner, K. 1997. Performance parameters of oxygen delignification. *Tappi Journal* 80(10):111-117.

Chirat, C., and Lachenal, D. 1994. Minimizing pulp degradation during totally chlorine free bleaching sequences including an ozone stage. In *1994 International Pulp Bleaching Conference Papers*. Montreal: Canadian Pulp and Paper Association.

Coghill, R.S., Dahl, S., and Thurley, D. 1995. Wastewater management at Australian newsprint mills, Albury: Responding to community expectations. *Appita Journal* 48(1):26-30.

Cook, R.A. 1991. A bleaching process for minimizing AOX discharges. *Appita Journal* 44(3).

Courchene, C.E. 1998. The tried, the true and the new – Getting more pulp from chips. In *Proceedings of the 1998 Tappi 'breaking the pulp yield barrier' symposium*, Atlanta, GA.

Dahl, S. 2003. Personal email communication email. 1/30/2003.

Danielsson, G., and Håkansson, M. 1996. Steam stripping of contaminated condensates from the black liquor evaporation plants. In *Proceedings Tappi 1996 Minimum Effluent Mill Symposium*. Atlanta: Tappi Press.

Devic, M., Pralus, C., and Suty, H. 1998. Stabilizers in pressurized peroxide bleaching of kraft pulps. In *Proceedings of the 1998 International Pulp Bleaching Conference*, Helsinki, Finland.

Dillner, B. 1993a. Isothermal cooking (ITC) - lower kappa number and easy-bleaching pulp. *Svensk Papperstidning* 96 (2): 22-24.

Dillner, B. 1993b. Isothermal cooking. *International Papermaker* 56 (2): 35-36.

Dubé, M., McLean, R., MacLatchy, D., and Savage, P. 2000. Reverse osmosis treatment: Effects on effluent quality. *Pulp & Paper Canada* 101:8.

duManoir, J.R., Hamilton, J., Senior, D.J., Bernier, R.L., Grant, J.E., Moser, L.E., and Dubelsten, P. 1991. Biobleaching of kraft pulp with cellulase-free xylanase. In *Preprints, 1991 International Pulp Bleaching Conference*. Stockholm.

Earl, P.F., and Reeve, D.W. 1989. Chlorinated organic matter in bleached chemical pulp production: Part III – The effect of chlorination stage variables on chlorinated organic matter in effluent. In *1989 TAPPI Environmental Conference Proceedings*. Atlanta, GA: Tappi Press.

Edelmann, K. 2001. CACTUS: *Water management in papermaking: Final report*. Finland: TEKES. Summary available at http://www.tekes.fi/julkaisut/cactus_final/. Accessed 11/18/2002.

Eklund, H. 1995. ECF vs. TCF - A time to assess and a time to act. Keynote address 1995 Non-chlorine bleaching conference.

EKONO, Inc. 1998. *Pulping and bleaching technologies: a comparative literature review of TCF and ECF pulp manufacture*. Washington, DC: American Forest and Paper Association.

Emilsson, K., Håkansson, M., and Danielsson, G. 1997. Extended stripping and usage of evaporator condensates at Varo Mill, Sweden. *1997 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta: Tappi Press.

Engström, J.G.J., and Hjort, L.A. 1995. Black liquor impregnation and ITC™ isothermal cooking. In *Proceedings of the 1995 ATCP meeting*, Chile.

Engström, J.G.J., and Hjort, L.A. 1996. Important parameters for elimination of inhomogeneity in kraft pulping. In *Proceedings of the 1996 SPCI meeting*, Stockholm, Sweden.

Environment Australia. 2001. Eco-efficiency and cleaner production case studies – Cleaner production – Closing the water loops - Norse Skog Paper Mills (Australia) Ltd.

Erickson, R.L., Zacher, D., and DeCrease, D. 1996. Minimum-impact manufacturing - Creating sustainable value for our shareholders. *1996 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta, GA: Tappi Press.

Ernerfeldt, B., Södersten, P-A., Eriksson, H-O., and Näsholm, A-S. 1999. Bleach plant presses reduce chemical consumption. *6th International Conference on Newly Available Technologies*, Stockholm, Sweden.

European Integrated Pollution Prevention and Control (IPPC) Bureau. 2000. *Integrated Pollution Prevention and Control (IPPC) Draft Reference Document on Best Available Techniques in the Pulp and Paper Industry*. Draft dated February 2000. Seville, Spain: European Commission.

Farrell, R.L., Viikari, L., and Senior, D. 1996. Section IV: The technology of pulp bleaching, Chapter 7: Enzyme treatments of pulp. In *Pulp Bleaching Principles and Practices*. Dence and Reeve (eds.). Atlanta, GA: Tappi Press.

Ferguson, K. 1996. Champion moves toward closure with BFR startup at Canton, N.C. *Pulp & Paper* 70:4.

Finnish BAT Report. 1997. *Finnish background report for the EC documentation of best available techniques for pulp and paper industry*. The Finnish Environment 96, Ministry of Environment in Finland, Edita Ltd., Helsinki.

Fosberg, T, Lloyd, I., and Kelland, C. 1993. Case study: CRMP effluent recycling system at the Australian Forest Industries Myrtleford Mill. In *47th Appita Annual General Conference*.

Frederick, W.J. Jr, Rudie, A.W., Schmidl, G.W., Sinquefeld, S. A., Rorrer, G.L., Laver, M.L., Yantasee, W., and Ming, D. 2000. *Control of the accumulation of non-process elements in pulp mills with bleach filtrate recycle: A chemical equilibrium approach to predicting the partitioning of metals in pulp mill streams*. DOE/ID/13441. Washington DC: Energy Efficiency and Renewable Energy, U.S. Department of Energy.

Fredström, C., Idner, K., and C. Hastings, 1992, Current state-of-the-art of EO, EP and EPO technologies. In *1992 Non-Chlorine Bleaching Conference Proceedings*, Hilton Head, SC.

Fujisaki, A., Tateishi, M., Baba, Y., and Arakawa, Y. 2001. Plugging prevention of recovery boiler by character improvement of the ash which used potassium removal equipment (part II). In *Proceedings of the International Chemical Recovery Conference*. Pulp and Paper Technical Association of Canada.

Fuller, W.S. 1983. In *Pulp and Paper Manufacture Volume 1, Properties of Fibrous Raw Materials and Their Preparation for Pulping, 3rd ed*. Kocurek, M.J., and Stevens, F. (eds.). Montreal: Technical Section Canadian Pulp and Paper Association.

Galloway L., Gleadow, P., Hastings, C., and Lownertz, P. 1994. *Closed-cycle technologies for bleached kraft pulp mills*. Technical Report No 7. Canberra, Australia: National Pulp Mills Research Program, CSIRO.

Gerbasi, B., Stuart, P.R., Arsnault, F., and Zaloum, R. 1993. Techno-economic assessment of several closed cycle technology alternatives for an existing TMP-Newsprint mill. *Pulp & Paper Canada* 94(12):123-128.

Gleadow, P. 1999. Personal notes from mill site visits to Metsä-Rauma Pulp Mill, UPM Pietsaari (WisaForest), and KCL, Helsinki.

Gosling, C.D., Lamparter, R.A., and Barna, B.A. 1981. Wet oxidation of paper mill wastes to recover filler materials. *Tappi* 64(2):75-79.

Griggs, B. 1997. *Union Camp route to bleach plant closure*. CPPA TECH'97 Process Closure Course, Montreal, Canada.

Hakulinen, R., and Salkinoja-Salonen, M.S. 1981. An anaerobic fluidized bed reactor for the treatment of industrial waste water containing chlorophenols. In *Biological fluidized bed treatment of waster and wastewater*. Copper and Atkinson (eds.). Ellis Harwood Ltd.

Hauptmann, E.G., Gairns, S.A., and Modell, M. 1994. Strategies for treating mixtures of bleach plant and waste water treatment sludges by supercritical water oxidation. In *Proceedings of the 1994 CPPA Annual Meeting*, Montreal, January 25-28. p. B71-B77.

Headley, R.L., 1996. Pulp cooking developments focus on fiber yield, lower chemical use. *Pulp and Paper* 70(10) 49-57.

Herschmiller, D.W. 1997. A new process for pulping with high initial hydrosulphide concentration. *Tappi Journal* 80(3):115-121.

Histed, J.A., and Nicolle, F.M.A. 1973. Water reuse and recycle in kraft bleacheries. *Pulp Paper Canada* 74(12):T386.

Hoddenbagh, J.M.A., Wilfing, K., Miller, K., Hardman, D., Tran, H., and Bair, C. 2001. Borate autocausticizing – A cost effective technology. In *International Chemical Recovery Conference*, oral proceedings. p. 336-345.

Höglund, O., Pehu-Lehtonen, K., and Hjort, A. 1994. Kraft pulping with black liquor pre-treatment. In *Proceedinsg of 1994 Tappi Pulping Conference*, San Diego, California.

Holmbom, B. 2001. Research projects on measuring techniques. *Water management in papermaking – Final report* (English version). Helsinki, Finland: Åbo Akademi, TEKES. bholmbom@aton.abo.fi.

Hupa, M., Backman, R., Skrifvars, B.-J., and Hyöty, P. 1990. The influence of chlorides on the fireside behavior in the recovery boiler. *Tappi Journal* 73(6).

Ichinose, L.Y. 1983. Midtec takes the high ground. *PIMA* July:23-25.

Jaegel, A. 1997. Cluster Rules compliance and advanced technologies – Mill applications and operating experience. In *Proceedings of the 1997 Minimum Effluent Mills Symposium*, San Francisco.

Jaegel, A., Gleadow, P., and Bruce, D. 1999. *Energy Use Characterization At Louisiana-Pacific, Samoa, Ca.* Johan Gullichsen Colloquim, Helsinki, Finland.

Janka, K., Backman, R., and Wallén, J. 2001. Prediction of dust content and properties in kraft recovery boilers: Comparison of theory and experimental results. In *Proceedings of the International Chemical Recovery Conference*. Pulp and Paper Technical Association of Canada.

Jemaa, N., Paleologou, M., Thompson, R., Richardson, B., Brown, C., and Sheedy, M. 1999. Chloride removal from the kraft recovery boiler ESP dust using the precipitator dust purification (PDP) system. *Pulp & Paper Canada* 100:7.

Johnson, A.P. 1992. Worldwide survey of oxygen bleach plants: Examples and case studies. Presentation at the Non-chlorine bleaching conference, Hilton Head, SC.

Johnson A.P., Herschmiller D., Trepte, R., Santos, C., Palmiere, M., and Purdie D. 1996. AlPac and Bahia Sul – Current design and environmental performance of ECF in the Americas. In *Proceedings of the 1996 International Pulp Bleaching Conference*, Washington.

Joseph, J.C., and White, D.E. 1996. The use of modeling in mill closure activities. In *1996 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta: Tappi Press.

Kaijaluoto, S. 2001. VTT Energy, 2001. *Water management in papermaking – Final report* (English Version). Helsinki, Finland: TEKES.

Katz, G. 1993. Anthraquinone and anthraquinone polysulfide pulping for extended digester delignification. In *Proceedings 1993 Tappi Pulping Conference*. Atlanta, GA: Tappi Press.

Knorr, P., and Fromson, D.A. 1993. World-scale production of BCTMP with zero liquid effluent. In *Proceedings of the EUCEPA 18th Mechanical Pulping Conference*, Oslo.

Knuutinen, J., Alén, R., Pallonen, R., Kauko, S., Harjula, P., Kilpinen J., and Jurvela, V. 2001. Analysis of paper mill process waters (Pappro). *Water management in papermaking – Final report* (English version). Helsinki, Finland: TEKES. Jyväskylä, Finland: University of Jyväskylä Department of Chemistry.

Koivo, H. 2001. Summary of process chemistry research area. *Water management in papermaking – Final report* (English version). Helsinki, Finland: TEKES.

Krotscheck, A., Sixta, H., Peter, W., and Gerzar, T. 1995. The effects of bleach plant closure: Laboratory bleaching plus computer simulation versus actual mill data. In *International Non Chlorine Bleaching Conference Proceedings*, Orlando, Florida.

Kubes, G.J., Lunn, R., and Keskin, A. 1994. *Wet air oxidation of waste effluent from thermo-mechanical pulping*. Miscellaneous Report - MR285. Pointe Claire, QC: Pulp and Paper Research Institute of Canada.

La Fond, J.F., Verloop, A., and Walsh, A.R. 1992. Engineering analysis of recovery boiler superheater corrosion. *Tappi Journal* 75(6):101-106.

Lange, H.B., Bick, M.P., McIlroy, R.A., and Foster, E.P. 1975. Chemical recovery and sulfur control using the Tampella recovery process. *Tappi Journal 58:2*.

Ledbetter, R., Pettit, R.R., Jaegel, A.F., Beer, C., Marcoccia, B., Gu, Y., and Edwards, L. 1997. Impact of falling film, cross-flow green liquor filtration and modified cooking on mill closure at Louisiana Pacific, Samoa Mill. In *1997 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta, GA: Tappi Press.

Liebergott, N. 1994. Peracid delignification and bleaching. In *1994 Tappi Pulping Conference Proceedings*. Atlanta, GA: Tappi Press.

Liebergott, N., and van Lierop, B. 1981. Ozone delignification of black spruce and hardwood, kraft-anthraquinone, and soda-anthraquinone pulps. *Tappi Journal* 64(6):95

Liebergott, N., van Lierop, B., Nolin, A., Faubert, M., and Laflamme, J. 1991. Modifying the bleaching process to decrease AOX formation. *Pulp and Paper Canada* 92:3.

Lindberg, H., Engdahl, H., and Puumalinen, R. 1994. Strategies for metal removal control in closed cycle mills. In *1994 Proceedings International Pulp Bleaching Conference*. Montreal: CPPA.

Lindström, L-A. 1990. Oxygen stage design and performance. In *1990 Tappi Bleach Plant Operations Short Course*, Hilton Head, SC.

Lindström, L-A., and Norden, S. 1990. Efficient post oxygen washing – Crucial for low bleach plant emissions. *Appita Journal*, 43(5):373.

Marcoccia, B.S., Laakso, R., and McClain, G. 1996. Lo-Solids™ pulping: Principles and applications. *Tappi Journal* 79(6).

Maples, G.M., Ambady, R., Caron, J.R., Stratton, S.C., and Vega Canovas, R.E. 1994. BFR™: A new process toward bleach plant closure. *Tappi Journal* 77(11).

McCubbin, N. 1997. Effect of oxygen delignification on overall pulp yield. In *Proceedings of the International Emerging Technologies Conference*, Orlando, Florida.

McCubbin, N. 2001a. Spill control: Assessing your situation. *Solutions!* 84(11).

McCubbin, N. 2001b. Spill control, part II: Reducing spills. *Solutions!* 84(12).

McDonough, T.J. 1990. Oxygen delignification. In *1990 Tappi Bleach Plant Operations Short Course*, Hilton Head, SC.

McKeough, P. 2001. Final treatment of concentrates. VTT Energy. *Water management in papermaking – Final report* (English version). Helsinki, Finland: TEKES.

Metsä-Botnia. 2001. Environmental report Botnia 2001.

Millar Western. 2003. Information provided by mill staff.

Minday, A.M., Burke, M.A., Reid, D.W., and Brown, C.J. 1997. An overview of various strategies for balancing saltcake, chloride and potassium levels in an ECF kraft mill. In *1997 Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta, GA: Tappi Press.

MoDo. 1996. MoDo environmental report 1996. www.holmen.com/Pdf/miljo96_uk.pdf (November 2002).

MoDo. 1997. MoDo environmental report 1997. www.holmen.com/Pdf/miljo97_uk.pdf (November 2002).

MoDo. 1998. MoDo environmental report 1998. www.holmen.com/Pdf/miljo98_uk.pdf (November 2002).

Morin, R. 2002. Personal email communication. 12/19/2002.

Myreen, B. 1993. Recirculation of bleach plant waste liquors. In *Proceedings of the 1993 Tappi Environmental Conference*, Boston, MA.

National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). 1993. *Regression models to estimate adsorbable organic halide (AOX) levels in bleached kraft mill wastewaters*. Technical Bulletin No. 654. New York, NY: National Council of the Paper Industry for Air and Stream Improvement, Inc.

National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). 1998. *Membrane technology applications in the pulp and paper industry*. Technical Bulletin No. 763. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

Nevalainen, A. 1996. *Green liquor crystallization: A method to manage Na/S balance*. Technical seminar, Ahlström Machinery Group, Concepción, Chile, Dec. 4-6.

New South Wales Environmental Protection Agency (NSWEPA). 1995. SOE95: Industrial Activity: Environmental Conditions and Pressures Case Study: Australian Newsprint Mills.

Nordén, S., Reeves, R., and Dahl, M. 1992. Bleaching of extremely low kappa southern pine, cooked by the SuperBatch™ process. In *Proceedings of the 1992 Tappi Pulping Conference*, Boston, MA.

Nutt, W.E., Eachus, S.W., Griggs, B.F., and Pikulin, M.A. 1993. Development of an ozone bleaching process. *Tappi Journal* 76(3).

Nyblom, I. 2001. Disturbances in paper making of closed water cycle. *Water management in papermaking – Final report* (English version). Helsinki, Finland: TEKES.

Obrien, H. 1995. Swedes chase closed-mill but goal is not yet apparent. *Pulp & Paper International*, June.

Onysko, K.A., and Hall, E.R. 1993. Anaerobic membrane bioreactor treatment of segregated bleach plant wastewater. In *Proceedings of the 1993 Tappi Environmental Conference*, Boston, MA.

Paleologou, M., Mahmood, T., Voss R., and Berry R. 2001. Progressive system closure: A Canadian perspective. In *JAPAN TAPPI Annual Meeting and Pan Pacific Conference Proceedings*, International Session, Sendai, Japan.

Parker, W.J., Hall, E.R., and Farquahar, G.J. 1991. Dechlorination of segregated kraft mill bleach plant effluents in high rate anaerobic reactors. In *Proceedings of the 1991 Tappi Environmental Conference*, San Antonio, TX.

Pikka, O., Vesala, R., Vilpponen, A., Dahllöf, H., Germgärd, U., Norden, S., Bokström, Steffes, F., and Gullichsen, J. 1999. Chapter 9 – Bleaching applications. In *Chemical Pulping*, *Papermaking Science and Technology*, book 6A. Gullichsen, J. and Paulapuro, H. (eds.). Atlanta, GA: Tappi Press.

Pradt, L.A. 1972. Developments in wet air oxidation. *Chemical Engineering Progress* 75(8):72-77.

Qian R., and Botsaris G.D. 2001. *A new freeze concentration process for minimum effluent process in bleached pulp*. Final report, 08/01/1997 – 01/31/2000 R. March 2001. Work performed under Contract No. DE-FC07-97ID13534 for U.S. Department of Energy Assistant Secretary for Energy Efficiency and Renewable Energy, Washington, DC, by Tufts University, Medford, MA National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI), Northeast Regional Center.

Qiu, R., and Ferguson, J.F. 1987. Anaerobic/aerobic treatment of kraft pulping wastes. *Proceedings of the 1987 Tappi Environmental Conference*, Portland, OR.

Ramamurthy, P., and Wearing, J.T. 1998. System closure: A Canadian perspective. In *84th Annual Meeting, Technical Section CPPA Proceedings*, PAPTAC, Montreal.

Rampotas, C., Terelius, H., and Jansson K. 1996. The Netfloc System – The Tool to remove Extractives and NPE. In *Proceedings of the 1996 Minimum Effluent Mills Symposium*, Atlanta.

Rapson, W.H. 1967. The feasibility of recovery of bleach plant effluent to eliminate water pollution by kraft pulp mills. *Pulp & Paper Canada* 68(12): T635-T640.

Rapson, W.H. 1982. The status of kraft pulp bleaching. *Pulp & Paper Canada* 83(6).

Reeve, D.W. 1984. The effluent-free bleached kraft pulp mill – part XIII: The second fifteen years of development. *Pulp & Paper Canada* 85(2).

Reeve, D.W., Pryke, D.C., Lukes, J.A., Donovan, D.A., Valiquette, G., and Yemchuk, E.M. 1983. Chemical recovery in the closed cycle mill, part I: Superheater corrosion. *Pulp & Paper Canada* 84(1).

Reside, D. 1994. Water use reduction in mechanical pulp production. In *Water use reduction in the pulp and paper industry 1994 – A monograph*. Canada: Canadian Pulp and Paper Association.

Reside, D. A. 2001. Water use reduction in mechanical pulp production. In *Water use reduction in the pulp and paper industry - second edition.* Canada: Canadian Pulp and Paper Association

Riebel, P. 1998. Alberta-Pacific's environmental program leaves nothing to chance. *Pulp & Paper Canada* 99:4.

Ryham, R., and Lindberg, H. 1994. Chemical recovery technology for future fiber production. In *80th Annual Meeting Proceedings*, CPPA Technical Section.

Ryösö, K., and Manner, H. 2001. The feed of paper chemicals with impure dilution water. *Water management in papermaking – Final report* (English version). Helsinki, Finland: TEKES. Lappeenranta University of Technology, Chemical Technology, Laboratory of Paper Technology.

Reid, B., and Lozier, A.G. 1996. Retrospective of closed-cycle CTMP operations. In *Tappi Minimum Effluent Mills Symposium Proceedings*. Atlanta, GA: Tappi Press.

Rogers B., and Arac. C. 1997. Louisiana-Pacific Chetwynd Pulpmill – From freezing cold to boiling hot. *TECH 97 Process Closure Course*, April 1997, CPPA.

Salkinoja-Salonen, M.S., Valo, R., Apajalahti, J., Hakulinen, R., Silakoski, L., and Jaakkola, T. 1983. Biodegradation of chlorophenolic compounds in wastes from wood-processing industry. *Current Perspectives in Microbial Ecology, Third International Symposium Microbial Ecology*, M.J. Klug and C.A. Reddy (eds.). Michigan State University.

Santos, C.A., and Caldas, P.G. 1996. Bleaching plant operation and its environmental relationship at Bahia Sul - A mill case. In *1996 International Pulp Bleaching Conference Proceedings*. Atlanta, GA: Tappi Press.

Savolainen, R., Norborg, K., and Lindberg, H. 1998. A modern ECF bleaching concept: Experience and eco mill perspectives at Stora Skoghall. In *Proceedings of the 1998 International Pulp Bleaching Conference*, Helsinki, Finland.

Senior, D.J., and Hamilton, J. 1992. Xylanase treatment for the bleaching of softwood kraft pulps: The effect of chlorine dioxide substitution. In *1992 Tappi Pulping Conference Proceedings*. Atlanta, GA: Tappi.

Shivgulam, N., Barham, D, and Rapson W.H. 1979. Sodium, chloride, potassium: Their effects on kraft smelt. *Pulp and Paper Canada* 80(9):T282-T285.

Södra. 1998. 1998 Environmental report. http://www.sodra.com/mediaservices/. 1999.

Södra. 1999. 1999 Environmental report. http://www.sodra.com/mediaservices/. 2000.

Södra. 2001. 1999 Environmental report. http://www.sodra.com/mediaservices/. 2002.

STFI. 2002. Mistra Projects and Sub Projects. http://www.stfi.se/documents/mistra/projects.htm. last updated 2002-04-15.

Stigsson, L.L. 1996. Pressurized black liquor gasification – Advanced technology for electric power production and recovery of pulping and bleaching chemicals. In *1996 Tappi Pulping Conference Proceedings*.

Stora Enso. 2001. Environmental Statement 2000, Kotka Mill, 20 April.

Stratton, S.C., and Ferguson, M. 1998. Progress report on the BFR™ technology demonstration: December 1996. *Pulp & Paper Canada* 99(3).

Suur-Hamari, T. 2003. Personal email communication. 1/30/2003.

Tannik. 1997. Non chlorine bleaching experiences. *Panel discussion on mill experiences with closed cycle operation, International Emerging Technologies Conference*, Orlando, FL.

Tateishi, M., Arakawa, Y., Tokunaga, K., and Maeda, T. 1998. Plugging prevention of recovery boiler by character improvement of the ash which used potassium removal equipment. In *Proceedings of 1998 International Chemical Recovery Conference*. Atlanta, GA: Tappi Press.

Teder, A., Andersson, U., Littecke, K., and Ulmgren, P. 1990. The recycling of acidic bleach plant effluents an their effect on preparing white liquor. *Tappi Journal* 73(2).

Tench, L., and Harper, S. 1987. Oxygen bleaching practices and benefits: An overview. *Tappi Journal* 70(11):55.

Thompson, R., Paleologou, M., Wong P-Y., and Berry, R.M. 1997. Separation of sulfide and hydroxide in white liquor by electrodialysis. In *83rd Annual Meeting Proceedings*, CPPA Technical Section.

Tolan, J.S., and Thibault, L. 2000. Mill scale implementation of enzymes in pulp bleaching. In *Proceedings 2000 Pulping / Process & Product Quality Conference*. Atlanta, GA: Tappi Press.

Thurley, D., Niemczyk, B., and Turner, G. 1997. Use of dissolved air floatation to clean process water. *Appita Journal* 50(2):109-112.

Tran, H.N., Barham, D., and Reeve, D.W. 1989. Chloride and potassium in the kraft chemical recovery cycle. In *1989 Proceedings of the Chemical Recovery Conference.* Atlanta, GA: Tappi Press.

Tsai, S-P., Pfromm, P., Henry M.P., and Fracaro, T. 1999. Recycling of water in bleached kraft pulp mills by using electrodialysis. In *Proceedings 1999 Tappi Environmental Conference*, Atlanta, GA: Tappi Press.

Uhlin, L. 2003. Personal email communication. 1/29/2003.

Ulmgren, P., and Rådeström, R. 1997. The build-up of phosphorus in a kraft pulp mill and the precipitation of calcium phosphate from green and white liquors. *Journal Pulp and Paper Science* 23(2).

United States Environmental Protection Agency (USEPA). 1996. *Summary report for pulp and paper mill sampling program*. Radian Corporation.

United States Environmental Protection Agency (USEPA). 1998. Code of Federal Regulations, 40 CFR Part 430 Effluent limitations guidelines, pretreatment standards, and new source performance standards: The pulp, paper, and paperboard point source category. Revised April 15, 1998. In *Federal Register* Vol. 63, No. 72.

University of Toronto. 1997. Tappi International Student Chapter at the University of Toronto, Notes on the University of Toronto Pulp and Paper Technology Tour, Brazil.

Van Lierop, B., Skothos, A., and Liebergott, N. 1996. Section IV: The technology of pulp bleaching, Chapter 5: Ozone delignification. In *Pulp Bleaching Principles and Practices*. Dence and Reeve (eds.). Atlanta, GA: TAPPI Press.

Voss, R. 2000. Compilation of research projects on environmental problems in the pulp and paper industry in Canada, Finland, Norway, Sweden and the United States of America. International Environmental Committee for the Forest Industries, May 2000, Paprican, Pointe Claire, Quebec, Canada.

Wahlberg, T. 1995. Closure affects the recovery cycle – report on the 1994 Swedish Recovery Boiler Conference (in Swedish). *Svensk Papperstidning* 98 (2): 38-39.

Wannenmacher, P.N., Frederick, W.J., Hendrickson, K.A., and Holman, K.L. 1998. The solubility of aluminosilicates in kraft green and white liquors. In *Proceedings of the 1998 International Chemical Recovery Conference*. Atlanta, GA: Tappi Press.

Warnqvist, B., Idner, K., Hastings, C., Barynin, J., and Gleadow, P. 1995. Impact on recovery cycle capacity by extended delignification and effluent recycle. *International Chemical Recovery Conference*, Toronto, Ontario, Canada.

Warnqvist, B. 1996. Handling alkali and sulfur balances in closed-cycle bleached kraft pulp mills – Options, technology and costs. In *Minimum Effluent Mills Symposium Proceedings*, Atlanta, GA.

White, K. 2003. Personal email communication. 1/30/2003.

Wickstrom,P. 1997. Membrane filtration in the closed-cycle bleach plant. In *1997 Tappi Minimum Effluent Mill Symposium Proceedings*. Atlanta, GA: Tappi Press.

Wizani, W., Eder, S., and Kubelka, V. 1993. Enerbatch - A technology for the production of bleachable grade pulp. In *Proceedings of the 25th EUCEPA Conference 1993.* Vienna, Austria, Book I.

Wright, R.H. 1956. The separation of sodium chloride from precipitator salt cake. *Pulp & Paper Canada* 57(11):T121-T123.

Ylén, J.-P. 2001. Multistaged strategy of pH control in the production of printing paper. *Water management in papermaking – Final report* (English version). Helsinki, Finland: TEKES.

Ylhäisi, M. 2001. *Water management in papermaking – Final report* (English version). Helsinki, Finland: TEKES. Available at http://akseli.tekes.fi/Resource.phx/plaza/tekes/bike1-cactus-en.htx.