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Environmental Protection
Agency

Office of Research and
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Washington, DC 20460

Office of
Enforcement
Washington, DC 20460

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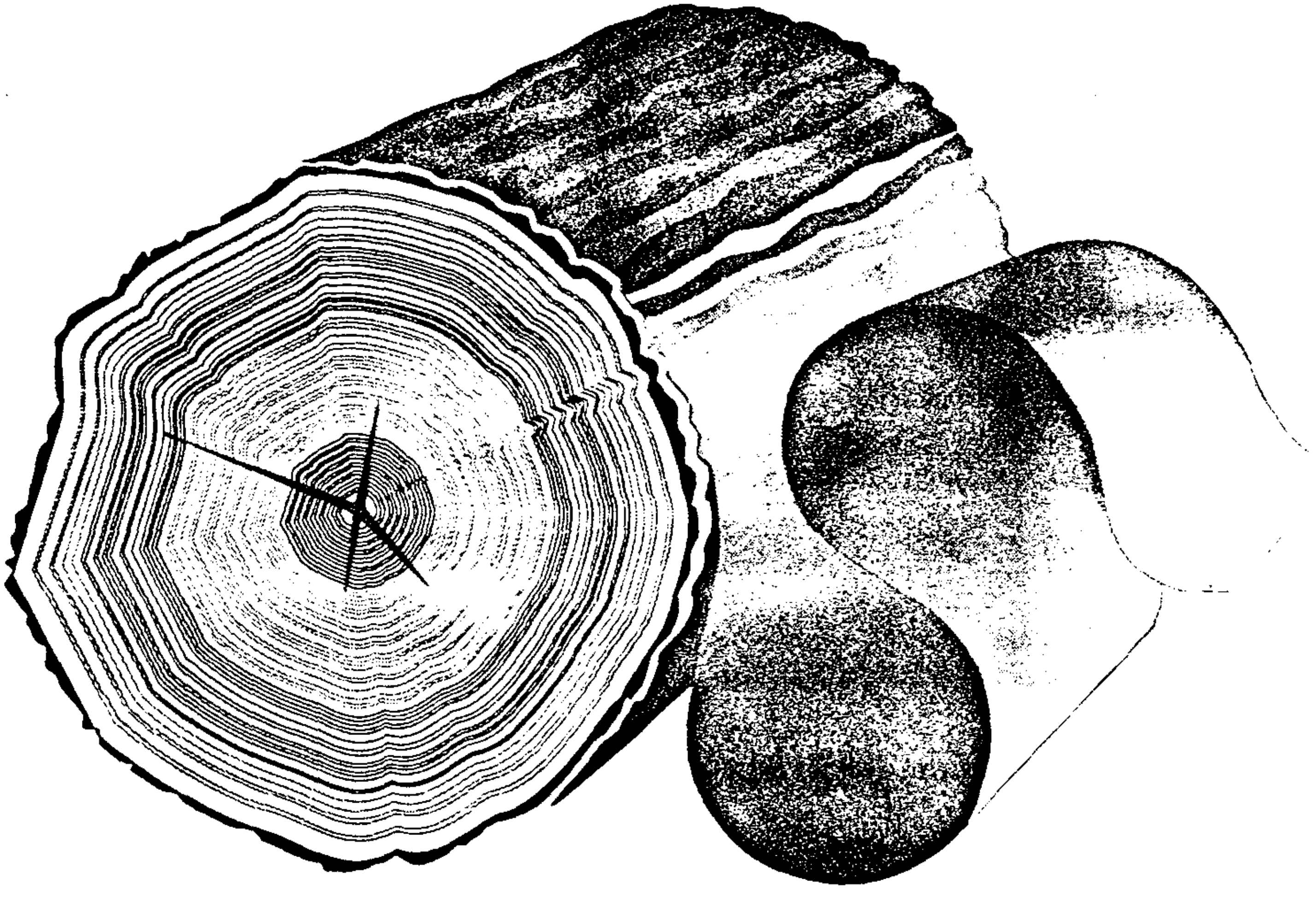
Handbook on Pollution Prevention Opportunities for Bleached Kraft Pulp and Paper Mills



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUL 13 1993

OFFICE OF ENFORCEMENT

MEMORANDUM

SUBJECT: Handbook On Pollution Prevention Opportunities For Bleached Kraft Pulp and Paper Mills

FROM: Steven A. Herman
Assistant Administrator

TO: Addressees

Pursuant to the Pollution Prevention Act of 1990 ("PPA"), the United States Environmental Protection Agency ("U.S. EPA") is directed to implement a source reduction training program for state and Federal enforcement officials and to facilitate adoption of source reduction techniques by businesses. Indeed, as clearly expressed by Administrator Browner in Pollution Prevention Policy Statement: New Directions for Environmental Protection (June 15, 1993), it is the policy of U.S. EPA to encourage pollution prevention as a means of compliance with environmental standards.

The purpose of this handbook is to familiarize environmental enforcement personnel, the regulated community, and others with currently available opportunities to prevent the formation of pollutants generated by pulp and paper mills, with a particular emphasis on the bleached kraft segment of the industry. The handbook was developed by the Office of Research and Development (ORD) in support of the enforcement program. The handbook is adapted from a more comprehensive in-depth ORD study of pollution prevention technologies for the bleached kraft segment of the pulp and paper industry, which relied on information generated through contacts with vendors, review of technical literature, and reports from operators of bleached kraft pulp and paper mills in the United States, Canada, and Europe.

To promote the consideration of pollution prevention opportunities by government and industry representatives in enforcement proceedings, the handbook is intended to be easily understandable, and to provide a basis for more detailed research into feasible pollution prevention alternatives. The concept of developing an industry-specific pollution prevention handbook for the use by the enforcement program is new. We encourage recipients to provide us with feed-back on the document, which will allow us to assess its usefulness as a pollution prevention promotional tool, and to consider whether additional industry-specific handbooks would be helpful to enforcement personnel. Comments should be directed to either Peter Fontaine (LE-134W) (phone 202/260-6240; fax 202/260-4201) or Pete Rosenberg (LE-133) (phone 202/260-8869; fax 202/260-7553), at the Office of Enforcement, U.S. EPA, 401 M Street, S.W., Washington, D.C. 20460. A limited number of additional copies of the handbook can be obtained by contacting the above persons.

The process of resolving noncompliance at regulated facilities presents unique opportunities to influence the future direction of residuals management at the facilities. In resolving an enforcement action, enforcement officials and facility operators must decide on the best means to return the facility to compliance, usually through the investment in additional treatment technologies or through some other means to reduce pollution to authorized levels and preferably to levels significantly below legal limits. This decision point is a critical juncture in the overall process of implementing environmental controls at a facility, as the outcome will determine for years to come the magnitude, character, and potential environmental impacts of pollutants released by the industrial source.

However, information on feasible options to prevent pollutant formation at industrial facilities, including kraft pulp and paper mills, is not always readily available to industry and government environmental managers. Furthermore, the prevailing "end-of-pipe" culture of these same managers, in part a product of the single-medium orientation of our environmental protection statutes, regulatory programs, and permitting and compliance monitoring systems, is not subject to rapid change. In short, instituting a prevention ethic both within EPA and the regulated community, and developing the technical knowledge to practice it, is an ongoing incremental process.

This handbook is designed to encourage the adoption of source reduction options at pulp and paper facilities in connection with environmental enforcement actions, in furtherance of the PPA, U.S. EPA's "Interim Policy on the Inclusion of Pollution Prevention and Recycling Provisions in Enforcement Settlements" (February 25, 1991) ("Interim policy"), and U.S. EPA's "Policy on the Use of Supplemental Environmental Projects in EPA Settlements" (February 12, 1991) ("SEP policy").

The Interim and SEP policies encourage EPA enforcement personnel and facility operators to consider pollution prevention projects in resolving noncompliance. Essentially, the Interim policy encourages the inclusion of pollution prevention projects as the basis for injunctive relief (the measures necessary to return a facility to compliance), while the SEP policy outlines the minimum prerequisites for acceptance of pollution prevention projects as the basis for off-setting penalty liability. Acceptable SEPs can include those that substantially reduce or prevent the creation of pollutants through use reduction or application of closed-loop processes, and projects that go substantially beyond compliance with discharge limitations to further reduce the amount of pollution that would otherwise be discharged. All SEPs must have some nexus to the violation(s) underlying the enforcement action.

The adoption of one or several of the pollution prevention options discussed in this handbook has the potential to significantly reduce pollution discharges to a number of different environmental media, thereby reducing risks to human health while improving the quality of the environment. For those pulp and paper mills in violation of pollutant limits, the options discussed in the handbook offer possible solutions to noncompliance while also providing a basis for EPA enforcement officials to consider reducing potential penalty liability, assuming fulfillment of the requirements contained in the SEP policy.

Addressees:

Deputy Regional Administrators
Regional Counsels
Region Counsel Branch Chiefs
Headquarters National Program Managers
Regional Program Division Directors
Regional Program Enforcement Branch Chiefs
Enforcement Counsel
Director, National Enforcement Investigations Center

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SECTION ONE
INTRODUCTION

This handbook examines the current state of the art, economics of adoption, and level of adoption of selected pollution prevention technologies in the U.S. pulp and paper industry.[1] The focus in the handbook is on the bleached kraft segment of the industry, due to the heightened concern over its environmental impacts. This concern is related primarily to the use of chlorine-based compounds in the manufacturing of bleached pulps, and the nature of the byproduct pollutants associated with conventional pulpmaking processes. In particular, it is the persistence, non-biodegradability, and toxicity of some of the chlorinated organic compounds formed during chlorine-based bleaching that explains the high level of attention directed toward this segment of the industry. The bleached kraft segment accounts for approximately 35 percent of the pulp mills and 47 percent of the pulp production capacity in the U.S. industry (API, 1992).

The control of chlorinated pollutants from the bleached kraft process through end-of-pipe treatment is difficult due to their persistence and low concentration in effluents. Conventional treatment technologies are relatively ineffective at destroying such compounds and instead may result in their transfer to other environmental media (e.g., wastewater treatment sludge). As a consequence, further reductions must focus on changes in the production process that can reduce or eliminate their formation. For prevention of chlorinated organics, the available technologies include a variety of techniques that enable the mill to reduce the use of chlorine-based compounds in the bleaching process. Because these technologies enable further recycle of the mill's effluent, they can also have a significant impact on more traditional pollutants such as BOD_5, COD, and TSS, as well as on effluent color, an increasing concern in some areas. Emissions of chloroform, an air toxic, are also reduced as a result of many of these technologies.

Recently, scientists in Canada and Scandinavia have suggested that non-chlorinated substances make a significant contribution to the effects of biologically treated pulp mill wastes on the receiving waters. At this time, there is little information available concerning these findings, although some of the results are expected to be published shortly. Most of the pollution prevention technologies discussed in this handbook, however, will also reduce the discharges of such non-chlorinated substances, particularly those which involve routing wastes to the recovery boiler that would otherwise have been discharged to the effluent treatment system.

The economics of adopting process changes are explored in detail in this handbook. An important conclusion from reviewing available information is that, while it is possible to cite representative capital and operating cost information, the actual costs and savings at an individual mill will be very site-specific. Facility costs will depend closely on the age, type, and condition of the existing equipment at the mill. A key consideration affecting the attractiveness of any of these options is the relative age and obsolescence of equipment it will replace, and the future investments that may be avoided.

The costs presented in this handbook are for specific examples drawn from the literature for the purposes of putting the economic aspects in perspective. Due to the wide variation in situations among mills, it

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[1] The technical information contained in this report is based upon a more detailed, peer-reviewed technology report prepared for the Office of Pollution Prevention and Toxics (OPPT) under an Office of Research and Development (ORD) contract (EPA, 1993b). A copy of the main report may be obtained from Jocelyn Woodman (Mail Code 7409) of the Pollution Prevention Division, OPPT (202-260-4418).

is recommended that evaluations of these technologies for a particular mill be based only on site-specific engineering reports that clearly identify the scope of the project, detail the necessary capital equipment and operating costs, and are explicit with regard to any savings assumed to accrue.

It should also be noted that a substantial amount of technical information and data presented in this handbook is based on published and unpublished sources at equipment vendor and system supplier companies. Since many of the technologies discussed in the handbook are available from only a small number of supplier companies, these suppliers offer a valuable and unique perspective on overall system performance and economics. Mention of specific vendors in the context of this handbook does not, however, constitute endorsement by the U.S. Environmental Protection Agency, nor does it imply that those mentioned are the only companies capable of supplying the technology.

Regardless of the situation, most pollution prevention technologies for the pulp and paper industry result in lower operating costs, but do not usually generate sufficient savings to justify the investment themselves. Thus, environmental compliance or market factors often play a deciding role in whether to go ahead with a project or not. In many cases, the decisionmaking process of a mill will be substantially affected by the market and/or regulatory environment it expects to face in the future. Many mills are undoubtedly concerned about the future direction of environmental regulations in their industry and the possible implications on the processes they use. Market forces are equally important. In particular, mills that sell pulp or paper into more environmentally discerning international markets may be forced to adopt further pollution prevention measures in order to comply with the demands of their customers for "environmentally responsible" paper and pulp products.

One factor to consider when evaluating the viability of pollution prevention technologies is that operating costs may be sensitive to the target pulp brightness level. This is especially true in totally chlorine-free (TCF) processes, which may use expensive hydrogen peroxide in the final bleaching stage to bring pulp to final brightness. The higher the producer's brightness requirements, the more peroxide must be used, leading to higher bleaching costs.

Traditionally, mills that produce "market pulp" for sale to other mills have had to meet higher brightness standards than most integrated mills -- mills that produce pulp for their own use in papermaking -- require. Pollution prevention technologies involving non-chlorine bleaching stages are more competitive with conventional processes in the 70 to 80 brightness range. Unless market pulp brightness levels fall, therefore, integrated mills that can use lower brightness pulps will be better positioned than maret pulp producers to take advantage of some of the pollution prevention technologies discussed in this handbook.[2]

Much of the information contained in this handbook is by necessity very recent. Many of the current concerns over the environmental impacts of the U.S. pulp and paper industry have arisen only since 1985, with the discovery of dioxin in bleached kraft mill effluents and solid wastes (EPA, 1988). Although prior to this some of these technologies were in use elsewhere in the world, only lately has there been an incentive for U.S. producers to investigate them. Since the discovery of the dioxin problem, however, the U.S. and international research and development effort has been impressive, and the rate of adoption of many of these technologies has been increasing rapidly. Information on their use, effectiveness, and cost

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[2] The market issues surrounding pulp brightness and pollution prevention are addressed in several papers contained in the proceedings from the EPA-sponsored *International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper - Opportunities and Barriers* (EPA, 1993a).

has been spreading through all of the major trade publications and at numerous industry conferences. As experience with the technologies grows, it is likely that costs will decline further and effluent quality will further improve, providing additional incentives for adoption.

This handbook is organized into five sections. Section Two presents a brief overview of the unit processes typically found at an integrated bleached kraft mill. Section Three covers technologies that can be applied in the woodyard and chipping areas of the mill. Section Four identifies pollution prevention opportunities in the pulping or pre-bleaching stages of the process, while Section Five discusses pollution prevention opportunities in the bleach plant of the mill.

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EPA, 1988. *U.S. EPA/Paper Industry Cooperative Dioxin Screening Study.* U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington, D.C., March 1988. EPA 440-1-88-025.

EPA, 1993a. *International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper - Opportunities and Barriers*, August 18-20, 1992, Washington, D.C. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. EPA-744R-93-002. February 1993.

EPA, 1993b. *Pollution Prevention Technologies for the Bleached Kraft Segment of the U.S. Pulp and Paper Industry.* U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington, D.C. EPA/600/R-93/110. July, 1993.

SECTION TWO
CONVENTIONAL BLEACHED KRAFT MILL OPERATIONS

This section briefly describes the unit operations common to most bleached kraft mills in North America and introduces two terms -- *kappa number* and *pulp brightness* -- essential to an understanding of the pollution prevention technologies discussed in this handbook.

The point of departure for this discussion is the typical bleached kraft mill as it existed in the mid- to late-1980s. Since that time the configuration of the "typical" mill has been evolving gradually, however the basic processes are still in place, perhaps with some modification, at most mills today.

Figure 2-1 shows the process flow for an integrated bleached kraft pulp mill. The mill operations are segregated according to the following major process areas: (1) wood preparation, (2) pulping, (3) bleaching, and (4) chemical recovery.

Wood Preparation/Pulping

In the wood preparation area, pulpwood (logs)[1] are debarked in a rotating drum and then chipped to uniform size and shape. The chips are steamed and mixed with *cooking liquor* (or *white liquor*), a mixture of sodium hydroxide and sodium sulfide. The liquor-impregnated chips are then fed into a large reaction vessel known as a digester. In the digester, the cooking chemicals react with the chips (at elevated temperature and pressure) to break down *lignin*, the substance that holds the individual wood fibers together.

The progress of the cook (as well as most downstream processes) is monitored via a parameter known as the *kappa number.* The kappa number reflects the amount of lignin remaining in the pulp. Since it is lignin that imparts color to the pulp and is responsible for yellowing and aging of paper, the primary objective of the bleached kraft process is to reduce the pulp's lignin content (or kappa number) as much as possible. While lignin removal can be enhanced using more severe process conditions (higher temperature and pressure, longer cooking times), the process yield is generally an inverse function of these variables. Thus, kraft mills must balance further lignin removal against the yield loss that may result.

Bleaching

Following discharge from the digester, the cooked pulp is washed and screened, at which point it is known as *brownstock.* The brownstock moves on to the bleach plant, where it undergoes a series of acidic and alkaline treatments. In the typical mill shown in Figure 2-1, the bleach sequence is as follows:

- Reaction with chlorine gas (C);
- Washing and extraction (E) with sodium hydroxide (caustic);

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[1] The diagram shows tree-length logs (roundwood) being used as feedstock for the pulping and bleaching operations. In the modern kraft mill, fiber may be derived from a variety of sources including logs, chips, and sawmill residues (including sawdust).

- Reaction with chlorine dioxide (D);
- Caustic extraction (E);
- An additional chlorine dioxide stage (D);
- A final caustic extraction stage (E).

The letters representing each stage of the bleaching sequence are commonly used as a shorthand way to describe the sequence used at a particular mill (e.g., CEDED).

The goal of the bleaching sequence is to remove additional lignin and to *brighten* (i.e., remove color from) the pulp. Chlorine acts as a very powerful delignifying agent, while the first caustic extraction stage is used to neutralize the pulp and facilitate removal of the dissolved lignin solids during washing. Chlorine dioxide is a more "selective" brightening agent that destroys chromophoric groups within the pulp without attacking the individual cellulose fibers.

Pulp brightness is an objective measure of the amount of light reflected by the pulp and is determined using standard measuring techniques and instruments.[2] Brownstock pulp registers a brightness level of 15 to 30 percent and is basically the color of unbleached kraft paper (e.g., grocery sack). Most pulp mills have traditionally applied bleaching chemicals to achieve a target brightness level of 90 percent. In particular, market pulp (i.e., pulp sold to other mills for use in papermaking) has always been bleached to 90 percent brightness according to the requirements of pulp buyers. Many integrated mills (i.e., mills that produce pulp for their own use in papermaking) are able to make quality paper products using pulp bleached to somewhat lower brightness levels (between 80 and 88, depending on the source). The target brightness level for the bleach plant is important since many of the pollution prevention technologies discussed in this handbook become more competitive at somewhat lower target brightness levels.

Chemical Recovery

The bottom half of Figure 2-1 shows the rather complex chemical recovery system that is characteristic of all kraft mills. Chemical recovery begins with the spent cooking chemicals and solubilized lignin that is flushed from the cooked pulp at the brownstock washers. This mixture, known as *weak black liquor*, is concentrated in a series of multiple effect evaporators to form *strong black liquor*, with a solids content of between 60 and 80 percent. The strong black liquor is fired into the recovery boiler, where the heat content of the organic lignin solids is released to generate steam for process use.

Smelt from the bottom of the furnace (consisting of sodium/sulfur salts and inorganic chemicals) runs into a dissolving tank where it is mixed with weak wash, the filtrate from lime mud washing (see below) to form *green liquor*. The green liquor is clarified to remove carbonaceous ash residues and other impurities. These *dregs*, as they are known, are washed to remove soluble sodium salts while the remaining residue is removed and generally disposed of in a landfill. The clarified green liquor moves next to the calcining system, where it is mixed with calcium hydroxide in the slaker to convert sodium carbonate to sodium hydroxide (caustic), one of the principal pulping chemicals.

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[2] Several alternative techniques for measuring pulp brightness are used, including the GE, Elephro, and ISO methods. The difference in readings obtained using these three methods is small, perhaps one or two points on a scale of 0 to 100. In this handbook, brightness levels cited are obtained using the ISO method unless otherwise indicated.

Calcium carbonate precipitates out of the causticizers and is removed in the white liquor clarifier. The clarified solution then contains the two major cooking chemicals, sodium hydroxide and sodium sulfide. The regenerated white liquor is now ready for use in the pulp digester(s).

The final stage in the recovery process involves recycle of the precipitated calcium carbonate removed from the white liquor clarifier. This mixture is thickened, washed, and introduced into the lime kiln, which converts it to calcium oxide. The calcium oxide is recovered and used in the slaker, as described above.

Wastewater Treatment

In Figure 2-1 it can be seen that filtrate from the bleach plant (the C-, D-, and E-stages) is not recycled and instead is discharged, via the alkaline and acid sewers, to the wastewater treatment system. Most North American mills operate both primary and secondary wastewater treatment facilities to treat these wastes. Primary treatment removes suspended solids (as primary sludge) while secondary treatment uses biological processes to remove dissolved and suspended solids from the effluent. Sludge from primary and secondary treatment is often combined prior to dewatering and final disposal. Landfills are the most common disposal method used for sludge, although surface impoundments, incineration, and land application are also widely used.

Bleach plant effluent from chlorine-based bleaching stages cannot be recycled due to the potential for corrosion of process equipment. From an environmental standpoint, there are two disadvantages to this. First, additional organic solids washed from the pulp during bleaching cannot be recovered for their heat value and are lost to the sewer system. Second, the chlorination of pulp in the first C-stage has been linked to the formation of chlorinated organics, including dioxin and furan, which are difficult to remove or destroy using conventional wastewater treatment. Major efforts are underway within the industry to either reduce the lignin content (kappa number) of the pulp prior to bleaching, or to substitute more environmentally-benign chemicals for chlorine in the bleach plant. In the former case, reducing the kappa number of the pulp entering the bleach plant means that (1) more effluent and solids can be recycled, and (2) less bleaching chemicals (including chlorine) will be needed to reach a target brightness level. In the latter case, reduction of chlorine will result in improved effluent quality but will not increase the level of effluent closure within the mill. Strategies for achieving some of these benefits are discussed in detail in Sections 4 and 5.

The remainder of this handbook discusses opportunities for prevention of pollution from the woodyard, pulping, and bleaching areas of the mill. While the chemical recovery process also contributes to emissions from the mill (especially to air), there are comparatively fewer opportunities for prevention of pollutants.[3] For a recent review of techniques to control emissions from the recovery process, the reader is referred to the Office of Air Quality Planning and Standards (OAQPS) recent *Background Information Document*, prepared in support of the proposed air and water regulations for the pulp, paper, and paperboard industries (EPA, 1993).

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[3] The configuration and operation of the chemical recovery system does, however, impact the technical and economic feasibility of adopting many of the pollution prevention technologies that are discussed here. For this reason, reference to the chemical recovery system is made throughout the document.

SECTION TWO REFERENCES

EPA, 1993. *Pulp, Paper and Paperboard Industry - Background Information for Proposed Air Emission Standards*. Preliminary Draft. April 1993. Office of Air Quality Planning and Standards, Emissions Standards Division. Research Triangle Park NC.

SECTION THREE

POLLUTION PREVENTION OPPORTUNITIES IN WOODYARD AND CHIPPING OPERATIONS

The woodyard is the name given to the areas at the mill where the raw pulping materials (logs, chips, and, increasingly, sawdust and other sawmill residuals), are stored, prepared, and fed to the pulping equipment. This section reviews the operations in the pulp mill woodyard and identifies opportunities for prevention of pollution associated with these activities.

3.1 RAW MATERIAL SELECTION

In the past, mills may have purchased wood, chips, or sawdust from sawmills that used preservatives such as pentachlorophenol (PCP) to treat the wood for stain resistance. These chemicals were found to contain CDDs/CDFs and CDD/CDF precursors which, following chlorination in the bleach plant, led to formation of dioxins and furans. This problem has been widely recognized within the industry and most mills are believed to have ceased purchasing treated wood.

3.2 RECYCLE OF LOG FLUME WATER

Log flumes are used to transport wood from storage areas to debarkers and chippers at some mills. The water used in such systems can be recycled to the wastewater treatment plant at minimal cost. Alternatively, treated wastewater can be used in the flume. In both cases, bark and fiber collected in the flume water can be removed and burned in "hogged" fuel boilers to recover energy values.

3.3 DRY DEBARKING

Wet debarkers rotate logs in a pool of water and remove bark by knocking the log against the side of the drum. The water used in this process is recycled but a certain amount is lost as overflow to carry away the removed bark. Resin acids and highly colored materials leach out of the bark and into this waste water stream. The effluent is collected and routed to the wastewater treatment system, where it contributes to BOD_5 and TSS loadings.

Dry debarking methods such as dry drum debarkers (see Figure 3-1) or shearbarkers eliminate the water stream and the pollutants associated with it. Water savings in the range of 2,000 to 3,000 gallons per ton of wood barked can be obtained, and BOD_5 and TSS loading reductions should be in the range of 6 to 55 pounds and 1 to 10 pounds per ton. Dry debarkers already dominate the industry, and wet systems have been in the process of being phased out since the 1970s (Smook, 1982).

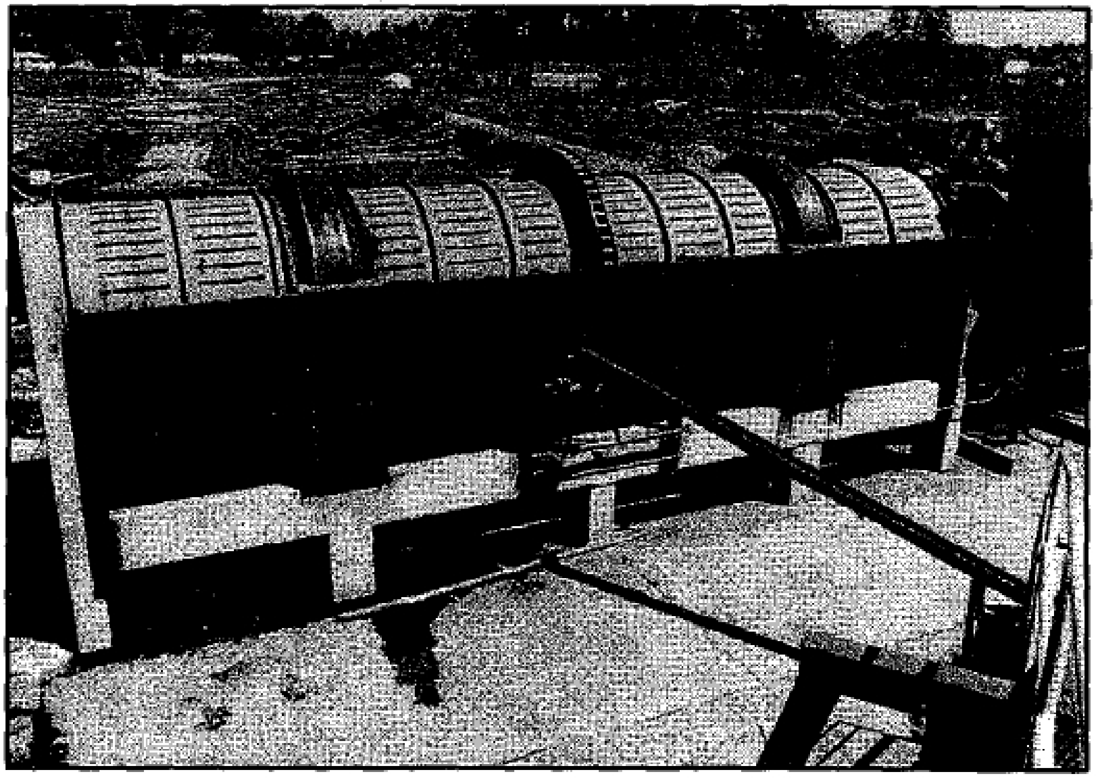

Figure 3-1. Debarking drum.

Source: Beak, 1978.

The costs of dry drum debarkers should not differ significantly from a wet system. Costs for replacing both types of equipment are in the range of $10 to 20 million.

3.4 IMPROVED CHIPPING AND SCREENING

In most mills, chips are passed over a vibrating screen that removes undersized particles (fines) and routes oversized chips for rechipping. Chips are normally segregated only according to chip length. Chip thickness screening has become important as mills realize the need to extend delignification. Both absolute chip thickness and thickness uniformity have a significant impact on delignification, since the kraft cooking liquor can only penetrate the chip to a certain thickness (Tikka et al., 1992). Thin chips are easier to cook to lower kappa numbers. Uncooked cores from overly thick chips will lower the average kappa of a cook, reducing yield and contributing to higher bleaching chemical demands. To improve thickness uniformity, mills are adopting screening equipment that separates chips according to thickness as well as length (Strakes and Bielgus, 1992). Chips that exceed the maximum acceptable thickness can be diverted to a chip slicer, that cuts them radially and reintroduce them to the screening system (see Figure 3-2).

Costs for chip thickness screening systems in a new installation may range from $200,000 to $400,000 (higher for a retrofit).

3.5 STORM WATER MANAGEMENT

Storm water runoff from wood storage and handling areas may contain significant amounts of BOD_5, TSS, and color. Mills may control storm water discharges by installing curbs, dikes, and drainage collection systems around wood and chip piles and wood processing areas. Collected stormwater can be collected and transported to the wastewater treatment facility which should effectively remove the pollutants of concern.

Costs for stormwater collection and treatment are variable and quite site-specific. They depend more on the current configuration of the mill woodyard and location of treatment facility than on the particular type of controls installed.

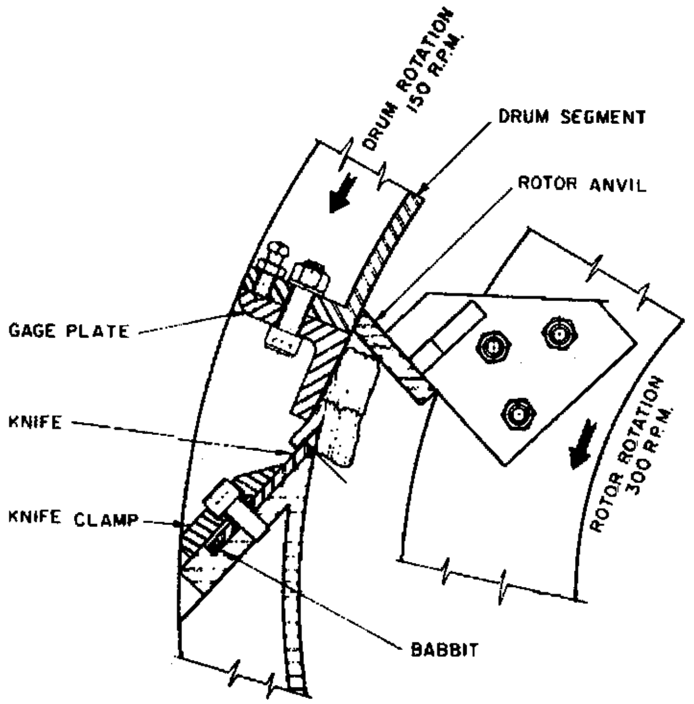

Figure 3-2. Chip thickness slicer showing oversize chip being split.

Source: Smook, 1982.

SECTION THREE REFERENCES

Beak, 1978. *Technical, Economic and Environmental Aspects of Wet and Dry Debarking*. Prepared by Beak Consultants, Ltd. for the Water Pollution Control Directorate, Environmental Protection Service, Fisheries and Environment Canada. Report No. EPS 3-WP-78-3. March, 1978.

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Strakes and Bielgus, 1992. George Strakes and Joe Bielgus. "New Chip Thickness Screening System Boosts Efficiency, Extends Wear Life," *Pulp and Paper*, July 1992, p. 93.

Tikka et al., 1992. "Chip Thickness vs. Kraft Pulping Performance, Part I: Experiments by Multiple Hanging Baskets," Proceedings, *1992 TAPPI Pulping Conference*, Boston MA, November 1992, p. 555.

SECTION FOUR
POLLUTION PREVENTION OPPORTUNITIES IN PULPING OPERATIONS

This section identifies pollution prevention technologies that may be applied in the kraft pulp mill to effect environmental improvements. This section (and the rest of the report) retains the traditional distinction between pulping and bleaching, which is to classify stages that occur prior to the application of chlorine-based bleaching agents as pulping stages, and those that occur following application of these agents as bleaching stages. With the increased use of non chlorine-based delignification agents, however, these distinctions are becoming less and less meaningful. For optimum pollution prevention potential, many experts would recommend viewing pulping and bleaching as integrated processes.

4.1 EXTENDED DELIGNIFICATION

What it is

Modification of the pulping equipment to achieve a more uniform reaction of chips with the pulping chemicals. Results in greater delignification, leading to reduced requirements for chlorine-based bleaching chemicals and their associated environmental impacts.

How it works

In conventional kraft pulping, the digester is filled with chips and given a one-time charge of cooking chemicals. The alkali concentration in the reactor is initially high, but then falls as the cook progresses and the cooking chemicals are consumed. Normal reaction times are between one and three hours. Longer cooks will further reduce pulp lignin content but will also begin to degrade the cellulose, as the reactions become less selective towards lignin.

By applying principles developed by the Swedish Forest Products Research Institute (STFI), it has become possible to extend pulp cooking times without impacting pulp quality or yield. These principles are embodied in technology offered by the major equipment suppliers. The Modified Continuous Cook (MCC®) and Extended Modified Continuous Cook (EMCC®) processes are available from Kamyr for continuous pulping operations.[1] In the MCC® process liquor is introduced at several different points to maintain a constant alkali concentration throughout the cook (see Figure 4-1). In EMCC®, about 20 to 25 percent of the white liquor is added to the wash liquor in the bottom zone of the digester for counter-current cooking (see Figure 4-2). EMCC® can be implemented without MCC® and in fact is the normal way of converting a conventional digester to extended cooking.

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[1] Both Kamyr AB (Karlstad, Sweden) and Kamyr, Inc. (Glens Falls, New York) can supply the technology in North America.

Single Vessel Hydraulic Digester

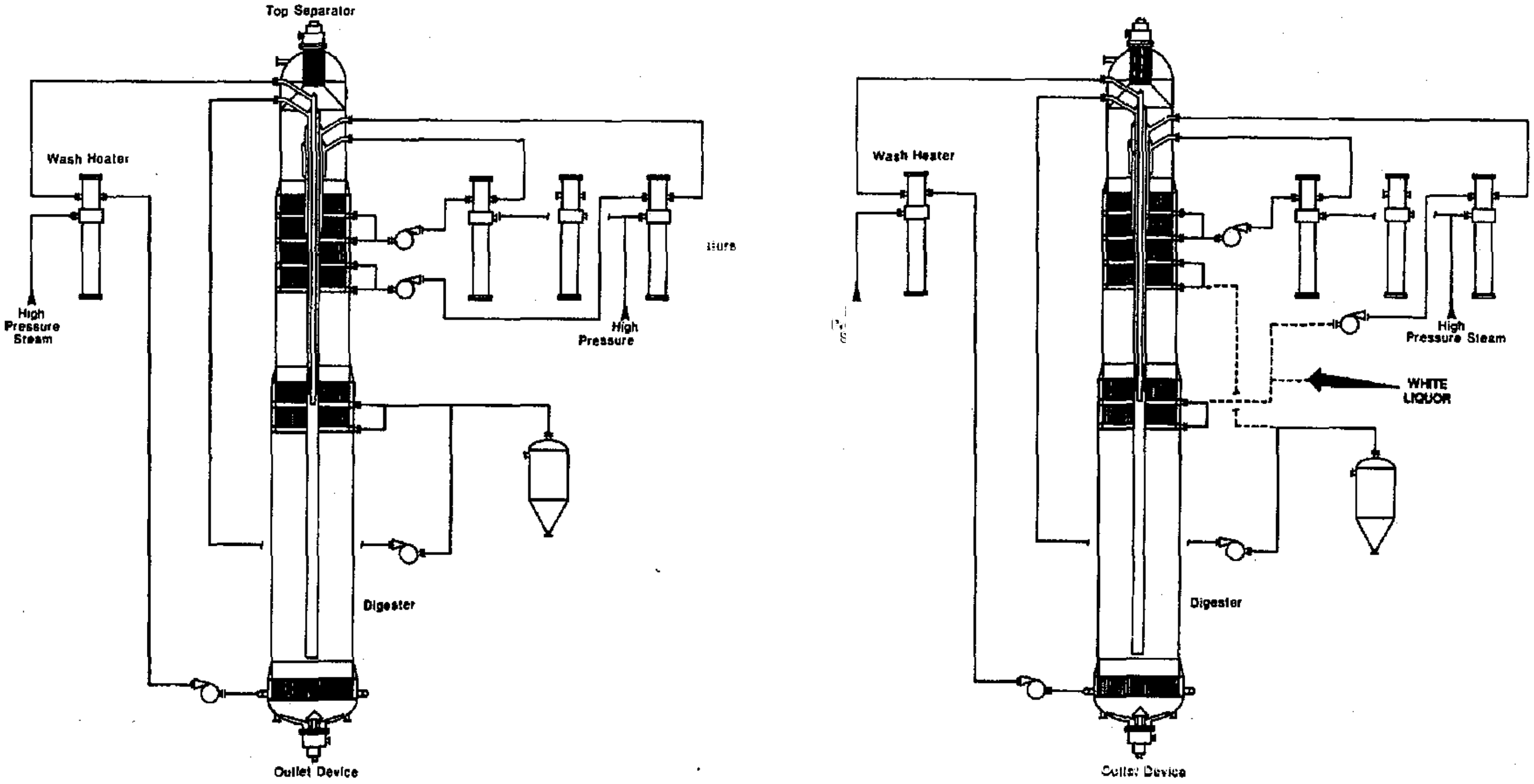
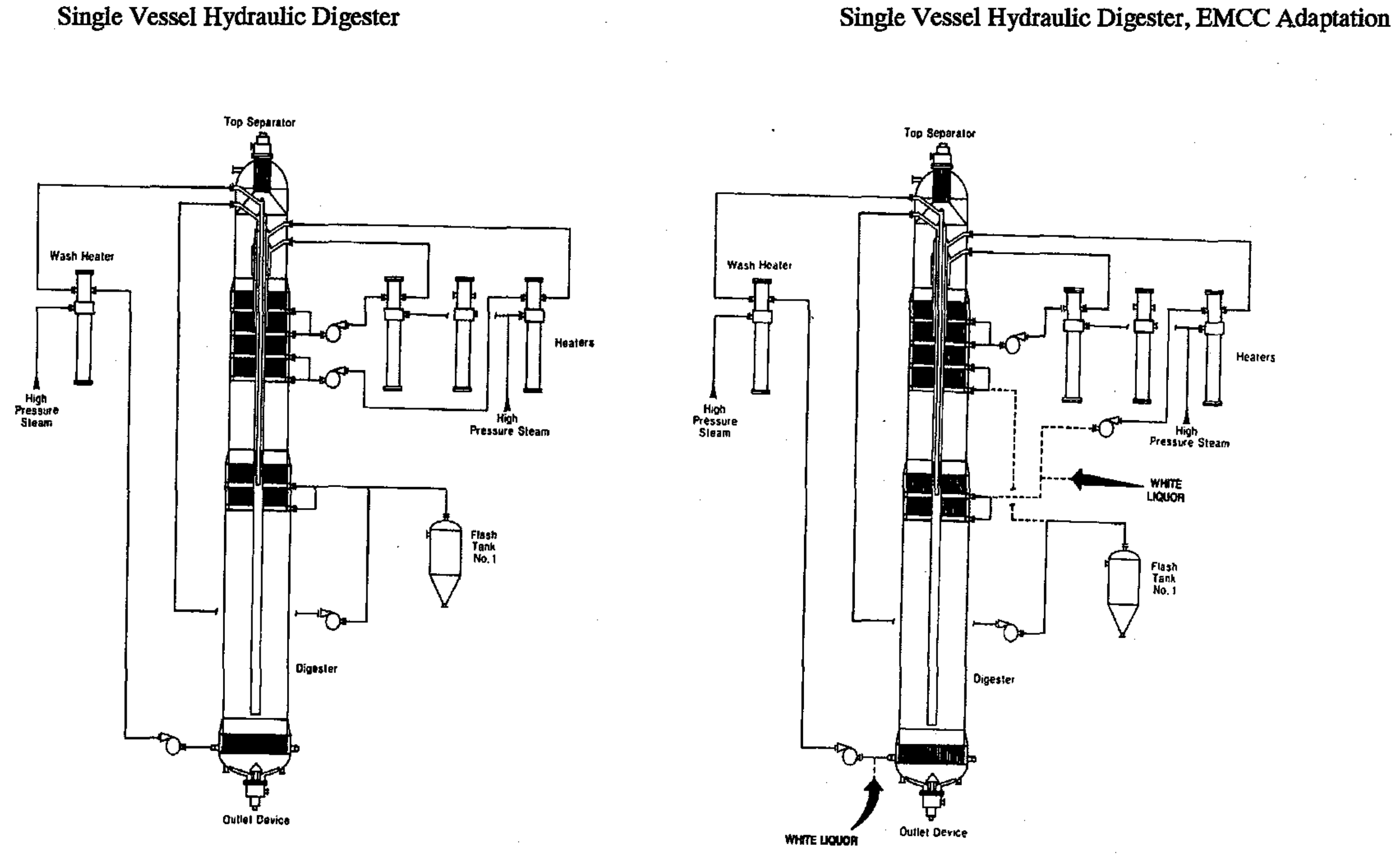


Figure 4-1. Equipment diagram for MCC extended cooking, showing multiple liquor addition points.

Source: Kamyr, Inc.



Single Vessel Hydraulic Digester

Single Vessel Hydraulic Digester, EMCC Adaptation

Figure 4-2. Equipment diagram for EMCC extended cooking, showing multiple liquor addition points and liquor addition to wash zone.

Source: Kamyr, Inc.

For batch pulping, the cook can be extended using the Rapid Displacement Heating (RDH) process or one of its variations. RDH was originally developed by the Beloit Corp. (Beloit, Wisconsin). Adaptations of the RDH principles are available in the SuperBatch™ technology of Sunds Defibrator (Sundsvall, Sweden; Norcross, Georgia) and the Enerbatch® process of Voest-Alpine (Linz, Austria).

The chemical delivery demands of an RDH-type batch system require additional equipment and a sophisticated process control system. This is especially true where the mill may run as many as 20 batch digesters at a time, sharing common process equipment (accumulator tanks, pumps, piping)). Production scheduling can be thrown off if there are disruptions due to equipment malfunction or operator error. Much of the work done since the discovery of the RDH principles has involved refinement of the "tank farm" configuration and improvement to the distributed control system that oversees the process.

Installations

Presently, world capacity for extended cooking is near 11 million tons per year (tpy), representing 20 percent of bleached kraft capacity (see Table 4-1). Worldwide, 31 new MCC®/EMCC® systems and 15 retrofits have been installed or are currently underway. Twenty-five of these projects are in the United States, including 16 new installations and 9 retrofits. Combined U.S. MCC® and EMCC® capacity (installed and underway) is 35,255 tpd, representing about 25 percent of U.S. bleached chemical pulp capacity. The average capacity of these installations is over 1,100 tpd. All new Kamyr digesters sold since 1985 have been equipped with (or prepared for) MCC® operation, hence retrofitting newer continuous digesters is technically quite straightforward.

Installations of extended batch cooking are also shown in Table 4-1. As of this writing, Beloit's RDH system had been installed at four U.S. mills plus one each in Canada, Finland, Spain and Taiwan. All four U.S. installations were new installs as opposed to retrofits. The Sunds SuperBatch™ digester system is currently operating at the Jefferson Smurfit mill in Jacksonville, Florida, at three Scandinavian mills, and at one South African mill.

Note that some mills may retrofit their existing pulping equipment without the input of the vendor companies discussed above. While technically not MCC®, EMCC®, or RDH, the equipment and principles applied are essentially the same.

Economics

Capital costs for extended delignification equipment have been quoted at $15 to $16 million for a new, 1,200 air dried short tons (ADST) per day MCC® digester, with the installed cost estimated at $40 to $45 million. Retrofits will range in cost from under $1 million for simple wash zone upgrades on digesters installed after 1980 to $15 to $30 million for a more complicated two-vessel conversion.

Costs for new RDH systems have been quoted at around $1.5 million for each new batch digester plus $5 million for the accumulator tank farm, with a turnkey system running approximately three times that amount or around $35 million for a 5-digester system. Costs for converting an existing pulping system to RDH would likely range around $0.5 million per digester. The retrofit potential for existing batch systems in the United States is somewhat limited, however, by the age of the digesters. Most U.S. batch digesters are of 1940-1970 vintage and hence many would not be suited for the complex modifications required for application of RDH. Space requirements for the RDH tank farm may also limit their applicability at some mills.

TABLE 4-1
Installations of Extended Delignification Systems Worldwide

Company	Location	Fiber Furnish	Capacity (tons/day)	Start-Up
New Kamyr MCC®/EMCC® Continuous Digesters North American Mills				
Federal Paperboard	Augusta, GA	HW/SW	770	1988
Domtar	Windsor, Que.	HW	1145	1988
Longview Fibre	Longview, WA	SW	1060	1988
Howe Sound	Port Mellon, B.C.	SW	1450	1990
Weyerhaeuser	Columbus, MS	SW	1575	1990
Daishowa Canada	Peace River, Alta.	HW/SW	1360	1990
Weldwood of Canada	Hinton, Alta.	SW	1460	1990
Federal Paperboard	Augusta, GA	HW	1520	1991
Champion International	Courtland, AL	SW	1180	1991
Union Camp	Eastover, SC	HW	1250	1991
Stone Savannah River	Port Wentworth, GA	HW/SW	865	1991
Alabama Pine Pulp	Clairborne, AL	SW	1620	1991
Gulf States Paper	Demopolis, AL	HW/SW	865	1992
Temple-Inland	Silsbee, TX	HW	1085	1992
Union Camp	Savannah, GA	SW	2450	1992
Alberta-Pacific	Boyle, Alta.	HW/SW	2020	1993
Celgar Pulp	Castlegar, B.C.	SW	1605	1993
Temple-Inland	Silsbee, TX	HW	1250	1994
Weyerhaeuser	Longview, WA	HW/SW	1455	1994
Weyerhaeuser	Plymouth, NC	HW/SW	700	1994
Weyerhaeuser	Plymouth, NC	HW/SW	1100	1994
Willamette	Johnsonburg, PA	HW	780	1994

TABLE 4-1 (cont.)
Installations of Extended Delignification Systems Worldwide

Company	Location	Fiber Furnish	Capacity (tons/day)	Start-Up
MCC®/EMCC® Retrofits of Kamyr Continuous Digesters North American Mills				
Consolidated Papers	Wisconsin Rapids,WI	SW	500	1987
International Paper	Georgetown, SC	SW	1300	1990
International Paper	Mobile, AL	HW/SW	1200	1990
Champion Int'l	Courtland, AL	HW	900	1990
Champion Int'l	Quinnesec, MI	HW	1000	1990
E.B.Eddy	Espanola, Ont.	SW	525	1991
Georgia Pacific	Ashdown, AR	SW	900	1991
Georgia Pacific	New Augusta, MS	HW/SW	1800	1991
Northwood	Prince George, B.C.	SW	1100	1991
Union Camp	Savannah. GA	SW	2450	1992
James River	Camus, WA	HW	580	1993
New Kamyr MCC®/EMCC® Continuous Digesters European, Asian, South American Mills				
Metsa-Botnia	Aanekoski, Finland	HW/SW	1210	1985
Korsnas	Gavle, Sweden	HW/SW	1160	1988
Kemi Oy	Kemi, Finland	HW/SW	800	1988
Iggesund Paperboard	Iggesund, Sweden	SW	690	1988
Oji Seishi	Kasugai, Japan	SW	800	1989
Nagoya Pulp	Kanishi, Japan	HW	800	1990
Oji Seishi	Yonago, Japan	HW	1200	1991
Celulosa Arauco	Arauco, Chile	SW	1210	1991
Celulosa Pacifico	Mininco, Chile	SW	1220	1991

TABLE 4-1 (cont.)
Installations of Extended Delignification Systems Worldwide

Company	Location	Fiber Furnish	Capacity (tons/day)	Start-Up
MCC®/EMCC® Retrofits of Kamyr Continuous Digesters European, Asian, South American Mills				
Enso Gutzeit	Varkaus, Finland	HW	590	1983
NCR	Vallvik, Sweden	SW	515	1990
Stora	Skutskar, Sweden	HW	420	1990
Iggesund Paperboard	Iggesund, Sweden	HW	800	1990
Beloit RDH Batch Extended Cook Systems North American Mills				
Packaging Corp	Valdosta, GA	HW/SW	1,000	1984
S.D. Warren (Scott)	Westbrook,ME	HW/SW	450	1989
Bowater	Calhoun, TN	HW/SW	1200	1990
Fletcher Challenge	Crofton, B.C.	SW	775	1990
Willamette	Bennettsville, SC	HW/SW	900	1990
Beloit RDH Batch Extended Cook Systems Rest of World				
Joutseno Pulp	Joutseno, Finland	HW/SW	950	1986
Nymolla	Nymolla, Sweden	SW	860	1987
Cellulosas de Naviron	Durango, Spain	SW	350	1989
Chung-Hwa	Hualien, Taiwan	HW	400	1992
Sunds SuperBatch Batch Extended Cook Systems Worldwide				
Jefferson Smurfit	Jacksonville, FL	SW	690	1990
ASSI	Karlsborg, Sweden	SW	875	1984
Mondi Paper	Richard's Bay, S. Africa	HW/SW	1500	1984
Sodra	Varo, Sweden	SW	900	1988
Enocell	Uimaharju, Finland	HW/SW	1800	1993

Source: MacLeod (1992).

Pollution prevention

Extended delignification can reduce the kappa number of brownstock softwood pulp from a range of 30 to 32 for conventional pulping to a range of 12 to 18 (although target ranges are currently around 20 to 25). Hardwood kappas can be reduced from around 20 to a range of 8 to 10, with current targets generally around 12 to 15. The impact of brownstock kappa number reductions on bleaching chemical demands and formation of many chlorinated organics is now well understood. AOX and polychlorinated phenols will be reduced in approximate proportion to reductions in the brownstock kappa number. Declines in conventional pollutants such as BOD_5, COD, and color characteristics of MCC® pulps are also well documented (Heimberger et al., 1988).

Compatibility

When used in combination with oxygen delignification, extended delignification has produced softwood pulps in the range of kappa number 6 to 10. These pulps are extremely bleachable and could be brought to full brightness using elemental chlorine-free (ECF) or totally chlorine-free (TCF) sequences.[2] Such sequences are associated with extremely low levels of AOX and CDD/CDF, and will allow closure of much of the mill's effluent cycle.

Extended delignification increases the amount of lignin and organic solids removed during the cooking process, and it is beneficial for the mill to burn these in the recovery boiler. Many boilers currently operate at or near capacity, thus it is often a challenge to find ways to accommodate the increase in solids load. A range of options are available, however, for increasing solids handling by 5 to 10 percent, and retrofits and rebuilds can boost capacity by significantly more at less than the $50 to $100 million cost of a new recovery boiler. Many mills already practice some of these techniques:

> **Additional evaporator** - Additional evaporation stages will increase the concentration of the black liquor, resulting in improved combustion (reduced gas flow) as well as lower sulfur emissions. Although this is a common upgrade option, the higher consistency solids are more difficult to handle and will necessitate improved pumping and firing equipment;
>
> **Transport black liquor solids offsite for disposal** - Where other kraft mills with excess recovery boiler capacity are within 500 miles of the mill, it may be feasible to ship additional solids offsite for firing. This has become common practice in some areas of North America and Europe;
>
> **Reduce boiler load per ton of solids** - Although boiler load is discussed in terms of pounds of solids burned, in practice the capacity ultimately depends on the heat content of the black liquor solids:

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[2] ECF pulps are produced using 100 percent chlorine dioxide substitution for chlorine; no elemental chlorine or hypochlorite are used. In TCF sequences, chlorine dioxide is also eliminated. Note that no bleached kraft mills in the U.S. are currently producing high brightness TCF pulps on a sustained basis. Louisiana-Pacific Corp. has agreed to eliminate chlorine-based bleaching at its Samoa, California kraft mill by 1995 (BNA, 1992), although as indicated in a company statement some brightness may be sacrificed: "Our expectation is that in the interest of a cleaner environment, consumers will accept paper products that are not quite as bright as they are accustomed to using."

(1) In at least one Swedish mill, black liquor oxidation has been used to reduce heat value of liquor solids sufficiently to accommodate an 8 to 10 percent increase in capacity;

(2) Mills can separate soap from the liquor solids for incineration or sale offsite. Soap removal can reduce the heat value of the liquor solids by 4 to 8 percent, thereby enabling further capacity increases;

Increase black liquor storage capacity - Some mills may lack sufficient black liquor storage capacity, resulting in insufficient supply to keep the boiler operating steadily at capacity (essential for efficient operation). By constructing additional supply capacity the mill may be able to obtain a higher liquor solids throughput from the existing boiler;

Black liquor gasification - A relatively recent technology, this proprietary process involves gasification of strong black liquor in a closed vessel. This produces a smelt similar to that from a conventional recovery furnace. A single Chemrec® unit is capable of processing the excess solids generated from oxygen delignification of 3,000 tpd of pulp;[3]

Anthraquinone addition in pulping - The use of an anthraquinone catalyst in the digester can increase the yield from kraft pulping by up to 2.5 percent (see Section 4.4) and decrease the production of black liquor solids by up to 6 to 10 percent;

Reduce boiler water feed temperature and/or temperature of combustion air - If steaming rate is the limiting factor on boiler capacity, these actions can reduce the steaming rate by several percent;

Enrich combustion air with oxygen - For mills limited by gas flow, it may be possible to boost boiler load capacity by introducing oxygen into the feed air;

Add incremental boiler capacity - Clement (1992) has presented case studies that illustrate a variety of options for increasing boiler capacity incrementally. In the four U.S. projects cited, capacity increases ranged from 10 to 63 percent. The costs have ranged from $3 to $63 million;

Boiler rebuild/replacement - Recovery boilers are among the most complex and expensive pieces of equipment at the pulp mill. The costs of constructing a new boiler could range from $50 to 100 million. While this may seem exceedingly costly, for an older mill a modern boiler will bring substantial additional benefits in the form of greater efficiency, easier maintenance, and reduced air pollution;

Production penalty - Mills may choose to decrease production to accommodate the additional solids per ton of pulp that results from oxygen or extended delignification. This operational penalty, however, is generally considered excessive.

In addition, it is always possible for the mill to discharge the effluent containing any additional (non-chlorinated) solids that cannot be accommodated in the recovery boiler. These will be treated in the existing wastewater treatment system.

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[3] The Chemrec® process is offered by the Swedish company Götavarken (U.S. subsidiary located in Charlotte, North Carolina).

The kraft liquor recovery system produces air emissions (from the recovery furnace) and solid wastes such as dregs (from the dregs washer) and grits (from the lime slaker). The modern recovery furnace is equipped with sophisticated air emissions control equipment such as electrostatic precipitation (ESP). Precipitates (primarily sodium sulfate and sodium carbonate) are returned to the liquor makeup system, hence the only material losses are the dregs and grits. These are usually landfilled. A higher degree of delignification would probably result in a minor (i.e., less than 5 percent) increase in the quantity of these materials going to landfill.

Extended delignification will cause an increase in steam demand (due to the longer cooking period), though more energy will be recovered from the additional lignin solids. The greatest energy impacts may be observed indirectly though, through reductions in bleaching chemical demands. Most bleaching agents are manufactured by applying energy to raw inorganic minerals (e.g., chloride, for the manufacture of sodium chlorate, caustic, and chlorine). McCubbin (1992) has modeled the onsite and offsite energy impacts of a variety of pollution prevention measures. Conversion of a model 1,000 tpd C_DEDED mill to extended delignification would result in no net increase in onsite power requirements but would reduce offsite power requirements (through decreased chemical use) by 3.4 MW (or around 800 kWh/ton).

4.2 OXYGEN DELIGNIFICATION

What it is

Installation of an oxygen reaction tower between the pulping and bleaching stages. Oxygen (a powerful bleaching agent) is mixed with the pulp and allowed to react. Lignin content in the pulp is further reduced prior to the bleaching stages, leading to decreased bleaching chemical demands and associated environmental impacts.

How it works

The brownstock pulp from the digester is first washed and then mixed with oxygen as it enters the reactor (see Figure 4-3). In high consistency systems, a press is required to remove excess water from the pulp prior to reaction. In the reactor, the pulp undergoes oxidative delignification. The pulp is then washed again to remove dissolved lignin solids before proceeding to the bleaching line. Oxygen systems are available from all of the major pulp equipment vendors.

Installations

Until recently, oxygen delignification had been more widely adopted outside of North America. In recent years the adoption rate within the U.S. and Canadian industries has increased. Presently, there are close to 150 mills worldwide that operate oxygen delignification systems, representing 26 million tons of annual production. Oxygen is currently installed or planned for 27 U.S. mills (see Table 4-2). Of these, 16 will have come online since 1989 only. U.S. capacity is currently around 8.1 million tons per year.

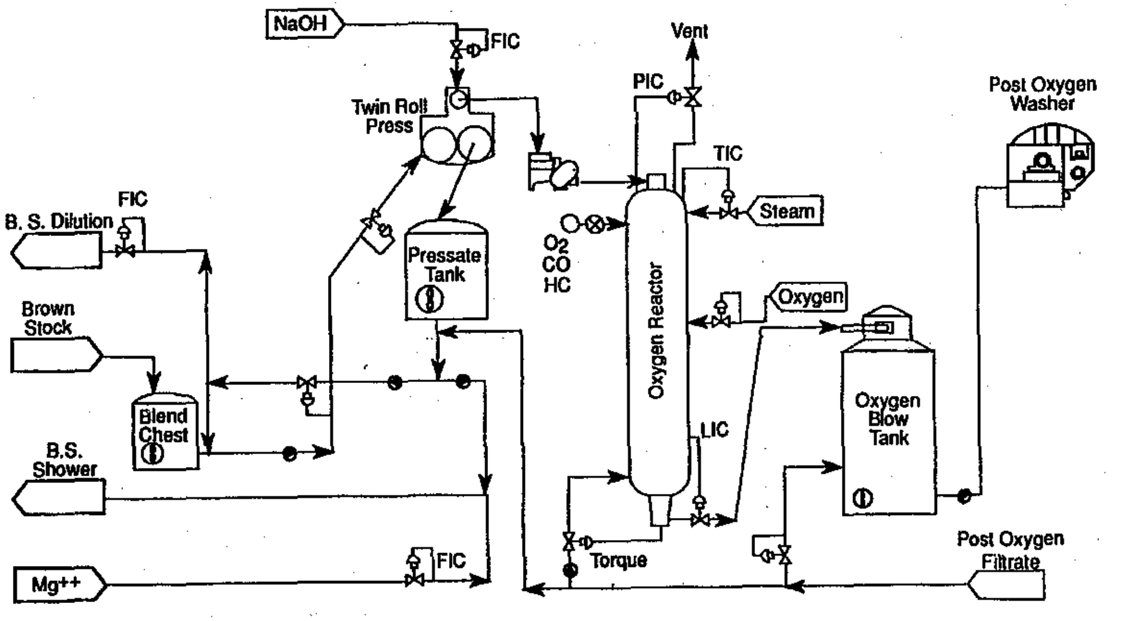

Figure 4-3. Process flow for high-consistency (HC) oxygen delignification.

Source: Miller, 1992.

TABLE 4-2
U.S. Installations of Oxygen Delignification Systems

Company Name		Location of Mill	Production Capacity (tpd)	Consistency [a]	Year of Startup
1	Chesapeake	W. Point, VA	550	HC	1972
2	Weyerhaeuser	Oglethorpe, GA	1,000	HC	1980
3	Union Camp	Franklin, VA	800	HC	1981
4	Union Camp	Eastover, SC	650	HC	1984
5	Consolidated Paper	Wisconsin Rapids, WI	500	MC	1985
6	Champion International	Pensacola, FL	800	MC	1986
7	Champion International	Pensacola, FL	600	MC	1987
8	Flambeau Paper	Park Falls, WI	200	MC	1987
9	Bowater Corp.	Calhoun, TN	1,300	MC	1988
10	Louisiana-Pacific	Samoa, CA	750	MC	1988
11	Willamette Industries	Bennettsville, SC	840	MC	1988
12	Champion International	Quinnesec, MI	1,150	MC	1989
13	Wausau Paper	Brokaw, WI	290	MC	1989
14	Westvaco	Covington, VA	915	MC	1990
15	Weyerhaeuser	Columbus, MS	1,400	MC	1990
16	Alabama Pine	Clairborne, AL	1,415	MC	1991
17	Champion International	Courtland, AL	1,150	MC	1991
18	Confidential client	Southern U.S.	1,385	MC	1991
19	Simpson Paper	Eureka, CA	850	MC	1991
20	Union Camp	Eastover, SC	1,100	HC	1991
21	Weyerhaeuser	Cosmopolis, WA	540	MC	1991
22	Weyerhaeuser	New Bern, NC	1,080	MC	1991
23	Champion International	Canton, NC	660	MC	1992
24	Champion International	Canton, NC	700	MC	1992
25	Champion International	Courtland, AL	1,245	MC	1992
26	Potlatch Corp.	Lewiston, ID	1,130	HC	1992
27	Union Camp	Franklin, VA	900	HC	1992
	Total capacity		23,900		

[a] HC = High consistency, MC = Medium consistency

Source: Johnson (1992).

Economics

The capital costs of the oxygen reaction tower and related equipment (pumps, washers) have been estimated at between $8 and $16 million (see Table 4-3). At the low end of this range, the savings in chemical costs, plus savings on current or future effluent treatment requirements, may favor the switch to oxygen. Installation of an oxygen delignification stage may also help mills avoid the costs of installing a new chlorine dioxide generating system or replacing an aging C-stage in their bleaching line. At other mills considerably greater investment may be required, particularly to upgrade pulp washing equipment. Successful implementation of oxygen delignification requires effective pulp washing both in front of and following the oxygen stage. For mills that require a considerable upgrade in pulp washing equipment, the cost of conversion may be closer to $15 million.

Most mills today using oxygen for bleaching will generate it onsite using non-cryogenic systems provided by equipment vendors. Typically, the mill enters into a 10- to 20-year "over the fence" supply contract with the vendor. The mill supplies the land for construction of the plant, while the vendor installs the equipment and in some cases operates the plant as well. The technologies for onsite generation are much smaller in scale and produce slightly lower purity oxygen compared to cryogenic methods, although this does not appear to affect pulp properties or mill operations to any significant degree. Advances in pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) technologies have enhanced the attractiveness of onsite generation.

In one comparison, capital costs for a PSA oxygen system ranged from $220,000 to $525,000 and produced oxygen at a cost of $50 to $75 per ton. This compares to prices of $100 per ton for liquid oxygen (Bansal, 1987). Onsite oxygen plants are available from numerous industrial gas vendors such as Liquid Air, Air Products, Airco, and Union Carbide.

Pollution prevention

Since effluent from the oxygen stage can be recycled to the mill's recovery system, oxygen delignification will reduce discharges of pollutants such as BOD_5, color, and organochlorines. Table 4-4 shows BOD_5 declining by approximately 32 percent, COD by 43 percent, and TOCl by 50 percent following installation of an oxygen stage. Oxygen and extended delignification can also reduce the overall wastewater flows from the mill by up to 25 percent each, putting it on the track towards zero effluent pulping and chlorine-free bleaching.

Compatibility

Oxygen delignification is compatible with most conventional bleaching sequences. In addition, since oxygen delignification has the potential to lower the pre-bleach stage kappa number by as much as 50 percent, a variety of innovative bleaching methods may also be applied. In a typical application, the mill follows the oxygen stage with a mixture of chlorine and chlorine dioxide, followed by a caustic extraction stage, another ClO_2 bleaching and extraction stage, and a final bleaching stage, i.e. OC_DEDED. A significant benefit of oxygen delignification is that it allows the mill to increase the substitution rate of chlorine dioxide for chlorine in the C_D stage without requiring additional chlorine dioxide generating capacity. A typical mill currently operating at 30 percent ClO_2 substitution, for example, could operate at 70 percent by increasing its dioxide generating capacity, or by adding an oxygen delignification stage and using existing dioxide capacity at 70 percent. Drawing from a database of actual installations,

TABLE 4-3
Capital Cost Estimates for Oxygen Delignification Systems

Information Source	Description	Size	Capital Cost ($millions)
Literature	Short sequence OD system	500 tpd	$8.8
Supplier	OD	500 tpd	$9-11
	OD	1000 tpd	$14-16
	MC	1000 tpd	$13-16
Consultant	Hardwood MC	n.a.	$13.5
	Softwood HC	n.a.	$19.5
EPA (1990)	Louisiana-Pacific, Samoa, CA, MC	680 tpd	$8.0
	Simpson Paper, Fairhaven, CA, MC	600 tpd	$11.5
	Weyerhaeuser Cosmopolis, WA, MC	400 tpd	$9.5
Idner (1988)	Softwood HC, Sweden	n.a.	$11-14.5
	Softwood, MC Sweden	n.a.	$6.5-$8.1
	Hardwood, HC Sweden	n.a.	$11-14.5
	Hardwood, MC Sweden	n.a.	$6.5-$8.1

MC = medium consistency oxygen
HC = high consistency oxygen

Sources: As indicated in table.

TABLE 4-4
Pollutant Impacts of Oxygen Delignification Versus Conventional Bleaching

	Softwood (Pine)			Hardwood (Birch)		
Parameter	Conven -tional	HC	MC	Conven -tional	HC	MC
Kappa no.	32	18	15	20	14	12
BOD_7, kg/mt	14	10.5	9.5	14.5	11.5	10
COD, kg/mt	80	50	45	50	40	35
TOCl, kg/mt	5 to 5.5	3 to 3.5	2.5 to 3	2 to 2.5	1.5 to 2	1.5
Reduction in acute toxicity to fish, % of reference	--	50 to 60	60 to 70	--	n.a.	n.a.

n.a. = not available.
HC = high consistency oxygen
MC = medium consistency oxygen

Source: Idner (1988).

Brunner and Pulliam (1992) have recently presented data for a model 1,000 tpd mill that indicated the latter option results in both lower capital and operating costs.

Other options include "short sequence" bleaching, in which oxygen delignification is followed by two rather than three bleaching stages (i.e., OC_DED or $ODE_{OP}D$). While short sequence bleaching has the benefits of lower capital costs and reduced effluent flow, its feasibility for an individual mill will depend on the pulp quality requirements, including the target brightness level. With fewer bleaching stages there is less opportunity for "fine tuning" the pulp characteristics and probably more variability in pulp quality. Integrated mills are more likely to consider short-sequence bleaching than market pulp producers.

Finally, when combined with extended delignification, mills may be able to produce oxygen delignified pulps with kappa numbers below 8 to 10 and without loss of strength or yield. These pulps are extremely bleachable and may be bleached to 80+ brightness using small amounts of chlorine dioxide (ECF bleaching), to 70+ percent ISO using one or more peroxide-based stages (e.g., the Lignox process), or to 85+ with ozone and peroxide (OZEP).

As with extended cooking, the addition of an oxygen stage increases the amount of recovered black liquor solids available for heat recovery. The recovery of 80 percent of the oxygen stage solids will generally increase the solids going to the boiler by 50 to 55 kg per metric ton (approximately 3 percent) for hardwoods and by 30 to 35 kg per metric ton (approximately 2 percent) for softwoods. Additional post-oxygen washing stages can increase this further still. At older mills where pre-chlorination washing is currently inefficient, the increase could be as much as 10 percent. Section 4.1 discusses a range of options a mill might take to accommodate demands for additional boiler capacity created by oxygen bleaching.

4.3 OZONE DELIGNIFICATION

What it is

Installation of an ozone reactor between the pulping and bleaching stages, and normally following an oxygen stage. Ozone (an extremely powerful bleaching agent) is mixed with the pulp which undergoes a rapid exothermic reaction. Lignin content in the pulp is greatly reduced. Since this occurs prior to any chlorine-based bleaching stages, dramatic decreases in bleaching chemical demands and associated environmental impacts can result.

How it works

Ozone delignification is performed using techniques and equipment similar to that used in oxygen delignification (see Figure 4-4). Peak ozone delignification efficiency has been found to occur at low pH, thus pulp is normally pretreated with sulfuric acid prior to ozonation. As with oxygen, both medium and high consistency systems are available. The acidified pulp is fluffed and deposited in the ozone reactor. Ozone gas generated onsite is delivered to the pulp in an oxygen carrier gas. During reaction, the ozone is consumed and the carrier gas is recovered and either returned to the ozone generator or used elsewhere in the mill.

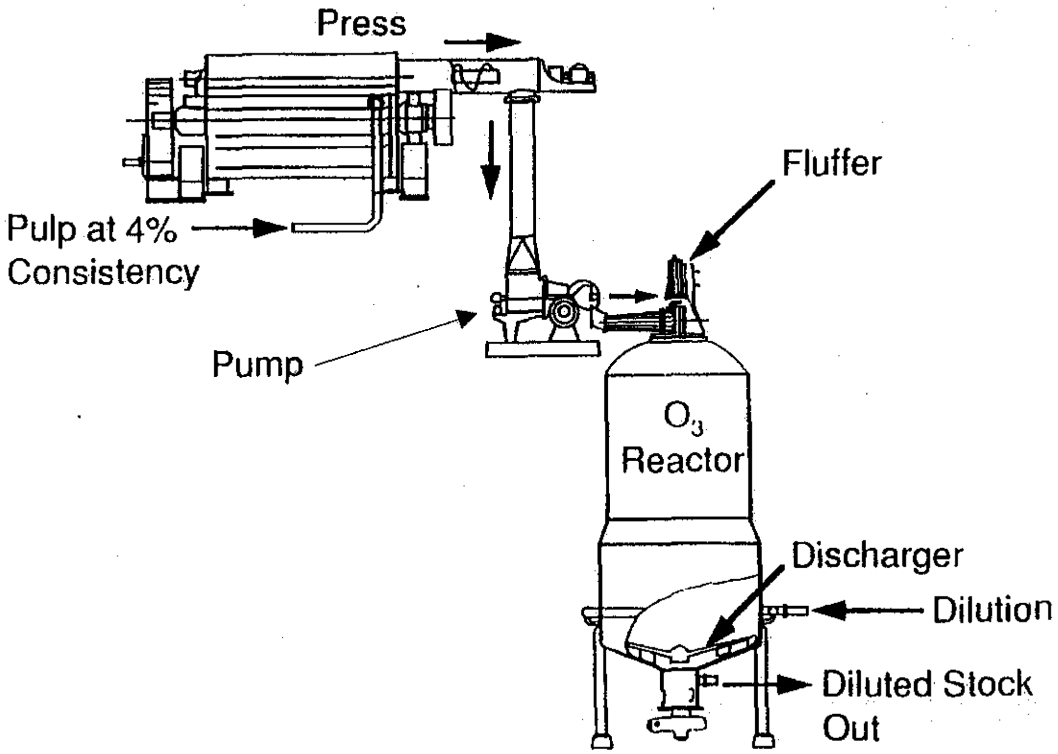

Figure 4-4. Equipment for high-consistency (HC) ozone delignification.

Source: Miller, 1992.

Until recently, the use of ozone in pulp bleaching was limited because of the detrimental effects it can have on pulp quality and strength properties. The successful "taming" of ozone has been greatly anticipated, however, since it opens the door to elimination of chlorine compounds in bleaching and raises the possibility of complete closure of the mill's bleach plant. As a result of a considerable research effort, the past year has seen the startup of the first two full-scale mills (1,000 tpd or more) operating ozone bleaching lines. Ozone bleaching equipment is now being offered by the following suppliers:

Ozone Generating Equipment	Onsite/Over-the-Fence Supply
Ozonia	Liquid Air
Emery-Trailgaz	Air Products
Capital Controls	Praxair (formerly Linde)
Sumitumo	MG Industries

Ozone generation requires large amounts of power, about 8 kWh per kilogram of ozone.[4] The ozone is most commonly generated from oxygen using the corona discharge method. This technology consists of a series of tubes through which the feed oxygen or air flows. As high voltage is applied across the discharge gap, free electrons in the corona collide with the diatomic oxygen and cause disassociation of the O_2 molecules, which recombine to form ozone. Ozone is unstable with a half life of only 15 minutes and will decompose to regular oxygen, thus ozone must be generated onsite and fed immediately to the pulp reactor.

Installations

Table 4-5 shows the chronology of ozone pilot plant and full-scale installations worldwide. Early work was done at the Scott Paper mill in Muskegon, Michigan and then at Longview Fiber in Washington state. PAPRICAN was also involved in early research work at their Pointe Claire, Quebec headquarters. In 1989, Union Camp (Wayne, New Jersey) installed a pilot plant at its mill in Eastover, SC. This $6 million experimental project has provided promising results over a four-year period. Based on their pilot experiences, the company just recently (September 1992) completed the startup of a full-scale ozone bleaching line at its 1,000 tpd mill in Franklin, Virginia -- the first in the world to operate at that scale. The mill uses oxygen, ozone, and chlorine dioxide to produce elemental chlorine-free (ECF) pulp from southern pine. All of the pulp will be used for onsite production of bleached uncoated free sheet and coated and uncoated bleached board. Target brightness is 83 to 85 GE, and the bleaching sequence is OZE_OD.

Other commercial-scale ozone projects are now in the startup or planning stages:

- The Mönsterås mill in Sweden started up a 1,000 tpd medium consistency ozone bleach line at approximately the same time as Union Camp's startup. The mill is reported to be using 30 kilos of peroxide per ton of pulp to produce totally chlorine-free market pulp (TCF) at 88 to 89 ISO brightness for sale in Germany;
- The Lenzing mill in Austria has installed medium consistency ozone in an $E_{OP}ZP$ configuration at its 100 tpd dissolving pulp mill. The mill is reportedly converting a separate 300 tpd line at this time;

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[4] Note that chlorine dioxide generation requires approximately the same amount of energy as ozone, but that ozone is twice as powerful a bleaching agent.

TABLE 4-5
Ozone Pilot and Full-Scale Plants Worldwide

Year	Location		Capacity (tpd)	Consistency	Bleaching sequences	Pulp type
1971	PAPRICAN	Pointe Claire, Quebec	10	HC	Z, (PZ)	Mechanical
1973	Scott Paper	Musckegon, MI	15	HC	Z	Hardwood kraft
1975	PAPRICAN	Pointe Claire, Quebec	10	HC	Z	Sulfite, kraft
1976	CTP	Grenoble, France	0.5	HC	Z	Mechanical
1982	Myrens Verksted	Hofmen-Hellefos, Norway	5	HC	Z	Mechanical, sulfite
1982	Weyerhaueser	Longview, WA	20	LC	OZD, OZDED	Softwood kraft
1988	PWA	Stockstadt, Germany	3	HC	Z	Sulfite
1989	Union Camp	Eastover, SC	25	HC	OZEDED	Kraft
1990	Wagner-Biro AG	Graz, Austria	1	LC	OZP	Sulfite, kraft, nonwood fiber
1990	Kraftanlagen Heidelberg	Beienfurt, Germany	5	HC	OZEP	Mg bisulfite
1991	Lenzing AG	Lenzing, Austria	100	MC	(EOP)ZP	Hardwood, dissolving
1991	OZF	Gratkorn, Austria	15	LC/HC	any sequence	Kraft, sulfite
1991	E.B. Eddy Forest Products	Espanola, Ontario	5	LC/MC/HC	O(Z)...	Softwood kraft, hardwood kraft
1991	PAPRICAN	Pointe Claire, Quebec	5	MC	OZEP, OZED O(pZE)P	All types
1991	CTP	Grenoble, France	3	MC/HC	...	All types
1992	Lenzing AG*	Lenzing, Austria	400	MC	(EOP)ZP	Hardwood, dissolving
1992	Union Camp*	Franklin, VA	1000	HC	OZE$_{O}$D OZE$_{O}$P (potential)	Kraft, integrated
1992	Sodra*	Monsteras, Sweden	1000	MC	OZEP	Market kraft, HW/SW (HW only so far)

... Represents any subsequent sequences
* Commercial installation.
LC = low consistency ozone
MC = medium consistency ozone
HC = high consistency ozone

Source: Liebergott et al. (1992).

- MoDo has purchased an ozone system from Kamyr for installation at their mill at Husum, Sweden;
- SCA Wifsta-Östrand in Sweden has entered into an agreement to produce pulp at their Timra kraft mill using ozone technology licensed from Union Camp;
- The E.B. Eddy mill in Espanola, Ontario is considering installation of a full-scale ozone plant following successful operation of their pilot plant.

Union Camp has formed a worldwide marketing alliance with Sunds Defibrator of Sweden to license its ozone bleaching technology in the pulp and paper industry under the name C-Free^{TM}. The technology is based on use of oxygen delignification, gas phase ozone, and a small amount of chlorine dioxide, which enables the licensee to produce ECF pulp at full market brightness.

Economics

Capital costs for the ozone delignification equipment will depend on type of system selected (i.e., high or medium consistency). Mills using ozone as a "bulk delignification" stage, that is, as the primary delignifying agent, may choose high consistency due to the decreased ozone consumption per ton of pulp. Others using ozone as a "polishing stage" for pulp brightening may favor medium consistency.

In comparison with chlorination stage bleaching, ozone requires additional process equipment (pulp press, high shear mixers, acid handling system) but benefits from the ability to use cheaper construction materials (corrosion problems are less severe compared to chlorine bleaching). Depending on how close the mill comes to closing its effluent cycle and whether it maintains one or more D stages, there should be reduced costs for effluent treatment and bleach plant scrubbing systems. The final cost for the Franklin mill installation has been recently cited as $113 million for a full 1,000 tpd bleach plant.

Bleaching costs, including ozone generation, are lower than for conventional sequences. Union Camp reports that bleaching costs at their Franklin mill are approximately 68 and 43 percent lower than the costs of a modern mill's DEDED sequence running at 100 percent chlorine dioxide substitution (see Table 4-6).

Union Camp's decision to retain a chlorine dioxide stage was based on the expectation that elimination of elemental chlorine would be sufficient to guarantee satisfactory effluent levels. The use of ozone in the bleach line, however, introduces the possibility of eliminating all chlorine-containing compounds to produce totally chlorine-free (TCF) pulp. Hydrogen peroxide would be used as a replacement for chlorine dioxide in a TCF sequence. The company estimates that replacing ClO_2 with peroxide would raise operating costs back to the level of a CEDED sequence if 90 brightness were required (peroxide costs would be around $30 to 40 per ton). Lower brightness TCF pulps (low 80s ISO) could be produced at significantly lower costs (under $10 per ton premium) if there was greater market acceptance.

Since either oxygen delignification or extended cooking (or both) are considered prerequisites for successful ozone bleaching, the more widespread adoption of these technologies will undoubtedly increase interest in ozone. Also, ozone's cost vis-à-vis conventional bleaching sequences has improved as it is now more likely to replace more expensive chlorine dioxide rather than less expensive chlorine.

TABLE 4-6
Bleaching Chemical Costs of Ozone Versus Conventional Sequences at Union Camp's Franklin, Virginia Mill

Sequence	Relative Costs	
	Pine	Hardwood
C-E-D-E-D	100	100
O-Z-E-D	48	83

D-E-D-E-D	100	100
O-D-E-D	56	73
O-Z-E-D	32	57

Note: Bleaching chemical costs of ozone-based sequences are shown relative to those of conventional sequences (costs equal to 100 for the conventional processes). Assumptions for costing purposes are shown below.

Source: Nutt et al. (1992).

ASSUMPTIONS

Chlorine	$153.00 per ton	Includes byproduct saltcake credit
Chlorine Dioxide	$0.32 per lb	
Oxygen	$53.00 per ton	
Magnesium sulfate	$485.00 per ton	
Caustic co-purchased with chlorine on ECU basis	$215.00 per ton	Used for CEDED requirements and used for ½ of O(DC)ED requirements
Caustic purchased independent of chlorine	$340.00 per ton	Used for OZED requirements and used for ½ of O(DC)ED requirements
Cost of preparing oxidized white liquor	$29.00 per ton as NaOH	
Sulfuric acid	$68.00 per ton	
Chelant	$0.51 per lb	
Ozone	$0.29 per lb	Based on power costs of $36/MwH and Union Camp's design of a recirculating ozone generation system

Pollution prevention

Due to its powerful bleaching effect, ozone has the potential to replace most if not all of the chlorine-based bleaching agents used in conventional pulp bleaching. At Union Camp, the bleaching sequence has been simplified to OZED, eliminating all elemental chlorine and retaining just one stage of chlorine dioxide bleaching. Emissions from the process are extremely low because of the ability to recycle all of the O, Z, and E stage effluents (see Table 4-7). Total organic halides (TOX) are below 0.1 kg per adt in effluent, chloroform is a very low 0.0015 kg per adt, BOD is below 2, COD is below 6, and color is below 1.5 (traditional color levels are around 100 to 300 kg per ton). The mill has been unable to detect dioxins using the most sensitive testing methods available, even after boosting chlorine dioxide consumption in the final stage

Among the numerous bleaching sequences being investigated that make use of ozone are: OZE_P, OZED, OZPY, OZEPY, $ZO_{ZW}PY$, and OZE_DPY. (Note: O_{ZW} refers to an oxygen stage using a wash of ozone stage effluent and Y is sodium hydrosulfite.) The absence of elemental chlorine in these sequences and the elimination of all chlorine-based compounds in some indicates that effluents from future mills using ozone will be extremely low in pollutants of current concern.

Compatibility

One concern raised by some in the industry is that ozone-bleached pulps tend to be of lower strength and hence lower quality than those produced by conventional bleaching processes. Most of these concerns center around observed decreases in the viscosity of pulps bleached using ozone. Viscosity has traditionally been used as an indicator of pulp strength, and ozone-bleached pulps have in fact been found to have lower viscosities than conventionally-bleached pulps of similar kappa number. However, numerous researchers have found that the viscosity-strength relationship is different for non-conventionally bleached pulps, so that despite the lower viscosities ozone bleaching does not impair pulp strength properties.

It should be noted that ozone is a toxic gas that must be handled properly. Ozone generators are equipped with sensors that will shut off power to the unit if any leaks are detected. Ozone production stops as soon as the power is cut. Under pressure, ozone may also present explosion hazards. For this reason, high consistency systems that operate at or near atmospheric pressures may be considered safer than medium consistency systems that operate under pressure.

One distinct safety advantage of ozone over chlorine is that the ozone is generated onsite. Chlorine is generally shipped to the mill in 100-ton tanker cars; this gas must then be transferred and stored onsite. Since ozone is produced on demand there is no onsite storage, hence only the small quantities contained in the pipeline (several kilograms) would pose a danger.

TABLE 4-7
Emissions from Ozone Bleach Line at Union Camp's Franklin, VA Mill [a]

Parameter		Pine	Hardwood
TOX, kg/ADT	Pulp	0.04	0.03
	Effluent	0.075	0.06
Chloroform, kg/ADT		0.0015	0.0015
BOD_5, kg/ADT		2.0	1.0
COD, kg/ADT		6.0	2.0
Color, kg/ADT		1.5	0.5
Effluent Volume	m^3/ADT	7.5	7.5
	gal/ADT	1,800	1,800

[a] Running an OZED bleaching sequence to produce 83 brightness pulp.

Source: Nutt et al. (1992).

4.4 ANTHRAQUINONE CATALYSIS

What it is

Small amounts of anthraquinone (AQ) added during pulping will act as a catalyst to speed up the cooking process and increase pulp yield. Alternatively, the technique can be used to reduce the amount of lignin solids generated per ton of pulp, thereby facilitating adoption of extended cooking or oxygen delignification.

How it works

The AQ is added to pulp during cooking using an application rate of around 0.05 to 0.1 percent on cooking liquor. The AQ catalyzes or accelerates the fragmentation of lignin, rendering it more vulnerable to attack and dissolution by the cooking chemicals.

Installations

AQ pulping is used in an estimated 60 percent of Japanese mills to improve yield from what are relatively expensive wood sources, and in at least two mills in Canada. The trade journal *Paper Age* has reported that over 100 mills worldwide use anthraquinone. There is reported to be increasing interest in AQ as a means of achieving extended delignification and overcoming boiler capacity bottlenecks.

Economics

By increasing yield or reducing chemical requirements, anthraquinone catalysis offers a potential means to offset the tendency of oxygen delignification or extended delignification to overload the kraft recovery system. It has been estimated that AQ could compensate for an increase in chemical recovery load of up to 7 or 8 percent. An AQ charge of 0.04 percent on wood in a 1,000 adt per day mill would have the following effects: (1) raise yield by 0.75 percent (or an additional 7.5 tons per day); (2) increase net costs by $5,262 per day or $5.15 per adt; and (3) reduce boiler load 4.6 percent. In some mills, a 4 to 5 percent reduction in boiler load will be sufficient to enable the mill to accommodate the additional solids load that results from oxygen delignification. The additional cost of AQ would, of course, offset the cost savings that would otherwise result from using oxygen.

Pollution prevention

Anthraquinone addition has the potential to alternatively decrease bleaching chemical requirements or facilitate adoption of oxygen delignification. In either role, anthraquinone will have a positive (i.e., beneficial) impact on the formation and release of chlorinated organics. By producing brownstock pulp with lower lignin content, the mill can decrease overall bleaching chemical requirements. And by improving the feasibility of oxygen delignification, the mill can recycle additional effluent as well as cut back on bleaching chemical usage. As with other delignification modifications that lower the pre-chlorination kappa number, chlorinated organics formation should decrease in approximate proportion to the drop in lignin content.

Compatibility

Most of the reacted AQ is removed with the spent liquor and presents no difficulties in the recovery system. AQ is not detectable in pulps subject to further chemical bleaching.

Anthraquinone is produced from coal tar generated in the coking process at steel mills. The chemical is used in several industries, including textiles where it serves as an intermediary in dyestuff manufacture. No negative environmental effects are known.

4.5 BLACK LIQUOR SPILL CONTROL AND PREVENTION

What it is

Accidental losses of black liquor may occasionally occur due to equipment failure, design flaws, or human error. Losses can result from overflows or leaks from process equipment (spills), or as a consequence of deliberate operator action (dumps) taken to avoid much more serious consequences. Equipment modifications can result in fewer spills or mitigate spill impacts, while spill prevention programs can potentially have even greater impacts.

How it works

Where no spill recovery system is in place, losses of black liquor will flow through the sewer to the wastewater treatment system. Depending on the volume of the spill, the high level of BOD and COD in the black liquor can shock the microbial action of the system, throwing it off balance and degrading the quality of treated effluent. Production interruptions may be necessary to allow time for the treatment system to return to equilibrium.

Effective loss control is achieved through good design, engineering, and operator training. Design changes that can be implemented include: 1) physical isolation of individual pieces of equipment so that spills can be collected and recovered, 2) modifications to the general floor drainage system so that spills are collected and returned to the recovery system, 3) provision of additional backup storage capacity, 4) sensors and other systems that provide immediate warning of potential or actual spill conditions, and 5) replacement of open-stage washing and/or screening equipment with closed equipment.

An effective spill control system design is shown in Figure 4-5. The system would include conductivity and pH probes in the process sewer to detect and identify the spill. Once detected and identified, the spill can be diverted to either a spill lagoon (in the case of weak spills that would not overload the treatment plant) or to a spill tank, where the spill would be held until it could be reintroduced into the recovery system.

Operator training and awareness is equally important to prevention. Control of spills requires an appreciation of the overall process, knowledge about locations where spills are likely to occur, and an understanding that spill control and environmental protection is part of every employee's job.

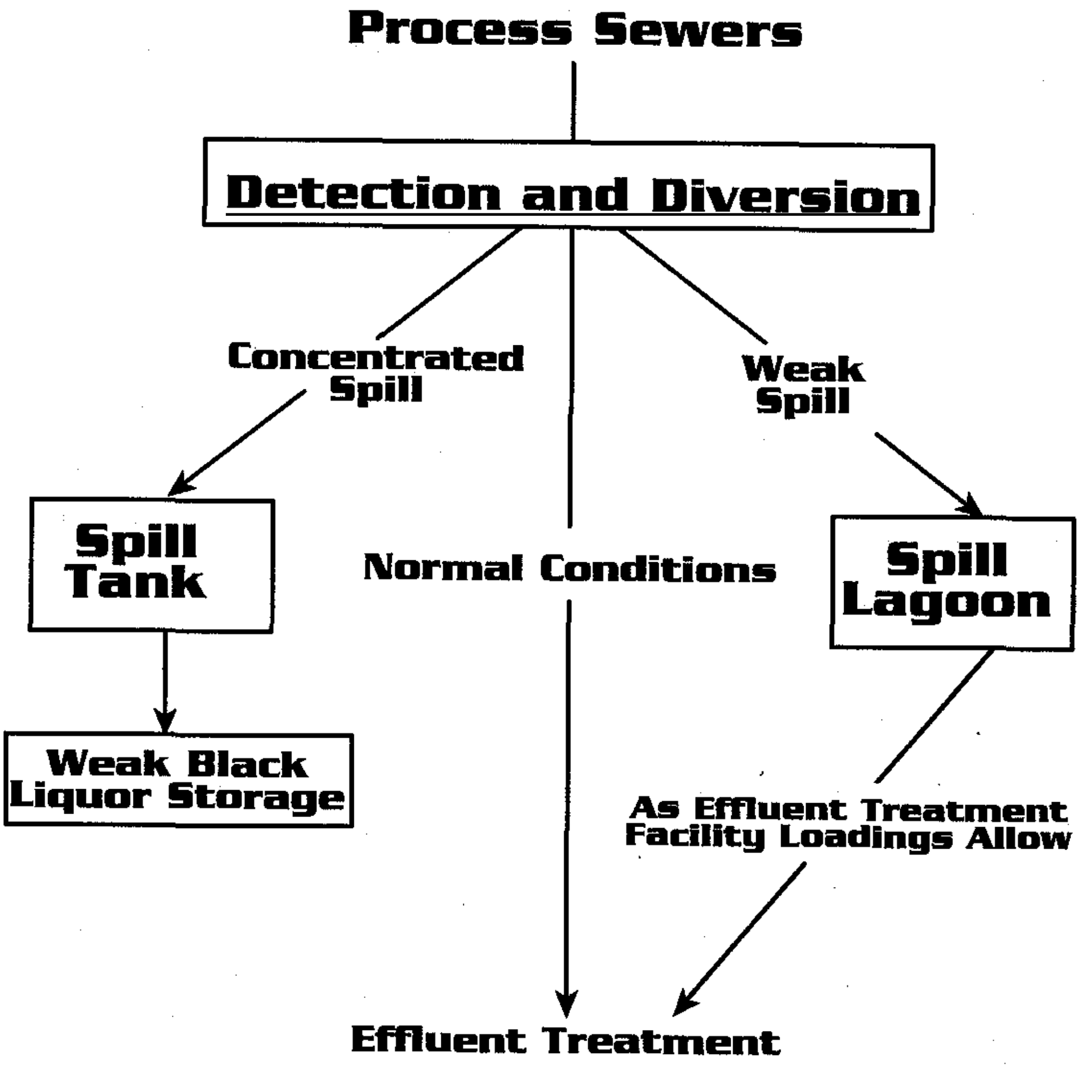

Figure 4-5. Spill control system flow design.

Source: Edde, 1984.

Installations

Improved spill control is recognized as an essential element in the overall environmental control of a modern pulp and paper mill. Newer mills are likely to have advanced spill warning and control systems designed into the plant from the start, and to use newer equipment design that is less prone to spillage. In an older mill, the retrofitting of floor drains and other spill collection systems can be quite difficult and very expensive, but some degree of improvement over the practices of the 1960s is generally possible. Instrumentation to warn of spills and facilitate rapid implementation of corrective measures can normally be retrofitted relatively easily.

Economics

Costs for improving spill control are quite site-specific, as they depend more on the physical layout of the plant than on the particular process in use. Capital costs are more likely to be in the range of hundreds of thousands rather than millions of dollars, while operating costs are low and will be partially or totally offset by recovered chemical and/or heat value, provided the spill is routed to the recovery cycle.

Pollution prevention

Raw black liquor contains high levels of BOD, COD, as well as some persistent non-chlorinated organics. As increased recycling of mill effluents is achieved through use of extended delignification and oxygen, spills will account for an increasing percentage of total mill effluent, and efforts to minimize or control spills will become more important.

Compatibility

When spills are not recovered the heat and chemicals value of the black liquor solids is lost. A high loss rate due to spills could result in a significant economic penalty in terms of lost heat and chemicals.

4.6 ENZYME TREATMENT OF PULP

What it is

Brownstock pulp is pretreated with cultured enzymes that catalyze the delignification reaction. This reduces subsequent bleaching chemical demands and the associated environmental impacts.

How it works

Research in the field of biotechnology has isolated specific, naturally-occurring microorganisms that produce enzymes capable of weakening the lignin bonds in pulp fibers, thereby providing a boost to delignification. The enzymes of most interest in pulp bleaching are the xylanases, which are secreted by wood-inhabiting microbes. Xylanases catalyze the hydrolysis of xylan, the main bonding agent between lignin and cellulose. This action is believed to improve the accessibility of bleaching chemicals to the pulp and enhance the extractability of the solubilized lignin.

Xylanase application in the mill has proven to be relatively simple. Conditions favorable for xylan reaction with pulp include: pH between 4 and 6, temperatures of 40 °C to 55 °C, reaction times of between 30 and 180 minutes, and pulp consistency between 2.5 and 12 percent. These conditions can be easily obtained by mixing sulfuric acid and xylanases with pulp coming off the brownstock washer as it enters the high density storage chest, in effect using the brownstock storage as a reaction vessel.

Installations

Xylanases suitable for use in pulp bleaching are available from several biotechnology and chemical concerns around the world, including: Genencor International, Iogen, Novo Nordisk, Sandoz, ICI Canada, and Voest-Alpine. Xylanase application rates are expressed in terms of International Units (IU) of xylanase activity, as applied per ton of pulp. The commercial enzymes are prepared to deliver a specific dose of IU's per kilogram to enable application on about a 1 kg per ton of pulp basis.

The exact number of mills running enzyme trials or using enzymes for production quantities is not known but it is believed that interest is high at this time. Given that the modifications necessary to accommodate enzyme treatment are quite minor, observers believe there to be many mills carrying out their own trials. According to a recent report, 10 mills were using enzymes in full scale commercial application and 85 mills were running trials (Juracek and Paice, 1992). Six of the 10 mills running full time were in Europe and the other four were in Canada.

Economics

The equipment necessary to apply enzymes to pulp is quite modest. Costs for an enzyme delivery system and pH adjustment are likely in the range of $10,000 to $100,000. The enzyme cost per ton of pulp is variable and depends on the type, activity level, and recommended application rate for the enzymes. Costs in the range of $5 to $10 per ton of pulp have been indicated by supplier firms. These costs will be partially or completely offset by savings in chemical costs.

Pollution prevention

In mill trials, reductions in active chlorine requirements of between 15 and 50 percent are being reported. Figure 4-6 shows the lower AOX levels associated with xylan-treated pulps versus control pulps in a 20 percent chlorine dioxide substitution bleaching sequence. Some improvement in brightness ceilings have also been observed, as shown in Figure 4-7. The reduction in demand for downstream bleaching chemicals can be used by mills in a variety of situations, including boosting of brightness levels, higher substitution of chlorine dioxide, or to facilitate production of totally chlorine-free pulp.

Compatibility

Xylanases appear to have no discernible impact on pulp quality or yield. Enzyme trials to date have been found there to be no impacts on pulp quality, strength or other attributes.

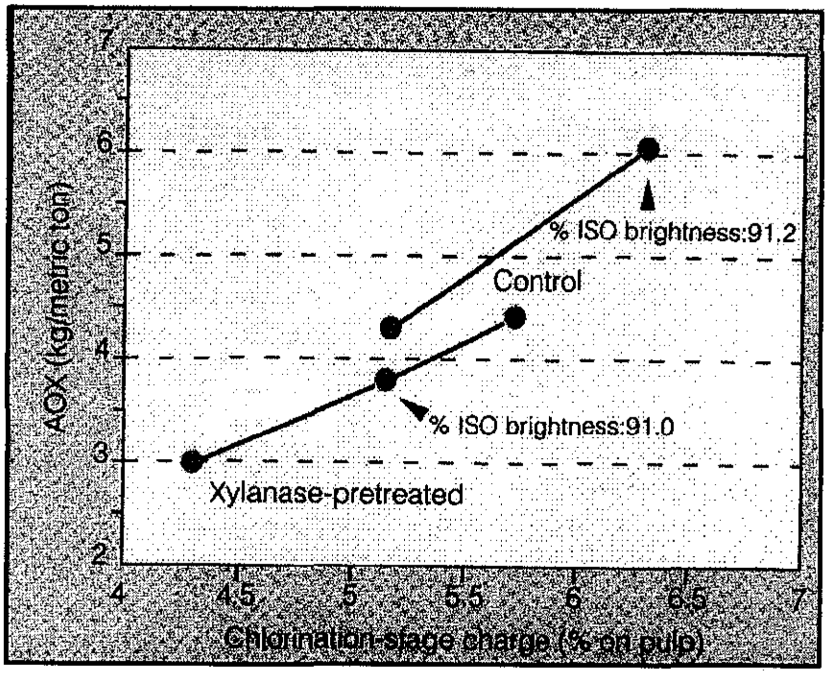

Figure 4-6. Impact of xylanase treatment on AOX.

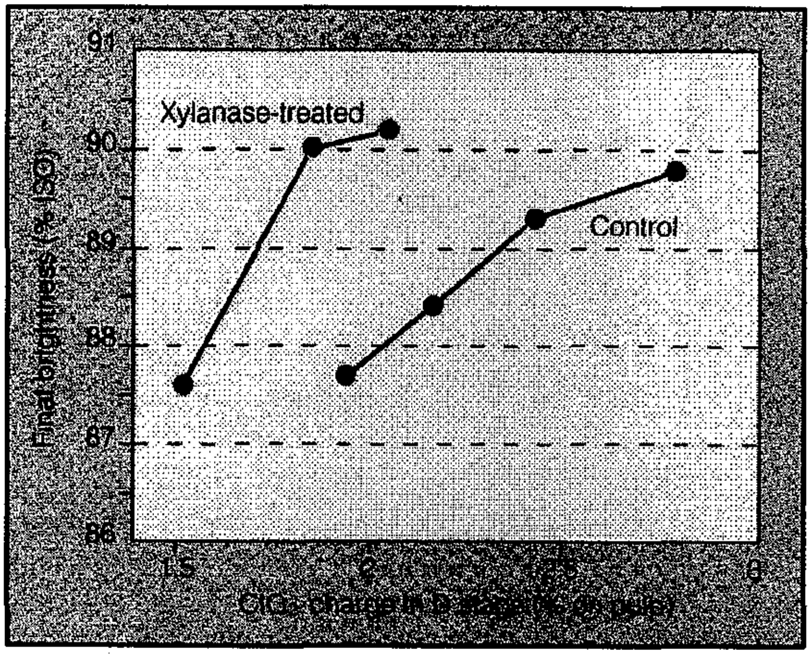

Figure 4-7. Impact of xylanase treatment on brightness.

Source: Senior and Hamilton, 1992.

So far, the potential for recycling enzymes has apparently not been investigated. Enzymes are washed from the pulp and eventually are destroyed in the mill's normal recovery cycle. The development of a method for recycling enzymes would greatly enhance their attractiveness. Likewise, developments that would permit enzyme application under closer to normal brownstock pH and temperature conditions would be welcome.

4.7 IMPROVED BROWNSTOCK WASHING

What it is

Upgrading of the pulp washing systems used to remove lignin solids dissolved during the pulping and bleaching stages. Good pulp washing will reduce downstream bleaching chemical demands and is essential for oxygen delignification and ozone.

How it works

Conventional pulp washers create a vacuum inside the drum to hold the fiber mat in place while it is sprayed with wash water to displace dissolved solids. Normally, a series of three or four washers are configured in series and operated in countercurrent fashion.

Current state-of-the-art washing systems replace the vacuum pressure units with pressure, diffusion, or belt washers, or with pulp presses. These systems are all capable of more effective solids removal from the pulp.

The efficiency of brownstock washing is often measured in terms of the "sodium carryover" and is indirectly measured as the amount of Na_2SO_4 (saltcake) lost. Sodium losses that in the 1970s were commonly in the range of 50 kg per ton have been reduced to 7 kg per ton in new, up-to-date pressure washing systems.

Installations

The importance of efficient brownstock washing is now well-recognized throughout the North American pulp and paper industry. The amount of upgrading taken place is difficult to estimate, however, since improvements can be made through several means, including better utilization of existing equipment, onsite refurbishment of old equipment, or replacement of equipment through new orders placed with vendors. One industry observer contacted vendors and verified orders for 38 brownstock washing systems between January 1988 and mid-1991 (Pulliam, 1991). Others confirm through discussion with vendors and paper companies that washing practices have been considerably upgraded in recent years.

Economics

Costs for improved washing could range from negligible in the case of relatively simple optimization of existing equipment to close to $20 million for a completely upgraded system in a 1,000 tpd mill. A recent case study evaluated modern washer systems from three established vendors and found that capital costs for all three ranged from $10.2 to $12.3 million for a hypothetical mill (Ricketts, 1992).[5] It should be noted that these costs include costs of constructing an appropriately-sized building to house the equipment. Depending on the circumstances, it may be possible to utilize existing space.

Major operational requirements for each system are shown in Table 4-8 and net incremental requirements compared to the existing 25-year old system are converted to dollar values in Table 4-9. Each of the newer systems will require less electric power and/or steam. The Chemi-Washer system was shown to result in operating savings of $4.67 per ton, while the Compaction Baffle Filtration system saved $2.32 per ton and the Drum Displacer saved $2.13 per ton. Additional cost savings will result from reduced bleaching chemicals requirements. These costs were not shown in the analysis because the hypothetical mill produces unbleached linerboard.

Pollution prevention

Lignin solids travelling with the pulp will compete with pulp fibers for reaction in the bleaching stages, leading to higher chemical consumption and increased formation of chlorinated organics. Improved pulp washing will reduce the amount of organic lignin solids carried through to the bleaching stages and reduce the formation of chlorinated organic compounds such as dioxin and furan. Improvements in conventional pollutants such as BOD, COD, resin acids, and color can also be expected. Improved washing also removes highly colored material and some of the persistent, non- biodegradable black liquor fraction which would otherwise be discarded.

Compatibility

As with other processes that remove additional solids from the pulp, upgraded pulp washing tends to increase the quantity of solids recovered from the condensed pulping effluent. Recovery boilers must be able to accommodate this increase in load to obtain maximum environmental and economic benefits.

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[5] The systems evaluated were: Black Clawson's Chemi-Washer, IMPCO's Compaction Baffle Filter, and the Kamyr/Ahlstrom Drum Displacement Washer. Diffusion washers, which may be the best option for a retrofit, were not considered in their analysis.

TABLE 4-8
Major Operating Cost Items for Existing Washing Line Versus Three Modern Alternatives - Hypothetical Mill Retrofit

Operating Cost Item	Existing System	Chemi-Washer	CB Filters	Drum Displacer
Connected horsepower, hp	870	820	910	270
Net steam savings, mlb/hr	0	39.3	12.6	3.0
Defoamer usage, lb/odt	3.0	20	1.0	0.5
No. of pieces rotating equipment (motor driven)	9	15	13	10
Washer facewire replacement	1 per yr	2 per yr	none	none

TABLE 4-9
Annual Incremental Operating Costs Saved for Three Modern Alternative Washing Systems - Hypothetical Mill Retrofit
($000)

Incremental Cost Item	Chemi-Washer	CB Filters	Drum Displacer
Power at $0.0525/kWhr	$12	($12)	$158
Steam at $3.50/1,000 lb	$1,555	$370	$88
Defoamer at $0.45/lb	$118	$236	$297
Maintenance - labor and materials for facewire change	($60)	$15	$15
Total annual savings	$1,225	$609	$558
Savings per odt ($)	$4.67	$2.32	$2.13

Source: Ricketts (1992).

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SECTION FIVE
POLLUTION PREVENTION OPPORTUNITIES IN BLEACHING OPERATIONS

This section examines the major pollution prevention technologies that can be implemented in the bleaching areas of the mill. The "bleaching areas" are defined according to the traditional distinction as those stages that include and follow the first chlorination stage in a conventional kraft mill. As discussed previously, however, with the advent of numerous pre-chlorination stages and the replacement of chlorine-based chemicals, these distinctions are becoming blurred.

5.1 HIGH CHLORINE DIOXIDE SUBSTITUTION

What it is

High substitution is generally defined as the replacement of 70 percent or more of the elemental chlorine (Cl_2) used in the first bleaching stage with equivalent amounts of chlorine dioxide (ClO_2).[1] At substitution rates above 70 percent, chlorinated organics formation is very low.

How it works

Chlorine reactions with lignin fall into three categories: substitution, addition, and oxidation. The first two reactions result in the formation of chlorinated organics. Oxidative reactions, meanwhile, generally result in fragmentation of the lignin. Chlorine dioxide is more of an oxidative bleaching agent than elemental chlorine. As a result, chlorine dioxide substitution increases the proportion of oxidative reactions and reduces the formation of chlorinated organic compounds.

Because chlorine dioxide is unstable and cannot be shipped, it is generated onsite at the mill. The principal feed material for chlorine dioxide is sodium chlorate ($NaClO_3$), produced using electrolysis technology similar to that used in chlor-alkali production. Onsite generators produce gaseous chlorine dioxide by reducing sodium chlorate in the presence of a reducing agent. Table 5-1 summarizes most of the various chlorine dioxide generating processes operated at North American pulp mills. A major distinction between systems is the amount and type of byproducts produced, which can include Cl_2, Na_2SO_4, H_2SO_4, and NaCl.

Installations

Chlorine dioxide substitution was adopted rapidly as a proven method for reducing dioxin in bleaching effluent. Figure 5-1 below shows the trend in U.S. chlorate consumption between 1955 and 1987. Over 90 percent of U.S. demand for chlorate (the feedstock for chlorine dioxide production) is accounted for

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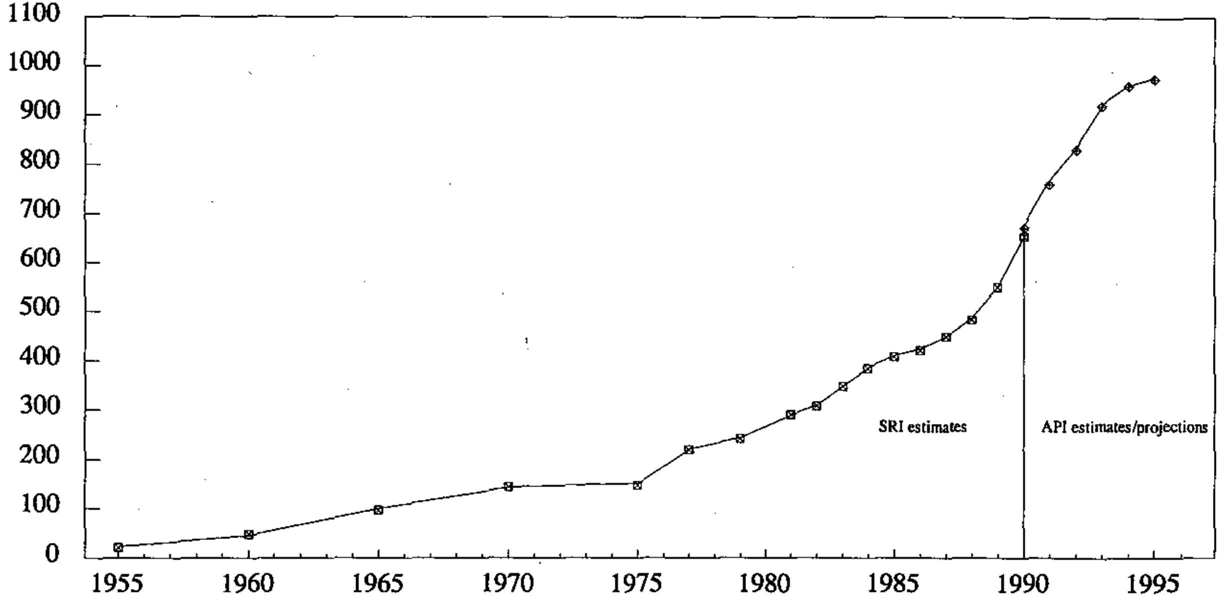
[1] Chlorine dioxide is a more powerful bleaching agent and replaces chlorine at a rate of 1:2.63 weight basis (i.e., 1 kg ClO_2 has the equivalent bleaching power of 2.63 kg Cl_2). In substituting chlorine dioxide for chlorine, total bleaching chemical demand (in kg) decreases.

TABLE 5-1
Summary of Chlorine Dioxide Generation Processes

Process	Reaction Equation	Reducing Agent	Byproducts
Mathieson	$2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2ClO_2 + 2NaHSO_4$	SO_2	spent acid solution
Solvay	$2NaClO_3 + CH_3OH + H_2SO_4 \rightarrow 2ClO_2 + 2H_2O + HCHO + Na_2SO_4$	CH_3OH	spent acid solution
R2	$NaClO_3 + NaCl + H_2SO_4 \rightarrow ClO_2 + 0.5Cl_2 + Na_2SO_4 + H_2O$	NaCl	spent acid and chlorine
R3/SVP	$NaClO_3 + NaCl + H_2SO_4 \rightarrow ClO_2 + 0.5Cl_2 + Na_2SO_4 + H_2O$	NaCl	saltcake and chlorine
R6/Lurgi/Chemetics/Vulcan	1)$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$ 2)$Cl_2 + H_2 \rightarrow 2HCl$ 3)$NaClO_3 + 2HCl \rightarrow ClO_2 + 0.5Cl_2\ NaCl + H_2O$	HCl	none
R8/SVP-MeOH/SVP-Lite	$9NaClO_3 + 2CH_3OH + 6H_2SO_4 \rightarrow 9ClO_2 + 3Na_3H(SO_4)_2 + 0.5CO_2 + 1.5HCOOH + 7H_2O$	CH_3OH	acid saltcake

Source: Stockburger (1992).

Figure 5-1
North American Consumption of Sodium Chlorate for Chemical Pulp Bleaching



Note: units are thousand short tons.

Sources: SRI (1989 and 1993); API (1992).

by the pulp and paper industry. By 1987, annual consumption had risen to 499,000 tons. Recent estimates by the American Paper Institute pegged the 1989 level of consumption at 540,000 tons per year, and projected growth to 900,000 tons per year by 1994 (API, 1992).

A recent report indicated that there are approximately 166 chlorine dioxide generators in North America, representing installed capacity of 3,194 short tons/day (Britt, 1992; cited in Stockburger, 1992). Table 5-2 summarizes the number and type of generators installed. The modern methanol- based generating systems (R8/SVP-MeOH/SVP-Lite) account for 52 percent of the generators and 76 percent of installed capacity.

According to market researchers Law, Sigurdson & Associates, most bleached kraft mills are currently using their chlorine dioxide generators to practice 45 to 50 percent substitution. This percentage is likely to increase to 60 to 65 percent in the future, depending upon the stringency of future environmental regulations and the direction taken by the industry to meet them (Shapiro, 1992). Further increases will require more generating capacity at most mills.

Economics

While most mills currently have chlorine dioxide generating capacity onsite, increasing production to enable 700 percent plus substitution rates may be quite expensive. Estimates of capital costs for ClO_2 generating systems range from $2.8 million for equipment only to $10 to $20 million for installed systems with upgraded ancillary equipment.

Two very recent studies have examined the economics of increased substitution and are worth noting:

- An analysis presented at the U.S. EPA's *Symposium on Pollution Prevention in the Manufacture of Pulp and Paper* (McCubbin, 1992) compared the costs and environmental affects of alternative upgrades to an existing 1,000 tpd model mill (see Table 5-3). One of the options considered was to increase chlorine dioxide substitution from 11 percent to 50 and 100 percent. At 50 percent substitution the mill would require an incremental capital investment of $5 million and increased annual operating expenses of $1.9 million. This upgrade was assumed to be achieved by expanding the capacity of the existing chlorine dioxide generator (approximately doubling capacity). At this point the generator would be at its maximum capacity; further expansions would require a new generator. An upgrade to 100 percent substitution would require a capital investment of $15.9 million (for a new generator, among other things) and an increase in annual operating costs of $7.1 million.

- A similar study by Brunner & Pulliam (1992) compared alternative bleaching technologies for a greenfield mill. Their 1000 tpd model mill was assumed to be practicing 30 percent substitution under the baseline scenario. Table 5-4 displays the incremental costs and environmental improvements that would result by modifying the mill design to use 70 percent chlorine dioxide substitution. No decline in pulp yield would result at 70 percent substitution (i.e., wood chip costs would not rise). The capital costs for the mill would be less than 1 percent higher than for the baseline mill (an incremental $0.5 million for a $284 million mill). Shifting from 30 to 70 percent substitution would increase bleaching chemical costs by 23 percent. Total operating costs, however, would only increase by 4 percent. The total cost for this hypothetical greenfield mill, including both capital and operating expenses, would presumably increase by 2.6 percent with the higher substitution rate.

TABLE 5-2
North American Chlorine Dioxide Generators

Process	Number	Installed Capacity (short t/d)	Percent of N. American Capacity
Mathieson	27	190	6%
Solvay	17	127	4%
R2	13	92	3%
R3/R3H/SVP	14	198	6%
R6/Lurgi/Chemetics	9	144	5%
R8/SVP-MeOH/SVP-Lite	86	2443	76%
TOTAL	166	3194	100%

Source: Britt (1992); cited in Stockburger (1992).

TABLE 5-3
Cost and Environmental Comparison of Chlorine Dioxide Substitution

Parameter		Chlorine Dioxide Substitution Level				
		Baseline Model Mill 11% ClO_2 Substitution	Maximum Substitution w/E_{OP} and existing ClO_2 Capacity	50% ClO_2 Substitution	100% ClO_2 Substitution	100% ClO_2 Substitution (w/E_{OP})
Incremental Capital Cost ($ Million)		$0.0	$2.8	$5.0	$15.9	$13.6
Incremental O&M Costs ($ Million)		$0.0	($0.5)	$1.9	$7.1	$3.2
AOX in Bleach Plant Effluent (kg/ton)		5.3	3.4	1.9	2.1	1.5
Dioxin/Furan Detect?		Yes	Perhaps	Marginal	No	No
BOD Reduction (kg/day)		0	0	0	0	0
Incremental Power Requirements	On-Site (MW)		0	0	0	0
	Off-Site (MW)		(2.6)	(2.7)	5.3	1.7

Note: Baseline mill is a 1,000 tpd softwood kraft pulp mill. Bleach sequence is C_DEDED.

Source: McCubbin (1992).

An alternate route to increased substitution is the addition of extended delignification and/or oxygen delignification upstream of the bleach plant. By reducing total bleaching chemical demands by as much as 50 to 70 percent, these technologies permit existing chlorine dioxide capacity to be used at higher rates of substitution. The enhanced bleachability of these low-kappa pulps will permit the mill to cut back elemental chlorine usage substantially or even facilitate its complete elimination.

Pollution prevention

The amount of chlorinated organics formed during bleaching is proportional to the quantity of atomic chlorine consumed. Both elemental chlorine and chlorine dioxide contain atomic chlorine, of which roughly 10 percent will end up as AOX. The substitution of chlorine dioxide for elemental chlorine is effective at reducing the formation of AOX for several reasons. First, chlorine dioxide contains only one-half the atomic chlorine as elemental chlorine. Secondly, less chlorine dioxide is needed, since it contains 2.63 times the oxidative power as elemental chlorine. Overall, chlorine dioxide bleaching results in only one-fifth the amount of chlorinated organics as traditional chlorine bleaching.

Brunner and Pulliam indicated that shifting from 30 percent to 70 percent substitution would reduce chlorinated discharges and color, but would have little impact on BOD (see Table 5-4). Their study suggests, however, that at substitution rates above 70 percent, improvements in BOD could result. McCubbin's (1992) comparison of upgrading a model mill from an 11 percent substitution rate suggests similar improvements in bleach plant effluent (see Table 5-3).

Chlorine dioxide use is also related to the formation of chloroform, a volatile organic and a toxic air pollutant. A study for the National Council for Air and Stream Improvement, the environmental arm of the U.S. pulp and paper industry, found that total chloroform emissions from the bleach plant vents and the acid and alkaline sewers fell from below 0.35 kg per ton at 15 percent substitution to below 0.01 kg per ton at 100 percent, though adding ClO_2 before chlorine increased the amounts by 1.6 to 4.9 times (Crawford et al., 1991). Thus, high chlorine dioxide substitution can be very effective in reducing emissions of chloroform.

Chlorine dioxide is generated by a variety of commercial processes, some of which generate byproduct chemicals. The Mathieson process, for example, uses sulfur dioxide (SO_2) as a reducing agent and generates chlorine gas as a byproduct. Sulfur dioxide is generated either onsite by burning sulfur, or is shipped in. The R3 and Hooker SVP processes use sodium chloride and also produce byproduct chlorine gas. Byproduct hypochlorite is produced in some chlorine dioxide generators. At one time hypochlorite was used in the bleaching process, but it has since been largely abandoned because of its close link to chloroform formation.

At higher substitution rates, the generation of byproducts such as sodium sulfate and sulfuric acid will exceed the mill's capacity to incorporate them in the chemical recovery cycle. It is likely that excess byproducts would be discharged to the sewers where it would be subject to whatever treatment technologies are in place.

TABLE 5-4
Cost and Environmental Comparison of Chlorine Dioxide Substitution Greenfield Mill

	Bleaching Scenario	
Parameter	Baseline Model Mill 30% ClO_2 Substitution	70% ClO_2 Substitution
Incremental Capital Cost ($ Million)	$283.88	$284.39
Incremental O&M Costs ($ Million)	$180.53	$187.77
Total Incremental Cost ($ Million)	$285.53	$292.96
Pulp Yield	92.1%	92.1%
AOX in Bleach Plant Effluent (kg/metric ton)	4.1	2.8
BOD in Bleach Plant Effluent (lbs/bleached ton of pulp)	37	37
Effluent Color (lbs/bleached ton of pulp)	298	176

Note: Baseline mill is a greenfield 1000 tpd softwood kraft pulp mill. Baseline bleach sequence is C_DE_ODED.

Source: Brunner and Pulliam (1992).

Compatability

Kraft pulp mills have traditionally been able to use of most of the ClO_2 byproducts for bleaching or as makeup chemicals in the recovery cycle. With increased substitution rates, however, the generation of byproducts frequently exceeds the mills' makeup requirements. Technologies that limit byproduct generation, therefore, have gained importance. A newer generating technology (R8/SVP-Lite^{TM}) virtually eliminates the generation of byproduct chlorine gas by using methanol as a reduction agent. This process was developed in the late 1980s and is now used in many mills.

Equipment specifications for ClO_2 generators are stringent due to the extremely corrosive and unstable nature of the product. Storage and handling of ClO_2 solution must be performed with care due to the explosion potential. In particular, contamination of feed equipment with oxidizable materials such as rubber, grease, iron, etc. must be avoided.

The corrosiveness of chlorine dioxide will affect the mill's ability to recover chemicals and recycle process water. Many pulp mills are now striving to close the process water loop in the bleaching plant. A closed water system can lower costs by increasing the recovery of makeup chemicals, reducing costs for obtaining and pumping raw water, and limiting wastewater treatment requirements. The use of chlorine dioxide can promote chloride corrosion in mill equipment (although to a lesser degree than elemental chlorine) thus making closed systems more difficult to achieve. In order to increase water recycling and chemical recovery, the waste streams containing chlorinated compounds should be isolated and excluded from the rest of the closed system.

5.2 SPLIT ADDITION OF CHLORINE/IMPROVED pH CONTROL

What it is

Splitting the charge of elemental chlorine in the first C-stage and improved pH control have been found to be effective in reducing formation of chlorinated organics.

How it works

By splitting the chlorine addition into several charges, introduced at multiple points throughout the reaction tower, it is believed that oxidation reactions between lignin and chlorine will be favored over substitution reactions. While substitution reactions are associated with the formation of chlorinated organics, oxidation reactions are not.

The technique of split chlorine addition follows from research by the Westvaco Corp. into ways to reduce the formation of chlorinated organics (Hise and Hintz, 1989). The research has focused on close control of the chlorine concentration in the chlorination stage as a means for reducing formation of chlorinated organics. This is in contrast to other approaches that may emphasize reducing the total amount of chlorine used.

The control of pH in the chlorination stage has also been used as a means for affecting the type of pulp reactions that occur. At higher pH, more of the chlorine is converted to hypochlorous acid (HOCl), a more powerful oxidizing agent. In the absence of other modifications, higher pH would also reduce pulp yield. For this reason, pH control is combined with split chlorine addition to reportedly reduce chlorinated organics formation without loss of yield.

Installations

Westvaco has implemented split chlorine addition at its bleached kraft mills at Luke, Maryland, Covington, Virginia, and Wickliffe, Kentucky. These are the only mills known to have adopted this technique.

Economics

Separate costs for conversion of the chlorination stage to implement split chlorine addition and improved pH control have not been reported. The necessary equipment for splitting the chlorine charge and for monitoring pH are likely to be quite modest.

Pollution prevention

Westvaco's studies indicate that split chlorine addition using three smaller chlorine charges reduced the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF by 70 and 50 percent, respectively. By incorporating advanced pH control, these discharges reportedly fell by 90 percent. Mill trials have shown that non-detect levels of TCDD and TCDF of 6 ppt can be obtained.

Compatability

While splitting the addition of chlorine and closer pH control has been shown to reduce dioxin formation, many mills are seeking to increase the recycle of their effluent as well. This requires reductions in overall use of chlorine-based bleaching agents, since effluents from chlorine compound bleaching stages cannot be recycled and must be discharged.

5.3 OXIDATIVE EXTRACTION

What it is

Addition of gaseous oxygen to the first caustic extraction stage. The oxygen aids in the removal of dissolved lignin and provides additional bleaching power. This reduces overall requirements for chlorine-based bleaching agents.

How it works

In a conventional bleaching sequence, chlorination is followed by an alkaline extraction stage (using NaOH), which completes the solubilization of chlorinated and oxidized lignin molecules and facilitates their removal. Lab and mill trials have found that the addition of gaseous oxygen to the extraction stage can enhance the removal of lignin and provide additional bleaching power, thereby reducing the requirements for chlorine and chlorine dioxide. Chlorine dioxide savings of approximately 2 kg per ton of pulp in subsequent D-stages are normal. Delignification following first-stage chlorination and extraction has been found to increase by approximately 25 percent.

Oxygen is normally added to the extraction stage via a high-intensity mixer or sparger at the discharge of the medium consistency pump. Between 4 and 6 kg of oxygen per ton of pulp are typically applied.

Oxidative extraction has also been used to help mills cut back on hypochlorite, a more expensive chemical and the one that is most associated with chloroform emissions.

Installations

Since its introduction in the late 1970s, oxygen extraction has been widely adopted in North America and elsewhere. Although recent data for the U.S. industry are not available, in 1987 it was estimated that 80 percent of Canadian mills were practicing oxidative extraction. The percentage in the U.S. is similarly quite high.

Economics

Equipment requirements for oxidative extraction will depend on the current configuration of the extraction stage. According to vendor information, an upflow extraction tower (or upflow pre-retention tube in front of a downflow extraction tower) is necessary to ensure the hydrostatic pressure needed to keep oxygen in suspension. Additional costs will be incurred for the oxygen mixing equipment, and washer upgrades following extraction may be desirable.

One source has reported estimated costs for a 1983 installation at a 450 tpd mill of $0.5 million (Ducey, 1984). At another mill, conversion to a pressurized E_O-stage required installation of a pressurized pre-retention tube, a medium consistency pump, and an oxygen sparger. Total costs of that project, including engineering and installation, were under $2 million dollars (Hastings et al., 1992).

Pollution prevention

The formation of chlorinated organic compounds is primarily associated with the use of elemental chlorine in the first bleaching stage. Since the E_1 stage follows the application of elemental chlorine, the benefits from oxidative extraction will accrue as the mill is able to reduce chlorine usage in the first stage, or increase its level of chlorine dioxide substitution. In most cases mills can realize a savings in active chlorine of about 2 kg per kg of oxygen charged in the E_O-stage. With the addition of a pressurized pre-retention tube, savings of approximately 11 kg of active chlorine per ton pulp have been obtained and reductions in AOX of approximately 0.5 kg per ton were observed (Hastings et al., 1992).

Oxygen extraction has proven effective in reducing loadings of other pollutants. In particular, E_O has been widely adopted as a means for reducing hypochlorite consumption and, consequently, generation of chloroform.

5.4 PEROXIDE EXTRACTION

What it is

Addition of hydrogen peroxide (H_2O_2) to the E_1 extraction stage (denoted then as an E_P stage). Similar to oxidative extraction, the addition of peroxide has been found to promote additional removal of lignin solids during extraction. It is very common to combine both peroxide and oxygen in the extraction stage, i.e., E_{OP}.

How it works

Peroxide is produced offsite and shipped to the mill via tanker as a 70 percent solution in water. Configuration for an E_{OP} stage is shown in Figure 5-2. The peroxide is generally added at the inlet of the oxygen mixer when oxygen is used, and at the inlet of the stock pump when there is no oxygen. Since it decomposes to water and oxygen gas, peroxide is essentially environmentally benign.

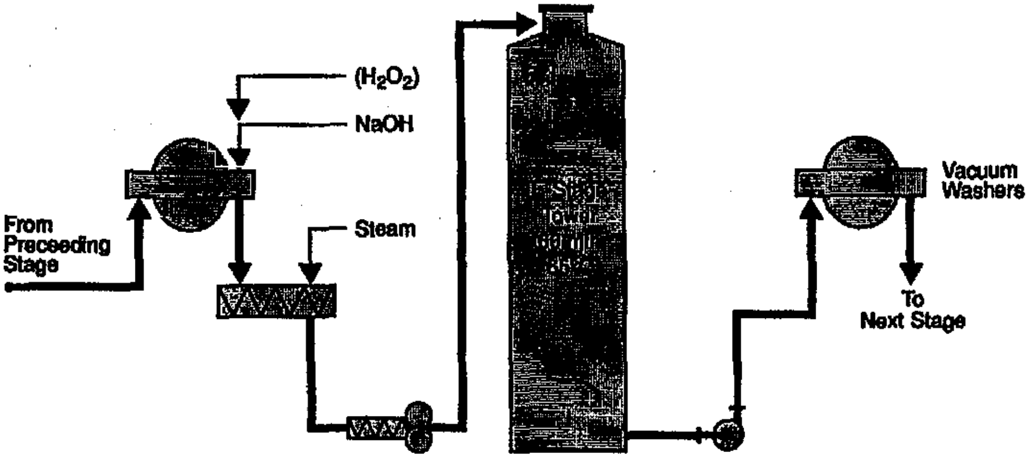
Although more commonly used for brightening mechanical pulps, peroxide can also be used as a full bleach stage in low-chlorine and chlorine-free bleaching sequences. Peroxide would be an essential part of any totally chlorine-free (TCF), full brightness sequence using ozone, e.g., OZEP. To protect the pulp, a prior chelation stage is crucial to ensure removal of metal ions that accumulate as chlorine is removed from the sequence. The only kraft mill currently producing "full" brightness TCF pulp is at Mönsterås, Sweden. The pulp produced is 88 percent ISO hardwood.

Installations

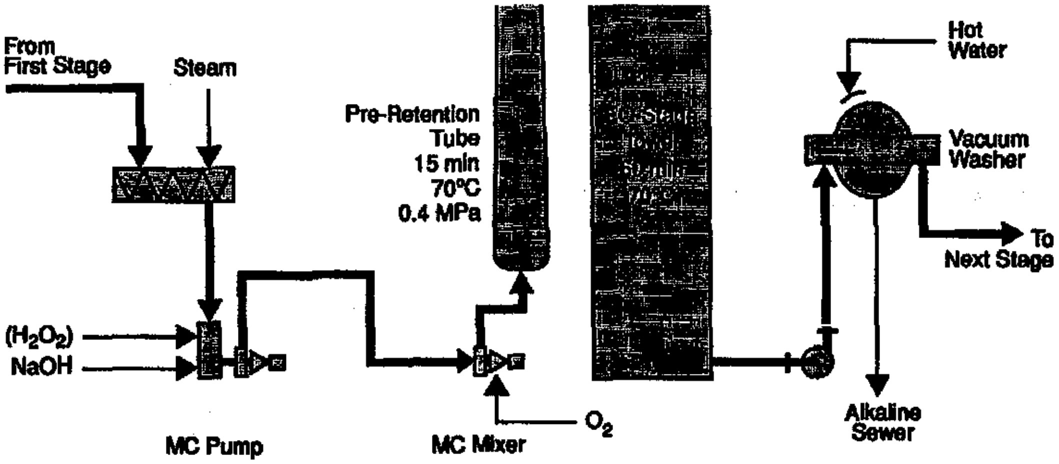
It has recently been estimated that 60 U.S. and Canadian mills use approximately 28,000 tpy of peroxide for enhanced extraction (Strunk, 1990). At an average application rate of 0.25 percent by weight on pulp, this suggests that 11 million tons of pulp are bleached using peroxide. In the past, the high cost of peroxide has been cited as a barrier to further adoption. In recent years peroxide prices have dropped considerably (see below).

Economics

Capital costs for storage tanks, mix tank, and piping will be in the neighborhood of $100,000. Application of peroxide at rates of 2 to 20 lbs per ton will add $0.75 to $7.00 per ton at current peroxide prices. When peroxide was first introduced to the pulp and paper industry, the limited number of suppliers provided significant technical support and accordingly high prices for their product. Now that peroxide capacity has expanded and the use of peroxide has become more prevalent in the industry producers has



Conventional alkaline extraction stage



Oxygen/peroxide-reinforced alkaline extraction stage

Figure 5-2. Modification of extraction stage for peroxide/oxygen reinforcement.

Source: Hastings et al., 1992.

become far more cost competitive. Prices for peroxide has recently dropped from roughly $2.00 per kg three or four years ago to $0.75 per kg today.

Pollution prevention

The use of hydrogen peroxide in the caustic extraction stage has been shown to increase delignification and decrease the kappa number of pulp following chlorination and extraction. By assuming some of the delignification load, peroxide-enhanced extraction will enable mills to reduce bleaching chemical consumption either upstream or downstream of the extraction stage without impacting pulp brightness or other properties. Reductions in bleaching chemical use, particularly in the first chlorination stage, are associated directly with reduced levels of chlorinated organics.

Webster (1990) has described a strategy to achieve significant environmental and economic benefit from the use of peroxide, without increasing ClO_2 requirements. Using a C_DE_ODED mill as an example, the first step is to add H_2O_2 to the last extraction stage. This permits reductions in chlorine dioxide use in the final D-stage to be made without sacrificing pulp brightness. Then, peroxide is added to the first E-stage, enabling the mill to cut the chlorine charge to maintain the same chlorination-extraction kappa number. Finally, the chlorine dioxide saved in the final D-stage can be shifted forward to raise the chlorine dioxide substitution in the C_D-stage to a higher level. This will accomplish the goal of lowering elemental chlorine without the need for expensive increases in chlorine dioxide capacity and without sacrificing pulp quality.

Recent mill trials using peroxide at various locations in the bleaching sequence showed that, depending on the current bleaching sequence, the use of peroxide in the extraction stage enabled each mill to cut back on chlorine or chlorine dioxide to effect reductions in kraft process pollutants (Webster, 1990). The most significant reductions -- over 80 percent for all five mills -- were for dioxin. AOX declined by close to 30 percent, while chloroform was reduced at two of the mills by approximately 50 percent.

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