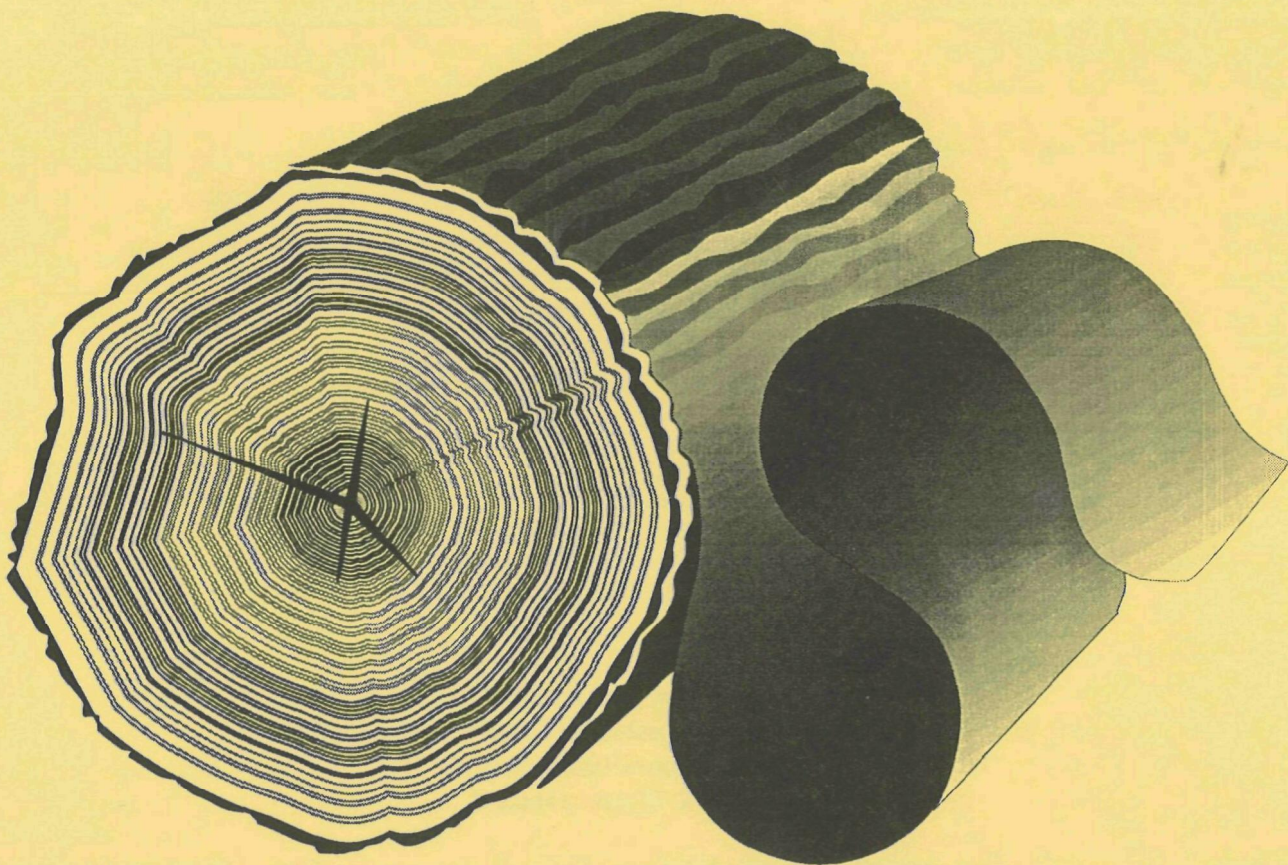


Pollution Prevention Technologies for the Bleached Kraft Segment of the U.S. Pulp and Paper Industry



EPA/600/R-93/110
August 1993

**POLLUTION PREVENTION TECHNOLOGIES FOR THE BLEACHED
KRAFT SEGMENT OF THE U.S. PULP AND PAPER INDUSTRY**

Contract No. 68-C0-0068

Work Assignment Manager

Jocelyn Woodman
Pollution Prevention Division
Office of Pollution Prevention and Toxics

Office of Pollution Prevention and Toxics
Office of Prevention, Pesticides, and Toxic Substances
U.S. Environmental Protection Agency
Washington, DC 20460

Office of Environmental Engineering and Technology Demonstration
Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460

Notice

This document is intended to provide technical and economic information on approaches to pollution prevention in the pulp and paper industry. Compliance with environmental and occupational safety and health laws is the responsibility of each individual business and is not the focus of this document. Mention of trade names or commercial products within this report does not constitute endorsement or recommendation for use. Users are encouraged to duplicate this publication as needed.

Acknowledgements

This report was prepared by ERG, Inc. of Lexington, Massachusetts under EPA Office of Research and Development Contract No. 68-C0-0068 for the EPA Office of Pollution Prevention and Toxics. The OPPT Work Assignment Manager was Jocelyn Woodman, while Jeff Cantin managed the development of the document for ERG.

The report has been subjected to the U.S. Environmental Protection Agency's peer review process. The following individuals participated in the review. Their helpful comments are greatly appreciated:

Gary A. Amendola Amendola Engineering 1052 Kenneth Drive Lakewood, Ohio 44107	Karl C. Ayers Director, Env. Programs Mead Corporation Courthouse Plaza, N.E. Dayton, Ohio 45463	Betsy Bicknell Radian Corporation 2455 Horsepen Road, Suite 250 Herndon, Virginia 22071
Danforth G. Bodien U.S. EPA Region X 1200 Sixth Ave. Seattle, Washington 98101	Jens Folke, Managing Director European Environmental Research Group, Ltd. Pinievangen 14 DK-3450 Allerød, Denmark	Steve Geil U.S. EPA Office of Water 401 M Street SW Washington, D.C. 20460
David P. Graves Director, Env. Management Weyerhaeuser Paper Company 33663 Weyerhaeuser Way South Federal Way, Washington 98003	George Heath U.S. EPA Office of Water 401 M Street, SW Washington, D.C. 20460	K.C. Hustvedt U.S. EPA Office of Air Quality Planning and Standards RTP, North Carolina 27711
Thomas J. Holdsworth U.S. EPA Office of Research and Development 26 W. Martin Luther King Drive Cincinnati, Ohio 45268	Anna Klein U.S. EPA Office of Water 401 M Street, SW Washington, D.C. 20460	Neil McCubbin N. McCubbin Consultants 140 Fishers Point Foster, Quebec JOE 1R0 Canada
Debra Nicoll U.S. EPA Office of Water 401 M Street, SW Washington, D.C. 20460		

TABLE OF CONTENTS

	<u>Page</u>
SECTION ONE INTRODUCTION	1-1
SECTION ONE REFERENCES	1-5
 SECTION TWO POLLUTANTS OF CONCERN IN THE PULP AND PAPER INDUSTRY	 2-1
2.1 Effluents	2-1
2.1.1 Solids	2-2
2.1.2 Biological Oxygen Demand	2-4
2.1.3 Color	2-6
2.1.4 Chlorinated Organic Compounds	2-8
2.1.5 Other Toxic Compounds	2-13
2.2 Solid Wastes	2-14
2.2.1 Wastewater Treatment Sludge	2-14
2.2.2 Boiler and Furnace Ash and Scrubber Sludge	2-16
2.2.3 Wood Processing and Other Wastes	2-17
2.3 Air Pollutants	2-17
2.3.1 Reduced Sulfur Compounds	2-17
2.3.2 Particulates	2-18
2.3.3 Volatile Organic Compounds	2-18
2.3.4 Chloroform	2-19
2.3.5 Other Hazardous Air Pollutants	2-20
SECTION TWO REFERENCES	2-22
 SECTION THREE POLLUTION PREVENTION TECHNOLOGIES IN WOODYARD AND CHIPPING OPERATIONS	 3-1
3.1 Raw Material Selection	3-1
3.2 Recycle of Log Flume Water	3-2
3.3 Dry Debarking	3-2

TABLE OF CONTENTS (cont.)

Page

SECTION THREE POLLUTION PREVENTION TECHNOLOGIES IN WOODYARD AND CHIPPING OPERATIONS (cont.)

3.4	Improved Chipping and Screening	3-3
3.5	Storm Water Management	3-6
	SECTION THREE REFERENCES	3-7

SECTION FOUR POLLUTION PREVENTION TECHNOLOGIES IN PULPING OPERATIONS

		4-1
4.0	Introduction	4-1
4.1	Conventional Kraft Pulping	4-4
	4.1.1 Batch Pulping	4-4
	4.1.2 Continuous Pulping	4-8
	4.1.3 The Kraft Recovery Cycle	4-8
4.2	Extended Delignification	4-10
	4.2.1 Number of Installations	4-16
	4.2.2 Costs and Economics	4-20
	4.2.3 Pollution Prevention Potential	4-21
	4.2.4 Compatibility with Downstream Bleaching Stages	4-23
	4.2.5 Impacts on Other Aspects of Mill Operations	4-28
4.3	Oxygen Delignification	4-32
	4.3.1 Number of Installations	4-39
	4.3.2 Costs and Economics	4-42
	4.3.3 Pollution Prevention Potential	4-47
	4.3.4 Compatibility With Downstream Bleaching Stages	4-47
	4.3.5 Impacts on Other Aspects of Mill Operations	4-51
4.4	Ozone Delignification	4-52
	4.4.1 Number of Installations	4-57
	4.4.2 Costs and Economics	4-60
	4.4.3 Pollution Prevention Potential	4-62
	4.4.4 Impacts on Other Aspects of Mill Operations	4-64

TABLE OF CONTENTS (cont.)

Page

SECTION FOUR POLLUTION PREVENTION TECHNOLOGIES IN PULPING OPERATIONS (cont.)

4.5	Anthraquinone Catalysis	4-69
4.5.1	Number of Installations	4-69
4.5.2	Costs and Economics	4-70
4.5.3	Pollution Prevention Potential	4-70
4.5.4	Impacts on Other Aspects of Mill Operations	4-72
4.5.5	Environmental Effects	4-72
4.6	Black Liquor Spill Control and Prevention	4-73
4.6.1	Number of Installations	4-75
4.6.2	Costs and Economics	4-75
4.6.3	Pollution Prevention Potential	4-75
4.6.4	Impacts on Other Aspects of Mill Operations	4-76
4.7	Enzyme Treatment of Pulp	4-76
4.7.1	Number of Installations	4-78
4.7.2	Costs and Economics	4-80
4.7.3	Pollution Prevention Potential	4-81
4.7.4	Compatibility With Other Aspects of Mill Operations	4-81
4.8	Improved Brownstock Washing	4-81
4.8.1	Number of Installations	4-83
4.8.2	Costs and Economics	4-84
4.8.3	Pollution Prevention Potential	4-84
4.8.4	Impacts on Other Aspects of Mill Operations	4-87
4.9	Closed Screen Room	4-89
4.10	Miscellaneous Pulping Technologies	4-89
4.10.1	The Lignox Process	4-90
4.10.2	Solvent Pulping	4-90
4.10.3	Polysulfide Cooking	4-93
4.10.4	Demethylation	4-94
	SECTION FOUR REFERENCES	4-96

TABLE OF CONTENTS (cont.)

	<u>Page</u>
SECTION FIVE POLLUTION PREVENTION TECHNOLOGIES IN BLEACHING OPERATIONS	5-1
5.1 Conventional Kraft Pulp Bleaching	5-1
5.2 Chlorine Dioxide Substitution	5-5
5.2.1 Number of Installations	5-10
5.2.2 Costs and Economics	5-14
5.2.3 Pollution Prevention Potential	5-20
5.2.4 Other Impacts	5-24
5.3 Split Addition of Chlorine Charge/Improved pH Control	5-25
5.3.1 Number of Installations	5-26
5.3.2 Costs and Economics	5-26
5.3.4 Pollution Prevention Potential	5-26
5.4 Oxygen-Reinforced Extraction	5-26
5.4.1 Number of Installations	5-28
5.4.2 Costs and Economics	5-28
5.4.3 Pollution Prevention Potential	5-29
5.5 Peroxide Extraction	5-30
5.5.1 Number of Installations	5-32
5.5.2 Costs and Economics	5-34
5.5.3 Pollution Prevention Potential	5-35
5.6 Additional Technology Options in the Bleaching Area	5-36
5.6.1 Improved Chemical Controls	5-37
5.6.2 Improved Chemical Mixing	5-37
5.6.3 Jump-Stage, Counter Current Washing	5-37
SECTION FIVE REFERENCES	5-38

LIST OF TABLES

<u>Number</u>		<u>Page</u>
2-1	Typical Sources and Quantities of Suspended Solids Generated in Pulp and Papermaking	2-3
2-2	Typical Sources and Amounts of BOD ₅ Generated in Kraft Pulp and Papermaking	2-5
2-3	Contribution of Bleaching Stages to Effluent Color in Conventional Kraft Process	2-7
4-1	Installations of Extended Delignification Systems Worldwide	4-17
4-2	Characteristics of Conventional and MCC Pulps	4-22
4-3	Impact of Modified Continuous Cooking on Effluent Characteristics	4-24
4-4	Characteristics of Conventional and RDH Pulping	4-25
4-5	Impact of Rapid Displacement Heating Cooking Techniques on Effluent Characteristics	4-27
4-6	Sample Boiler Upgrade and Rebuild Projects	4-30
4-7	Typical Operating Data for Oxygen Delignification of Kraft Softwood Pulp	4-34
4-8	U.S. Installations of Oxygen Delignification Systems	4-41
4-9	Capital Cost Estimates for Oxygen Delignification Systems	4-43
4-10	Potential Oxygen Demand at Bleached Kraft Mill	4-45
4-11	Change in Total Costs for Oxygen Bleaching vs. Conventional Bleaching in a 600 mt/d Swedish Mill	4-46
4-12	Pollutant Impacts of Oxygen Delignification Versus Conventional Bleaching	4-48
4-13	Change in Energy Consumption for HC Oxygen Delignification Using Softwood Kraft at 50% Oxygen Delignification	4-53

LIST OF TABLES (cont.)

<u>Number</u>		<u>Page</u>
4-14	Ozone Pilot and Full-Scale Plants Worldwide	4-58
4-15	Bleaching Chemical Costs of Ozone Versus Conventional Sequences at Union Camp's Franklin, Virginia Mill	4-61
4-16	Emissions from Ozone Bleach Line at Union Camp's Franklin, Virginia Mill	4-63
4-17	Effluent Properties of Ozone Bleaching Sequences	4-65
4-18	Properties of Pulps Produced Using Alternative Bleaching Sequences	4-66
4-19	Costs of Anthraquinone Treatment	4-71
4-20	Major Operating Cost Items for Existing Washing Line Versus Three Modern Alternatives Hypothetical Mill Retrofit	4-85
4-21	Annual Incremental Operating Costs Saved (\$1,000) for Three Modern Alternative Washing Systems Hypothetical Mill Retrofit	4-86
4-22	Impacts of Improved Washing Practices on Formation of Dioxin	4-88
4-23	Capital Costs for Chiyoda Polysulfide Process	4-95
5-1	Summary of Bleaching Chemicals	5-4
5-2	Most Common Bleaching Sequences at U.S. Kraft Mills	5-6
5-3	Summary of Chlorine Dioxide Generation Processes	5-9
5-4	Levels of Chlorine Dioxide Substitution at U.S. Kraft Mills	5-13
5-5	North American Chlorine Dioxide Generators	5-15
5-6	Cost and Environmental Comparison of Chlorine Dioxide Substitution	5-17
5-7	Cost and Environmental Comparison of Chlorine Dioxide Substitution, Greenfield Mill	5-18
5-8	Impact of Chlorine Dioxide Substitution Levels on Chemical Requirements and Costs	5-19

LIST OF TABLES (cont.)

<u>Number</u>		<u>Page</u>
5-9	Effect of Split Chlorine Addition on Formation of TCDD and TCDF Formation	5-27
5-10	Impact of Use of Peroxide in Extraction Stages on Chlorine Consumption and Substitution Rate	5-33

LIST OF FIGURES

<u>Number</u>		<u>Page</u>
3-1	Dry Debarking Systems	3-4
3-2	Chip Slicer Showing Oversize Chip Being Split	3-5
4-1	Process Flowsheet for Conventional Integrated Bleached Kraft Mill	4-2
4-2	Batch Digester and Ancillary Equipment	4-5
4-3	Countercurrent Brownstock Washing	4-7
4-4	Continuous Digester and Ancillary Equipment	4-9
4-5	Kamyr Two-Vessel Hydraulic Digester MCC Adaptation	4-13
4-6	Kamyr Single Vessel Hydraulic Digester EMCC Adaptation	4-14
4-7	The Rapid Displacement Heating (RDH) Cycle for Batch Pulping Systems	4-15
4-8	Process Flows for High Consistency Oxygen Delignification	4-35
4-9	Equipment Diagrams for High-Consistency Oxygen Delignification	4-36
4-10	Process Flows for Medium Consistency Oxygen Delignification	4-38
4-11	Installations of Oxygen Delignification Systems U.S. and Worldwide	4-40
4-12	Illustration of Typical Wastewater Flows at Bleached Kraft Mill	4-49
4-13	Equipment for High Consistency Ozone Delignification	4-55
4-14	Spill Control System Flow Diagram	4-74
4-15	Hypothesized Reaction of Xylanase with Pulp	4-77
4-16	Equipment Configuration for Xylanase Application	4-77
4-17	Impact of Xylanase Treatment on AOX	4-79

LIST OF FIGURES (cont.)

<u>Number</u>		<u>Page</u>
4-18	Impact of Xylanase Treatment on Brightness	4-79
4-19	Alternative Pulp Washing Equipment	4-82
5-1	North American Consumption of Sodium Chlorate for Chemical Pulp Bleaching	5-12
5-2	Modification of Extraction Stage for Oxygen Reinforcement	5-31

SECTION ONE INTRODUCTION

The Pollution Prevention Act of 1990 asserts that there are significant opportunities for industry to reduce or prevent pollution at the source, and establishes that pollution should be reduced at the source whenever feasible.¹ In keeping with this national objective, and in an attempt to develop and provide information on the benefits of source reduction, EPA has produced this report which examines: (1) the current state of the art, (2) the economics of adoption, and (3) the level of adoption, of selected pollution prevention technologies in the U.S. pulp and paper industry.

The focus of this report is on the bleached kraft segment of the pulp and paper industry, due to the heightened concern over its environmental impacts. This concern is related primarily to the use of chlorine-based compounds in the manufacture of bleached pulps, and the nature of the byproduct pollutants associated with conventional pulp making 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, 1992a).

The removal or destruction 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 in destroying such compounds and instead may result in their transfer to other environmental media (e.g., wastewater treatment sludge), or even their partitioning into final products. As a consequence, reduction efforts must focus on changes in the production process that can reduce or eliminate their formation. The technology options described in this report thus include a variety of techniques that enable the mill to *reduce the use of* chlorine-based compounds in the bleaching process. Because these technologies may enable further recycle of the mill's effluent, they can also lead to reductions in more traditional pollutants such as biological oxygen demand (BOD₅), chemical oxygen demand (COD), and total suspended solids (TSS), and may further reduce effluent color, water use, and

¹ Public Law 101-508, November 5, 1990.

sludge volumes generated from the mill's wastewater treatment plant. Emissions of chloroform and other air pollutants will also decrease as a result of some of these technologies.

Pollution prevention technologies can also further reduce discharges of non-chlorinated pollutants. Scientists in Canada and Scandinavia have recently suggested that such non-chlorinated substances can make a significant contribution to the effects of (treated) pulp mill wastes on the receiving waters (see Section 2.1.5).² By increasing the volume of effluent recycled through the recovery boiler, most pollution prevention technologies reduce the discharges of such non-chlorinated substances to the treatment system and receiving waters.

The economics of adopting process changes are explored in detail in this report. It is important to note that, while it is possible to cite representative capital and operating cost information, the actual costs and savings for any particular mill are very site-specific, and 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 as a consequence of adopting in-plant pollution prevention measures. Additional savings in the form of reduced or avoided treatment and compliance costs and, potentially, exposure to liability from pollution-related litigation may also factor into the decision to adopt prevention technologies.

The costs presented in this report 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 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 that are explicit with regard to any savings assumed to accrue.

In general, pollution prevention technologies in kraft pulping and bleaching result in higher capital but lower operating costs for the mill. Using conventional project evaluation techniques, in-plant prevention measures may not generate sufficient savings to justify the investment costs themselves. The decisionmaking process at an individual mill, however, can be substantially affected by the market and/or regulatory environment it expects to face in the future. Many mills are undoubtedly concerned about the

² At this time, only limited information is available concerning these findings, although further results are expected to be published shortly.

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 certain 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, and the higher the 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.³ Unless market pulp brightness levels fall, therefore, integrated mills that can use lower brightness pulps will be better positioned than market pulp producers to take advantage of some of the pollution prevention technologies discussed in this handbook.⁴ This may become significant since market pulp producers in the U.S. sell much of their product to European customers, who are increasingly looking at the processes used to manufacture the pulps they buy.⁵

³ Most pulp mills have traditionally applied bleaching chemicals to achieve a target brightness level of 88 to 90 percent ISO. In particular, market pulp (i.e., pulp sold to other mills for use in papermaking) has always been bleached to high brightness according to the demands 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 percent, depending on the source). Brightness targets above 85 percent ISO are both technically more difficult and substantially more costly to achieve using alternative and emerging technologies. For further discussion of pulp brightness, see Section 5.1.

⁴ 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, 1993).

⁵ In 1991, U.S. exports of paper grade wood pulp to Western Europe totalled 2.1 million metric tons (or 41.3 percent of the total) (API, 1992b).

Much of the information contained in this report is by necessity very recent. Many of the current concerns over the environmental problems 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 1985 some of these alternative and emerging technologies were in use elsewhere in the world (and were under active investigation in North America), only lately has there been a move by U.S. producers to adopt them. Since the discovery of dioxins in pulp mill effluent, however, the U.S. and international research and development effort has been impressive, and the rate of adoption of many of these in-process pollution prevention technologies has been increasing rapidly. Information on their use, effectiveness, and cost has been spreading through all of the major trade publications and at numerous industry conferences. As experience with the technologies grows, it is inevitable that costs will decline and effluent will further improve, providing additional incentives for adoption.

This report is organized into four sections. Section Two covers the primary pollutants of concern in the pulp and paper industry. This section provides background for discussion in further sections on technologies that reduce these pollutants. Sections Three, Four, and Five cover pollution prevention technologies that are available to reduce or minimize the generation of some of these pollutants. Section Three covers technologies that can be applied in the woodyard and chipping areas of the mill. Section Four addresses technologies associated with the pulping or pre-bleaching stages of the process, while Section Five deals with alternative bleaching technologies. The first parts of Sections Four and Five include information on the conventional processes used in kraft pulping and bleaching to facilitate discussion of alternative techniques.

It should be noted that in addition to the pollution prevention technologies presented in this report there are numerous additional technologies, not necessarily meeting the definition of pollution prevention, that may be of interest to some readers. These include water conservation, solid waste reduction, and treatment technologies that can be applied in the woodyard, pulping, bleaching, and papermaking areas of kraft mills. Further information concerning these technologies can be found in a separate EPA report (EPA, 1992).

SECTION ONE REFERENCES

- API, 1992a. American Paper Institute. *1992 Statistics of Paper, Paperboard, & Wood Pulp*, New York.
- API, 1992b. American Paper Institute. *Exports of Pulp, Paper, Paperboard and Converted Products to World Markets 1991*. International Department. New York.
- EPA, 1988. U.S. Environmental Protection Agency. *U.S. EPA/Paper Industry Cooperative Dioxin Screening Study*. Office of Water Regulations and Standards, Washington, D.C., March 1988. EPA 440-1-88-025.
- EPA, 1992. U.S. Environmental Protection Agency. *Model Pollution Prevention Plan for the Kraft Segment of the Pulp and Paper Industry*. U.S. EPA Region 10, Seattle, WA, September 1992. EPA 910/9-92-30.
- EPA, 1993. *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.

SECTION TWO

POLLUTANTS OF CONCERN IN THE PULP AND PAPER INDUSTRY

This section discusses the sources, types, and quantities of pollutants found in the waste streams of bleached kraft pulp and paper mills, and the methods currently in use for their control. Section 2.1 describes effluent discharges, including conventional pollutants, toxics and, in particular, chlorinated organic compounds. Section 2.2 discusses the solid wastes, while Section 2.3 discusses air emissions.

2.1 EFFLUENTS

Pulp and paper mills require large quantities of water for wood handling, pulping, washing, bleaching, and papermaking operations. Water consumption has declined considerably over the past three decades, however, as mills have initiated water reuse programs to “close up” the process water flow. For example, in 1959 the U.S. pulp and paper industry consumed 57,000 gallons of water per ton of production. By 1988, this figure had dropped to 16,000 to 17,000 gallons per ton (Miner and Unwin, 1991). Nevertheless, at these rates a 600 tpd mill still requires approximately 10 million gallons of influent water per day, and must treat and discharge approximately the same amount (net of evaporative losses).

Effluent guidelines for the pulp and paper industry were first promulgated in November, 1982. The main categories of aquatic pollutants addressed in these effluent guidelines were: suspended solids, biochemical oxygen demand (BOD₅), color, and toxics.¹ Conventional pollution abatement in the U.S. has concentrated on reducing solids, oxygen demand, and aquatic toxicity. Color has been perceived as a problem only in isolated instances, and until late has not received significant regulatory attention at the national level.² Recent investigations have found toxic contaminants in bleach mill effluents that were

¹ The November 18, 1982 effluent limitations guidelines (47 FR 52006) established limits for the conventional pollutants BOD₅, TSS, and pH, and for the priority pollutants zinc, pentachlorophenol, and trichlorophenol.

² State water criteria and standards have addressed color in some localities, and these requirements will be reflected in the NPDES permits of affected mills.

not confirmed prior to 1985 (e.g., dioxins). These pollutants are now included in the current (scheduled) revisions of effluent guidelines for the industry under the Clean Water Act.

2.1.1 Solids

Solids consist of both suspended and dissolved materials carried in the effluent stream. In a conventional integrated kraft mill, the solids load in untreated effluent consists mainly of: (1) dirt, grit, and fiber from the wood preparation stages, (2) screen rejects and spills from the pulping area, (3) fiber and dissolved lignin solids from the pulp bleaching stages, and (4) fiber and additives washed from the early stages of papermaking.

Virtually all U.S. mills have installed primary and secondary effluent treatment designed, in part, to remove solids from the effluent before it is discharged to the receiving waters. Suspended solids are normally removed by settling or flotation processes that take place during primary wastewater treatment. Dissolved solids not removed by primary treatment are subjected to the biological processes that occur during secondary wastewater treatment.³ Some of the inorganic (mineral) fraction of the suspended solids pass through both primary and secondary processes and are discharged with the final effluent. Typical quantities of suspended solids produced at various pulp- and papermaking stages are shown in Table 2-1.

In the past, the release of settleable suspended solids in pulp and paper mill effluents was significant, and posed an environmental hazard after their release to the receiving waters. These particles can blanket the bottom of the receiving waterbody and destroy the habitat of bottom-living organisms. As the solids blanket decomposes, anoxic conditions may develop, resulting in the release of methane, hydrogen sulfide, and other noxious and/or toxic gases. In extreme cases, suspended fibers can also be lethal to fish. Nowadays, well-operated primary treatment systems are capable of removing most of the

³ Dissolved organic solids are associated with the effluent's biochemical oxygen demand, and are addressed in the following section.

TABLE 2-1

**Typical Sources and Quantities of Suspended Solids
Generated in Kraft Pulping and Papermaking**

Source	Solids Contribution (lb/ton)	Key factors
Wood Yard	1 to 100	Dry vs. wet debarking; use of log flumes.
Pulping	0 to 60	Amount of screen rejects sewered; whether screen room is closed; level of spill controls.
Recovery	5 to 10	Amount of lime mud sewered; fate of liquor grits; condensate stripping and fate of condensates.
Bleaching	2 to 6	Intra-stage washing efficiency.
Papermaking	10 to 60	Save-all efficiency; paper grade (amount of fillers, sizing, etc. added).

Source: Various industry observers.

settleable solids. Concern remains, however, because heavy metals, dioxins, and other chlorinated and unchlorinated compounds tend to adsorb to any remaining particles.

2.1.2 Biochemical Oxygen Demand

Biochemical oxygen demand (BOD₅) is a measure of the tendency of an effluent to consume dissolved oxygen from receiving waters.⁴ The consumption of oxygen results from natural biochemical degradation that occurs as complex organic materials are consumed by microorganisms present in the water. High levels of BOD₅ in the effluent stream can deprive nonphotosynthetic organisms (i.e., fish, shellfish, fungi, aerobic bacteria) of the oxygen they need to survive. BOD₅ has been used as a generic term for all organic material because organic compounds are the substrate responsible for the measured oxygen demand. Any regulation or procedure which reduces BOD₅ will thus reduce the total organic content of the water as well.

High-BOD₅ effluent is produced at many stages throughout the pulping and bleaching processes, including: debarking, washing, cooking, condensing of spent liquors, and bleaching. The BOD₅ in effluent from wet drum or hydraulic debarking is associated with wood particles and dissolved organics that remain in the wash water after the logs are stripped. Dry debarking generates no effluent load at this stage, but results in higher BOD₅ levels from pulping operations (because more bark remains on the logs, requiring a higher volume of cooking liquor). Spent cooking liquor (weak black liquor) contains much of the lignin and other organic materials originally contained in the wood. The weak black liquor is concentrated and routed to the recovery system, however, where much of the BOD₅-causing substances are incinerated.

Digester condensates and condensates from weak black liquor concentration may contain up to one-third of the untreated wastewater loadings BOD₅ at bleached kraft mills. Chlorination and extraction stages generate BOD₅ during bleaching operations; this BOD₅ is associated with dissolved lignin, other carbohydrates, and fiber that is dissolved during bleaching. Typical quantities of BOD₅ produced during pulp and paper production are shown in Table 2-2.

⁴ BOD₅, representing the 5-day biochemical oxygen demand of effluents, is the most common pollutant parameter used in the U.S. and will be used throughout the remainder of this report.

TABLE 2-2

**Typical Sources and Amounts of BOD₅
Generated in Kraft Pulping and Papermaking**

Source	BOD Contribution lb/ton	Notes
Wood Yard	0 to 10	Dry vs. wet debarking, use of log flumes.
Pulping	0 to 50	Level of spill control
Recovery	2 to 20	Level of spill control
Bleaching	3 to 40	Amount of bleach plant effluent that can be recycled to recovery (depends on bleach sequence)
Papermaking	5 to 30	Type of product (amount of additives).

Source: Various industry observers.

During secondary treatment of effluent, most BOD₅ is removed. In an oxidation lagoon, a 30-day retention period removes 85 to 90 percent of BOD₅, while an aerated lagoon requires a fraction of that time to produce similar results.

2.1.3 Color

“Color” is a measure of an effluent's interference with the transmission of light. Because it reduces light levels in receiving waters, high doses of color can disrupt photosynthesis and aquatic life. The primary concern over effluent color is its undesirable aesthetic effect on receiving waters. The compounds contributing to color are also associated with water taste problems and can stabilize some bivalent metal ions by chelation.⁵ Although materials that impart color to mill effluent are generally nontoxic, and are not known to cause harm to the receiving waters (except at very high loadings), their impact on the aesthetic qualities of some waterways has led to increased regulatory attention at the local level.⁶

High molecular mass materials, primarily dissolved lignin and lignin derivatives, hold the bulk of the chromophores (color bodies) present in pulp and paper effluent. The molecules responsible for color break down slowly in the aquatic environment, eventually reaching a size small enough to be incorporated into microbial metabolism. This process is reflected in a long-term biochemical oxygen demand over a period of 20 to 100 days or longer, which is not measured by the conventional BOD₅ test.

Table 2-3 indicates that over half of the color load in kraft pulp mill effluents comes from the first caustic extraction stage in the bleach plant; most of the remainder is generated during the first chlorination stage. As noted in the table, color is usually measured in “platinum cobalt units” (PCU), expressed as pounds PCU per ton of pulp. Effluent from a 1970s-era integrated CEDED softwood kraft pulp mill may contain approximately 300 lbs of color per ton pulp (hardwood pulping contributes less than half this amount). Of this total, pulping contributes about 20 percent and the bleach plant contributes about 70

⁵ Technically, taste problems are caused by the pollutants that cause color. It follows that actions taken to reduce color will also reduce taste problems as well.

⁶ Color regulations are normally established based on narrative criteria contained in the facility's NPDES permit (e.g., “no significant impact on receiving water color”).

TABLE 2-3

**Contribution of Bleaching Stages to
Effluent Color in Conventional Kraft Process**

Bleaching Stage	Softwood		Hardwood	
	kg/ADT	% of Total	kg/ADT	% of Total
1 C - Chlorination	50	17.0	26	22.6
2 E Caustic extraction	226	76.9	78	67.8
3 D Chlorine dioxide	11	3.7	6	5.2
4 E Caustic extraction	6	2.0	4	3.5
5 D Chlorine dioxide	1	0.3	1	0.9
TOTAL	294	100.0	115	100.0

Note: Units are Am. Pub. Health Assoc. (APHA) chloroplatinate units, kg/ton.
For further details on bleaching chemicals see Section 5.

Source: Ontario Ministry of the Environment (1988). Data based on Rush and Shannon (1976).

percent. The remainder is generated from a number of minor sources, including wood preparation, chemical recovery, and papermaking operations. Within the bleach plant, caustic extraction is the largest single source of color, contributing some two-thirds of the color in bleach plant effluents, or nearly half of all color generated at an integrated mill (Springer 1986).

Conventional biological treatment removes less than 10 percent of the effluent color (Ho et al., 1991). Although water quality standards in many states address color, color standards are currently included in the NPDES permits of only five pulp and/or paper mills (Geil, 1993).^{7,8} Where it is necessary, some mills employ a separate clarification stage to remove effluent color. Most pollution prevention technologies discussed later in this report will reduce color substantially.

2.1.4 Chlorinated Organic Compounds

Discharges of chlorinated compounds are associated almost exclusively with bleach plant operations at pulp mills that use elemental chlorine or chlorine-containing bleaching chemicals. Discharges may also occur from paper mills (or papermaking operations at integrated mills) which use chlorine-bleached pulps, but these discharges are small in comparison.

Terminology, Units of Measurement, and Test Methods

A number of alternative test methods have been developed and/or adapted to yield quantitative estimates of chlorinated compounds in pulp and paper mill effluents. This is an active area of research, as scientists attempt to develop methodologies that accurately reflect the biological activity and potential impacts of the many classes of chlorinated compounds that are present in these effluents. The most common tests include the following:

⁷ State water quality criteria generally do not specify color limits; rather they include language requiring, for example, that effluent be “free” of color. It is then up to the NPDES permit writer to determine whether the mill’s discharge permit should address color, including whether monitoring and reporting of color levels is required.

⁸ A further ten mills have standards for turbidity (cloudiness) which, according to Geil (1993), may be a surrogate for color.

Total Organic Chlorine (TOCl) This test measures all organically bound chlorine in an effluent (or other) sample. The sample is passed through one or more media in which organic compounds are captured. The medium is combusted to destroy all organics, and chlorine is captured and measured from the combustion byproducts. Chlorine concentration is expressed as a proportion of the initial sample (e.g., g chlorine per kg pulp, kg chlorine per metric ton pulp).

Total Organic Halogens (TOX) Identical to TOCl in procedure, except that all of the halogens (fluorine, bromine, and iodine, in addition to chlorine) are measured. Results are typically nearly identical to TOCl results, because only traces of fluorine, bromine, and iodine are generally present in effluents.

Adsorbable Organic Halogens (AOX) - Conceptually very similar to TOCl or TOX, except that organics are adsorbed onto granular activated charcoal in the initial step. The primary advantage of this test is that it can be completed much more rapidly than TOCl. Results are also expressed as the proportion of chlorine to total sample weight (e.g., g chlorine per kg pulp, kg chlorine per metric ton pulp), and are generally highly correlated with TOCl results.

Extractable Organic Halogens (EOX) - Procedurally identical to AOX, except that effluents are first extracted with a nonpolar solvent. EOX compounds include those that can be expected to be lipophilic, i.e., to show a tendency to bioaccumulate in the fatty tissues of living organisms.

Historically, TOCl has been most often used to express the total organic chlorine content of pulp and paper mill effluents and other wastes. In recent years, however, AOX has become a more or less standard measure. Most regulatory requirements in European countries and Canada are based on the AOX measurement, and AOX monitoring requirements have begun to be incorporated into some NPDES permits in the United States. It has been suggested however, that EOX or other measurements that are more closely correlated with biologically active chlorinated compounds should be used as the basis for regulating chlorine discharges (e.g., Folke et al., 1991; MacKay, 1989), and research toward this end remains active.

Organic chlorine in effluents can also be estimated as a function of the amount of chlorine used in the bleaching process. Germgard (1983) proposed the following relationship:

$$\text{Organic chlorine} = k * \left\{ C + \frac{H}{2} + \frac{D}{5} \right\} \text{ kg/metric ton pulp}$$

Where:

C, H, and D . represent the molecular chlorine, hypochlorite and chlorine dioxide charges in kg per tonne pulp, (with H and D expressed as equivalent molecular chlorine); and

k equals a constant in the range of 0.07 to 0.15.

Liebergott (1991) has since shown that the values for k depend on the level of chlorine dioxide substitution. To estimate AOX, McCubbin et al. (1992) add the factor (1-e_B) to the equation, and adjust k depending on the substitution level:

$$AOX = k * \{C + \frac{H}{2} + \frac{D}{5}\} * \{1 - e_B\} \text{ kg/metric ton pulp}$$

Where:

e_B equals the AOX removal efficiency of the biological treatment system (40 percent for aerated stabilization and 33 percent for activated sludge);

k equals 0.08 when the bleach plant operates with less than 70 percent chlorine dioxide substitution; and

k equals 0.08 x [1.7 (%subst. ÷ 100)] where substitution is greater than 70 percent.

Identified Chlorinated Organic Compounds

More than 300 individual chlorinated organic compounds have been identified to date in bleach plant effluents. The major classes of compounds that have been identified include: chlorinated acids, chlorinated phenolics, chlorinated aldehydes, ketones, and lactones, and chlorinated hydrocarbons.

These compounds contain only a small fraction of the total mass of chlorine contained in effluents, however. By far the larger proportion of all organically bound chlorine (75 to 90 percent) is incorporated into very large molecules (molecular weight > 1,000), many of which have not been specifically characterized. These molecules typically consist of chlorinated fragments of complex lignin species, which are not amenable to precise characterization. Because of their large size, such high molecular weight

compounds are difficult to break down in treatment. The extent of their breakdown during treatment, the nature of possible breakdown products, and the potential magnitude of their related environmental impacts has been extensively investigated, though few conclusions have been reached.

Although many of the chlorinated compounds identified in pulp and paper mill effluents have some potential to damage living systems, to date only a small number have been the subject of specific scientific and regulatory attention.⁹ Those which have been widely studied include dioxins and furans, chloroform, and chlorates; they are addressed individually in the following paragraphs.

Dioxins and furans Dioxins and furans (specifically, dibenzo-*p*-dioxins and furans) are a class of chlorinated organic compounds that contain two aromatic carbon rings joined by a bridge of carbon-carbon and carbon-oxygen bonds. A total of 75 dioxins and 135 furans have been identified. The biological activity and impacts of these compounds depend on the number of chlorine molecules attached to the double ring structure and their location on the dioxin/furan molecule. The most toxic are 2,3,7,8-TCDD (2,3,7,8-tetrachloro-dibenzo-*p*-dioxin) and 2,3,7,8-TCDF (2,3,7,8-tetrachloro-dibenzo-furan), both of which contain four chlorine molecules.

Like all of the chlorinated organics found in pulp and paper effluents, dioxins and furans are not formed as a planned product of the bleaching process, rather they are a byproduct generated by the chlorination of nonchlorinated precursors during the complex reactions that occur during bleaching. The concentration of these chemicals is not great -- even in uncontrolled effluents, concentrations are typically measured in parts per trillion to parts per quadrillion. Concern has arisen from their high toxicity, persistence, and potential for bioaccumulation rather than high effluent concentrations per se. Lignin contains chemical structures from which dioxins may be generated, and is thought by some to provide most or all of the precursors associated with dioxin formation. Other sources have been suggested, including natural compounds in mill influents (Ontario Ministry of the Environment, 1988), and oils used as defoamers during pulping and bleaching (Berry et al., 1989).¹⁰

⁹ Many individual compounds have been studied on a collective basis (e.g., AOX, EOX, TOCI).

¹⁰ In the last several years the replacement of precursor-containing defoamers has caused a significant decrease in dioxin production.

Secondary wastewater treatment is moderately effective at removing dioxins and furans from effluents, and developing technologies have promised removal efficiencies of greater than 90 percent (OTA, 1989). Wastewater treatment does not, however, result in the destruction of dioxins and furans, but simply in their transfer to treatment sludges, where disposal remains a significant problem. It is for this reason that scientific and regulatory attention has generally focused on technologies that prevent the formation of dioxins and furans during bleaching, and not on biological or chemical effluent treatment. The U.S. industry has also recognized the role of pollution prevention techniques in reducing dioxin and furan formation. According to estimates from the National Council of the Paper Industry for Air and Stream Improvement (NCASI),¹¹ more than \$2 billion has been spent on water pollution control in the U.S. since 1985, much of this aimed at reducing dioxins and furans (API, 1992).

Chloroform The hypochlorite bleaching stage (used in a large but decreasing number of mills) is by far the major source of chloroform generated during pulp bleaching. The chlorination and extraction stages are also associated with chloroform generation, and are the major sources when a hypochlorite stage is not used. A number of factors influence chloroform generation, the most important being the amount of hypochlorite used and the variation in pH during bleaching and extraction. Chlorine dioxide substitution generally results in a reduction in chloroform formation (because it replaces hypochlorite), as does a reduction in chlorination stage temperature (although this is not a useful control parameter) (Dallons et al., 1990; Crawford et al., 1991).

Because chloroform is an extremely volatile compound, 60 percent or more of all discharges are typically released as fugitive air emissions through bleach plant vents (Dallons et al., 1990; see also Section 2.3.4). In plants that employ secondary wastewater treatment, as much as 80 percent of the remaining chloroform may escape as fugitive emissions from water treatment facilities (aeration basins, aerators, primary and secondary clarifiers) (Ontario Ministry of the Environment, 1988). The remainder will volatilize gradually following release to the receiving waters. Because its aquatic toxicity and bioaccumulation potential are low, chloroform in pulp and paper effluents is not considered to be a significant aquatic hazard. However, it is considered both a toxic pollutant under the Clean Water Act and a hazardous air pollutant (HAP) under the Clean Air Act, and will be subject to regulation under the upcoming integrated pulp and paper rulemaking.

¹¹ NCASI is the environmental arm of the American Forest Products Association (AFPA), formerly the American Paper Institute (API).

Chlorate Chlorate (ClO_3^-) is a by-product formed during chlorine dioxide bleaching. The quantity of chlorate produced is insignificant in most mills, but up to 3 kg per ton of pulp can be generated and found in untreated wastewater when high rates of chlorine dioxide substitution are used (Germgard, 1988). Chlorates are a potential concern because some compounds are known to harm plant life; for example, sodium chlorate has been used as an herbicide for weed control. At concentrations found in untreated effluents, chlorate damage to marine algae populations in Sweden has been documented (e.g., Germgard, 1988). Chlorate is effectively removed from effluents during secondary treatment providing they have an anoxic section installed deliberately (or otherwise), and similar biological processes also remove chlorate from natural receiving waters. Since U.S. mills have only recently begun using high substitution bleaching, there are no reports of damage to freshwater species so far. At the present time, chlorates in pulp and paper effluents do not pose a serious threat to the environment, but with higher rates of chlorine dioxide substitution they may become a focus of concern in the future.

2.1.5 Other Toxic Compounds

Resin acids and fatty acids are pulping byproducts which form a “soap” that is skimmed from the pulp during the recovery process. About eighty kilograms of soap are produced per ton of pulp. This soap is generally incinerated, though in some cases it is captured for processing into tall oil (sold as a pulping byproduct). Occasionally, the soap causes foam overflows, which can escape into the effluent stream. The environmental effects from soap spills can be severe, since these compounds are acutely toxic to many aquatic species. Their impact can be felt on both the biota of receiving waters and on the populations of bacteria and fungi that are responsible for biological wastewater treatment.

Recently, scientists in Canada and Scandinavia have suggested that non-chlorinated substances represent a large portion of the remaining toxicity of effluents from mills that have reduced discharges of chlorinated organics to below traditional levels (Lehtinen, 1991; MFG, 1991; Van der Krakk et al., 1992). Lehtinen, for example, has concluded that there is no correlation between the amount of AOX formed during bleaching and the composite biological response of fish retained in dilute mill effluents (Lehtinen, 1991). In other studies, the effluent from unbleached kraft mills showed a stronger response than that obtained from mills producing up to 4 kg per ton AOX (Brunsvik, 1991; Ladner, 1991). While these findings are preliminary, it has been hypothesized that the biological effects are due to steroids present in wood extractives, which may not be eliminated during secondary treatment. In-plant measures

that would reduce the total discharge of organics would have the added benefit of reducing the amount of such non-chlorinated substances discharged from the mill.

2.2 Solid Wastes

The significant solid waste streams from pulp and paper mills include bark, wastewater treatment sludges, lime mud, lime slaker grits, green liquor dregs, boiler and furnace ash, scrubber sludges, and wood processing residuals. Because of the tendency for chlorinated organic compounds (including dioxins) to partition from effluent to solids, wastewater treatment sludge has generated the most significant environmental concerns for the pulp and paper industry. To a lesser extent, concern has also been raised over whether chlorinated organics are partitioned into pulp products, a large portion of which becomes a post-consumer solid waste. This section discusses disposal of wastewater treatment sludge, scrubber ash and sludge, and wood residues

2.2.1 Wastewater Treatment Sludge

With the exception of bark, wastewater treatment sludge is the largest volume solid waste stream generated by the pulp and paper industry. Pulpmaking operations are responsible for the bulk of these wastes, although treatment of papermaking effluents also generates significant sludge volumes. For the majority of pulp and integrated mills that operate their own wastewater treatment systems, sludges are generated onsite. A small number of pulp mills, and a much larger proportion of papermaking establishments, discharge effluents to publicly-owned wastewater treatment works (POTWs). Sludges associated with these mills are generated at public facilities, where they form a portion of total sludge generated from mixed industrial, commercial, and residential sewage.

Wastewater treatment sludges themselves do not pose a significant environmental concern. Potential environmental hazards are associated with trace constituents (e.g., chlorinated organic compounds) that are partitioned from the effluent. The 1988 results of the "104-Mill Study" showed that dioxins and furans were present in bleached pulp mill sludges, resulting in calls to regulate both landfill disposal and land application of such sludges. Landfill and surface impoundment disposal are most often

used for wastewater treatment sludge; in 1988 only eleven of 104 bleached kraft mills disposed of any sludge through land application or conversion to sludge-derived products (e.g., compost, animal bedding).¹²

Sludge generation rates vary widely among mills. For example, bleached kraft mills surveyed as part of EPA's 104-Mill Study reported sludge generation that ranged from 14 to 140 kg sludge per ton pulp (EPA, 1988). Total sludge generation for these 104 mills was 2.5 million dry metric tons per year, or an average of approximately 26,000 dry metric tons per year per plant.

Two different types of wastewater treatment sludge are generated at the mill, each of which exhibits very different physical and chemical characteristics. Primary sludge includes floating and suspended solids that are removed from the pulp by the physical processes (e.g., screening, skimming, sedimentation, flotation) used during primary wastewater treatment. Primary sludge may also contain chemical coagulants and/or flocculants that are added to effluents to promote settling of suspended solids. Primary sludge therefore consists primarily of unaltered constituents of the wood that is input to the pulp and papermaking process — bark and other wood residuals, knots and other rejects that enter pulping effluents, paper machine additives (clays, fillers), and fiber that is lost from pulping, washing, and bleaching operations.

The solids in secondary sludge consist almost exclusively of bacterial and fungal biomass that is generated during biological treatment of dissolved and suspended organic matter in wastewaters, including bleach plant effluents. Pollutants that are sequestered in these organic compounds tend to become concentrated in secondary sludges; it is for this reason that secondary sludges have become a focus of

¹² Under the terms of a 1988 consent decree (*EDF/NWF v. Thomas*, D.D.C. No. 85-0973, July 27, 1988) EPA announced in November, 1991 their finding that there was insufficient evidence of potential risk to justify regulation under the Resource Conservation and Recovery Act (RCRA) of landfill or surface impoundment disposal of bleached pulp and paper mill sludge. Under a separate consent decree, (*EDF v. Reilly*, D.D.C. No. 89-0598) EPA is required to "...promulgate a listing determination for sludges from pulp and paper mill effluent on or before the date 24 months after promulgation of an effluent guideline regulation under the Clean Water Act for pulp and paper mills," (p. 10). The decree specifies, however, that a listing determination would not be required if the final rule for the effluent guideline revision is based on "...the use of oxygen delignification, ozone bleaching, preox bleaching, enzymatic bleaching, hydrogen peroxide bleaching, oxygen and peroxide enhanced extraction, or any other technology involving substantially similar reductions in uses of chlorine-containing compounds," (pp. 10-11).

Also in response to the 1988 consent decree, regulatory actions to control land application under the Toxic Substances Control Act (TSCA) were proposed in April, 1991 and are still under development. Since that time, dioxin levels in mill effluent and, presumably in sludges, have declined considerably.

environmental concern. The largest volumes of secondary sludges are generated by activated sludge treatment systems, which aggressively promote biomass growth and turnover. Much smaller volumes are generated by aerated lagoon treatment systems, as a large percentage of the solids in these systems are aerobically and anaerobically destroyed.

Additional sources of wastewater treatment sludge include coagulation and/or flocculation treatment stages designed to capture specific pollutants. For example, lime or alum coagulation is used by a few pulp mills to control color discharges, and generates a sludge that must be collected and disposed. Depending on specific treatment process design, these sludges may be captured as a portion of primary sludge or may be collected in an independent step.

2.2.2 Boiler and Furnace Ash and Scrubber Sludge

The power boiler and recovery furnace are the major sources of ash from pulpmaking operations, while the lime kiln is a secondary and relatively minor source. Two different types of ash are generated by the combustion processes at pulp and paper mills. Fly ash consists of fine particles that are entrained in and subsequently captured from flue gases by emission control devices, while bottom ash consists of coarse noncombustible particles that are removed continuously or periodically from boiler and furnace combustion chambers. Although the volume of ash generated depends to some extent on boiler/furnace design and operating conditions, ash generation is primarily a function of the fuels that are consumed. Coal and wood fuel generate the largest volumes of ash, whereas liquid and gaseous fuels produce very little or no ash.

Scrubber sludges are also associated with ash generation. A number of mills use wet scrubbers to capture particulate (and occasionally other) emissions. Sludges generated by these scrubbers contain the captured particulate or gaseous pollutant species. The disposal of ashes and scrubber sludge is a concern in the industry, due to the generally low pH of these wastes. Many mills must raise the pH by mixing ash and scrubber sludges with lime, bark, or wood chips. This increases the bulk of the waste and

increases the cost of their disposal. Fly ash from hog fuel burners is also a concern due to the presence of dioxins and furans in the ash at some mills.

2.2.3 Wood Processing and Other Wastes

A number of other minor solid waste streams are associated with pulp and paper operations. Dry wood preparation operations and groundwood pulping generate significant volumes of residuals. To the maximum extent practicable, however, these wastes are captured and consumed as fuel in power and/or steam boilers. Knots, bark, and other pulping rejects may be captured as a solid waste stream separate from effluent flows. Mills also generate significant quantities of mixed industrial solid wastes including pallets, chemical shipping containers, construction debris, and other items.

2.3 Air Pollutants

The major air pollutants from kraft pulping and bleaching operations include reduced sulfur compounds, particulates, hazardous air pollutants (HAPs), including methanol and chloroform, and volatile organic compounds (VOCs), some of which may also be HAPs. SO_x , SO_2 and, to a lesser extent NO_x are also a concern. The following sections discuss emission sources for these pollutants and the associated environmental and health concerns.

2.3.1 Reduced Sulfur Compounds

Emissions of reduced sulfur compounds are associated with the kraft pulping process only. Four compounds are of concern: hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide [$(\text{CH}_3)_2\text{S}$], and dimethyl disulfide [$(\text{CH}_3)_2\text{S}_2$]. These compounds are all derived from sodium sulfide (Na_2S), one of the two primary cooking chemicals used in the kraft process, and are generated during the complex reactions that occur in the initial kraft cook. Major emission sources in the mill include digester blow and relief gases, evaporator vents, chemical recovery furnace emissions, and pulp washers. They are also released from vents during a number of other pulping unit processes. Small quantities are typically dissolved in liquid effluents, which escape from the effluent during wastewater collection and

treatment or after discharge to receiving waters. Approximately 12 to 13 kg of total reduced sulfur (or TRS) are generated per ton of pulp (EPA, 1993).

Even at small concentrations, TRS from kraft pulp mills can be a source of nuisance odors. Humans can detect the rotten egg and rotten cabbage odors of hydrogen sulfide and methyl mercaptan at as little as 1 part per billion (ppb). Detection thresholds for dimethyl sulfide and disulfide are about 10 ppb. In untreated kraft mill effluents, TRS may be present in sufficient quantities to taint the taste of fish. At much higher concentrations these compounds are acutely lethal to marine and terrestrial wildlife (including humans), but effluent concentrations sufficient to cause acute toxicity are not a concern associated with well-operated kraft pulp mills. These compounds are not persistent in the environment, and do not show tendencies to bioaccumulate.

2.3.2 Particulates

The major sources of particulates are fly ash from power boilers, chemical recovery furnaces, and lime kilns. The highest volume source is the power boiler. Depending on the age and efficiency of the equipment, the chemical recovery furnace can be a source of very fine particulates, which are a particular concern because they tend not to settle from the atmosphere and may be associated with more significant health impacts than larger particulates. The volume of ash generated is a function primarily of the fuel combusted in the power boiler. Coal and wood produce significant volumes of ash, while oil and other liquid fuels produce little or no ash.

Particulate emissions from pulp and paper mills are controlled under current EPA regulations (40 CFR Part 60.280), which limit emissions from both power boilers and recovery furnaces.

2.3.3 Volatile Organic Compounds

Volatile Organic Compounds (VOCs) are organic species that participate in the formation of photochemical oxidants. Derived from lignin, carbohydrates, and extractives in the pulp furnish, the largest proportion of these compounds are generated during pulping (and, where used, oxygen delignification), and the largest emission sources are digester blow gases, the chemical recovery

evaporators, and the brownstock washer and knotter hoods (EPA, 1993). Smaller quantities are generated and emitted during later stages of bleaching and papermaking, as residual VOCs are gradually released from the pulp. Typical VOC emissions include terpenes, alcohols, phenols, and chloroform (a HAP). Other VOC species known to be emitted include acetone, methyl compounds, and turpentine-based organics.

Several VOCs including chloroform, methanol, and other gaseous emissions (including hydrogen chloride and chlorine) are identified as Hazardous Air Pollutants (HAPs) under the 1990 Clean Air Act Amendments. Emissions of these compounds from pulp and paper mills will be subject to Maximum Achievable Control Technology (MACT) emission limitations. These limitations are currently under development.

2.3.4 Chloroform

Until recently, the pulp and paper industry has been the major industrial source of chloroform emissions in the United States.¹³ Chloroform is considered by the EPA, the American Council of Governmental Industrial Hygienists (ACGIH), and the International Agency for Research on Cancer (IARC) to be a probable human carcinogen, posing a significant cancer risk at an exposure level of 50 parts per million. In 1989, the Occupational Safety and Health Administration (OSHA) proposed revising its permissible exposure limit (PEL) for chloroform from 50 ppm to 2 ppm (54 FR 12, January 19, 1989). Chloroform is among the emissions that are being addressed under two ongoing EPA programs: The voluntary Industrial Toxics Program sponsored by the Administrator's office, and the MACT standard described above.

Chloroform generation is associated with chlorine-based bleaching of pulps. The largest chloroform source is the sodium hypochlorite (NaOCl) bleaching stage (where this stage is used), although

¹³ The identification of the hypochlorite bleaching stage as a major source of chloroform, and its subsequent steady elimination from bleach sequences, has led to significant decreases in chloroform emissions by the industry.

elemental chlorine and chlorine dioxide stages are also responsible for some chloroform generation. The rate of chloroform generation is a function of many variables, including:¹⁴

Hypochlorite charge - Chloroform generation increases with the charge of the hypochlorite used in bleaching, at a rate proportional to the square root of the amount of hypochlorite used;

Lignin content - Chloroform generation in the hypochlorite bleaching state is proportional to the lignin content of the bleached and extracted pulp that enters this stage (expressed at the chlorine extracted kappa number, or CEK);

Chlorine factor The chlorine factor expresses the ratio of molecular chlorine to pulp. Chloroform emissions increase with increasing chlorine factor;

pH Emissions tend to increase with increasing pH during bleaching and extraction. Acid sewer effluents containing chloroform precursors are often mixed with more alkaline waste streams, and the resulting pH increase is associated with significant chloroform formation;

Chlorine dioxide substitution Increasing chlorine dioxide substitution generally results in a reduction in chloroform formation; and

Chlorination stage temperature - A reduction in chlorination stage temperature tends to reduce chloroform emissions.

Chloroform discharges are divided between effluents and emissions to air. Sixty percent or more of total discharges are typically in the form of fugitive air emissions from bleach plant vents. The majority of chloroform that remains in bleach plant effluents is also ultimately released to the atmosphere in the form of evaporative emissions from the wastewater treatment system or from the receiving waters.

2.3.5 Other Hazardous Air Pollutants (HAPs)

In addition to chloroform, the kraft pulping and bleaching processes emit quantities of other HAPs including methanol, hydrogen chloride, and chlorine. Methanol is the largest volume HAP, and is emitted from several sources. The black liquor oxidation stage, where used, is the largest volume methanol source

¹⁴ Sources for all factors cited are NCASI: Dallons and Crawford (1990); Dallons et al. (1990); Crawford et al., (1991).

according to most recent estimates.¹⁵ Newer recovery boiler designs eliminate the black liquor oxidation stage in favor of indirect contact evaporation, thus newer mills will emit substantially lower amounts of methanol. Much smaller amounts of methanol are emitted from digester blow valves, knotter and washer hood vents, evaporator vents, and turpentine recovery processes, as well as from acid sewers at plants practicing high chlorine dioxide substitution.

Hydrogen chloride is emitted from several sources including washer and seal tank vents (especially under high or 100 percent ClO₂ substitution), while chlorine is released from C-, D-, and H-stage tower and washer vents (EPA, 1993).

¹⁵ The most recent document characterizing air emissions from pulp and paper facilities (EPA, 1993) covers only the evaporation portion of the recovery process and thus does not address emissions from black liquor oxidation. Additional recovery processes will be discussed in future drafts of this document.

SECTION TWO REFERENCES

- Berry et al., 1989. R.M. Berry, B.I. Fleming, R.H. Voss, C.E. Luthe, and P.E. Wrist, "Toward Preventing the Formation of Dioxins During Chemical Pulp Bleaching," *Pulp & Paper Canada*, September, 1990, p. 48.
- Brunsvik et al., 1991. "To CD or Not to CD. That is the Question," *Proceedings, 1991 TAPPI Pulping Conference.*, p. 159.
- Crawford et al., 1991. Robert J. Crawford, Victor J. Dallons, Ashok K. Jain, and Steven W. Jett. "Chloroform Generation at Bleach Plants With High Chlorine Dioxide Substitution and/or Oxygen Delignification," *Proceedings, 1991 TAPPI Environmental Conference*, p. 305.
- Dallons et al., 1990. Victor J. Dallons, Dean R. Hoy, Ronald A. Messmer, Robert J. Crawford. "Chloroform Formation and Release From Pulp Bleaching," *TAPPI Journal*, June 1990, p. 91.
- EPA, 1988. U.S. Environmental Protection Agency. *U.S. EPA/Paper Industry Cooperative Dioxin Screening Study*, Office of Water Regulations and Standards, Washington, D.C. March 1988. EPA 440/1-88-025.
- EPA, 1993. U.S. Environmental Protection Agency. *Pulp, Paper, and Paperboard Industry - Background Information for Proposed Air Emission Standards*. Office of Air Quality Planning and Standards, Research Triangle Park, NC. Preliminary Draft. April 1993.
- Folke et al., 1991. Jens Folke, Karl Johan Lehtinen, Howard Edde. "The Scientific Foundation of Adsorbable Organochlorines (AOX) as a Regulatory Parameter for Control of Organochlorine Compounds," *Proceedings 1991 TAPPI Environmental Conference*, p. 517.
- Geil, 1993. Personal communication between Jeff Cantin of ERG and Steve Geil, EPA Office of Water, Office of Wastewater Enforcement and Compliance, Permits Division (Washington, D.C.). February 18, 1993. Based on data pulled from the Office of Water's Permit Compliance System.
- Germgard, 1988. Ulf Germgard. "Chlorate Discharges From Bleach Plants - How To Handle a Potential Environmental Problem," *Proceedings, 1988 TAPPI Pulping Conference* p. 315.
- Germgard, 1983. Ulf Germgard. "Oxygen Bleaching and its Impact on Some Environmental Parameters," *Svensk Papperstidning* 88(12).
- Ho et al., 1991. Bosco P. Ho, Randy R. Warner, Denis E. Hassick, Terrance J. McLaughlin, Charles Ackel. "Automatic Coagulant Dosage Control for Mill Wastewater Color Removal," *Proceedings 1991 TAPPI Environmental Conference*, p. 617.
- Lehtinen et al., 1991. K.-J. Lehtinen, B. Axelsson, K. Kringstad, L. Strombers. "Characterization of Pulp Mill Effluents by the Model Ecosystem Technique. SSVL Investigations in the Period 1982-1990," *Nordic Pulp and Paper Research Journal*. 6(2): 81-88.

SECTION TWO REFERENCES (cont.)

- MFG, 1991. Internal Reports of the European Environmental Research Group. Denmark, Sweden, and Finland.
- MacKay, 1989. Donald MacKay. "A Review of the Nature and Properties of Chemicals Present in Pulp Mill Effluents," *Chemosphere*, No. 7 1988, p. 248.
- Miner and Unwin, 1991. Reid Miner and Jay Unwin. "Progress in Reducing Water Use and Wastewater Loads in the U.S. Paper Industry," *TAPPI Journal*, August, 1991, p. 127.
- Ontario Ministry of the Environment, 1988. *Kraft Mill Effluents in Ontario*. Municipal-Industrial Strategy for Abatement. March 1988.
- OTA, 1989. U.S. Congress, Office of Technology Assessment. *Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp*, OTA-BP-O-54 (Washington, D.C.: U.S. Government Printing Office, May 1989).
- Reeve and Earl, 1989. Douglas W. Reeve and Paul F. Earl. "Chlorinated Organic Matter in Bleached Chemical Pulp Production: Part I Environmental Impact and Regulation of Effluents," *Pulp & Paper Canada*, April 1989, p. 65.
- Rush and Shannon, 1976. *Review of Color Removal Technology in the Pulp and Paper Industry*. Environment Canada, Water Pollution Control Directorate, Report EPS #WP 765.
- Springer, 1986. Aan M. Springer. *Industrial Environmental Control Pulp and Paper Industry*, John Wiley & Son, New York.
- Van der Krakk et al., 1992. "Receiving Water Environmental Effects Associated With Discharges from Ontario Pulp Mills," Proceedings, *19th Annual Toxicity Workshop*, Edmonton, Alberta, Canada, Oct. 4-7, 1992.

SECTION THREE

POLLUTION PREVENTION TECHNOLOGIES IN WOODYARD AND CHIPPING OPERATIONS

This section reviews the operations in the pulp mill woodyard and chipping areas and identifies technologies relevant to prevention of pollution associated with these activities. The main technologies discussed are raw material selection (Section 3.1), recycle of log flume water (Section 3.2), dry debarking (Section 3.3), improved pulp chipping and screening (Section 3.4), and stormwater management (Section 3.5).

3.1 RAW MATERIAL SELECTION

Increasingly, pulp mills have turned to using sawmill residues (logs, chips, sawdust) to supplement the virgin fiber used in kraft pulping and papermaking. While use of sawmill residues improves the industry's overall product yield from timber, problems may arise at the pulp mill if the raw material has been previously treated with wood preservatives, specifically pentachlorophenols (PCPs). Researchers at PAPRICAN (Pulp and Paper Research Institute of Canada) have found that these types of preservatives contain CDDs/CDFs or CDD/CDF precursors, which can carry over into the bleach plant (Luthe et al., 1992.; Berry et al., 1989; Voss et al., 1988). There, they may react with chlorine to form dioxins and furans.

While the use of chlorophenol-based preservatives has been more common in Canada (and particularly in British Columbia), raw material supplies for U.S. mills may include wood from a variety of sources. Mills should therefore try to avoid using chips, logs, or sawdust from unknown sources without first testing for the presence of chlorophenols.

The costs of using "cleaner" raw materials may be slightly higher if lower prices are paid for the treated wood or wood waste. It is widely believed, however, that contaminated wood fiber is not a major problem in the U.S. pulp and paper industry.

3.2 RECYCLE OF LOG FLUME WATER

Log flumes are used at some mills to transport wood from log piles to debarkers and chippers. The water used to convey the logs can be recycled, with fiber and bark being recovered and burned in a furnace (the "hogged fuel" boiler) for heat recovery. Alternatively, or in addition, treated wastewater can be used as makeup for the log flume.

The practice of log flume water recycle is common among mills that use log flumes. Costs of developing an appropriate recycle system may be in the range of \$100,000 to \$500,000. Recycle of log flume water will reduce the discharge of BOD₅ and TSS, as well as conserve water. BOD₅ and TSS reductions of up to 750 lbs per day have been previously estimated for a 3 MGD recycle system (U.S. EPA, 1982).

3.3 DRY DEBARKING

The bark of the tree comprises about 10 percent of the weight of the tree trunk. Bark does not yield good papermaking material because it is resistant to pulping, contains a high percentage of extractives, and retains dirt. In most pulping processes, bark is removed from the logs before they undergo chipping.

The most common debarking mechanism used for pulpwood is the debarking drum, which removes bark by tumbling the logs together in a large cylinder. Slots in the outside of the drum allow the removed bark to fall through. The bark collected from these operations is usually fed to the hogged fuel boiler and used to generate process heat or steam.

Wet drum debarkers rotate the logs in a pool of water and remove bark by knocking the log against the side of the drum, while hydraulic barkers employ high pressure jets of water to remove the bark. The water used for bark removal in these systems is typically recycled, but a certain amount is lost as overflow to carry away the removed bark. This overflow can contain resin acids and highly colored materials which leach out of the bark and into the waste water stream. This effluent stream is collected and routed to the wastewater treatment system, where the pollutants are normally removed quite effectively by the biological processes that take place there (Springer, 1986).

Dry debarking methods such as dry drum debarkers (see Figure 3-1) or shearbarkers eliminate the water stream and the pollutants associated with it. Dry debarkers already dominate the industry, and wet systems have been in the process of being phased out since the 1970s (Smook, 1982).

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

The purpose of chipping is to reduce the logs to a smaller size suitable for pulping. In the conventional chipper, logs are fed into a chute where they contact a disc outfitted with a series of radially-mounted blades. The blades project about 20 mm from the disc. Chip uniformity is extremely important for proper circulation and penetration of the pulping chemicals, hence considerable attention is paid to operational control and maintenance of the chipper. Chips between 10 and 30 mm in length, and 2 to 5 mm in thickness, are generally considered acceptable for pulping.

The chipped wood is passed over a vibrating screen that removes undersized particles (fines) and routes oversized chips for rechipping. Normally, fines are burned with bark as hogged fuel, although they may also be pulped separately in specialized "sawdust" digesters. In most mills, chips are segregated only according to chip length.

Chip thickness screening has become important as mills realize the need to extend delignification and reduce bleach plant chemical demands. 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 over-thick chips will lower the average kappa reduction of a cook and contribute to higher bleaching chemical demands. To improve thickness uniformity, many mills are now adopting screening equipment that separates chips according to thickness (Strakes and Bieligus, 1992). Chips that exceed the maximum acceptable thickness are diverted to a chip slicer that cuts them radially and reintroduces them to the screening system (see Figure 3-2). Costs for chip thickness screening and reprocessing of between \$2 and \$4 million have been cited for new installations (U.S. EPA, 1992). Costs for retrofits would generally be higher.

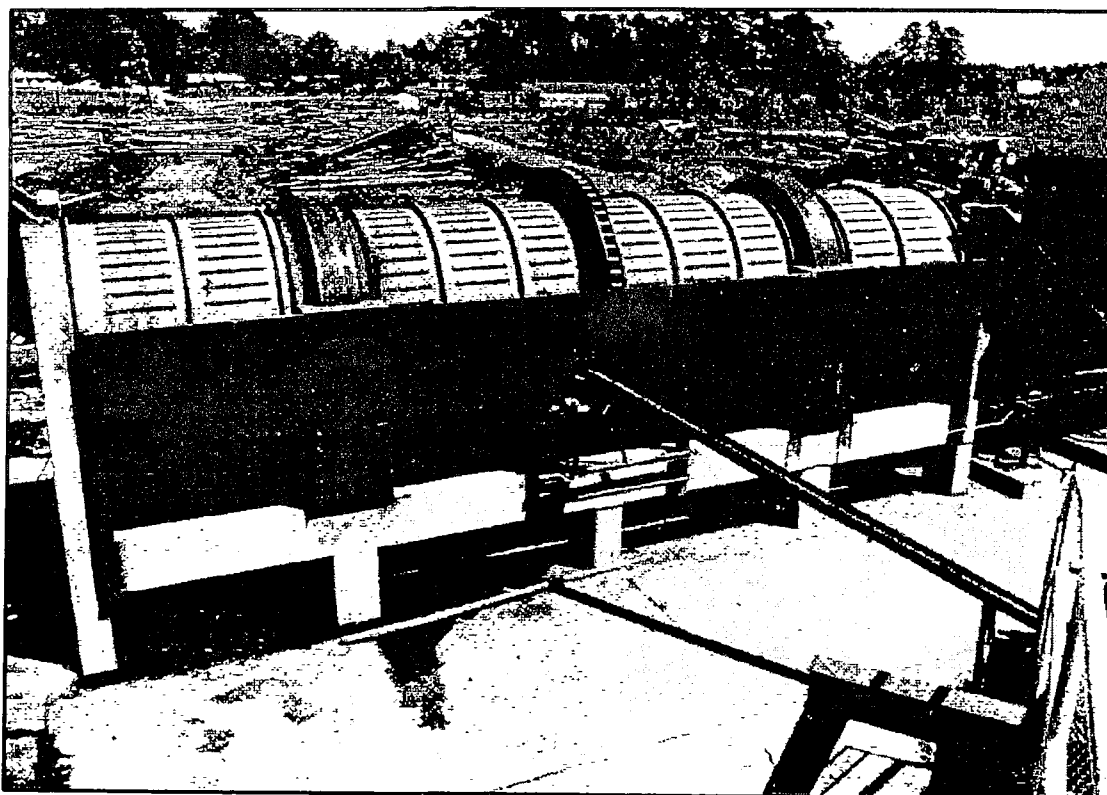


Figure 3-1. Debarking drum.

Source: Beak, 1978.

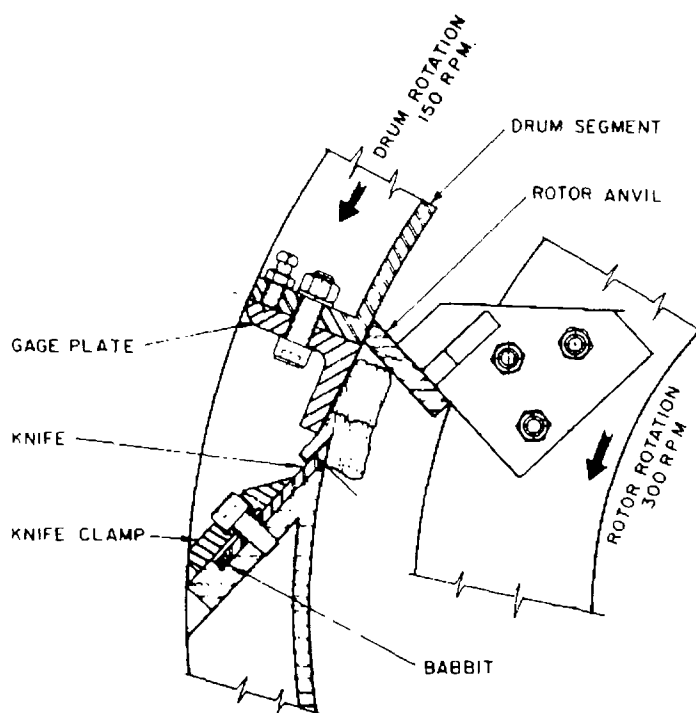


Figure 3-2. Chip thickness slicer showing oversize chip being split.

Source: Smook, 1982.

3.5 STORMWATER MANAGEMENT

The impact of storm water runoff from industrial facilities can be significant and has begun to be addressed by regulatory actions.¹ At the pulp mill, the runoff from wood and chip storage and processing areas is of greatest concern, as these streams may contribute substantially to BOD₅ and TSS loadings.

Options for reducing stormwater impacts on receiving waters include modifying wood yard operations to reduce storm run-off (i.e., moving operations inside, where feasible), and installing curbing, diking, and drainage collection for storm water from chip piles and wood processing areas. Storage and treatment of collected stormwater may be required. Collected stormwater can be 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.

¹ Regulations for permitting stormwater discharges from industrial facilities were promulgated in November, 1990 (55 FR 47990).

SECTION THREE REFERENCES

- Berry et al., 1989. R.M. Berry, L.H. Allen, B. I. Fleming, R.H. Voss, C.E. Luthe, P.E. Wrist. "Toward Preventing the Formation of Dioxins During Chemical Pulp Bleaching," *Pulp and Paper Canada*, 90(8), 1989, pp. 48-58.
- Edde, 1984. Howard Edde. *Environmental Control for Pulp and Paper Mills*. Noyes Publications, Park Ridge NJ.
- Luthe et al., 1992. C.E. Luthe, R.M. Berry, R.H.Voss. "Chlorinated Dioxins in the Production of Bleached Kraft Pulp Resulting from the Use of Sawmill Wood Chips Contaminated with Polychlorinated Phenols," *Proceedings, 1992 TAPPI Environmental Conference*, Richmond VA, April 1992. p. 859.
- Springer, 1986. Allan M. Springer. *Industrial Environmental Control Pulp and Paper Industry*, John Wiley & Sons, New York.
- 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. P.O. Tikka, H. Tahkenen, K.K. Korasin. "Chip Thickness vs. Kraft Pulping Performance, Part I: Experiments by Multiple Hanging Baskets," *Proceedings, 1992 TAPPI Pulping Conference*, Boston MA, November 1992, p. 555.
- U.S. EPA, 1982. *Development Document for Effluent Limitations Guidelines and Standards for the Pulp, Paper and Paperboard*. Effluents Guidelines Division, WH-552, Washington, D.C. EPA 440/1-82/025, October, 1982.
- U.S. EPA, 1992. *Model Pollution Prevention Plan for the Kraft Segment of the Pulp and Paper Industry*. Region 10, Seattle, WA. EPA 910/9-92-030, September, 1992.
- Voss et al., 1988. R.H. Voss, C.E. Luthe, B.I. Fleming, B.H. Allen. "Some New Insights into the Origins of Dioxins Formed During Chemical Pulp Bleaching," in *Proceedings, 1988 CPPA Conference*, Vancouver, B.C., October 25-26, 1988.

SECTION FOUR

POLLUTION PREVENTION TECHNOLOGIES IN PULPING OPERATIONS

This section discusses the conventional pulping processes and identifies pollution prevention technologies that can be implemented in the 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.

4.0 INTRODUCTION

The purpose of pulping is to separate the tightly-bound fibers in the wood chips into individual fibers so they can be formed into a sheet on the papermaking machine. The type of pulping process used depends first on the desired properties of the end product, and second on the relative economics of raw material costs, energy requirements, and, increasingly, effluent and emissions treatment and control costs.

Chemical pulping methods use various chemical solutions to dissolve the lignin that holds the wood fibers together, while mechanical methods use mechanical energy (e.g., grinding) to tear the fibers from the wood. Chemical pulping differs from mechanical methods in that lignin and other materials are dissolved and removed during processing. These losses are reflected in a lower yield (40 to 55 percent), in comparison with mechanical pulping methods (up to 95 percent yield). While the lower yield means that larger quantities of wood are required to produce the same quantity of paper, lignin removal enables the mill to produce a pulp with superior papermaking characteristics. Figure 4-1 shows the process flow for a typical chemical (kraft) pulp mill.

The amount of lignin remaining in the fiber following chemical pulping is an important pulping control parameter. The most common method for measuring lignin content is the kappa number test. The *kappa number* of a pulp is based on the amount of potassium permanganate required to oxidize the lignin

The flowsheet is divided into four main sections: WOOD PREPARATION, PULPING, BLEACHING, and CHEMICAL RECOVERY.

- WOOD PREPARATION:** Wood enters a chipper, producing chips and white liquor. The chips move to the pulping section.
- PULPING:** Chips are washed and then enter a digester with white liquor. The output goes through brownstock washers and a screen rejecter. Excess unbleached white liquor is recycled. The main stream goes to an unbleached high density storage tank (C), then through a series of bleach stages (E, D, E, D) with inputs of chlorine dioxide, sodium hydroxide, and oxygen. Wash water is added at several points.
- BLEACHING:** The final product is bleached high density storage tank, which feeds into a pulp dryer or paper mill. Wastewater from bleaching goes to an acid sewer.
- CHEMICAL RECOVERY:**
 - Black Liquor Recovery:** Weak black liquor from the pulping stage and strong black liquor from the bleach stage enter a multiple effect evaporator. The evaporator produces vapor (used for steam) and a concentrate that goes to a recovery boiler. The recovery boiler also receives feedwater and produces steam for the process. The bottoms from the recovery boiler go to a precipitator, which produces saltcake makeup and chlorine dioxide generator byproducts. The precipitator output goes to a blaker, which produces grits to landfill and fuel for a lime kiln.
 - White Liquor Recovery:** The blaker output goes to a white liquor clarifier, which produces recovered white liquor (to digester) and wash water. The wash water goes to a lime mud (CaCO₃) tank, which feeds into a lime kiln. The lime kiln produces lime mud and weak wash. The weak wash goes to a dissolving tank, which feeds into a green liquor clarifier. The green liquor clarifier produces dregs to landfill and a stream that goes to a steam stripper. The steam stripper produces stripped condensates (recycled) and gas to incineration. The gas to incineration also comes from the multiple effect evaporator. The incinerator produces surface condensate, which goes to a pool condenser, then to a steam condenser, and finally to a reboiler.

Legend:

- ▶ MAIN PULP LINE
- - -▶ BLACK LIQUOR
- ▶ OTHER FLOWS

contained in a standard sample of dry pulp. Although this is a strictly chemical test, pulp chemists have devised a number of rapid scanning techniques to provide on-line measurement of kappa number during pulping and bleaching.

Monitoring of the pulp kappa number provides feedback to the mill operators concerning how far along the pulping and bleaching reactions have proceeded. Lower kappa numbers correspond to a lower residual lignin concentration. A pulp with a kappa number of 35 has a lignin content of approximately 5 percent. Most pulp is cooked to a target kappa number, measured at the point in the process where pulp exits the brownstock washer following cooking and before proceeding to any bleaching stages (see Figure 4-1).¹ Kappa number targets are usually between 20 and 40 for softwood pulp and between 15 and 25 for hardwood.

The kappa number of brownstock pulp determines its bleachability in subsequent bleaching stages. The term “bleachability” refers to the amount and also the type of bleaching chemicals that will be required to produce pulp of the desired brightness. The more lignin that is removed in the pulping stages, the lower the downstream bleaching chemical demand. As brownstock kappa numbers fall, it also becomes possible to bring the pulp to target brightness levels using environmentally preferable bleaching chemicals (e.g., less chlorine and more chlorine dioxide, oxygen, or peroxide). Lowering the brownstock kappa number to reduce bleaching chemical demands is a major objective of the pollution prevention technologies discussed in this section.

Using conventional pulping methods, the brownstock kappa can be reduced below the target levels cited above, e.g. through longer residence times in the digester or more severe cooking conditions. While this will increase its bleachability, it also results in a loss of pulp yield and strength, as the pulping chemicals become less selective and begin to attack the cellulose material.² As discussed in this section, however, new techniques (generally known as extended cooking) have been devised that enable the lignin content to be reduced without further harming the pulp fibers.

¹ The term brownstock refers to the raw pulp exiting the pulping stage. At this point, the pulp still contains large amounts of reacted lignin and spent cooking chemicals. The brownstock pulp moves through a series of washing and screening/cleaning stages before it enters the bleach plant.

² The term selectivity refers to the differential rates of reaction between the pulping chemicals and lignin, and the pulping chemicals and cellulose.

4.1 CONVENTIONAL KRAFT PULPING

Kraft (or sulfate) pulping has become the most common chemical pulping process in use in the United States, accounting for approximately 77 percent of pulpmaking capacity in 1990 (API, 1992). The success and widespread adoption of the kraft process is due to several factors. First, because the kraft cooking chemicals are selective in their attack on wood constituents, the pulps produced are notably stronger than those from other processes. The kraft process is also flexible, in so far as it is amenable to many different types of raw materials and can tolerate contaminants that may be found in the wood (e.g., high resin content). Finally, the chemicals used in kraft pulping are readily recovered within the process (see below).

Kraft processing subjects the wood chips to a mixture of caustic soda (sodium hydroxide, or NaOH) and sodium sulfide (Na₂S) in a reaction vessel known as a digester. This chemical mixture is known as white liquor (or cooking liquor). The caustic in the liquor attacks the lignin in the fiber, breaking it into smaller segments that are soluble in the cooking liquor. The output of kraft pulping consists of the separated wood fibers (brownstock pulp) and a *black liquor* that contains the dissolved lignin solids in a solution of reacted and partially reacted pulping chemicals.

Kraft pulping techniques are available for both batch and continuous operation. These are discussed briefly in turn below.

4.1.1 Batch Pulping

In batch operation, the digester is charged with chips and the cooking liquor, a mix of sodium hydroxide (NaOH) and sodium sulfide (Na₂S). Figure 4-2 shows a diagram of a batch digester. The liquor is circulated through the digester, and the temperature and pressure are raised to the level required for reaction. Once the reaction is complete, the pulp is emptied by opening the “blow” valve at the bottom of the digester. Pressure built up inside the digester during reaction is sufficient to push most of the pulp out into the blow tank. Steam or waste cooking liquor may be used to flush the remaining pulp from the digester. As the pressure is relieved and the temperature of the cooking mixture drops, steam and gases formed during the reaction are released. These gases and liquids must be captured and

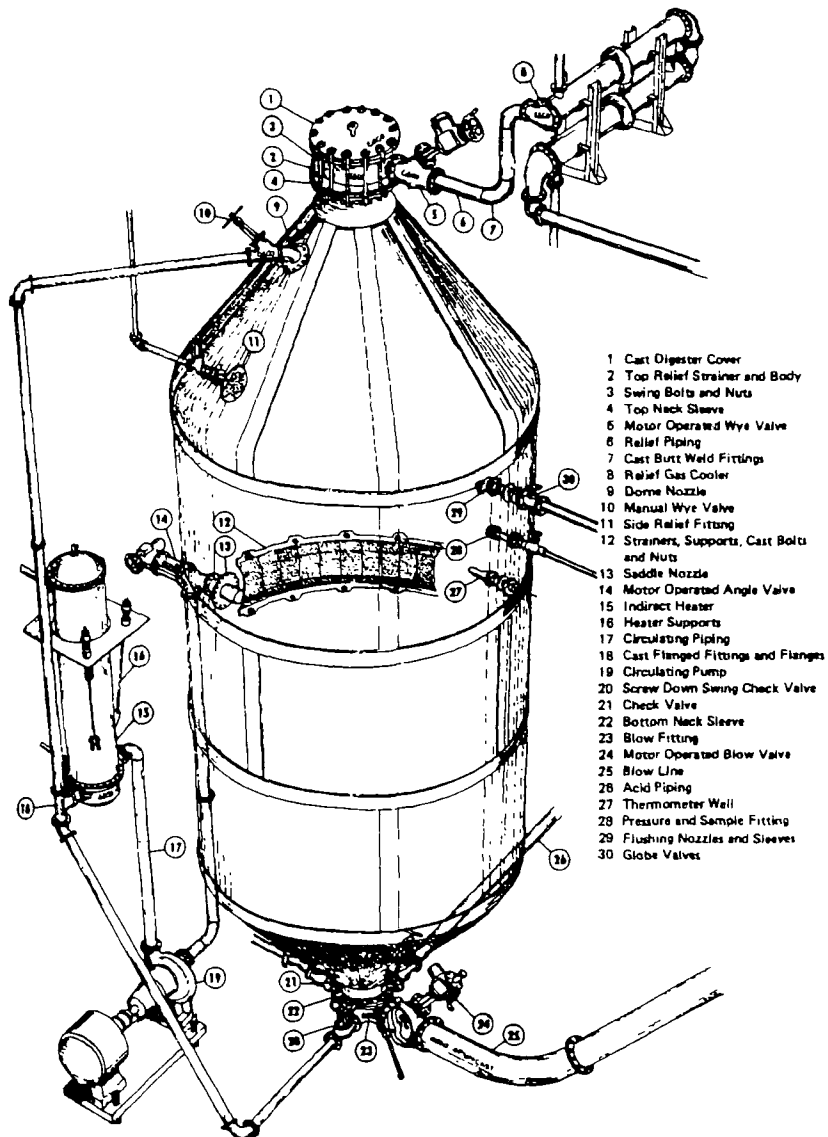


Figure 4-2. Batch digester and ancillary equipment.

Smook, 1982.

controlled, as they are a source of concentrated odor (TRS), volatile organic compounds (VOC), and biochemical oxygen demand (BOD₅) pollutants.

Although the digester operation is performed in batches, the downstream bleaching is performed continuously. To supply a continuous feed of pulp to the bleaching operation, a series of batch digesters are usually operated on a staggered basis. Individual digesters sometimes range in size from 6,000 to 8,000 cubic feet.

Following removal from the digester, the pulp may pass through a disc refiner to separate the fibers. It is then screened to remove knots and unreacted chips, or "rejects". These may be either sent through the digester again or used as fuel in the hog fuel boiler.

The screened pulp then passes through a series of washers. Washing is a key stage, since dissolved lignin that cannot be removed here will continue on to the chlorination stage, where it consumes a large amount of bleaching chemicals, reacts with the bleaching chemicals to form chlorinated organics, and will be discharged with the bleach plant effluent. The mixture of dissolved lignin and cooking liquor washed from the pulp is known as black liquor. The washing systems used to remove this spent cooking solution from the pulp are quite sophisticated. Most mill wash systems operate in a countercurrent fashion, with water flowing in a direction opposite to the pulp. The pulp is alternately thickened and diluted on the washing drums, with water sprayed onto the pulp mat to displace the suspended black liquor solids. As shown in Figure 4-3, the filtrate from each stage is used as washing liquid in the previous stage. This configuration conserves water and removes chemicals from the first washing stage most effectively.³

Final thickening of the pulp is performed using a gravity thickener or "decker". From the decker, the pulp may be blended with other pulps before it either continues on to the bleach plant or is dried for shipping to market.

³ Note that the figure illustrates countercurrent washing in conventional drum washers. More recently, the industry has shifted towards more advanced washing system designs (see Section 4.8). Although the washing equipment differs, the same principle of countercurrent wash water flow is generally applied.

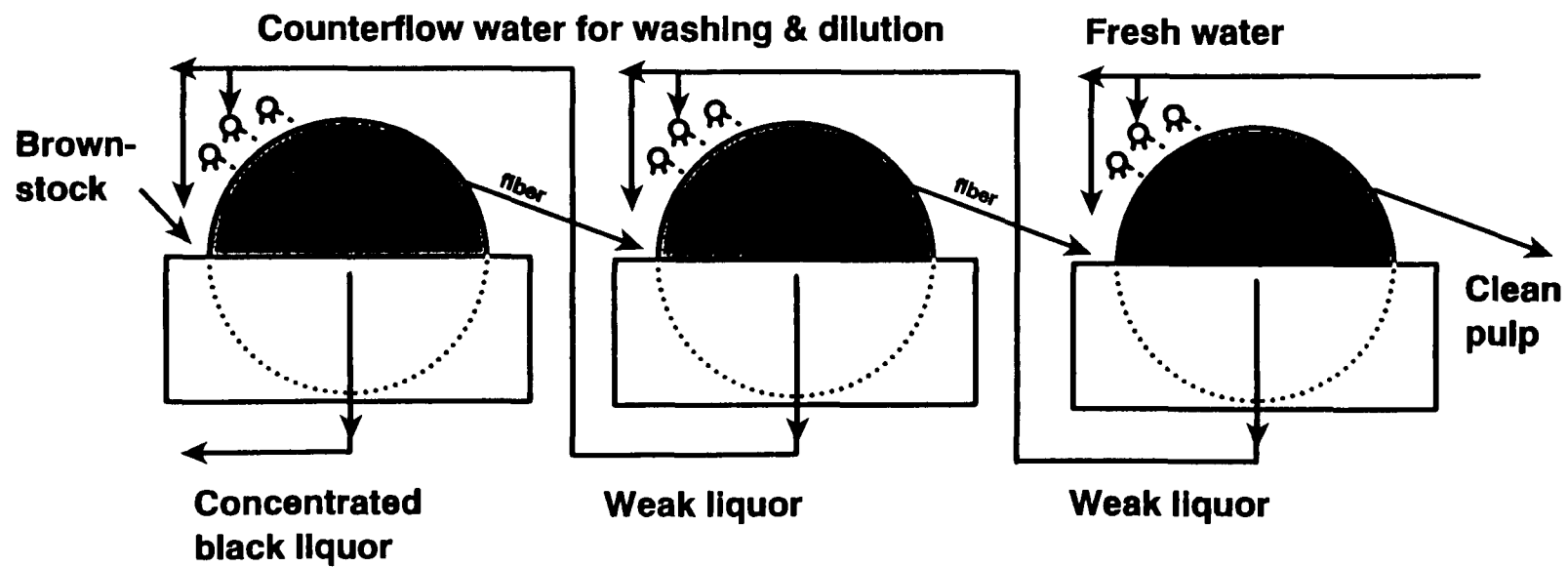


Figure 4-3. Countercurrent brownstock washing. using drum washers.

Source: Kline, 1982.

4.1.2 Continuous Pulping

In Figure 4-4, the continuous cooking process is diagrammed. The most common type of continuous digester is the Kamyr downflow digester, introduced by Kamyr in 1950. Chips are first fed from a chip meter into the steaming vessel. The chips are carried through a series of tubes and are injected with cooking liquor. The treated chips are then deposited into the top of the continuous reaction vessel. The chip mass travels downward through the digester via gravity, during which time the liquor penetrates the chips and the lignin is dissolved.

In continuous pulping, washing of the pulp takes place in a section of the digester known as the washing zone. Here, the spent liquor is siphoned off and hot water is introduced for washing. The wash water is circulated through a heat exchanger that gradually reduces the temperature of the chips, thereby avoiding the flashing of volatile gases that occurs during batch operation. This washing method, known as diffusion washing, also operates in a countercurrent fashion. It is capable of removing about 98 percent of the black liquor solids. To complete the washing, the pulp is diluted to approximately 2 percent consistency⁴ and is then washed over a series of rotary drum washers. As in batch pulping, a decker is normally used for final thickening of the washed pulp.

4.1.3 The Kraft Recovery Cycle

In addition to producing pulp with superior strength properties, a primary advantage of the kraft process is the relative ease of recovery of the pulping chemicals. The recovery side of the mill's operations consists of various stages that serve to concentrate, purify, and reconstitute the kraft cooking chemicals from the black liquor, while recovering energy value from the dissolved lignin and other solids removed during pulping and washing.

The bottom half of Figure 4-1 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*,

⁴ Pulp consistency is usually expressed as the ratio of the oven-dry weight of pulp solids to the total weight of the pulp slurry.

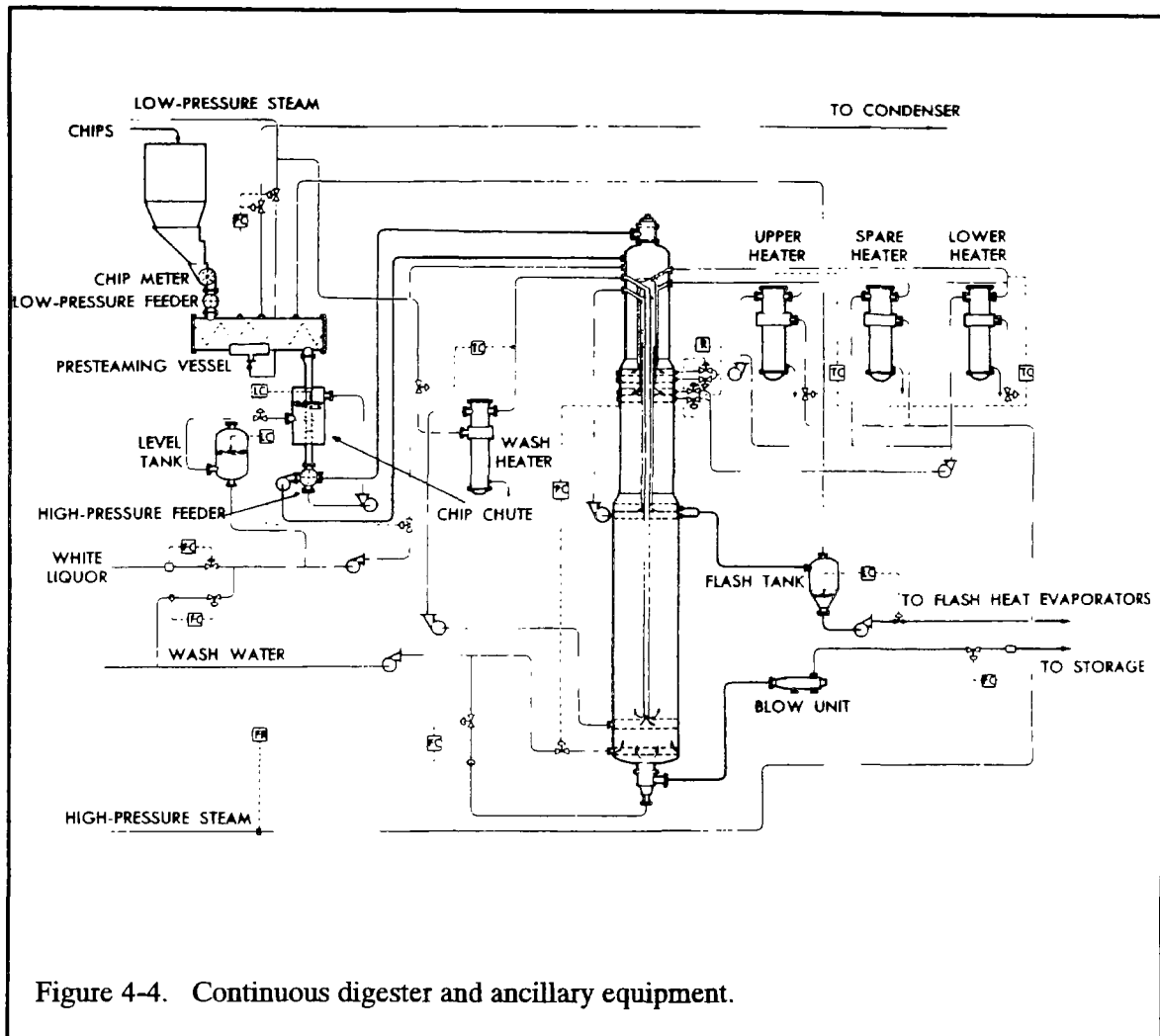


Figure 4-4. Continuous digester and ancillary equipment.

Source: Smook, 1982.

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. Most mills are able to generate 100 percent of their energy requirements in this manner.

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.

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 (NaOH) and sodium sulfide (Na₂S). This white liquor is then ready for reuse 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.

4.2 EXTENDED DELIGNIFICATION

The amount of bleaching power (or bleaching chemicals) required in the bleach plant to bring the pulp to the target brightness level is directly related to the kappa number (residual lignin content) of the brownstock pulp, i.e. the amount of lignin that remains in the pulp following chemical cooking. The mill can reduce the bleaching chemical demands (and subsequent environmental effects) by adopting techniques that reduce the brownstock kappa number. Over the last decade, methods and equipment have been developed that allow the pulp cooking time to be extended, enabling further delignification to occur before the pulp moves on to the bleach plant. At the same time, extended cooking, as it is known, protects the pulp from the detrimental effects (reduced quality and yield) that would normally accompany increased cooking time.

How It Works

In conventional kraft pulping, the digester is filled with chips and then given a one-time charge of cooking chemicals (sodium hydroxide and sodium sulfide). 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 lignin content but will also begin to degrade the cellulose, as the reactions become less selective towards lignin.

The ability to extend the cooking process without impacting pulp quality has been achieved by applying principles developed by the Swedish Forest Products Research Institute (STFI) in the late 1970s (Hartler, 1978). The technique involves charging the cooking chemicals at several points throughout the cook. This levels out the alkali profile in the pulp, permitting more lignin to be dissolved in the latter stages of the process. The specific techniques used to achieve this effect are proprietary, however their general operation is well-known and have been widely-adopted. Improved selectivity is obtained through careful application of the following principles:

- (1) Achieve a more uniform concentration of effective alkali ($\text{NaOH} + \frac{1}{2} \text{Na}_2\text{S}$) throughout the cook (lower at beginning, higher at end);
- (2) Maximize the concentration of hydrogen sulfide ions (HS^-), especially during the initial phase of the cook;
- (3) Minimize the concentration of dissolved lignin at the end of the cooking process; and
- (4) Maintain low temperatures at the beginning and end of the cook.

By attaining greater control over these conditions in the digester, the delignification reaction can be extended, and the lignin content of the brownstock pulp reduced by between 20 and 50 percent compared to conventional digesters. In the absence of such controls, similar lignin reductions could not be accomplished without significant losses in pulp yield and strength.

The Modified Continuous Cook (MCC®) and Extended Modified Continuous Cook (EMCC®) processes were developed by Kamyr for continuous pulping operations.⁵ MCC® has been described as “just in time chemistry” — the system is optimized to deliver the right amount of the right kind of chemicals at the right time. In MCC® cooking, the kraft digester is modified so that liquor is introduced at several different points to maintain a constant alkali concentration throughout the cook (see Figure 4-5). 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 4-6). This levels out the alkali profile through the cook, enabling further delignification to occur. EMCC® can be implemented without MCC® and in fact is the normal way of converting a conventional continuous digester to extended cooking.

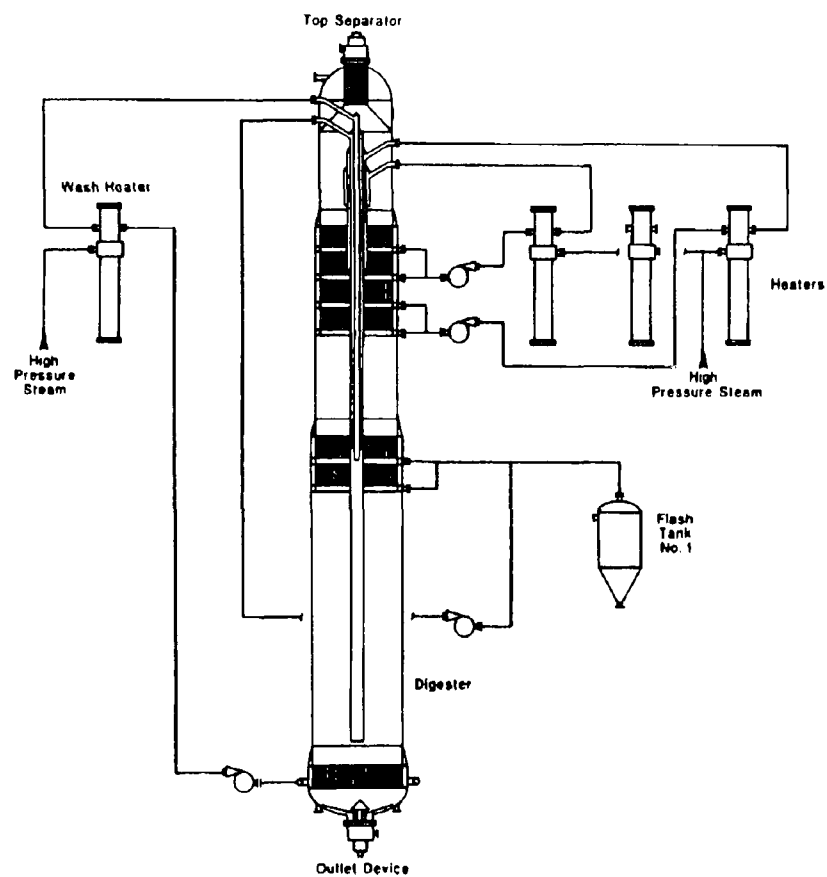
By splitting the addition of cooking liquor and improving liquor circulation and mixing, modified cooking processes level out the alkali concentration not only from the beginning to the end of the cook but also throughout the length of the digester. The more uniform cooking of chips throughout the digester helps maintain pulp yield, (fewer under- and over-cooked chips), and leads to easier bleachability and reduced bleaching chemical demand.

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 basic liquor displacement cycle for RDH pulping is illustrated in Figure 4-7 and includes five stages:

- (1) Chips are fed and steam packed into the digester;
- (2) Warm black liquor at about 115 °C is used to impregnate the chips, improving penetration of the cooking chemicals;
- (3) The warm liquor is displaced with hot black and hot white liquor (150°C to 155°C), which is raised to cooking temperature using indirect heating;
- (4) After time at temperature, the hot cooking liquor is displaced using brownstock washer filtrate, which is cooled using indirect cooling to below flashing temperature (95°C). The displaced hot liquor is stored and used in subsequent cooks; and

⁵ Both Kamyr AB (Karlstad, Sweden) and Kamyr, Inc. (Glens Falls, New York) were once part of the same company. Both now compete in the North American market subject to certain legal restrictions currently being litigated. Kamyr AB is owned by Kvaerner of Norway and Kamyr Inc. is owned by Ahlstrom of Finland.

Single Vessel Hydraulic Digester



Single Vessel Hydraulic Digester, MCC Adaptation

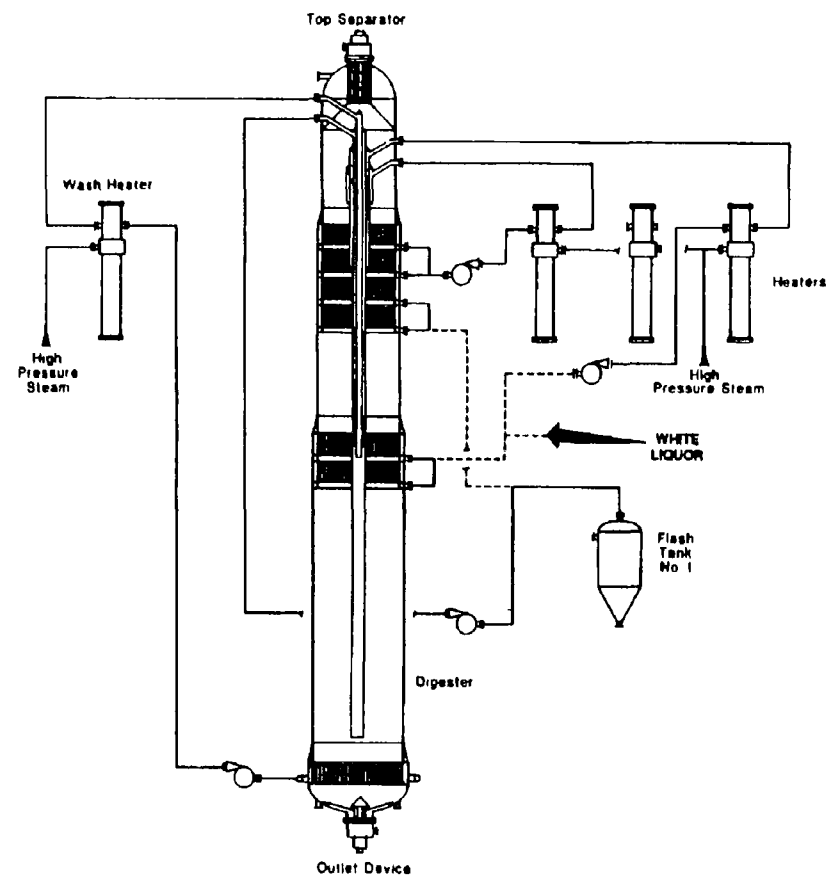
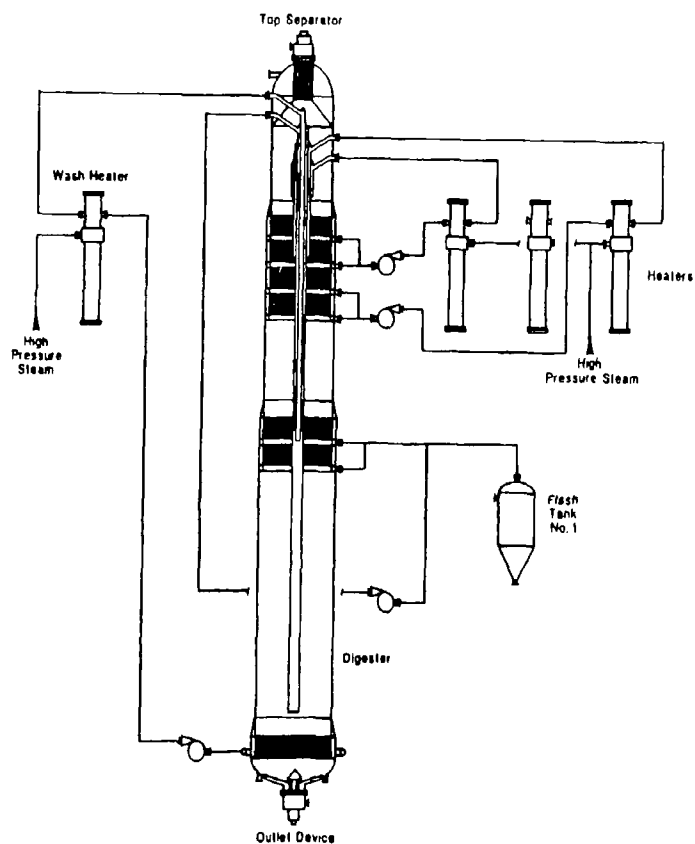


Figure 4-5. Equipment diagram for MCC extended cooking, showing multiple liquor addition points.

Source: Kamyr, Inc.

Single Vessel Hydraulic Digester



Single Vessel Hydraulic Digester, EMCC Adaptation

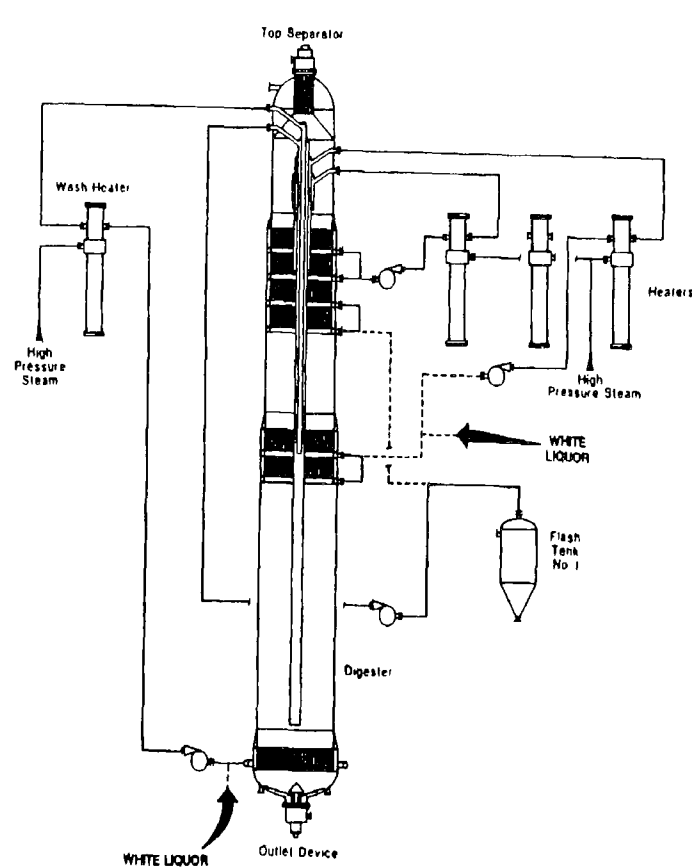
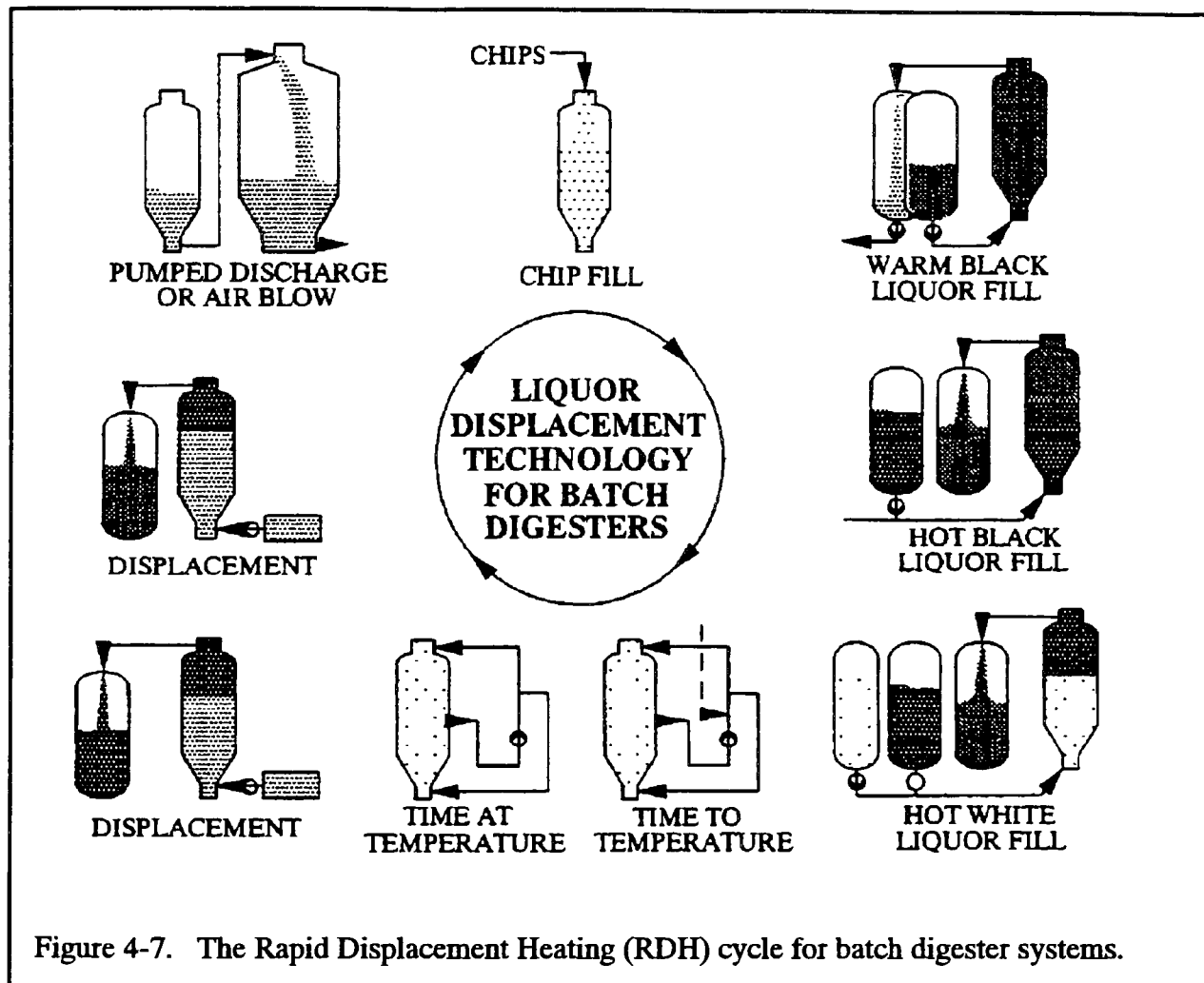


Figure 4-6. Equipment diagram for EMCC extended cooking, showing multiple liquor addition points and liquor addition to wash zone.

Source: Kamy, Inc.



Source: Macleod, 1992.

- (5) The reacted pulp is pumped or air blown out of the digester vessel.

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, and where common process equipment (accumulator tanks, pumps, piping) may be shared. Production scheduling can be thrown off if there are disruptions due to equipment failure 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.

4.2.1 Number of Installations

Macleod (1992) has recently presented a survey of extended cooking installations worldwide. These and additional listings compiled by other industry observers are shown in Table 4-1. At the time of this writing, world capacity for extended cooking was about 11 million tons per year, representing 20 percent of bleached kraft capacity.

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 tons per day (tpd), representing about 25 percent of U.S. bleached chemical pulp capacity. The average capacity of these installations is over 1,100 tpd. Stromberg (1993) reports that all new Kamyr digesters sold since 1985 have been equipped with, or prepared for, MCC® operation, hence retrofitting newer continuous digesters should be a relatively straightforward process.

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.

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).

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 the same.

4.2.2 Costs and 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 (Kamyr, Inc. 1990; cited in EPA, 1990a) with the installed cost closer to \$45 million.

Extended cooking can be retrofitted to most continuous digesters. Based on experience with mills in North America, McCubbin (1992) suggests there are three categories of retrofits, each having a different baseline set of conditions and subsequent upgrade costs:

- (1) Digesters operating with an upflow of wash water and a dilution factor of at least 0.5. This generally applies to digesters installed after 1980 that were not equipped for extended cooking. These require only a simple “wash zone” retrofit, costing under \$1 million dollars in most cases;
- (2) Overloaded conventional Kamyr digesters, or two-vessel digesters that are unsuitable for a wash-zone retrofit. These would have to be replaced with new digesters. The few continuous digesters in North America that are not of Kamyr manufacture, for which there is no demonstrated technology for retrofitting extended cooking, are also in this category. Capital costs for replacement would be in the \$30 to 40 million range.
- (3) Most other continuous digesters would require conversion to a two-vessel installation by adding another vessel downstream of the existing one, and retaining the existing vessel and its chip feed system to perform the functions of an impregnation vessel. This normally allows an increase in digester capacity and improved pulp washing. Costs would be in the \$15 to 30 million range for existing digesters.

In a study prepared for the paper industry, Phillips et al. (1992) suggest that costs for retrofit of a model 1,320 tpd continuous digester currently running at 50 percent chlorine dioxide substitution average \$4.9 million, assuming no need to upgrade recovery capacity. Annualized over 20 years at an 8 percent discount rate, the incremental annual capital costs per ton are \$1.08, but these are more than offset by operating cost savings (energy and bleaching chemicals) of \$6.19 per ton.

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 (Beloit Corp. 1990; cited in EPA, 1990a). Costs for converting an existing pulping system to RDH would likely range around \$0.5 million per digester. Direct steaming digesters would be much more expensive to retrofit compared to those with liquor circulation systems.

The retrofit potential for existing batch systems in the United States is somewhat limited due to the age of the digesters. Most U.S. batch digesters are of 1940 to 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.

Beloit, the vendor of the RDH system, has reported that the expected payback period on an RDH retrofit is approximately 18 months. Among the benefits cited are: (1) steam savings, (2) better pulp quality, (3) higher solids concentration in the liquor, leading to lower evaporation costs, and (4) savings in bleaching chemical costs of approximately 50 percent.

4.2.3 Pollution Prevention Potential

Extended delignification has been shown to 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. Target ranges, however, are currently around 20 to 25 (Stromberg, 1993). Hardwood kappas can be reduced from around 20 to a range of 8 to 10, with current targets generally around 12 to 15. Below these target ranges, at this time at least, yield losses may accelerate and pulp quality may be diminished. Ongoing refinements to these processes are expected to bring these kappa numbers down further, however, over the next few years.

The impact of brownstock kappa number reductions on bleaching chemical demands and formation of many chlorinated organics is now well-documented. AOX and polychlorinated phenols will be reduced in approximate proportion to reductions in the brownstock kappa number. Declines in conventional pollutants such as BOD₅, COD, and color from MCC® processes have also been widely realized. According to Heimbürger et al. (1988a), MCC® cooking reduced kappa by 22 percent, while BOD₅ and color declined by 29 and 31 percent, respectively (see Table 4-2).

TABLE 4-2
**Characteristics of Conventional
and MCC Pulps**

Parameter	Conventional	MCC	Percentage Decrease
Kappa number	32	25	21.9%
BOD, mg/dm ³	675	480	28.9%
COD, mg/dm ³	4,618	3,931	14.9%
TOC, mg/dm ³	1,579	1,220	22.7%
TOCl, mmol/dm ³	1.93	1.45	24.9%
Color, Pt mg/dm ³	10,202	7,065	30.7%

BOD = biochemical oxygen demand.

COD = chemical oxygen demand.

TOC = total organic carbon.

TOCl = total organic chlorine.

Source: Heimbürger et al. (1988a).

Due to the higher level of effluent recycle and recovery of solids from effluent achieved with extended delignification, the mill's chemical recovery system may experience an increase in load and there may be an increase in byproducts from the recycle system following implementation. Additional energy may be required to evaporate the increased effluent volume passing through the recovery boiler (although this will be more than offset by the heat recovered from the additional solids). Incineration of higher solids volumes will cause some increase in air emissions and solid wastes (recovery boiler ash), although these increases are expected to be minor.

4.2.4 Compatibility with Downstream Bleaching Stages

When used in combination with oxygen delignification (see Section 4.3), kappa number reductions to the range of 6 to 10 have been reported for softwoods (Galloway et al., 1989; Shin et al., 1990). Pulp in this range are extremely bleachable and could be brought to high brightness using elemental chlorine-free (ECF) and possibly totally chlorine-free (TCF) sequences.⁶

Data in Table 4-3 show the pollution reduction potential of extended delignification in combination with oxygen delignification (case C), as compared with conventional cooking (case A) or oxygen delignification alone (case B). In terms of organics discharge, the data show that oxygen delignification alone will decrease AOX from 7.9 to 4.7 kg per ton, while oxygen plus extended delignification decreases it to 3.6 kg per ton. A high chlorine dioxide substitution (70 percent or higher) can be further effective in reducing AOX to a level of 1.9 kg per ton (see Section 5.2). Table 4-3 also shows beneficial impacts of MCC® pulping and oxygen pre-bleaching on BOD₅, COD, and color. When extended cooking is combined with an oxygen stage, BOD₅ falls from 28 to 20 kg per ton, COD falls from 100 to 55 kg per ton, and color declines from 300 to 80 kg per ton.

Table 4-4 compare the characteristics of conventional and RDH pulps, both with and without an oxygen prebleaching stage (Heimberger et al., 1988a). Total active chlorine (percent on pulp) is reduced

⁶ 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, although Louisiana-Pacific has committed to do so at its Samoa, California mill by 1995 as part of a consent decree signed with EPA.)

TABLE 4-3

**Impact of Modified Continuous Cooking
on Effluent Characteristics**

Process	Flow m ³ /admt	BOD ₅ kg/admt	COD ₅ kg/admt	Color kg/admt	AOX kg/admt
Case A	50-55	28	100	300	7.9
Case B	50-55	22	70	100	4.7
Case C	50-55	20	55	80	3.6
Case D	50-55	20	55	65	1.9

Case A State of the art conventional kraft mill.

Case B - Case A with oxygen delignification.

Case C - Case B plus modified continuous cooking (ED).

Case D - Case C with 70% chlorine dioxide substitution.

Source: Galloway et al. (1989).

TABLE 4-4
Characteristics of Conventional
and RDH Pulping

Parameter	Conventional		RDH Pulping	
	No O ₂ Stage	O ₂ Stage	No O ₂ Stage	O ₂ Stage
Kappa No.	34	23	23	15
Total Active Cl ₂ , % o.d. pulp	11.7	7.5	9.0	5.3
Brightness, % ISO	89	90	88	88
COD, kg/ton	78	57	50	40
BOD, kg/ton	14	11	10	8.5

Source: Heimbürger et al. (1988a).

from 11.7 to 9.0 without oxygen and from 7.5 to 5.3 when oxygen prebleaching is practiced. Reductions in chlorine usage will generally lead to proportionate decreases in the formation of chlorinated organics.

Table 4-5 shows results from a series of laboratory investigations conducted by the Beloit Corp. and researchers at North Carolina State University (Shin et al., 1990). Conventional kraft pulps and pulps produced using the RDH extended delignification process were delignified using conventional techniques, as well as with pressurized oxygen (O) and atmospheric oxygen (E_O). For the conventional pulp, measured AOX levels were 3.1 kg per ton (Case 4). Pulping with RDH decreased the AOX level to between 1.28 and 1.40 kg per ton, or a decrease of 55 to 59 percent.

When conventional pulp was bleached with atmospheric oxygen, AOX fell to between 2.7 and 2.8 (Cases 2-3), while bleaching with pressurized oxygen reduced AOX to 1.74 kg per ton (Case 1). Thus, RDH by itself had a greater impact on AOX than oxygen.

In cases 7 through 11, the effectiveness of combining RDH and OD is seen. Bleaching the RDH pulps with atmospheric oxygen reduced the AOX levels to a range of 0.90 to 0.95 kg per ton (Cases 7-9), while pressurized oxygen produced even lower results of 0.54 to 0.60 per ton (Cases 10-11). In cases 12-15, chlorine dioxide substitution was increased from 75 to 100 percent, resulting in still greater decreases in AOX (to as low as 0.44 kg per ton in Case 15). Complete substitution of ClO₂, however, has been shown to result in less efficient delignification (Reeve, 1990). Continued improvement in effluent can be obtained, but it will come at the expense of some yield.

Researchers from Sunds recently delignified Southern pine to kappa numbers between 34.4 and 14.1 using an industrial SuperBatch™ digester (Norden et al., 1992). Each sample was then oxygen delignified, resulting in a 50 percent reduction in kappa number. Using 100 percent ClO₂ substitution, the 34.4 kappa pulp (oxygen-delignified to 15.2) consumed 48 kg active chlorine per ton during laboratory bleaching to 89 percent ISO brightness. The 14.1 kappa pulp, (oxygen-delignified to 7.7), consumed 30 kg active chlorine per ton. AOX levels of these two pulps were a very low 0.35 and 0.1 kg per ton, respectively.

In the same trials, two oxygen delignified pulps with kappa numbers 9.9 and 7.7 were bleached using TCF sequences OXP and OZXP, where X denotes treatment with EDTA and Z is ozone delignification (see Section 4.4). The 7.7 kappa pulp was bleached to 80 percent ISO with a peroxide

TABLE 4-5

**Impact of Rapid Displacement Heating Cooking
Techniques on Effluent Characteristics**

Pulping Sequence	Bleaching		Color		AOX	
	Case	Sequence	Trial A	Trial B	Trial A	Trial B
Conventional Kraft Pulping ¹ (kappa no. 33)	1	O(DC)(EO)D	44	44	1.66	1.74
	2	(EO)(DC)(EO)D	68	68	2.71	2.70
	3	(EO)(DC)(EO)(De)D	68	68	2.80	2.80
	4	(DC)(EO)(De)D	120	120	--	3.13
RDH Kraft Without Oxygen ¹ (kappa no. 16)	5	(DC)(EO)(D)	--	--	1.27	1.28
	6	(DC)(EO)(DE)D	62	60	1.32	1.40
RDH Kraft With Oxygen ¹ (kappa no. 16)	7	(EO)(DC)(EO)D	47	47	0.92	0.92
	8	(EO)(DC)(EOP)D	36	36	0.90	0.94
	9	(EO)(DC)(EO)(De)D	47	47	0.93	0.95
	10	O(DC)(EO)D	27	27	0.60	0.59
	11	O(DC)(EOP)D	20	20	0.54	0.55
100% Chlorine Dioxide Substitution (kappa no. 16)	12	(EO)(E)(EO)D	32	32	0.57	0.57
	13	(EO)(D)(EOP)D	56	26	0.64	0.64
	14	OD(EO)D	18	18	0.56	0.58
	15	OD(EOP)D	13	13	0.44	0.50

¹ClO₂ substitution 75% for all bleaching sequences

Source: Shin et al. (1990).

consumption of 30 kg per ton. When ozone was added to the sequence, a brightness of 89 percent ISO was achieved with the same peroxide consumption. In full scale production, this sequence would be expensive (due to the costs of peroxide) but possibly competitive.

Experiments with RDH pulps have also been performed using ECF and TCF sequences (Kumar et al., 1992). Various bleaching sequences involving several pretreatments and additions were investigated. Using oxygen delignification to reduce kappa by 50 percent, a brightness level of 85 to 87 percent ISO could be achieved using as little as 0.6 percent ClO_2 . AOX levels were not reported but are expected to be quite low. TCF sequences using ozone produced 85 ISO brightness pulps.

4.2.5 Impacts on Other Aspects of Mill Operations

Recovery Boiler Operations

Extended delignification increases the amount of lignin and organic solids removed during the kraft cooking process. As indicated earlier, the black liquor washed from the pulp is concentrated and burned in the recovery furnace. Boilers running at or near capacity (in terms of solids handling capability) may be unable to accommodate the additional solids without further process modifications. 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:

- (1) In at least one Swedish mill, black liquor oxidation has been used to reduce heat value of liquor solids sufficiently to accommodate an 8-10 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 installed at the Swedish Frövifors mill has boosted the recovery capacity by 3 tons dry solids per hour, the equivalent of 15,000 metric tons per year of pulp (Götavarken, 1993).⁷ Unlike other boiler modifications, the black liquor gasification unit can be installed without any lost production time.

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 3.4) 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 (1993) has recently presented several case studies that illustrate a variety of options for increasing boiler capacity incrementally through rebuilds and equipment upgrades (see Table 4-6). 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.

⁷ The Chemrec® process is offered by the Swedish company Götavarken (U.S. subsidiary located in Charlotte, North Carolina).

TABLE 4-6

**Sample Boiler Upgrade and Rebuild Projects
Babcock & Wilcox Company**

Company	Mill Location	Description of project
Stone Container	Florence, South Carolina	The recovery boiler was modified to achieve an increase in solids throughput of 10 percent. The air feed and liquor firing systems were substantially upgraded.
Potlatch Corporation	McGehee, Arkansas	The furnace at this mill was enlarged and a new three-level air system was added. Solids capacity was increased from 680 tons per day to 1,111 tons per day, an increase of 63 percent
Gaylord Container	Bogalusa, Louisiana	The boiler, already running at 22 percent over capacity, was upgraded to reduce the time between waterwashing and to cut TRS. After the rebuild, the mill was able to run at 28 percent above capacity with reduced TRS. Time between waterwashings was increased from six weeks to six months.
James River	St. Francisville, Louisiana	Conversion of the boiler to low odor configuration resulted in an increase in solids processing capacity to 1,224 tons per day from a level of 998 tons per day (design capacity was only 816 tons per day). In addition to upgrading the combustion, heating, and liquor firing systems, seven feet was added to the furnace depth and nine feet was added to the height.

Source: Clement (1993).

In addition, it is always possible (though less preferable) for the mill to discharge the effluent containing any additional solids that cannot be accommodated in the recovery boiler. The solids in this effluent were previously removed during the bleaching stages and could not be recycled. Thus, there would be no net increase in solids discharged to treatment, but the ratio of chlorinated to unchlorinated solids would decrease.

Air and Solid Waste Emissions

The kraft liquor recovery system produces air emissions (from the recovery furnace) and solid wastes such as ash and precipitates (from the recovery boiler), dregs (from the dregs washer) and grits (from the lime slaker). The volume of air emissions is related, all else being equal, to the volume of solids processed in the recovery boiler. Thus, increases in solids recovery through the recovery boiler could result in increased air emissions and solid wastes.

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 ash, 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 the landfill.

Energy Requirements

Extended delignification will cause an increase in steam demand (due to the longer cooking period), however 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 large amounts of energy to raw inorganic minerals (such as chloride to manufacture sodium chlorate, caustic, and chlorine). McCubbin (1993) has modeled the onsite and offsite energy impacts of a variety of pollution prevention measures. Conversion of his model 1,000 tpd C_pEDED 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 per ton).

Pulp Yield

Reductions in brownstock lignin content below the current target ranges of 20 to 25 on softwood and 12 to 15 on hardwood are possible using extended delignification. Full-scale mill trials have produced pulps with kappas below 10 (hardwood) and 15 (softwood), with no discernible effect on strength properties (Elliott, 1989; Whitley, 1990). With present technology, however, yield losses will begin to occur at these levels. Yields on softwood pulped drop from 45.0 to 43.5 percent when kappa is reduced from 20 to 15 (Gullichsen, 1991). As the technology develops further these results may improve.

At the same time, conventional digesters currently suffer a pulp yield loss of around 3 percent due to knots and rejects removed during post-digester screening. About half the mills grind these and reprocess them, at a cost, while the other half landfill them. In extended cooking, rejects are under 0.5 percent, hence any yield loss is significantly offset.

4.3 OXYGEN DELIGNIFICATION

Oxygen delignification provides an additional way to extend the pulp cooking process, thereby lowering the bleaching chemical demands and the amount of pollution associated with chlorine-based bleaching stages.⁸ The technique involves the integration of an oxygen reaction tower in between the kraft pulping stages and the bleach plant. The brownstock pulp from the digester is first washed and then mixed with oxygen and sodium hydroxide as it enters the pressurized reactor. There, the pulp undergoes oxidative delignification. The pulp is then washed again to remove additional dissolved lignin solids before proceeding to the bleaching line.

Installation of an oxygen delignification stage can reduce the kappa number of brownstock pulp from a range of 30 to 35 to perhaps 16 or 17 (i.e., a 50 percent reduction). At these kappa levels, a range of bleaching options are available. At a minimum, chlorine requirements will fall in approximate relation to the percent reduction in kappa number. When used in combination with other process modifications,

⁸ The term "oxygen bleaching" is sometimes used to refer to oxygen delignification, because it can be viewed as a replacement for chlorine in the first bleaching stage. Oxygen bleaching is also used by some to describe the addition of elemental oxygen to the caustic extraction stage, i.e., oxidative extraction (E_o). In this report, however, we avoid the term oxygen bleaching entirely.

oxygen delignification can reduce the requirements for chlorine-based bleaching agents still further, and under certain circumstances eliminate them completely.

High-Consistency Versus Medium-Consistency Systems

Two different types of oxygen systems have been designed and are in use around the world. The systems differ in terms of the reaction consistency of the pulp. In high consistency (HC) systems, pulp is reacted at 25 to 28 percent consistency, while in medium consistency (MC) systems the pulp consistency is typically between 10 and 12 percent. MC systems can take pulp directly from the brownstock washers while in HC systems a press is required to remove excess water from the pulp prior to reaction. Table 4-7 presents typical operating data for HC and MC oxygen systems.

The earliest oxygen delignification installations were of the high consistency type. Initially, it was believed that the higher consistencies promoted greater absorption of oxygen by the pulp fibers, leading to a higher degree of delignification. More oxygen is needed, however, and better mixing is required to achieve the same thoroughness and uniformity of reaction obtained in a medium consistency reactor.

Figures 4-8 and 4-9 show process flows and equipment used in an HC oxygen delignification process. In Figure 4-8, the process begins with cooked pulp which is taken from the brownstock washers at about four percent consistency. A small amount of magnesium salts (MgSO_4) are blended with the pulp in a mixing chest (2 to 3 lbs per ton pulp). The magnesium additive has been found to protect the cellulose fibers from oxidative degradation that may occur in pockets of high oxygen concentration inside the reactor. Thus, the magnesium permits a further degree of delignification without any loss of yield.

Following the addition of magnesium, the pulp is dewatered in a press to the desired consistency, about 25 to 28 percent. Fresh caustic solution or, more commonly, oxidized white liquor, is added at the press discharge. The pulp then passes through a fluffer which shreds the pulp. Shredding exposes more pulp surface area and promotes a more consistent reaction. The fluffed pulp is then deposited on the bed of the oxygen reaction vessel, steamed to around 90 to 120° C, and injected with gaseous O_2 . The pulp is swept down a series of trays inside the reactor by sets of rotating arms (see diagram in Figure 4-9). Gases generated during the lignin oxidation must be purged from the reactor to avoid a fire or explosion

TABLE 4-7

**Typical Operating Data for Oxygen Delignification
of Kraft Softwood Pulp**

Parameter	High Consistency	Medium Consistency
Pulp consistency, %	25-28	10-12
Delignification, %	45-50	40-45
Retention time, min.	30	50-60
Initial temp., °C	100-105	100-105
Pressure, kPa		
Inlet	500-600	700-800
Outlet	500-600	450-500
Steam consumption, kg/metric ton		
Low pressure (450 kPa)	--	70
Medium pressure (1,140 kPa)	75-100	200-300
Evaporator (450 kPa)	30-50	90-100
Power consumption, kWh/metric ton	40-50	35-45
Alkali consumption, kg/metric ton	21-23	25-28
Oxygen consumption, kg/metric ton	20-24	20-24
Magnesium ion, kg/metric ton	0.5	0.5

Source: Tench and Harper (1987).

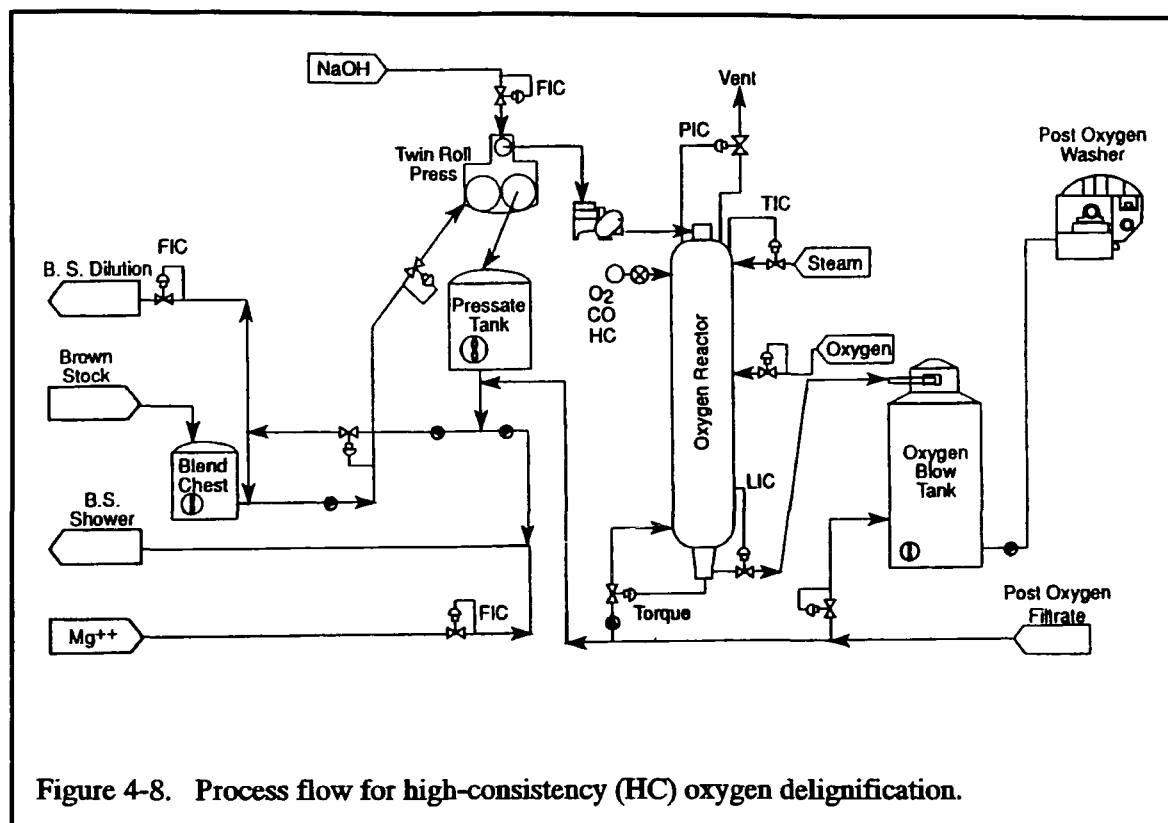
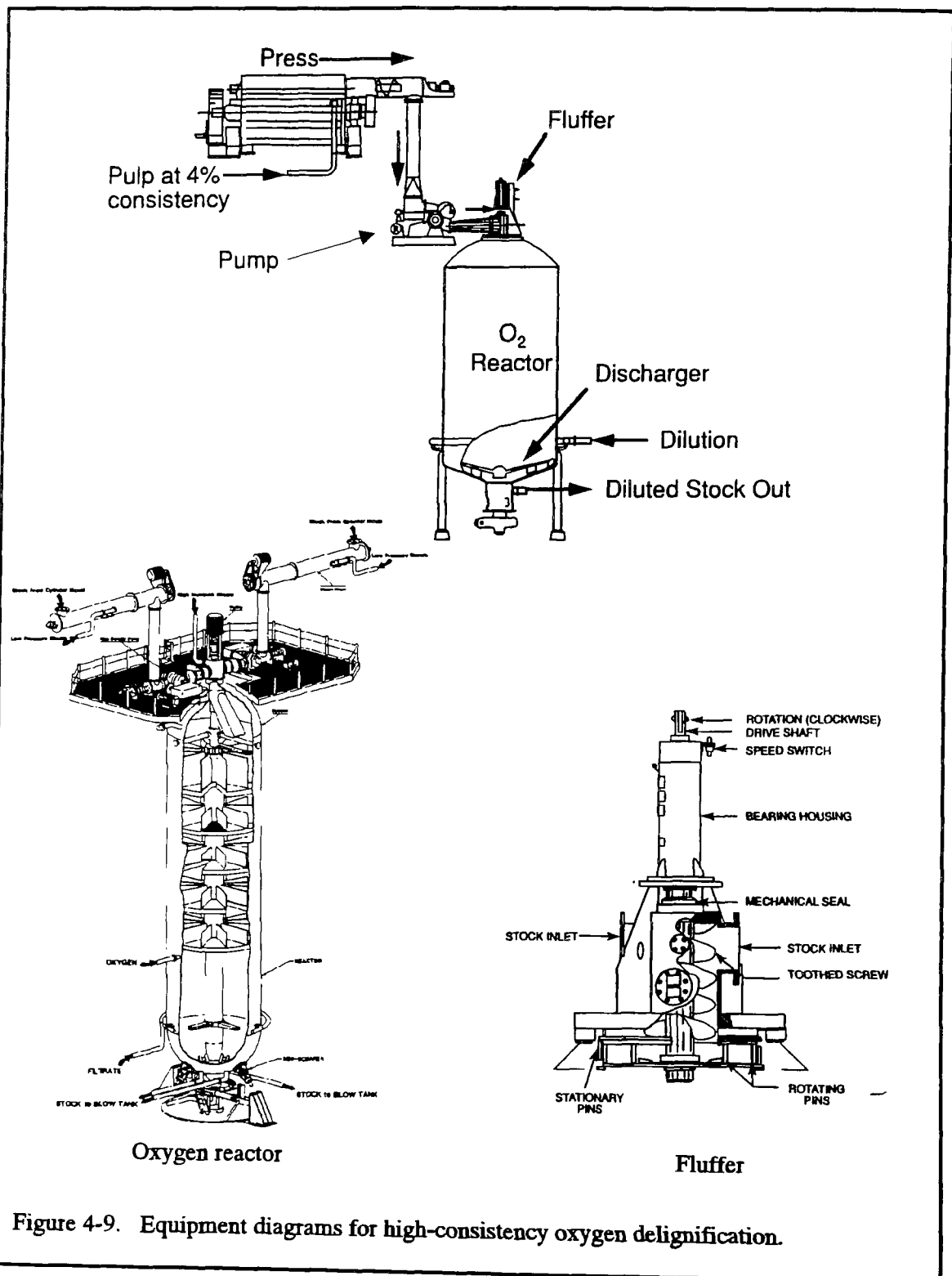


Figure 4-8. Process flow for high-consistency (HC) oxygen delignification.

Source: Miller, 1992.



Source: Miller, 1992.

hazard.⁹ The reacted pulp is diluted with post-oxygen filtrate to about six percent consistency and is then discharged to a blow tank, where the pulp is restored to atmospheric temperature and pressure. Post-oxygen washing stages are usually added to maximize the amount of solids removed prior to chlorination. Good pulp washing is the key to effective implementation of oxygen delignification.

The thickness of the stock in an HC system can lead to flow problems in the reactor and may create pockets of elevated oxygen concentrations. With a buildup of oxygen, malfunctions due to pump failures or blockages could present a risk of fire or explosion.

Medium consistency or MC oxygen systems operate at a lower solids concentration of approximately 10 to 14 percent. This consistency can be delivered directly from the brownstock washers, thereby eliminating the need for the pulp press. An equipment diagram for an MC system is shown in Figure 4-10. Note that the diagram of the MC system shows the upflow design of the reactor. Pulp is fluidized in the high shear mixers and then travels upwards through the reactor vessel. This contrasts with the HC systems, in which the pulp enters at the top of the reactor before being swept down towards the bottom.

In the MC process, the pulp is blended with oxygen using high shear mixers or pumps, which cause the pulp slurry to fluidize and the oxygen to form very fine bubbles. The development of the high shear mixer has allowed for faster and more uniform reactions between the oxygen and the lignin. Retention time is approximately 60 minutes for hardwood and 45 to 60 minutes for softwood. Research so far indicates that single-stage MC systems are capable of slightly less delignification than HC. Nevertheless, the MC system has several advantages: (1) no requirement for dewatering equipment, (2) reduced safety hazard, and (3) reduced potential for pulp degradation, which can reduce or eliminate the need for magnesium viscosity additives. For these reasons, the medium consistency system is now being recommended by vendors for most new oxygen installations (McCubbin et al., 1991), and accounts for almost all of the recent U.S. installations.

⁹ These gases are generally considered safe and are normally vented to the atmosphere, although there is some concern that these may contain VOCs such as methanol or acetone.

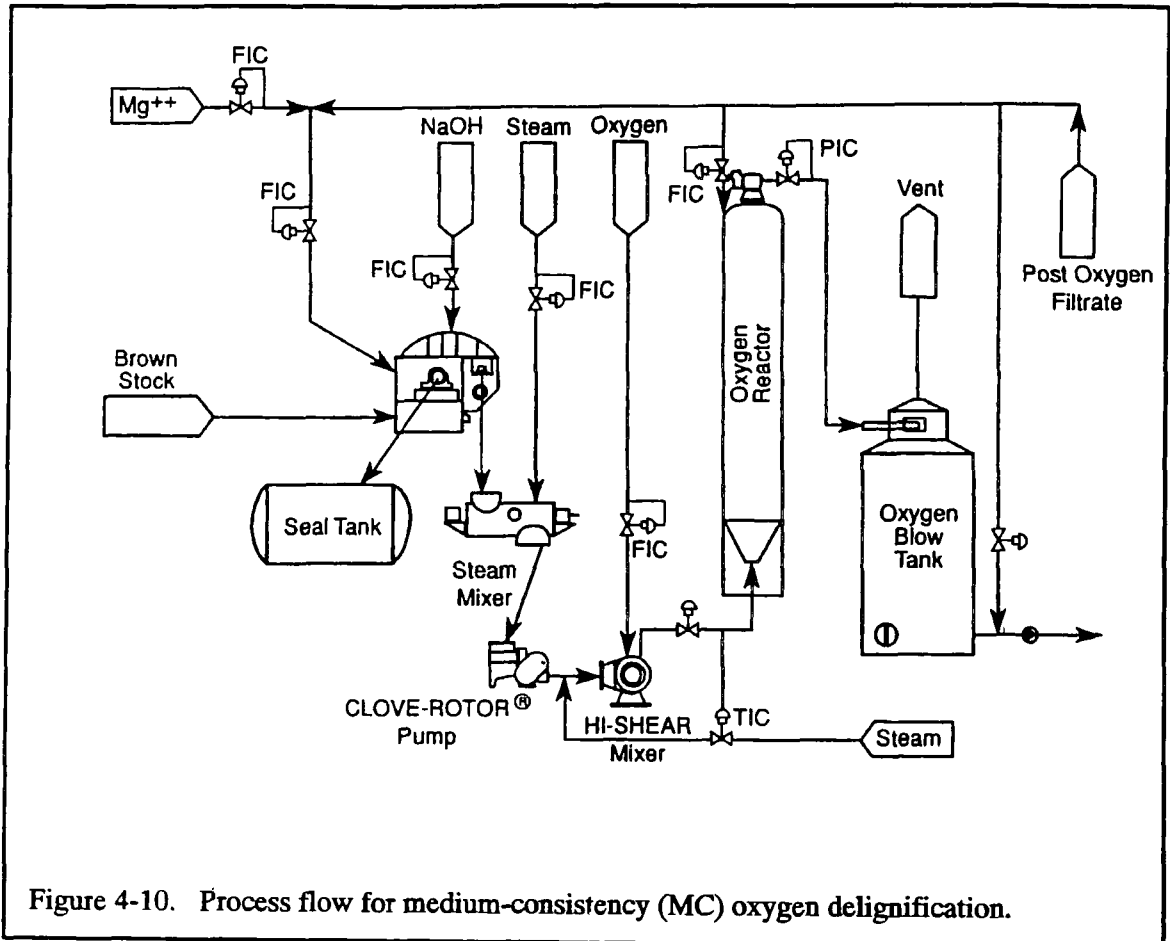


Figure 4-10. Process flow for medium-consistency (MC) oxygen delignification.

Source: Miller, 1992.

Two-Stage Oxygen Systems

One of the more recent developments has been the introduction of multiple-stage oxygen systems to further increase the delignification effectiveness. At least a dozen mills around the world, including two in the United States and two in Canada, now use two-stage oxygen delignification. Data from Johnson (1993) indicate that 2-stage systems account for eleven percent of oxygen capacity in 1993. This modification requires installation of two reactor vessels with additional mixing equipment installed in between. Lignin removal of between 60 and 65 percent has been reported for 2-stage systems (Deal, 1991), as opposed to 50 percent reductions with a single stage system.

4.3.1 Number of Installations

Oxygen delignification has been commercially available since the late 1960s, having been developed in Sweden and first applied successfully in a South African mill in 1970. The more widespread adoption of oxygen came with the development in France of magnesium additives that inhibited degradation of cellulose, a problem that had afflicted earlier implementation attempts.

Until recently, oxygen delignification had been more widely adopted outside of North America. In recent years, the adoption rate in the U.S. and Canada has increased. According to Johnson (1993), there are presently 155 mills worldwide operating oxygen delignification systems, representing 26 million tons of annual production or 34 percent of total world kraft output (see Figure 4-11). During 1992, 32 additional systems started up, and another 20 more systems have been sold and/or are under construction as of March, 1993.

Oxygen is currently installed or planned for 27 U.S. mills. Of these, 16 will have come online since 1989. U.S. capacity is currently around 8.1 million tons per year. Figure 4-11 illustrates the rapid rate of adoption of oxygen systems worldwide and in the United States, and Table 4-8 lists these installations.

Figure 4-11
Installations of Oxygen Delignification Systems

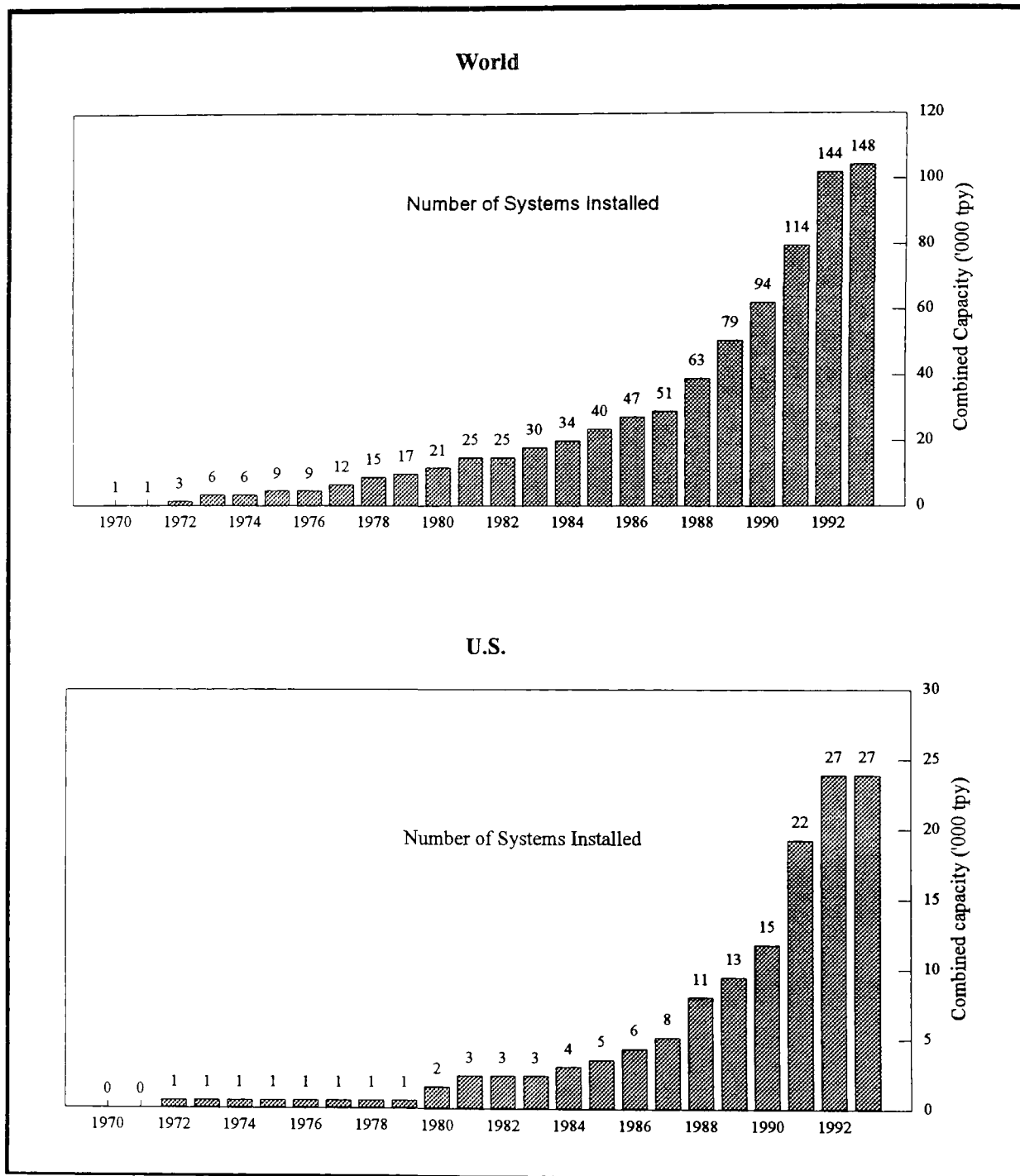


TABLE 4-8

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).

4.3.2 Costs and 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 4-9).¹⁰ At the low end of this range, the savings in chemical costs alone, plus savings on current or future effluent treatment requirements, may favor the switch to oxygen. 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, to avoid excess oxygen consumption and minimize potential for heat generation. For mills that require a considerable upgrade in pulp washing equipment, the cost of conversion may be closer to \$20 to \$25 million.

Installation of an oxygen delignification stage can help mills avoid the costs of installing a new chlorine dioxide generating system or replacing an aging C-stage in their bleaching line. By lowering the pre-bleaching kappa number by 50 percent, oxygen will permit some mills to shorten their bleach sequence (i.e., eliminate a C-stage) and/or increase the chlorine dioxide substitution rate without installing additional ClO_2 generating capacity.¹¹ By taking some of the delignification load off of the bleach plant, oxygen stages can also alleviate bleach plant capacity bottlenecks.

Historically, oxygen has been generated offsite and has been expensive for use as a bleaching agent. In North America, most oxygen for industrial applications is generated using cryogenic air separation (or fractional distillation), with nitrogen and argon produced as coproducts (SRI International, 1988). Cryogenic techniques produce oxygen in the purest form. Installations are large in scale and located in regions of heavy demand. 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

¹⁰ In a study prepared for the paper industry evaluating the impacts of adopting pollution prevention options, Phillips et al. (1993) used an average cost of \$37.7 million for the oxygen equipment alone. As seen, these costs are considerably higher than those reported elsewhere. The source for the equipment cost estimates is reported only as "national industry averages."

¹¹ The conventional approach to increasing the chlorine dioxide substitution rate involves boosting ClO_2 generating capacity and increasing the ratio of ClO_2 to Cl_2 . Alternatively, a mill can add an oxygen stage to first decrease the overall amount of bleaching chemicals required. Then, using existing ClO_2 generating capacity, they cut back on Cl_2 , effectively raising the ClO_2 substitution rate. In the latter case, the mill obtains the added benefit of being able to recycle the effluent from the O-stage and to decrease the flow of effluent going to the wastewater treatment plant.

TABLE 4-9

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 (1990a)	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
Phillips et al. (1992)	Model mill calculations	1320 tpd	\$37.7 (installed)
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

Sources: As indicated in table.

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 (van Lierop and Brown, 1987). 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), although costs for liquid oxygen depend closely on transportation distances and could be lower near major population centers. Onsite oxygen plants are available from numerous industrial gas vendors such as Liquid Air, Air Products, Airco, and Union Carbide. The cost advantage of onsite generation will depend on the volume demand and the proximity of the mill to sources of liquid oxygen. Onsite production becomes attractive once demand reaches around 10 tons per day. Other areas of the mill that may use oxygen include oxygen-reinforced extraction stages, wastewater treatment, and black liquor oxidation. Potential oxygen requirements for a 1,000 tpd mill (as reported by an equipment vendor) could reach as much as 110 to 150 tons per day, depending on the number of oxygen applications. These figures are shown in Table 4-10.

Data from Idner (1988) indicates that, based on Swedish experience, there are substantial savings in variable costs associated with oxygen and that these tend to offset higher capital costs. Table 4-11 suggests that variable costs would be lowered by 21 to 56 SEK (\$3.40 to \$9.08) per ton, depending on the wood species (hardwood or softwood) and consistency of the pulp. When annualized capital costs are added to operating and maintenance costs, the change in annual costs compared to conventional bleaching range from a decrease of 16 to 23 SEK (\$2.59 to \$3.73) per ton for MC softwood pulping to an increase of 25 to 41 SEK (\$4.05 to \$6.65) per ton for HC hardwood pulping. These figures assume no requirements for changes in recovery system capacity, and credits for avoided investment in C- or D-stage equipment are also not included.

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. Inadequate washing of brownstock pulp prior to oxygen delignification will result in increased oxygen consumption and possibly excess heat generation in the reactor. Post-oxygen washing must also be thorough in order to recover as much dissolved lignin as

TABLE 4-10

Potential Oxygen Demand at Bleached Kraft Mill

Area of Mill	Potential Oxygen Demand (tpd)
Oxygen delignification	25
White liquor oxidation	5
Oxidative extraction	5
Black liquor oxidation	60
Lime kiln enrichment	1-5
Wastewater treatment	15-50
TOTAL [a]	111-150

[a] The use of oxygen for black liquor oxidation is limited to mills with older recovery boilers. Oxygen use in wastewater treatment is predicated on the existence of an oxygen-activated sludge treatment system, which not all mills have. Thus, for most mills, oxygen demands will be considerably lower.

Source: Deal et al. (1991).

TABLE 4-11

**Change in Total Costs for Oxygen Bleaching vs.
Conventional Bleaching in a 600 mt/d Swedish Mill
(SEK/metric ton)**

	Softwood (Pine)		Hardwood (Birch)	
	HC	MC	HC	MC
Investment (SEK millions)	70 to 90	40 to 50	70 to 90	40 to 50
Variable costs	-56	-54	-29	-21
Maintenance ^[a]	10 to 13	6 to 7	10 to 13	6 to 7
Capital Costs ^[b]	44 to 57	25 to 31	44 to 57	25 to 31
TOTAL	-2 to 14	-23 to -16	25 to 41	10 to 13

Notes: Assumes no changes in recovery system required.

\$1.00 U.S. ~ 6.17 SEK (1988)

MC = medium consistency

HC = high consistency

^[a] 3% of the investment

^[b] Depreciation 15 years and 10% interest

Source: Idner (1988).

possible before chlorination. For mills that require a considerable upgrade in pulp washing equipment, the cost of conversion may be closer to \$15 million.

4.3.3 Pollution Prevention Potential

From an environmental standpoint, oxygen delignification offers two distinct advantages. First, by continuing the delignification process begun during kraft cooking, it reduces the amount of lignin carried through to the chlorination stages. Reductions in the amount of lignin entering the bleach plant translate directly into reductions in most pollutants of concern, i.e., BOD₅, color, and organochlorines (Tench and Harper, 1991). Table 4-12 shows the impacts of adopting oxygen delignification on pollutant parameters such as BOD₅, COD, TOCl, and acute fish toxicity. BOD₅ declines by approximately 32 percent, COD by 43 percent, and TOCl by 50 percent.

Second, the effluent from the oxygen stage is recycled through the pulp mill recovery cycle. In a conventional bleach plant, these solids would only be removed following chlorination. Such post-chlorination effluents cannot be recovered due to their corrosiveness to process equipment and must go to wastewater treatment (see Figure 4-12). Therefore, when coupled with increased recycle or close-up of the effluent stream, oxygen pre-bleaching normally reduces effluent flows (and associated sludge volumes) from the mill as well.

Oxygen also puts the mill on the track towards “zero effluent” pulping and chlorine-free bleaching. Should regulations or market forces require further reductions or elimination of chlorine compounds, mills that have previously installed oxygen delignification will be able to respond more rapidly.

4.3.4 Compatibility With Downstream Bleaching Stages

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 (and up to 65 percent for the newer two-stage systems), a variety of innovative bleaching methods may also be applied. In a typical application, the mill follows the oxygen stage with a mixture

TABLE 4-12

**Pollutant Impacts of Oxygen Delignification
Versus Conventional Pulping/Bleaching**

Parameter	Softwood (Pine)			Hardwood (Birch)		
	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.

MC = medium consistency

HC = high consistency

Source: Idner (1988).

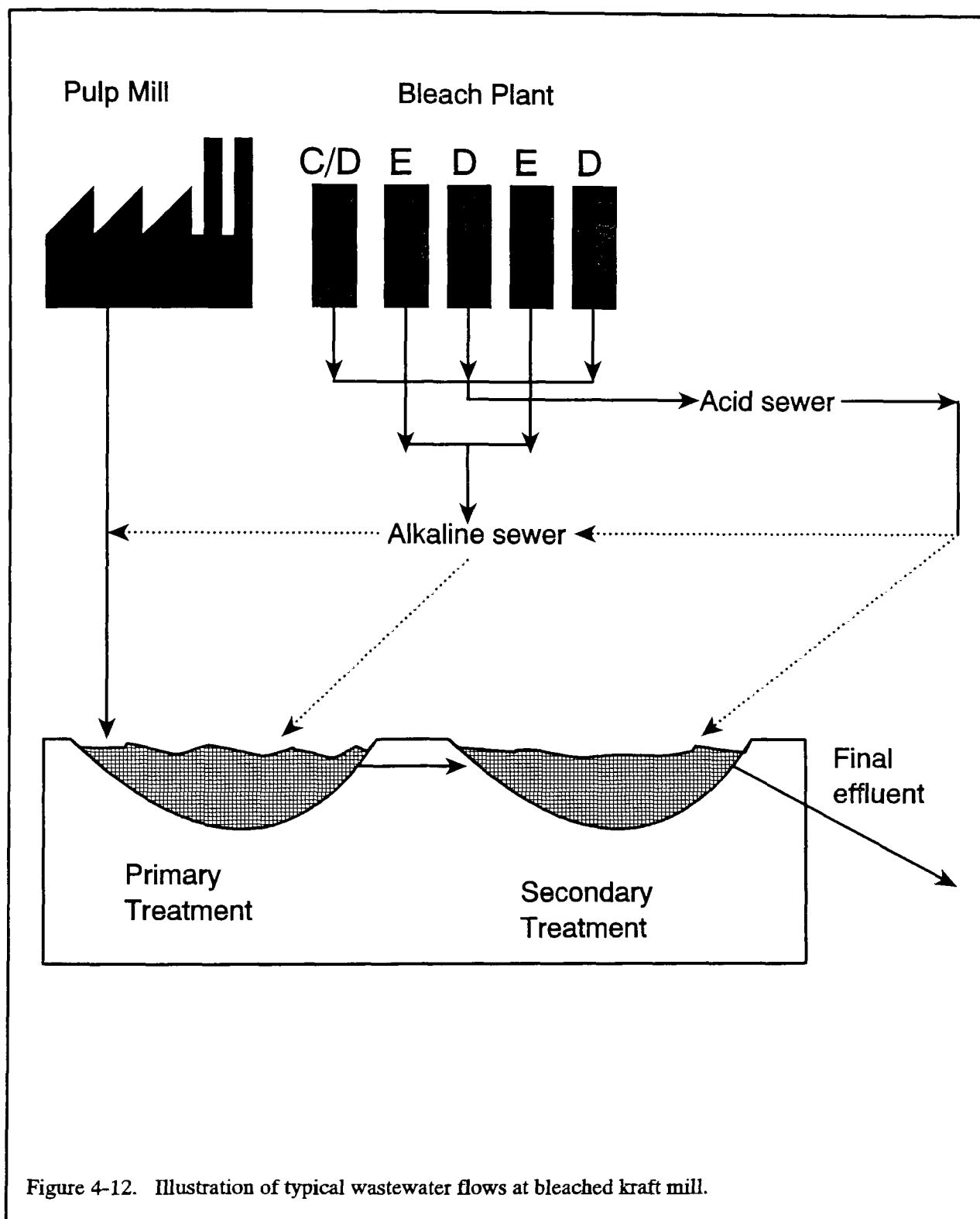


Figure 4-12. Illustration of typical wastewater flows at bleached kraft mill.

Source: Eastern Research Group, Inc.

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_pEDED .

A significant benefit of oxygen delignification is that it will allow the mill to increase the substitution rate of chlorine dioxide for chlorine without requiring additional chlorine dioxide generating capacity. A typical mill operating currently at 30 percent ClO_2 substitution, for example, could operate at 70 percent in one of two ways: (1) increase its chlorine dioxide generating capacity, or (2) add an oxygen delignification stage. Under the second option, the mill can cut back on the application of chlorine, thereby increasing the ratio of ClO_2 to Cl_2 (the substitution rate) using its existing chlorine dioxide capacity. Drawing from a database of actual installations, 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 possibilities include “short sequence” bleaching, in which oxygen delignification is followed by three rather than five bleaching stages (i.e., OC_pED or ODE_{op}D versus OCEDED). While short sequence bleaching has the benefits of lower capital costs and, if carefully engineered, 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. Some conventional CEDED mills have succeeded in raising capacity by a substantial amount by installing oxygen delignification and then splitting their single 5-stage line into two 3-stage lines.

Finally, when combined with extended delignification, mills may be able to produce oxygen delignified pulps with kappa numbers below 8 to 10, although minor losses in strength or yield may occur. These pulps are extremely bleachable and may be bleached to 80+ brightness using small amounts of chlorine dioxide (ECF bleaching), to 70+ using one or more peroxide-based stages (e.g., Lignox), or potentially to 85+ with ozone and peroxide (OZEP), depending on tree species.¹²

¹² Hardwoods are easier to bleach than softwoods.

4.3.5 Impacts on Other Aspects of Mill Operations

Recovery Boiler Operations

The main obstacle to more widespread adoption of oxygen delignification is likely to be the impact of an increased black liquor solids load on the recovery boiler. With the addition of a pre-chlorination oxygen delignification stage, the amount of solids recovered per ton of pulp that are subsequently directed to the recovery boiler system will increase. According to one analysis (Tench and Harper, 1987), 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. In particular, at older mills where pre-chlorination washing is currently inefficient the increase could be as much as 10 percent.

While some mills may operate with surplus boiler capacity, in other cases boiler throughput may represent a production bottleneck. The burning of additional solids beyond boiler design capacity will result in ash being built up on the boiler heat transfer surfaces, necessitating more frequent shutdowns to permit the boiler tubes to be washed out (Clement, 1993). Options for accommodating a higher level of solids per ton of pulp are available, however, and were reviewed in Section 4.2.5.

Air and Solid Waste Emissions

As with extended delignification, the introduction of an oxygen stage shifts some of the delignification load ahead of the bleach plant, permitting recovery of additional solids from the effluent. The processing of this additional effluent in the kraft recovery system may produce slight increases in air emissions (from the recovery furnace) and solid wastes such as ash and precipitates (from the recovery boiler), 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 ash, dregs and grits. These are usually landfilled. The introduction of an oxygen stage and subsequent recycle of oxygen filtrate will

probably result in a minor (i.e., less than 5 percent) increase in the quantity of these materials going to the landfill.

Energy Requirements

In substituting oxygen for chlorine, some changes in direct and indirect energy consumption will result. Chlorine is manufactured offsite in an energy-intensive process that consumes approximately eight times the amount of energy per unit of bleaching power compared to oxygen (McDonough, 1986). Oxygen may be produced offsite and transported to the mill, in which case the energy costs will be reflected in the delivered price, or manufactured onsite using energy supplied by the mill. In the latter case, the energy cost may be ignored by the mill since many mills self-generate 100 percent of their energy requirements through incineration of wood and pulping byproducts. The true cost of further energy requirements may depend, therefore, on whether energy can be sold offsite into the local power grid. Table 4-13 presents information on changes in energy requirements for a mill adopting high consistency oxygen delignification. Site-specific factors could result in substantial variations from these figures.

4.4 OZONE DELIGNIFICATION

Ozone (O_3) is an extremely powerful oxidant whose potential as a pulp bleaching agent has been recognized for some time. Until recently, the integration of ozone into the bleach line has been limited because of the detrimental effects it has had on pulp quality and strength properties. The successful "taming" of ozone has been greatly anticipated in the industry, 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 and ultimately the total mill's effluent cycle. 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.¹³ Ozone bleaching equipment is now being offered by all of the established vendors of pulp bleaching equipment.

¹³ To date, only limited details concerning these startups are available.

TABLE 4-13

**Change in Energy Consumption for HC Oxygen Delignification
Using Softwood Kraft at 50% Oxygen Delignification**

Energy Type	Source	$C_D E_O DED$	$OC_D E_O D$
Steam usage, kg/metric ton	Bleach plant	500	600
	Chemical preparation	370	250
	Evaporator, increase	0	40
	Recovery boiler, increase	0	-100
	TOTAL	870	790
Power usage, kWh/metric ton	Bleach plant and chemical preparation	160	170
	Turbine increase	0	-10
	TOTAL	160	160
Kiln fuel, increase in liters oil/metric ton		--	2

Source: Tench and Harper (1987).

The movement towards ozone bleaching has been achieved through advances in determining the optimum conditions for ozone bleaching, developments in ozone generation equipment, and the relative economics of ozone use. The key process conditions for ozone bleaching have been summarized by Shackford (1992):

Pulp pH The pH of the reaction is the most important variable. At pH greater than 3, ozone becomes less selective towards pulp and greater amounts of ozone will be consumed;

Pulp washing - The carryover of organic materials from brownstock or post-oxygen washing must be minimized (below 10 kg COD per ton pulp);

Reaction temperature - Ambient temperatures (around 20 °C) appear to be optimal for an ozone stage. At higher temperatures there will be increased ozone consumption for a given level of delignification;

Metals buildup - The ozone stage operates in an acid medium, and is generally situated between two alkaline stages. In this configuration, the ozone stage can become a “trap” for metal ions that are present in wood pulp. These metals will catalyze the decomposition of ozone, thereby releasing hydroxy radicals, which are destructive to pulp. To reduce metals buildup, a small purge of acid filtrates upstream of the ozone stage is probably necessary.

Reaction mechanisms and process economics will determine the best consistency for the system. Low, medium, and high consistency bleaching each have their own advantages and disadvantages:

- At low consistency, the stock is more homogenous and the reaction with ozone tends to be more uniform. The larger volumes of water reacted with the pulp, however, means larger-scale equipment;
- Advantages of “gas phase” or high consistency systems (35 to 45 percent) include potentially lower ozone consumption, the ability to operate the reaction at or near atmospheric pressure, greater ease of control of reaction temperature, and better water balance for recovery of all effluents. Disadvantages include the need for additional presses to dewater the pulp and the greater potential for pulp degradation (and hence lower yield). Note, however, that with a high-consistency oxygen stage prior to the ozone stage the mill can forego the investment in pulp pressing equipment;
- At medium consistency (12 to 14 percent) there may be an increase in ozone and acid consumption compared to a gas phase system, but pulp handling equipment is less complex.

Ozone delignification is performed using techniques and equipment similar to that used in oxygen delignification (see Figure 4-13). Peak ozone delignification efficiency has been found to occur at pH 1.0 to 2.0, thus pulp is normally treated with sulfuric acid prior to ozonation. In a high consistency system,

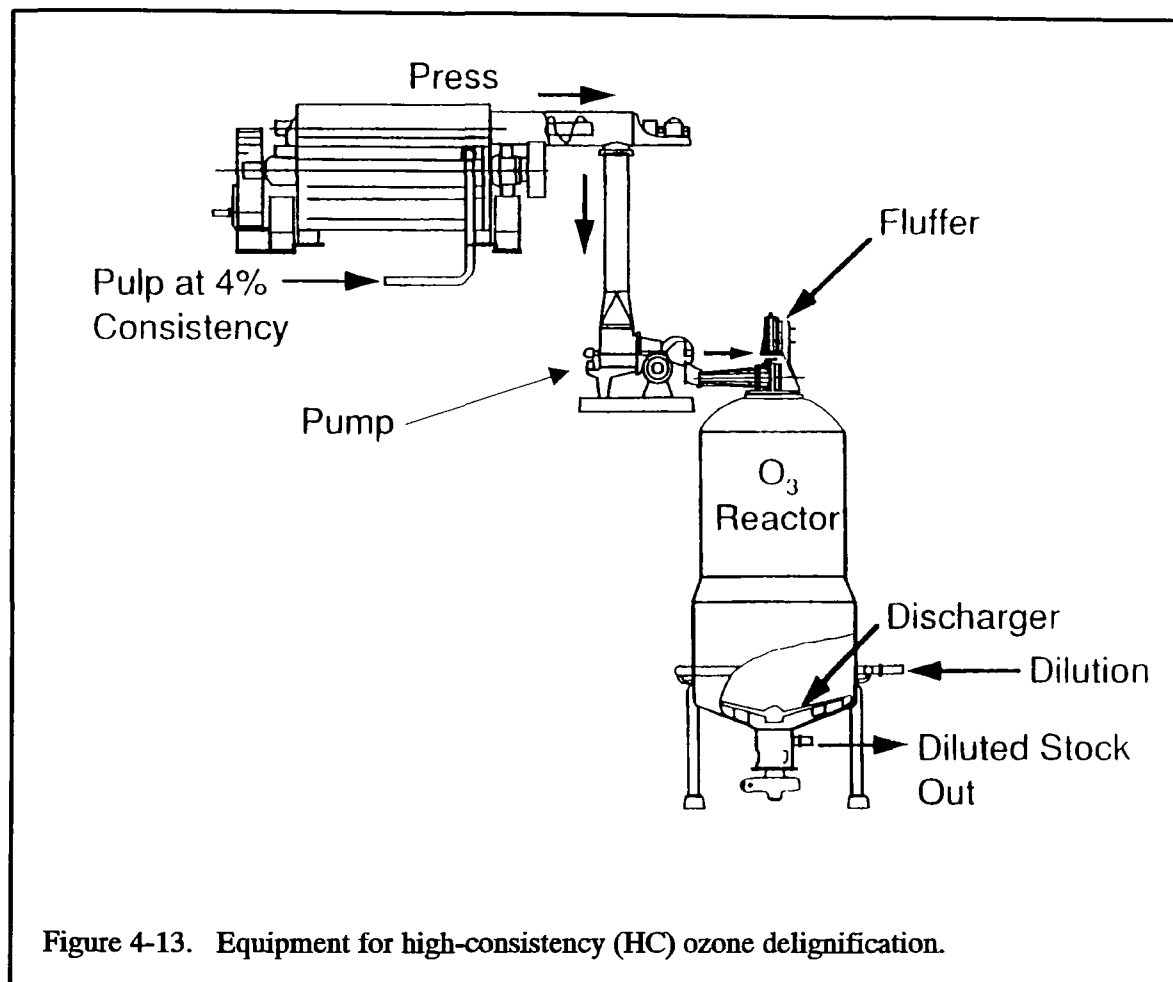


Figure 4-13. Equipment for high-consistency (HC) ozone delignification.

Source: Miller, 1992.

as shown, 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 (in an oxygen-reinforced extraction stage or in the wastewater treatment plant, for example). The equipment for ozone generation is a crucial part of the process and accounts for a high percentage of the costs. Ozone generation is discussed in the section below.

Ozone Generating Equipment

The technology for large-scale ozone generation has been used for many years in industrial applications such as bleaching of textiles, bleaching of clay in the manufacture of paper fillers, and in municipal drinking water systems. Its use in pulp bleaching, therefore, represents only a new application of an established technology. Major suppliers of ozone generating equipment and onsite ozone suppliers include:

Ozone Generating Equipment

Ozonia
Emery Trailgaz
Capital Controls
Sumitomo

Onsite/Over-the-Fence Ozone Supply

Liquid Air
Air Products
Praxair (formerly Linde)
MG Industries

Ozone generation requires large amounts of power, about 8 kWh per kilogram of ozone (Singh, 1982).¹⁴ Ozone is most commonly generated from oxygen or oxygen-containing gases (e.g., air) using the corona discharge method. The generating equipment 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 O₂ molecules, which recombine to form ozone. Ozone is unstable and will decompose to molecular oxygen, thus ozone must be generated onsite and fed immediately to the pulp reactor.

¹⁴ While chlorine dioxide generation requires approximately the same amount of energy as ozone, ozone is theoretically twice as powerful a bleaching agent.

The ozone reaction with pulp is exothermic, and a large amount of the energy required for production (up to 90 percent) is converted to heat. This heat must be dissipated, normally through the application of cooling water, and may be recovered.¹⁵ Cooling water requirements sufficient to keep the gas temperature stable and prevent ozone decomposition are in the range of 2,500 to 4,000 liters per kg of ozone.

Ozone can be generated from air, although the low concentration of oxygen in air make this commercially unfeasible. Instead, it is normally produced from oxygen. Recent articles suggest that most mills will purchase liquid oxygen (the purest form) for conversion to ozone, although it is very likely that ozone generation systems will also be coupled with on-site oxygen plants (Byrd and Knoernschild, 1992). Commercial ozone generators have a capacity of between 450 and 1,400 kg of ozone per day, and most mills will require several large-sized generators running in parallel.¹⁶

Since only a small percentage of the oxygen feed gas is converted to ozone, there is a substantial incentive to recycle the carrier gas back into the ozone generator. These off-gases pick up volatile components as a result of their contact with the pulp, however, and must be first passed through a purification system that combines wet scrubbers, catalytic converters, and desiccant dryers. Some work is being done on systems that separate the ozone from the oxygen gas prior to pulp contact. This would allow the oxygen carrier gas to be recycled directly to the ozone generator (Byrd and Knoernschild, 1992).

4.4.1 Number of Installations

Table 4-14 shows the history of ozone pilot plant and full-scale installations worldwide. Early work in the U.S. was done at the Scott Paper mill in Muskegon, MI and then at Weyerhaeuser's Longview mill in Washington State. PAPRICAN was also heavily involved in early research work at their Pointe Claire, Quebec headquarters. In 1989, Union Camp (Wayne, New Jersey) installed a 25 tpd ozone system at its mill in Eastover, South Carolina. This \$6 million experimental project has provided promising

¹⁵ Normally, this low level heat cannot be used in the mill and will be dissipated using a cooling tower.

¹⁶ The Union-Camp installation described in the next section operates five ozone generators.

TABLE 4-14

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	Muskegon, 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	Weyerhaeuser	Longview, WA	20	LC	OZD, OZDED	Softwood kraft
1988	PWA	Stockstadt, Germany	3	HC	Z	Sulfite
1989	Union Camp	Eastover, SC	25	HC	OZED	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*	Monstera, Sweden	1000	MC	OZEP	Market kraft, HW/SW (HW only so far)

* Full-scale installation.

Source: Liebergott et al., 1992.

results over a four-year period. Based on experiences at this mill, 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 OZE₀D (Nutt et al., 1992). Visits to the Franklin mill by EPA contractors have confirmed that there have been no major operational difficulties associated with the ozone bleaching process to date.

Among the commercial-scale ozone projects in the startup or planning stages (as of 1992) are the following:

- The Monsteras 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. To date, the mill has pulped only hardwoods;
- 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 has recently converted an adjacent 400 tpd line;
- MoDo has purchased an ozone system from Kamyr for installation at their mill at Husum, Sweden;
- SCA Wifsta-Ostrand in Sweden has licensed ozone technology from Union Camp for use at their Timra kraft mill;
- The E.B. Eddy mill in Espanola, Ontario is considering installation of a full-scale ozone plant following successful operation of Kamyr's pilot plant.

For the Franklin mill installation, Union Camp selected a high consistency gas phase ozone stage. The advantages claimed for gas phase reaction are possibly lower ozone consumption (compared to medium consistency), and the ability to operate at or near atmospheric pressures. In Union-Camp's case, the selection of high consistency may also have been influenced by the fact that a high consistency oxygen stage was already in place. This eliminated the need for installation of a high consistency pulp press prior to the ozone stage. Through redesign of the ozone reactor, Union Camp claims to have solved the problem of nonuniformity of reaction that had been experienced in previous HC lab and pilot plant trials (Nutt et al., 1992).

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™. 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 pulp at full market brightness.

4.4.2 Costs and Economics

Capital costs for the ozone delignification equipment will depend on the type of system selected (i.e., gas phase or medium consistency). This in turn is dependant on the charge of ozone required to achieve target pulp properties (brightness and yield) and the economics of the individual mill. Mills using ozone as a “bulk delignification” stage, (i.e., as the primary delignifying agent), may choose high consistency due to the potential for reacting more ozone in a single stage. Others using ozone at more moderate levels 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, as 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 (Deal, 1991). Cost savings from these areas would be greater for a greenfield mill compared to a retrofit. The final cost for the Franklin mill installation has been recently cited as \$113 million (Ferguson, 1992b).

Bleaching costs for ozone, including ozone generation, are lower than for conventional sequences. Power consumption for an oxygen feed ozone system producing 83 to 85 percent brightness pulp is about 8 to 9 kWh per kg O₃ or \$0.64 per kg based on a power value of \$0.04 per kWh (Nutt et al., 1992). Fuel values from additional solids recovery may provide further payback, depending on recovery capacity. Nutt et al. (1992) compared operating costs of the OZE₀D line at the Franklin mill with the mill's 1970s era CEDED bleaching sequence, and against two more contemporary processes (with 100 percent chlorine dioxide substitution) that might be found at numerous North American mills (costs are indexed with CEDED and DEDED bleaching set equal to 100). Table 4-15 indicates that bleaching costs for the OZE₀D line will run 48 and 83 percent of the costs for CEDED bleaching on pine and hardwood,

TABLE 4-15

**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 ₀ -D	48	83

D-E-D-E-D	100	100
O-D-E-D	56	73
O-Z-E ₀ -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 ozonegeneration system

respectively. When compared to a more contemporary DEDED line, OZE₀D bleaching costs will run at 32 and 57 percent of the costs.

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 final brightening agent, replacing chlorine dioxide in a TCF sequence. Nutt et al. (1992) indicate that replacing ClO₂ with peroxide would raise operating costs back to the level of a CEDED process (e.g., by 52 percent for softwood and 17 percent for hardwood) if 90 percent ISO brightness were required (peroxide costs would be around \$30 to 40 per ton).¹⁷ Lower brightness TCF pulps (low 80s) could likely 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 may increase interest in ozone. Also, ozone's cost vis-à-vis conventional bleaching sequences has improved as it is now more likely to be used as a replacement for more expensive chlorine dioxide rather than less expensive chlorine.

4.4.3 Pollution Prevention Potential

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 OZE₀D, 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 E₀ stage effluents. Table 4-16 summarizes the effluent quality of the new OZE₀D line at the Franklin mill under ozone bleaching. As seen, total organic halides are below 0.1 kg per ton in effluent, chloroform is a very low 0.0015 kg per ton, 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.

¹⁷ Note that the technical feasibility of producing 90 percent ISO softwood pulp using an OZEP sequence is debated within the industry. Softwoods are generally more difficult to bleach than hardwoods.

TABLE 4-16

**Emissions from Ozone Bleach Line at Union Camp's
Franklin, Virginia 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 OZE₀D bleaching sequence to produce 83 brightness pulp.

Source: Nutt et al. (1992).

Table 4-17 presents similar effluent data from the PAPRICAN ozone pilot plant running several bleach sequences. Compared to a conventional $C_D E_O DED$ sequence the $OZE_O D$ sequence resulted in the following reductions: BOD (62 percent), COD (53 percent), Color (88 percent), and TOC1 (98 percent). In comparison with a more modern $ODE_O DED$ sequence, BOD and COD levels of the $OZE_O D$ sequence were slightly higher (by 20 and 14 percent, respectively), while effluent color decreased by 48 percent and TOC1 fell by 80 percent.

Among the numerous ozone-based bleaching sequences currently being investigated in labs and pilot plants around the world are: OZE_P , $OZED$, $OZPY$, $OZEPY$, $ZO_{ZW}PY$, and OZE_PPY . (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.

4.4.4 Impacts on Other Aspects of Mill Operations

Pulp Quality

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. As discussed by Liebergott (1992b), however, numerous researchers have found that the viscosity-strength relationship is different for non-conventionally bleached pulps, and that despite their lower viscosities, ozone-bleached pulps maintain their strength properties.¹⁸ (The same is true to some extent for oxygen-delignified pulps.) Table 4-18 shows Union-Camp data on properties of conventional, oxygen-delignified, and ozone-delignified pulps. Although the viscosity of the pulps decrease with the use of low-chlorine bleaching sequences, the pulp strength properties (tear, breaking length) are maintained. Viscosity falls from 17 to 11 for softwood and from 14 to 12 for hardwood when moving from $CEDED$ bleaching to $OZE_O D$, while

¹⁸ Viscosity itself is not a functional end-use parameter, but it is used as a surrogate for strength.

TABLE 4-17

Effluent Properties of Ozone Bleaching Sequences

Bleach Sequence	Effluent Outfall (kg/ton)			
	Color	BOD	COD	TOCl
C _D E _O DED	228	31	101	7.7
OC _D E _O DED	75	18	50	4.4
ODE _O DED	52	10	41	0.5
OZED	27	12	47	0.1
OZE _O PY or OZEZP	28	13	49	

Basis: softwood kraft, brownstock kappa 30.2, final brightness 90% ISO

Source: Shackford, 1992 (based on PAPRICAN lab effluent data).

TABLE 4-18

**Properties of Pulps Produced
Using Alternative Bleaching Sequences**

Parameter	Units	CEDED		O(DC)ED		OZED	
		SW	HW	SW	HW	SW	HW
Breaking length	km	7.5	5.9	7.2	5.8	7.0	5.7
Zero span breaking length	km	13.8	14.2	12.4	13.3	12.5	13.7
Burst	m ³ /cm ³	53	39	62	41	59	39
Tear	dm ³	111	87	119	87	124	85
TAPPI viscosity	cp	17	14	13	13	11	12
Bulk	cm ³ /g	1.63	1.65	1.64	1.72	1.66	1.71
TAPPI opacity	577 nm	74	78	70	79	72	79
TAPPI scattering coefficient	577 nm	260	354	242	366	254	368

Experimental: 83 GE brightness pulp, Valley beater refined to 350 mL CSF. Nonstandard handsheet method used of acid sized pulp, fines retained, semistrained drying to simulate paper machine conditions.

Source: Nutt (1993).

burst and tear parameters are comparable or superior. Thus, the ozone-bleached pulps are different than, but not necessarily inferior to, pulps produced using conventional sequences.

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.

Recovery Boiler Operations

The main obstacle to more widespread adoption of oxygen delignification is likely to be the impact of an increased black liquor solids load on the recovery boiler. With the addition of a pre-chlorination oxygen delignification stage, the amount of solids recovered per ton of pulp that are subsequently directed to the recovery boiler system will increase. According to one analysis (Tench and Harper, 1987), 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. In particular, at older mills where pre-chlorination washing is currently inefficient the increase could be as much as 10 percent.

While some mills may operate with surplus boiler capacity, in other cases boiler throughput may represent a production bottleneck. The burning of additional solids beyond boiler design capacity will result in ash being built up on the boiler heat transfer surfaces, necessitating more frequent shutdowns to permit the boiler tubes to be washed out (Clement, 1993). Options for accommodating a higher level of solids per ton of pulp are available, however, and were reviewed in Section 4.2.5.

Air and Solid Waste Emissions

The addition of an ozone stage will have a significant impact the chemical recovery cycle due to the greatly reduced need for conventional bleaching chemicals and the ability to recycle the Z-stage effluents. Since the Z-stage operates without chlorine-based chemicals, all of the Z-stage effluents can be recycled through the recovery boiler, permitting recovery of additional solids from the effluent.¹⁹ The processing of this additional effluent in the kraft recovery system may produce slight increases in air emissions (from the recovery furnace) and solid wastes such as ash and precipitates (from the recovery boiler), 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 ash, dregs and grits. These are usually landfilled. The introduction of an ozone stage and subsequent recycle of ozone filtrate will probably result in a minor increase in the quantity of these materials going to the landfill.

Energy Requirements

As discussed above in Section 4.4, ozone generation is approximately as energy-intensive as chlorine dioxide, yet ozone is about twice as powerful a bleaching agent. Energy consumed onsite in the generation of ozone will replace energy used offsite to produce chlorine and sodium chlorate. Since most mills generate all of their onsite power requirements from pulping byproducts, it is possible that surplus energy exists for ozone generation, especially where the mill is unable to sell power back into the local utility grid.

¹⁹ A small purge of acid filtrates upstream of the ozone stage is generally necessary to avoid buildup of metals in the pulp. Metals naturally present in the wood can catalyze the hydrolysis of ozone to produce the hydroxy ion, which is destructive to pulp (Shackford, 1992).

4.5 ANTHRAQUINONE CATALYSIS

In the 1970s, the addition of anthraquinone (AQ) to the pulping liquor was discovered to speed up the kraft pulping reaction and increase the yield, with no deleterious effects on pulp properties (Holton and Chapman, 1977). The anthraquinone acts as a delignification catalyst, and can cause a combination of the following impacts: (1) increased pulp yield of up to 2 percent; (2) reduced chemical requirements by up to 10 percent; (3) increased pulp production, and (4) lower cooking temperature (and energy requirements).

The use of small amounts of AQ (around 0.05 to 0.1 percent on cooking liquor) catalyzes or accelerates the fragmentation of lignin, rendering it more vulnerable to attack and dissolution by the cooking chemicals. 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 (Blain, 1992).

By improving yield and lowering black liquor solids generation, anthraquinone addition has the potential to facilitate the use of extended cooking or oxygen delignification at some mills. This would include mills experiencing unacceptable yield drops from extended cooking, or where extended cooking or oxygen delignification increases the boiler load beyond capacity.

According to Blain (1992), mills will find AQ most attractive if they are in a situation to benefit from the “multiplicative” effects of AQ pulping. This refers to the effectiveness of AQ in (1) reducing the level of organic and inorganic solids, and (2) increasing yield per ton of fiber.

4.5.1 Number of Installations

AQ pulping is reported to be used extensively in Japan to improve yield from what are relatively expensive wood sources (Blain, 1992), and in at least two mills in Canada. This same source indicates significant current interest in AQ as a means of achieving extended delignification and overcoming boiler capacity bottlenecks. At current U.S. pulp wood and AQ chemical cost levels, the use of AQ is not attractive unless it solves some bottleneck problem, usually in the recovery boiler. The trade journal *Paper Age* (1990) has reported that over 100 mills worldwide use anthraquinone.

The patent on use of anthraquinone in pulping, held by ICI, is due to expire in a couple of years. According to some, several pulp and paper companies are considering sourcing AQ and becoming a supplier to the industry. One company is reported to be already importing AQ from India for use in pulp cooking.

4.5.2 Costs and Economics

The potential for anthraquinone to increase yield or reduce chemical requirements implies a reduction in the load on the recovery boiler. Thus, anthraquinone catalysis offers another potential means to buffer the impacts of oxygen delignification or extended cooking on the recovery system. Holton and Blain (1983) have examined the potential impacts of anthraquinone and concluded that its use could compensate for an increase in chemical recovery load up to 7 to 8 percent. Table 4-19 shows that a 0.04 percent AQ charge on wood at a 1,000 ton per day mill could have the following impacts:

- (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 ton; and
- (3) reduce boiler load 3.0 percent.

In some mills, this 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.

4.5.3 Pollution Prevention Potential

Based on the its potential for decreasing chemical requirements or facilitating adoption of oxygen delignification, anthraquinone catalysis will reduce the formation and release of chlorinated organics. 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 of the brownstock pulp.

TABLE 4-19
Costs of Anthraquinone Treatment

Parameter		Anthraquinone Charge (% on wood)				
		0.00%	0.03%	0.04%	0.06%	0.08%
Yield	%	48.00	48.56	48.75	49.13	49.45
Wood input	ODT/day	2,083	2,059	2,051	2,036	2,022
Effective alkali charge	% on wood	14.50	14.13	14.00	13.75	13.50
Price of AQ	\$/kg	11.00	11.00	11.00	11.00	11.00
Cost of softwood at mill	\$/ODT	140	140	140	140	140
Organics to black liquor	ODT/day	1,062	1,038	1,030	1,015	1,002
Actual chemical charge	ODT/day	569	548	541	527	514
Black liquor exit digester	ODT/day	1,631	1,586	1,571	1,542	1,516
Black liquor solids: pulp	kg/tonne	1,631	1,586	1,571	1,542	1,516
Boiler load reduction (organic)	%	0.0	2.2	3.0	4.4	5.6
AQ charge	kg/day	0	618	821	1,221	1,618
Cost of AQ charged	\$/day	0	6,796	9,026	13,435	17,796
Saving on wood	\$/day	0	3,364	4,487	6,679	8,552
Evap. steam @ \$9/tonne	\$/day	18,000	17,792	17,723	17,588	17,472
Saving on evap. steam	\$/day	0	208	277	412	528
Lime kiln fuel	\$/day	10,000	9,629	9,507	9,266	9,037
Saving on lime kiln fuel	\$/day	0	371	493	734	963
NaOH released for ox. delig.	kg/tonne	0	12.4	16.5	24.5	32.2
Net cost of AQ	\$/day	0	3,971	5,262	7,833	10,365
Net additional cost (\$/ton bleached pulp)	\$/ADT	0	3.88	5.15	7.66	10.14

Note: Under each option it is assumed there is no net change in pulp output. Costs shown are in 1992 Canadian dollars.

Source: Ontario Ministry of the Environment, (1992); calculated from data presented in Holton (1983) and Bonsor (1988).

4.5.4 Impacts on Other Aspects of Mill Operations

Recovery Boiler Operations

Depending on how it is used, anthraquinone could alternatively decrease, have no impact on, or increase the recovery boiler load. One strategy is to use AQ to produce the same quantity of pulp using less fiber. In this case, the solids load would decline. A more common application, however, is to use AQ to facilitate implementation of extended delignification without the increase in solids load that otherwise would occur (see Section 4.2). Finally, where maximum output from available fiber is the goal, the mill could use AQ to boost yield such that additional solids are produced.

Air and Solid Waste Emissions

To the extent that AQ is used in such a way that it results in an increased solids load, air emissions from the recovery boiler and solid waste byproducts from the recovery cycle may increase slightly.

Energy Requirements

The impacts of AQ on energy requirements are expected to be negligible.

4.5.4 Environmental Effects

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. Most anthraquinone used in pulping is likely destroyed during the recovery process (i.e., incinerated). To our knowledge, no negative environmental effects have been reported in the literature.

4.6 BLACK LIQUOR SPILL CONTROL AND PREVENTION

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.

Losses of up to 5 percent of liquor volume were not uncommon at some mills 30 years ago. In the absence of warning systems or detection procedures, many spills can go unnoticed for extended periods of time. As more of the mill effluent is recovered through the application of measures such as extended delignification techniques, accidental losses will comprise an increasing proportion of effluent, hence efforts to minimize spills and their impacts are important.

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 result in a shock to 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. A small but environmentally significant proportion of the black liquor solids are also non-biodegradable, so if spilled to sewer, will be discharged into the receiving waters. Spills are also a significant source of air emissions.

Effective loss control depends on a combination of 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 appropriate section of 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 4-14. The system would include conductivity and pH probes in the process sewer to detect and identify the spill. Once detected, the spill can be diverted to either a spill lagoon (in the case of weak spills that would not overload the treatment

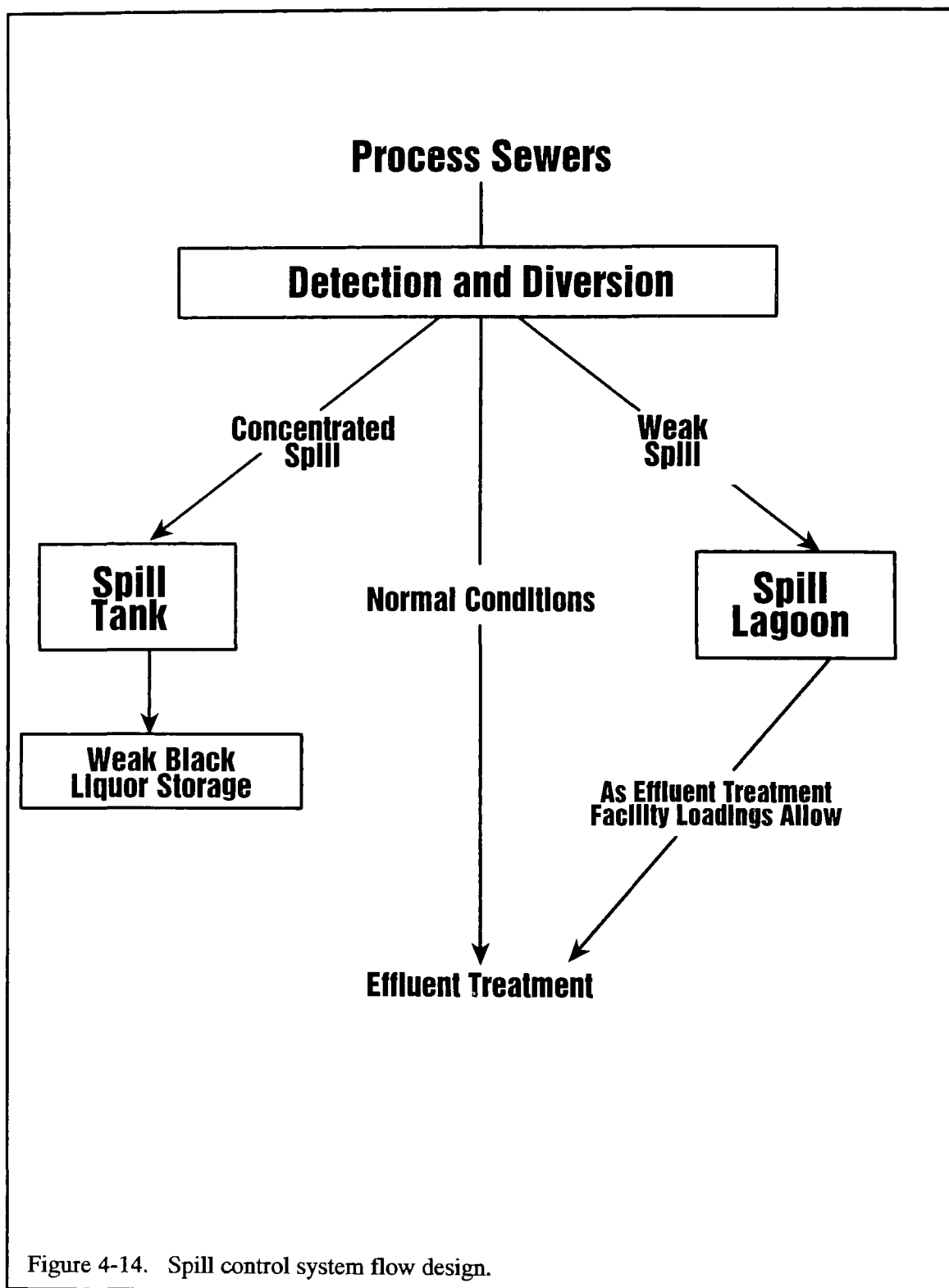


Figure 4-14. Spill control system flow design.

Source: Edde, 1984.

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.

4.6.1 Number of Installations

Improved spill control is now 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 often possible. Instrumentation to warn of spills and facilitate rapid implementation of corrective measures can normally be retrofitted relatively easily.

4.6.2 Costs and Economics

Costs for improving spill control are entirely site-specific, as they will depend more on the physical layout of the plant than on the particular process in use. No cost information has been collected. Capital costs are more likely to be in the range of hundreds of thousands rather than millions, 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.

4.6.3 Pollution Prevention Potential

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.

4.6.4 Impacts on Other Aspects of Mill Operations

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.

4.7 ENZYME TREATMENT OF PULP

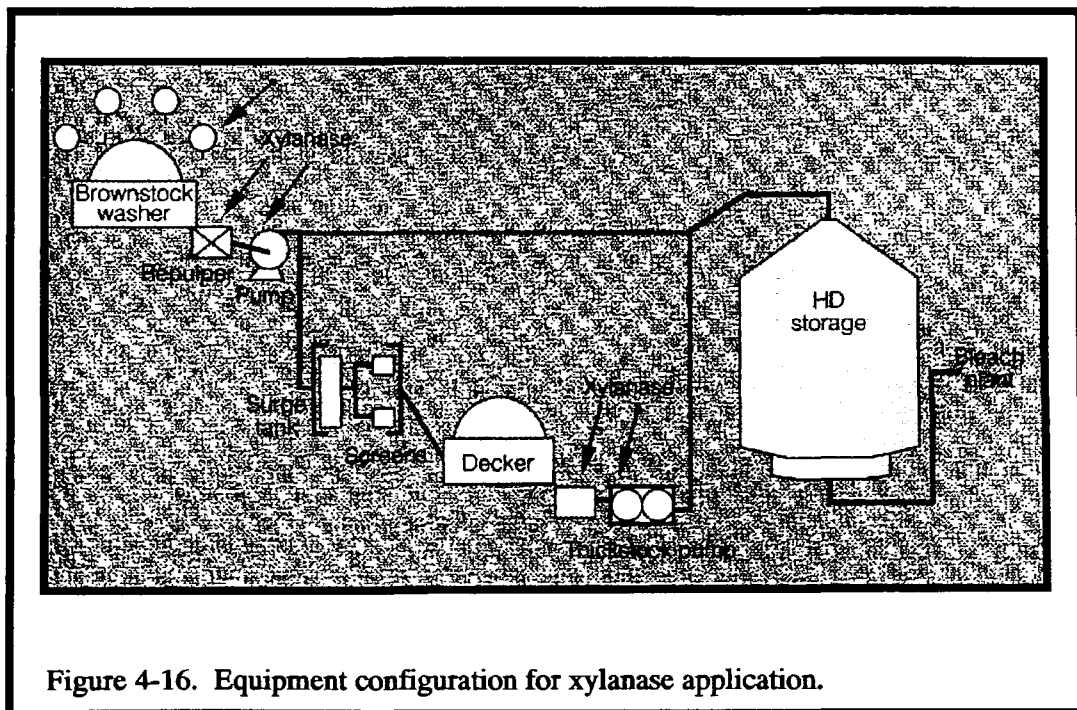
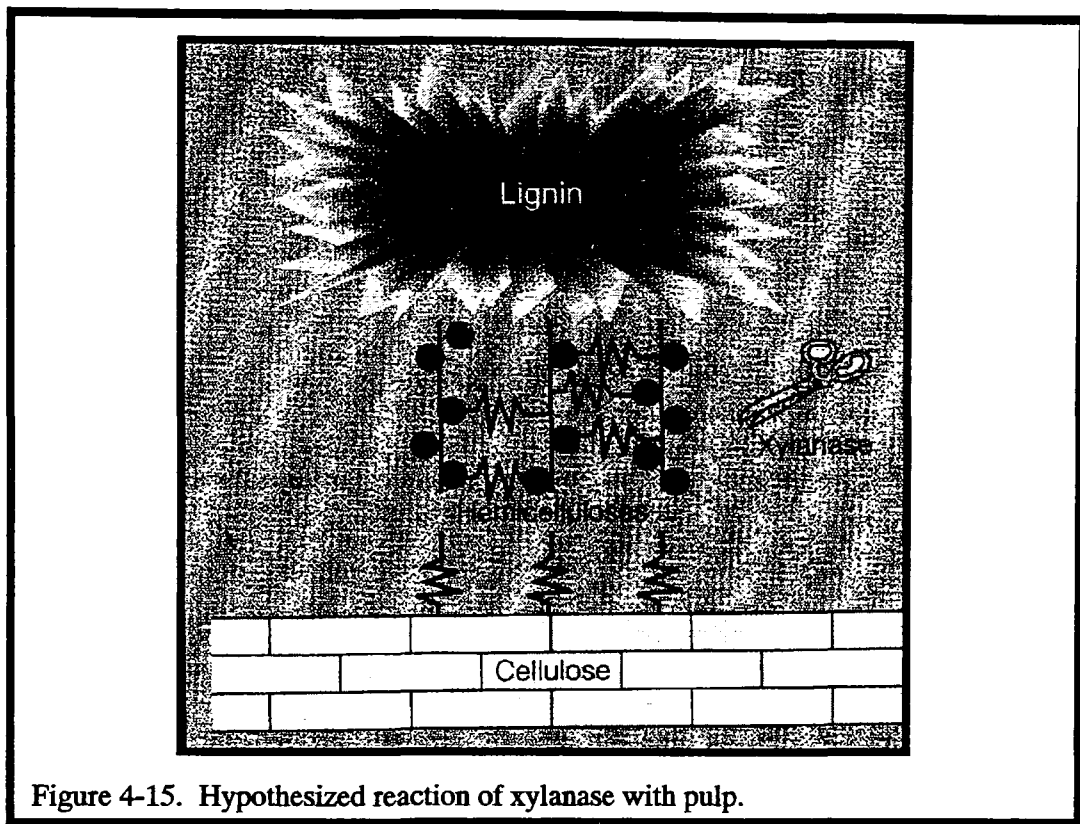
The potential for using cultured enzymes to assist in pulp bleaching has gained significant attention in the past few years. Research in the field of biotechnology has isolated specific, naturally-occurring microorganisms that produce enzymes capable of weakening the lignin bonds in pulp fibers, thereby providing a boost to delignification. Experimentation with these enzymes has accelerated recently and it is believed that numerous mills in North America and Scandinavia have been and are now running full-scale trials, some of which are sufficiently long to be considered as production campaigns.

The enzymes of most interest in pulp bleaching are the xylanases, which are secreted by wood-inhabiting microbes. There are numerous theories concerning how 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. Figure 4-15 shows the hypothesized reaction mechanism for xylanases. The xylan molecule “clips” the bonds of xylan within the long chain of the xylan molecule. This clipping is believed to disrupt the bonding between lignin and cellulose in pulps, thereby permitting easier attack of lignin by the pulping chemicals.

Xylanase application in the mill has proved to be relatively simple. Conditions favorable for xylan reaction with pulp include:

- pH between 4 and 6;
- temperatures of 40 to 55 °C;
- reaction times of between 30 and 180 minutes; and
- pulp consistency between 2.5 and 12 percent.

(Source: Farrell, 1992).



Source: Senior and Hamilton, 1992.

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 (see Figure 4-16). According to Senior and Hamilton (1992), the addition of a post-xylanase wash stage can significantly enhance the biobleaching effect, but this is not common practice.

Xylanase reaction appears to have no discernible impact on pulp quality or yield. In mill trials, vendors report reductions in active chlorine requirements of between 15 and 50 percent (Senior and Hamilton, 1992). Informal contacts indicate that actual reductions are nearer to the low end of these estimates. Figure 4-17 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 4-18. The reduction in demand for 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 (as at Aanekowski, Finland).

Xylanases suitable for use in mill bleaching trials 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.

4.7.1 Number of Installations

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, it would not be surprising to find large numbers of mills investing in small quantities of enzymes to carry out their own trials. Indications of the extent of interest in enzymes can be seen in the following observations:

- At the Nonchlorine Bleaching Conference in March 1992, mills in Canada and Finland were the only ones reporting use of enzymes in full-scale;

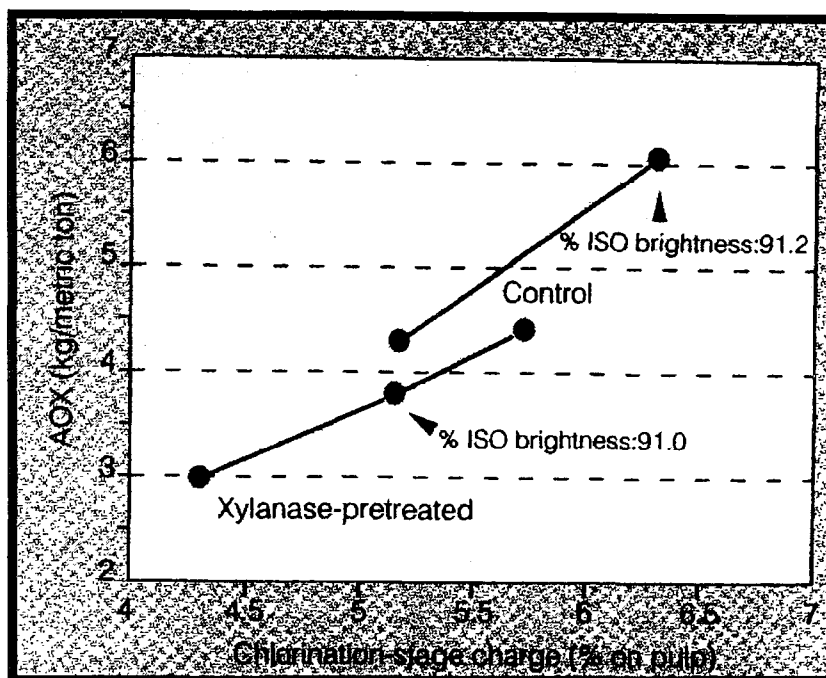


Figure 4-17. Impact of xylanase treatment on AOX.

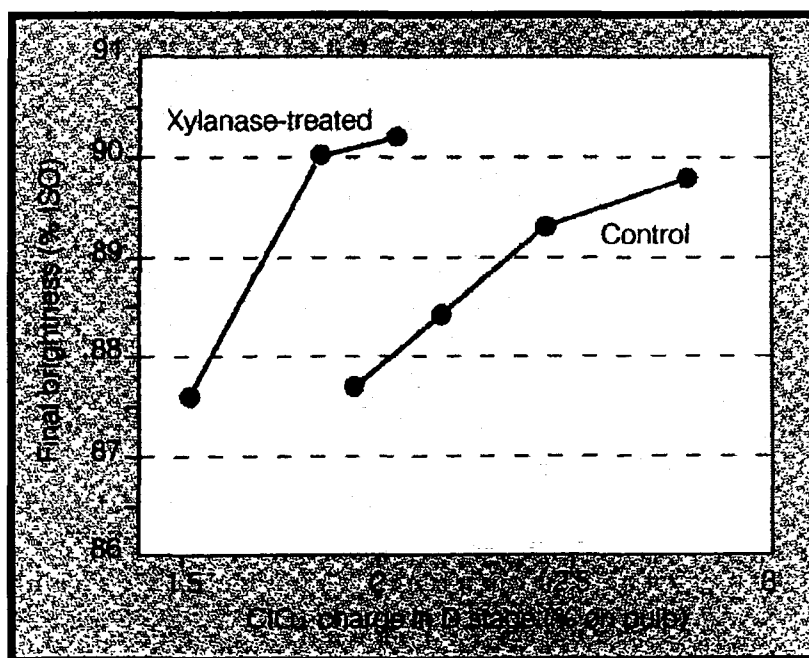


Figure 4-18. Impact of xylanase treatment on brightness.

Source: Senior and Hamilton, 1992.

- Juracek and Paice (1993) estimated in August, 1992 that 10 mills were using enzymes in full scale commercial application and that 85 mills were running trials. Six of the 10 mills running full time were in Europe and the other four were in Canada;
- In a paper published in September, Senior and Hamilton (1992) indicated that a “significant number” of mills in North America and Scandinavia are running enzyme trials;
- At the TAPPI Pulping Conference in November, 1992, industry observers suggested that there are more mills running full-scale trials than were prepared to disclose their process publicly.

Given that the biotechnology industry has only recently begun focussing on the pulp and paper industry, it is likely that enzyme applications will be improved in the future, further enhancing their attractiveness for mill usage. Thus, additional experimentation with enzymes and possible new uses can be expected.

4.7.2 Costs and Economics

The equipment necessary to apply enzymes to pulp is quite modest. Estimates of the costs for an enzyme delivery system and pH adjustment range from \$10,000 to \$100,000 (Juracek and Paice, 1993). 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 are probably appropriate, which will be partially or completely offset by savings in chemical costs.

So far, the potential for recycling enzymes has apparently not been investigated.²⁰ Enzymes are washed from the pulp and eventually are destroyed in the mill's normal recovery cycle. If a method was discovered to recycle enzymes, their cost of use might decrease, thereby enhancing their attractiveness.

Still another factor that would add to enzyme's appeal would be their ability to operate at closer to normal brownstock pH and temperature conditions. The necessity to lower the pH and temperature of the pulp before enzyme application imposes additional costs.

²⁰ Recovery of enzymes would have to take place in front of the mill's regular “recovery” process, which results in concentration and destruction of solids via incineration.

4.7.3 Pollution Prevention Potential

Enzymes are used primarily as a substitute brightening agent that permit the mill to cut back on the application of other, mostly chlorine-based bleaching chemicals. As a replacement for chlorine in the first bleaching stage, the effectiveness of enzymes in reducing formation of chlorinated organics will be approximately proportional to the percentage decrease in chlorine application that is possible.

4.7.3 Compatibility With Other Aspects of Mill Operations

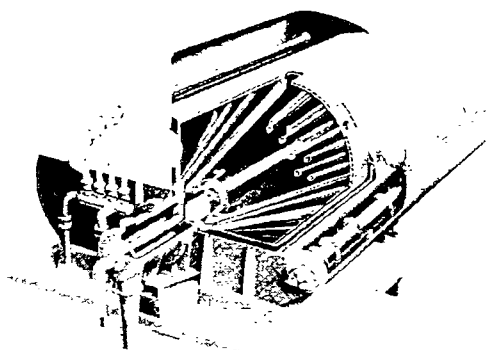
In enzyme trials held to date, no detrimental impacts on pulp quality, strength or other pulp characteristics have been found.

4.8 IMPROVED BROWNSTOCK WASHING

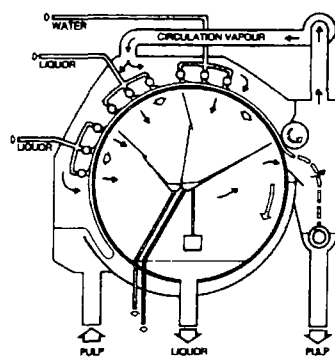
In recent years, substantial progress has been made in improving the efficiency of brownstock pulp washing systems. These advances have been aimed at reducing effluent flows, improving energy efficiency, and achieving better removal of dissolved lignin solids and spent liquor from the pulp. Since liquor solids carried over to the bleach plant will compete with lignin remaining in the pulp fibers for reaction, improved pulp washing can lower the consumption of bleaching chemicals and hence the formation of chlorinated organics. Efficient washing is also a prerequisite for successful operation of an oxygen delignification system.

Rotary vacuum washers represented the standard within the pulp industry until the 1980s, with approximately 5,000 units operating in North America (Nelson, 1992). These washing systems create a vacuum inside the drum to hold the fiber in place and draw the wash water through the pulp mat (see Figure 4-19). Normally, a series of three or four washers are configured in a wash line and operated in countercurrent fashion. This means that the filtrate from each washing stage is used as washwater for the previous (less clean) stage (see Figure 4-3).

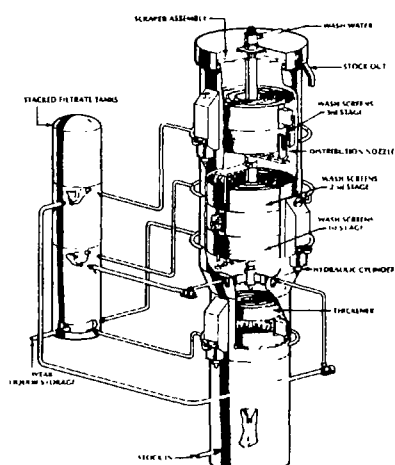
Current state-of-the-art washing systems may replace the vacuum pressure units with atmospheric or pressure diffusion washers, belt washers, or pulp presses (see Figure 4-19). Pressure washers apply external atmospheric pressure to the fiber mat. By removing the vacuum system from the inside of the



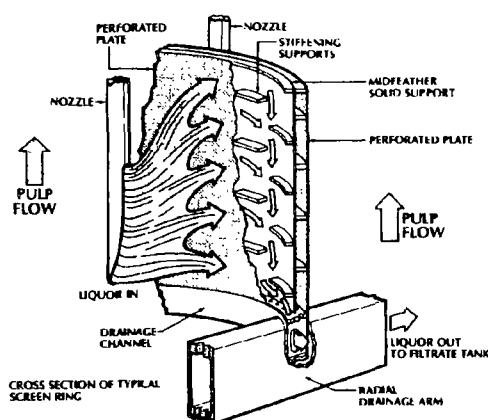
Single-stage vacuum washer



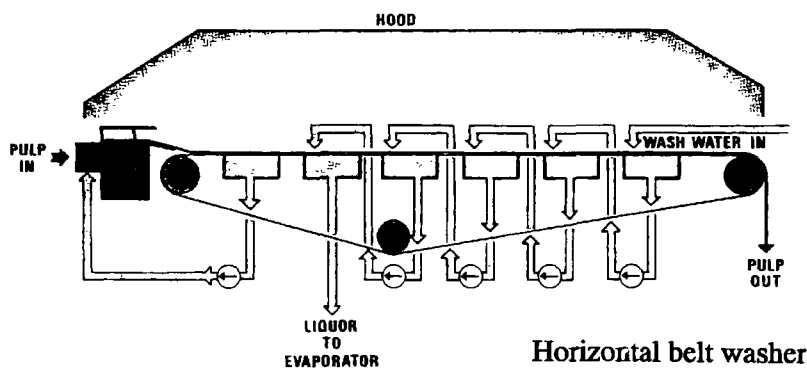
Pressure washer



Three-stage diffusion washer



Detail of diffusion washer



Horizontal belt washer

Figure 4-19. Alternative pulp washing equipment.

Source: Smook, 1982.

drum, the manufacturers can install a sophisticated filtrate collection and recirculation system. In diffusion systems, the washing takes place without dilution to low consistency, thereby avoiding the large flows of recycled filtrate required in the drum washing system. By avoiding free-falling liquid streams, diffusion washers also eliminate any problems with foaming and air entrapment. Belt washers pass the pulp under a series of showers (usually at least seven) with no mixing stages in between. These washing advances have been associated with reduced effluent flows, energy savings, and less foaming.

Improved lignin removal and energy efficiency is also being obtained through the application of sophisticated computer control systems and by improved attention to proper operation. Experiments using "neural networks" to determine the underlying relationships between washing variables such as mat density, mat consistency, and sodium loss, permitted additional fine tuning of washer operations that resulted in chemical and energy savings (Beaverstock and Wolchina, 1992).

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. According to one source, 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 (Ontario Ministry of the Environment, 1988). Since it is lignin solids, however, and not sodium that reacts with bleaching chemicals, it can be argued that sodium carryover reductions do not necessarily imply reduced bleaching demand. Stromberg (1990) showed that at the same sodium loss the dissolved organic solids loss (expressed as COD) varied by up to four times in different mills. For this reason, it is preferable to now measure washing efficiency using a COD reactivity test. Sodium losses, however, remain the principle design tool and are widely reported. The difference is minor in practice, since modifications that reduce sodium losses also reduce COD losses.

4.8.1 Number of Installations

The importance of efficient brownstock washing is now well-recognized throughout the North American pulp and paper industry. The extent to which the industry has adopted the various upgrade options 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.

4.8.2 Costs and Economics

Costs for improved washing could range from negligible in the case of relatively simple optimization of existing equipment to close to \$20 million to completely upgrade the wash 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).²¹ 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 4-20 and net incremental requirements compared to the existing 25-year old system are converted to dollar values in Table 4-21. 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, 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.

Due to their smaller size, pressurized diffusion washers are relatively easy to retrofit in an existing mill.

4.8.3 Pollution Prevention Potential

Improved pulp washing will reduce the amount of organic lignin solids carried through to the bleaching stages, thereby reducing the potential for formation of chlorinated organic compounds such as

²¹ 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 4-20

**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

Source: Ricketts (1991).

TABLE 4-21

**Annual Incremental Operating Costs Saved for
Three Modern Alternative Washing Systems - Hypothetical Mill Retrofit
(\$1,000)**

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 (1991).

dioxin and furan. Improvements in conventional pollutants such as BOD₅, COD, resin acids, and color can also be expected.

Researchers from Westvaco have published data that show the potential impacts of improved washing in the bleach plant on formation of 2,3,7,8-TCDD. In one set of mill trials, the brownstock wash volume was first increased above the normal rate and then decreased (Hise and Hintz, 1989). Results are shown in Table 4-22. With poor washing, C-stage pulp had a dioxin reading of 7.3 ppt while D₂-stage pulp had a reading of 9.3. When washing was improved (by increasing volume) C-stage pulp dioxin readings fell to 3.3 ppt and dioxin in D₂-stage pulp was non-detectable. It should be noted here, however, that the relative amounts of wash water used may not be a good predictor of the washing efficiency of state-of-the-art versus conventional washing systems.

The authors of the above study also measured the impact of surfactant use and ethanol wash during laboratory washing of pulp. Surfactants presumably could assist in the removal of reacted lignin solids, while ethanol is a more potent washing fluid. The results showed that surfactants reduced TCDD and TCDF levels in chlorination-stage pulp by 20 and 20 to 25 percent, respectively. Ethanol washing, further, reduced both TCDD and TCDF levels by approximately 80 percent. It seems unlikely that ethanol addition would be desirable, however, since it would add volatile components and BOD₅ to the effluent

Improved washing also removes highly colored material and some of the persistent, non-biodegradable black liquor fraction which would otherwise be discarded.

4.8.4 Impacts on Other Aspects of Mill Operations

Recovery Boiler Operations

As with other technologies that result in further removal of lignin solids from the pulp, upgraded brownstock washing increases the quantity of solids recovered from the condensed pulping effluent. These additional solids are processed in the recovery boiler, which recovers their heat value, instead of continuing to the bleach plant and eventually being discharged to the wastewater treatment system. The processing of these additional solids in the boiler may marginally impact air emissions and solid waste byproducts from the rest of the recovery process (grits and dregs).

TABLE 4-22

**Impacts of Improved Washing Practices on
Formation of Dioxin**

Bleaching stage	2,3,7,8-TCDD (ppt)	
	"Good" Washing	"Poor" Washing
C-Stage pulp	3.3	7.3
E-Stage pulp	2.1	6.3
D ₁ -Stage pulp	2.5	8.1
D ₂ -Stage pulp	ND (4.2)	9.3

ND non-detectable

Source: Hise and Hintz (1989).

Energy Requirements

According to available information, newer pressure washing systems are more energy efficient than previous types. The recovery of additional solids through the boiler will result in increases in boiler energy output.

Implementation of Further Pollution Prevention Technologies

Efficient brownstock washing is necessary to accomplish effective removal of solids prior to oxygen delignification, and is considered a prerequisite to introduction of an oxygen stage. Improved washing is also an essential part of the zero effluent mill proposed by Albert (1992).

4.9 CLOSED SCREEN ROOM

The term “closed screen room” refers to modification of the brownstock screening system to use only recycled unbleached white water from the decker as dilution water for the screeners and wash water for the washers. Complete closure of the screen room with little excess flow to sewer is difficult to achieve but will yield significant environmental benefits, including reduction of flow and loadings of BOD₅ and other pollutants.

Costs for closed screen room configuration in a new installation will range from \$10 to \$15 million. Costs in a retrofit situation will be site-specific.

4.10 MISCELLANEOUS PULPING TECHNOLOGIES

A number of additional technologies capable of reducing pollution generation in the pulping area are available and have been discussed to varying lengths in the literature. Those presented above currently represent the most promising and/or the most widely adopted options. The additional methods have in some cases been discussed for several years without making it into full-scale mill operation, or have seen only limited full-scale operations. Problems have been encountered in either scaling up the process from

lab-scale to pilot plant and full-scale operation, and for some facilities the economics have just not been favorable.

4.10.1 The Lignox Process

Lignox is a proprietary process developed by Eka Nobel in Sweden. The process involves a two-stage treatment of pulp, normally sandwiched between an oxygen delignification stage and a ClO_2 or non-chlorine bleaching sequence. The first stage, referred to as “X”, involves the application of the chelating agent EDTA to the pulp at a rate of about 2 kg per ton. This allows a specific profile of the trace metals contained in the pulp to be used in the application of the second “P” stage, which is an alkaline peroxide treatment. The process has shown the following results:

- When applied to a pulp with kappa 18, application of EDTA and peroxide at 25 kg per ton can produce 70 ISO brightness;
- When combined with extended cooking, a brightness of 75 ISO was attainable with peroxide charge of 30 kg per ton.
- Addition of ozone and an additional peroxide stage has been shown to produce a brightness of more than 85 ISO for softwoods and 89 ISO for hardwoods (Basta et al, 1992.)

The Swedish mill at Aspa utilizes the Lignox process to produce totally chlorine free (TCF) kraft pulp. The mill produces a paper with brightness of 70 to 75 ISO with good strength characteristics. The plant currently operates at full capacity at around 110,000 ADt/yr (Malinen, 1992.) Although other mills appear capable of incorporating the LIGNOX process in order to produce chlorine-free paper, the costs associated with the high peroxide application rates would tend to discourage it.

4.10.2 Solvent pulping

Three solvent-based kraft alternative pulping processes have been developed that avoid the use of sulfur-based chemicals. Because of this, they are characterized by low recovery costs. Two of these have been developed in Germany and one in North America.

Alcell® Pulping

The Alcell® process has been developed by Repap Enterprises (Valley Forge, PA). Alcell stands for alcohol-cellulose, and it uses an acidic water-alcohol mixture at 195 °C to solubilize and remove lignin from hardwood pulps. The process supposedly produces kraft-equivalent pulp with similar strength and optical properties (Harrison, 1991).

The simplified Alcell® recovery process reportedly makes the process viable at one-quarter the scale of a modern kraft mill. A methanol distillation tower replaces the recovery furnace, lime kiln, recausticizer, and other kraft recovery equipment. The three main steps in recovery are: 1) lignin precipitation (proprietary Alcell® technology), 2) methanol recovery, and 3) byproduct recovery.

The byproducts are an essential part of the economics of the process. They include Alcell® lignin, furfural, and a mix of hemicellulose sugars (Jamieson, 1991). Furfural is a commodity chemical that can be easily sold into existing markets for use in engineering plastics and other applications. The carbohydrate solution can be processed into a suitable supplement for animal feed. The mill must find markets for the lignin, however, that earn a credit above its value as hog fuel. Because the process lacks a recovery boiler, it is a heavy net energy consumer and the mill cannot afford to burn the lignin for energy. The lignin has properties different from other kraft lignins, namely the absence of sulfur or sodium, that make it interesting. While numerous uses for the lignin are being investigated, so far the uses are mostly experimental. The applications tried so far include: a replacement for phenol formaldehyde resin in building board manufacturing, a tackifying agent in rubber compounding, an additive for agrochemicals, and as a water reducer and plasticizer in concrete.

An Alcell® demonstration plant was started up in Newcastle, New Brunswick in 1989 to produce 15 tons per day at a cost of \$95 million. The success of this project prompted Repap to begin work on a full-scale, 300 tpd facility which is scheduled for startup in 1993 at the same Newcastle site. So far, this is the only pilot or full-scale installation to be built. The developers foresee opportunities in regions with small hardwood resources and for reopening small kraft or sulfite mills that have closed due to environmental or high cost reasons (Pye, 1990).

Organocell Pulping

Organocell has emerged in Germany as an alternative to kraft, which has never established itself as an industry in that country because of concerns over odor and safety. The process uses a soda-AQ-methanol liquor and currently is used only to produce fluff pulp (used as an absorbent in diapers, hygienic products, etc). The first full-scale application is at a converted sulfite mill in Kelheim, north of Munich. The mill currently produces 60,000 tpy of pulp from spruce chips generated by some 500 nearby sawmills, and will soon upgrade to 150,000 tpy capacity.

The organocell mill resembles a kraft mill but requires additional features to protect it from the dangers of methanol cooking. These include thicker digester walls to withstand the high pressure of the methanol vapor (Fleming, 1993). It includes a full recovery furnace plus a methanol recovery unit. Explosion-proof electrical equipment will also be necessary.

Fleming (1993) suggests that capital costs for a greenfield organocell mill will be similar to kraft, but that operating costs will be higher, in part due to the use of AQ at a cost of some \$17 per ton.

Alkaline Sulfite Anthraquinone Methanol (ASAM)

ASAM pulping is a low-alkalinity process developed at Heidelberg University. The process is reported to be capable of producing higher-strength pulps than kraft with good bleachability and at somewhat higher yields. Although classified as a solvent pulping method, it is not typical in that methanol is used as an additive only. The delignification is performed using a mixture of sodium hydroxide, sodium carbonate, sodium sulfate, AQ, and methanol.

ASAM has a liquor recovery cycle similar to kraft pulping with three separate loops to recover methanol, caustic, and sodium sulfite. The capital costs are expected to be about 10 to 20 percent higher than for kraft. Operating costs will also be higher; the AQ requirements alone amount to about \$17 per ton (Fleming, 1993).

So far, the only pilot plant in operation is a 5 tpd mill in southern Germany.

4.10.3 Polysulfide Cooking

The beneficial impacts of polysulfides on the kraft cooking process have been known for some time. These include the ability to increase yield at the same kappa number or to obtain the same yield at a lower kappa number. Polysulfides accomplish this by stabilizing the end groups of cellulose and hemicellulose polymer chains against “peeling” reactions (Smook, 1989.) In terms of environmental benefits, the key impact is a reduction in the thermal value of black liquor solids. This reduction means that an increased boiler load, such as that resulting from oxygen delignification or extended cooking, can be accommodated.

Until recently, it was necessary to inject cooking liquor with sulfite to obtain polysulfides. This technique increases the sulfidity of the liquor, however, and causes an increase in air emissions. Patented processes have now been developed that can partially oxidize the kraft white liquor. The oxidation converts sulfides in the liquor to polysulfides without the detrimental effect on air pollutants. The thermal load decrease is reported to be in the neighborhood of 6 percent, which should be sufficient to offset the extra solids load obtained with oxygen delignification.

Polysulfide liquor (known as orange liquor) is produced in an oxidation unit installed between the white liquor storage and the kraft digester. A patented catalyst used in the oxidization reactor is responsible for the white liquor oxidation (Lightfoot, 1990).

Polysulfide cooking has also been used in combination with anthraquinone (AQ) catalysis, where synergistic effects have been noted (Lightfoot, 1990). As shown in Section 4.5, AQ addition by itself can also improve the yield of the kraft cooking process. In combination with polysulfide cooking, however, the yield improvements are more than additive. Lightfoot cites data from the Shirakawa mill in Japan which indicate that polysulfide and AQ addition individually had increased yield by 1.1 percent. In combination, however, an increase of 3.1 percent was recorded.

Although the technology that has been available for several decades, polysulfide cooking has been viewed by the industry as unusable because the process has been associated with losses in strength. Researchers recently showed that when polysulfide cooking is combined with extended modified cooking, pulp yield and strength properties can be improved simultaneously. When compared with bleachable

conventional kraft pulps, the pulp combining extended delignification and polysulfide cooking produced a comparable property in terms of strength, kappa number and yield (Jiang, 1992.)

As of 1990, the polysulfide process developed by Mitsubishi and the Chiyoda Corporation was installed at 6 mills. Four of these were in Japan, and one each was located in Norway and Austria (EPA, 1990a). Installation data for the process developed by Mead Corporation (MOXY process) was not available. Estimates of capital costs for installation of the Chiyoda polysulfide system are shown in Table 4-23.

4.10.4 Demethylation

Demethylation of pulp has been shown in the laboratory to increase the number of reaction sites where delignification can take place (Pryke, 1985). If a commercial system could be implemented, a significant increase in the amount of delignification occurring prior to chlorination may be feasible. Demethylation followed by a treatment with 2 percent H_2O_2 on pulp produced a pulp with kappa number 7.5.

The demethylation process has been conducted by treating pulp with a solution of potassium thiophenoxide in diethylene glycol at 200°C. Due to the complexity and extreme conditions under which the demethylation reaction has been induced, however, no commercial process has been developed so far.

TABLE 4-23**Capital Costs for Chiyoda Polysulfide Process**

Mill Size (ADT/day)	Cost (\$millions)
500	1.28
750	1.89
1,000	2.23

Source: Chiyoda Corporation; cited in EPA (1990a).

SECTION FOUR REFERENCES

- Albert, 1992. Richard J. Albert. "The Effluent-Free Kraft Pulp Mill Technical and Economic Considerations," Proceedings, *1992 TAPPI Pulping Conference*, Boston, MA, November 1992.
- Anderson, 1992. Ross Anderson. "Peroxide Delignification and Bleaching," Proceedings, *Non-Chlorine Bleaching Conference*, Hilton Head SC, March 1992. Available from Miller-Freeman Publications, San Francisco.
- API, 1992. American Paper Institute. *1992 Statistics of Paper, Paperboard, & Wood Pulp*. New York.
- Bansal, 1987. Ravinder K. Bansal. "On-Site Pressure Swing Adsorption Systems for the Pulp and Paper Industry," Proceedings, *1987 TAPPI Oxygen Delignification Conference*, p. 151.
- Basta et al., 1992. J. Basta, L. Anderson, W. Hermansson. "LIGNOX and Complementary Combinations," Proceedings, *Non-Chlorine Bleaching Conference*, Hilton Head SC, March 1992. Available from Miller-Freeman Publications, San Francisco.
- Bauerlin et al., 1991. C.R. Bauerlin, M.H. Kirby, G. Berndt. "Vacuum Pressure Swing Adsorption Oxygen for Oxygen Delignification," *TAPPI Journal*, May 1991, p. 85.
- Beaverstock and Wolchina, 1992. Malcolm Beaverstock and Kenneth Wolchina. "Neural Network Helps G-P Ashdown Mill Improve Brownstock Washer Operation," *Pulp and Paper*, September 1992, p. 134.
- Beloit Corp., 1990. Cited in U.S. EPA, *Summary of Technologies for the Control and Reduction of Chlorinated Organics From the Bleached Chemical Pulping Subcategories of the Pulp and Paper Industry*. U.S. EPA, Office of Water Regulations and Standards. Office of Water Enforcement and Permits. April 27, 1990.
- Berry et al., 1991. R.M. Berry, C.E. Luthe, R.H. Voss, P.E. Wrist, P. Axegård, G. Gellerstedt, P.O. Lindblad, and I. Popke. "The Effects of Recent Changes in Bleached Softwood Kraft Mill Technology on Organochlorine Emissions an International Perspective," Proceedings, *CPPA Spring Conference*, Whistler, B.C., May 1991.
- Blain, 1992. T.J. Blain. "Anthraquinone Pulping: Fifteen Years Later," Proceedings, *1992 TAPPI Pulping Conference*, November 1992, Boston, MA.
- Boström and Hillström, 1992. "Status report from the Chemrec recovery booster at Frövifors," Proceedings, *1992 International Chemical Recovery Conference*, CPPA, Seattle, WA.
- Brenner and Pulliam, 1992. Lee Brenner and Terry Pulliam. "A Comprehensive Impact Analysis of Future Environmentally Driven Pulping and Bleaching Technologies," Proceedings, *1992 TAPPI Pulping Conference*, Boston, MA, November 1992.

SECTION FOUR REFERENCES (cont.)

- Byrd and Knoernschild, 1992. Medwick V. Byrd and Kevin J. Knoernschild, "Design Considerations for an Ozone Bleaching System," *TAPPI Journal*, May 1992, p. 101.
- Clement, 1993. John L. Clement. "Recovery Boiler Capability to Accommodate Alternative Kraft Mill Processes," Proceedings, *International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper*, August 18-20, 1992, Washington, DC. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. EPA-744R-93-002. February 1993.
- Deal et al., 1991. Richard Deal, Richard Hendrickson, William Lewis. "Onsite Oxygen Plants Can Reduce Pulp Mill Costs for Volume Users," *Pulp and Paper*, September 1991, p. 141.
- Deal, 1991. Howard Deal. "Environmental Pressure Causes Changes in Bleaching Technologies, Chemicals," *Pulp and Paper*, November 1991, p. 110.
- Elliot, 1989. R.G. Elliot. "Experience with Modified Continuous Cooking," presented at University of Washington, Pulp and Paper Foundation Annual Meeting, May 23-24, 1989.
- Farrell, 1992. Roberta L. Farrell. "Status of Enzyme Bleaching R&D and Mill Work," Proceedings *Nonchlorine Bleaching Conference*, Hilton Head SC, March 1992. Available from Miller-Freeman Publications, San Francisco.
- Ferguson, 1992b. Kelly Ferguson. "Union Camp Begins Ozone Era with New Kraft Bleaching Line at Franklin, VA," *Pulp and Paper*, November 1992, p. 42.
- Ferguson, 1992a. Kelly Ferguson. "P&W Starts Up Alabama Pine Pulp Mill with Plans to Produce 430,000+ tpy," *Pulp and Paper*, March, 1992. p. 71.
- Fleming, 1993. Bruce I. Fleming. "Alternative and Emerging Non-Kraft Pulping Technologies," Proceedings, *International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper*, August 18-20, 1992, Washington, DC. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. EPA-744R-93-002. February 1993.
- Galloway et al, 1989. L.R. Galloway, P.I. Helminen, D.N. Carter. "Industry's Effluent Problems Spawn New Engineering Technology and Design," *Pulp & Paper*, September 1989, p. 91.
- Götaverken, 1993. "Recovery Boiler Bottleneck Eliminated at Frövifors Mill," *TAPPI Journal*, Supplier Update, March, 1993, p. 249.
- Gullichsen, 1991. Johan E. Gullichsen. "Means to Reduce Effluent Pollution of Kraft Mills," Proceedings *1991 TAPPI Environmental Conference*, San Antonio, Texas, Book 1 pp 185-190. TAPPI Press, Atlanta, GA.
- Harrison, 1991. Andy Harrison. "Repap Produces High-Quality Pulp at Newcastle with Alcell Process," *Pulp and Paper*, February 1991, p. 116.

SECTION FOUR REFERENCES (cont.)

- Hartler, 1978. Nils Hartler, "Extended Delignification in Kraft Cooking A New Concept," *Svensk Papperstidning*, 81(15), (October 25, 1978), p 483.
- Heimbürger et al., 1988a. Stanley A. Heimbürger, Daniel S. Blevins, Joseph H. Bostwick, and G. Paul Donnini, "Kraft Mill Bleach Plant Effluents: Recent Developments Aimed at Decreasing Their Environmental Impact, Part 1," *TAPPI Journal*, October 1988, p. 51.
- Hise and Hintz, 1989. Ronnie G. Hise and Harold L. Hintz. "Effect of Brownstock Washing on Formation of Chlorinated Dioxins and Furans During Bleaching," *Proceedings, 1989 TAPPI Pulping Conference*.
- Idner, 1988. Kristina Idner. "Oxygen Bleaching of Kraft Pulp: High Consistency vs. Medium Consistency," *TAPPI Journal*, February, 1988, p.47.
- Jamieson, 1991. Scott Jamieson. "Alcell Pulping: World Class Research Right Here in Canada," *Pulp and Paper Canada*, 92:3 (1991), p. 16.
- Jiang, 1992. Jian Er Jiang. "Extended Modified Cooking With Polysulfide For Simultaneous Pulp Yield and Strength Improvement," *Proceedings, 1992 TAPPI Pulping Conference*, Boston MA, November 1992, p.683
- Johnson, 1992. Anthony P. Johnson. "Worldwide Survey of Oxygen Bleach Plants," *Proceedings, Nonchlorine Bleaching Conference*, Hilton Head, SC March 1992. Available from Miller-Freeman Publications, San Francisco.
- Johnson, 1993. Anthony P. Johnson. "Oxygen Delignification Systems Flourish as Mills Push for Lower Kappa Number," *Pulp & Paper*, March, 1993, p. 103.
- Jurasek and Paice, 1993. Lubomir Juracek and Michael Paice. "Saving Bleaching Chemicals and Minimizing Pollution with Xylanase," *Proceedings, International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper*, August 18-20, 1992, Washington, DC. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. EPA-744R-93-002. February 1993.
- Kamyr, Inc., 1990. Cited in U.S. EPA, *Summary of Technologies for the Control and Reduction of Chlorinated Organics From the Bleached Chemical Pulping Subcategories of the Pulp and Paper Industry*. U.S. EPA, Office of Water Regulations and Standards. Office of Water Enforcement and Permits. April 27, 1990.
- Kumar et al., 1992. Kumar, K., H.-m. Chang, H. Jameel, N.H. Shin. "Elemental Chlorine-Free (ECF) and Total Chlorine-Free (TCF) Bleaching of RDH Hardwoods," *Proceedings, 1992 TAPPI Pulping Conference*, November 1-5, Boston, MA. p. 169.

SECTION FOUR REFERENCES (cont.)

- Liebergott et al., 1992a. Norman Liebergott, Barbara van Lierop, Anastasios Skothos. "A Survey of the Use of Ozone in Bleaching Pulps, Part 2," *TAPPI Journal*, February 1992, p. 117.
- Liebergott et al., 1992b. Norman Liebergott, Barbara van Lierop, Anastasios Skothos. "The Use of Ozone in Bleaching Pulps," Proceedings, *1992 TAPPI Environmental Conference*, Richmond VA, April 1992.
- Lightfoot, 1990. W.E. Lightfoot. "New Catalyst Improves Polysulfide Liquor Makeup, O₂ Delignification," *Pulp and Paper*, January 1990, p. 88.
- Macleod, 1992. Martin Macleod. "Extended Cooking in the Mills," Proceedings, *Nonchlorine Bleaching Conference*, Hilton Head, SC, March 1992. Available from Miller-Freeman Publications, San Francisco.
- Malinen, 1992. Raimo Malinen. "Chlorine-Free Bleaching: State of the Art in Scandinavia," Proceedings, *Non-Chlorine Bleaching Conference*, Hilton Head SC, March 1992. Available from Miller-Freeman Publications, San Francisco.
- McCubbin et al., 1991. Neil McCubbin, Howard Edde, Ed Barnes, Jens Folke, Eva Bergman, Dennis Owen. "Best Available Technology for the Ontario Pulp and Paper Industry," Rep. ISBN 7729-9261-4, Ontario Ministry of the Environment, Toronto, Ontario.
- McCubbin, 1992. Memorandum from Neil McCubbin to ERG concerning extended cooking. November 18, 1992.
- McCubbin, 1993. Neil McCubbin. "Costs and Benefits of Various Pollution Prevention Technologies in the Kraft Pulp Industry," Proceedings, *International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper*, August 18-20, 1992, Washington, DC. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. EPA-744R-93-002. February 1993.
- McDonough, 1986. Thomas J. McDonough. "Oxygen Bleaching Practices," *TAPPI Journal*, June 1986, p. 46.
- Miller, 1992. Bill Miller. "Tutorial: Process Technology, Machinery, Advantages & Disadvantages," Proceedings, *Nonchlorine Bleaching Conference*, Hilton Head SC, March 1992. Available from Miller-Freeman Publications, San Francisco.
- Nelson, 1992. Phil Nelson. "Mills Improve Pulp Washer Performance with New Rotary Vacuum Filter Design," *Pulp and Paper*, November 1992, p. 101.
- Norden et al., 1992. Norden, S., M. Dahl and R. Reeves. "Bleaching of Extremely Low Kappa Southern Pine, Cooked by the SuperBatch Process," Proceedings, *1992 TAPPI Pulping Conference*, November 1-5, Boston, MA. p. 159.

SECTION FOUR REFERENCES (cont.)

- Nutt et al., 1992. . "Development of an Ozone Bleaching Process," Proceedings, *1992 TAPPI Pulping Conference*, Boston, MA November 1992.
- Nutt et al., 1993. W. E. Nutt, B.F. Griggs, S.W. Eachus, M.A. Pikulin. "Developing an Ozone Bleaching Process," *TAPPI Journal*, March, 1993, p. 115.
- Ontario Ministry of the Environment, 1988. *Kraft Mill Effluents in Ontario*. Municipal-Industrial Strategy for Abatement. March 1988.
- Paper Age* (1990). no author. March, 1990, p. 23.
- Phillips et al., 1993. Richard B. Phillips, Lindsay M. Lancaster, Jean J. Renard, Caifang Yin. "The Effects of Alternative Pulping and Bleaching Processes on Product Performance - Economic and Environmental Considerations," Proceedings, *International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper*, August 18-20, 1992, Washington, DC. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. EPA-744R-93-002. February 1993.
- Pye, 1990. E. Kendall Pye. "The Alcell Process A Proven Alternative to Kraft Pulping," Proceedings, *1990 TAPPI Pulping Conference*, p. 991.
- Reeve, 1990. Douglas W. Reeve. "Chlorine Dioxide Delignification Process Variables," Proceedings, *1990 TAPPI Pulping Conference*, p. 837.
- Ricketts, 1992. Drew Ricketts. "Three BSW Systems Studied to Find Best Fit for Mill Upgrade Project," *Pulp and Paper*, September 1991, p. 94.
- Senior and Hamilton, 1992. David Senior and Janice Hamilton. "Biobleaching with Xylanases Brings Biotechnology to Reality," *Pulp and Paper*, September 1992, p. 111.
- Shackford, 1992. Lewis Shackford. "Commercial Implementation of Ozone Bleaching Technology," Proceedings, *Nonchlorine Bleaching Conference*, Hilton Head, SC March 1992. Available from Miller-Freeman Publications, San Francisco.
- Shin et al. 1990. N.H. Shin, M. Sundaram, H. Jameel, H. Chang. "Bleaching of Softwood RDH Pulps With Low/No Chlorine Bleaching Sequences," Proceedings, *1990 TAPPI Environmental Conference*, p. 549.
- Singh, 1982. Rudra P. Singh. "Ozone Replaces Chlorine in the First Bleaching Stage Advances in Ozone Bleaching, Part 1," *TAPPI Journal*, February 1982.
- Smook, 1982. Gary A. Smook. *Handbook for Pulp and Paper Technologists*. (TAPPI/CPPA, Atlanta/Montreal).

SECTION FOUR REFERENCES (cont.)

- SRI International, 1988. Stanford Research Institute. *Chemical Economics Handbook Marketing Research Report: Air Separation Gases*.
- Stromberg, 1990. Bertil Stromberg, "Washing for Low Bleach Chemical Consumption," Proceedings, *1990 TAPPI Pulping Conference*, p. 883.
- Stromberg, 1993. Bertil Stromberg. "Low Kappa Continuous Cooking," Proceedings, *International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper*, August 18-20, 1992, Washington, DC. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. EPA-744R-93-002. February 1993.
- Tench and Harper, 1987. Larry Tench and Stuart Harper. "Oxygen Bleaching Practices and Benefits An Overview," Proceedings, *1987 TAPPI International Oxygen Delignification Conference*, p. 1.
- van Lierop and Brown, 1987. Barbara van Lierop and Gordon Brown. "Varying the Purity of Oxygen Gas Used in Oxygen Delignification and Oxidative Extraction Stages," Proceedings, *1987 TAPPI International Oxygen Delignification Conference*, p. 133. TAPPI Press, Atlanta.
- Whitley, et al., 1990. D.L. Whitley, J.R. Zierdt, D.J. Lebel. "Mill Experiences with Conversion of a Kamyr Digester to Modified Continuous Cooking," *TAPPI Journal*, January 1990, pp. 103-108.

SECTION FIVE**POLLUTION PREVENTION TECHNOLOGIES IN BLEACHING OPERATIONS**

This section examines 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.

Most of the technologies discussed in this section are aimed at reducing dioxin, AOX, and chloroform. With the exception of chlorine dioxide substitution, they all result in greater recycling of wood organics and associated chemicals through the recovery boiler. Their impact on reducing most chlorinated and unchlorinated pollutants is roughly proportional to the reductions in elemental chlorine usage that they facilitate.

This section begins with a discussion of conventional kraft mill bleaching practices in Section 5.1. Section 5.2 discusses high chlorine dioxide substitution as a means of reducing pollution, and Section 5.3 examines split addition of chlorine. Sections 5.4 and 5.5 provide information on oxygen and peroxide reinforcement of the alkaline extraction stages, respectively.

5.1 CONVENTIONAL KRAFT PULP BLEACHING

Bleaching is a process that lightens or whitens the cellulose fibers in the pulp through chemical actions. The bleaching action can involve either oxidative or reductive processes (or both) that increase the solubility of color bodies in the pulp, making them easier to remove. The bleaching of pulp is usually performed with two interrelated objectives: (1) whitening the fibers, which makes them more suitable for printing and other applications; and (2) increasing the permanence of the whiteness (to avoid yellowing or aging of final products).^{1,2} The ease with which pulp can be bleached depends on the amount of lignin that remains in the fibers following pulping. As indicated above, chemical pulping removes up to 90

¹ Bleaching chemicals and conditions may also be controlled in order to influence pulp properties such as absorbency and porosity.

² Bleaching is also used to remove dirt from the pulp, to the extent that dirt is in the form of uncooked fiber bundles (or "shives") that are harder to bleach. (Bleaching does not effectively remove carbon-based dirt particles.) In conventional pulping and bleaching, it has often been necessary to add excess chemicals in order to eliminate shives. One advantage of the newer technologies such as extended cooking and oxygen delignification is that shives are greatly reduced.

percent of the lignin present in the wood chips. Chemical bleaching applies progressively more selective agents in an effort to remove more and more of the remaining lignin fractions without further damaging the cellulose.

If the cooking reaction is extended in an effort to remove additional lignin, damage will result to the cellulose portions of the fiber, causing sharp decreases in pulp yield and paper strength characteristics. For this reason, the chemical cook is closely controlled so as to achieve the lowest possible kappa number (lignin content) while holding yield losses to an acceptable level.

The pulp kappa number is used as the primary control parameter up until the point where the pulp leaves the brownstock washers. After the pulp enters the bleaching stage, however, attention turns to measures of pulp brightness. Brightness is a measure of the amount of light reflected from the pulp. A number of specific brightness measurements are available, all of which measure the proportion of incident light that is reflected from the pulp. For example, a reading of 0 indicates that all incoming light is completely absorbed by the pulp, while a reading of 100 indicates perfect reflectance.³ Unbleached kraft pulp (brownstock) registers brightness readings in the range of 15 to 30 percent. The sulfite process produces pulps with a brightness in the range of 50 to 65 percent. For printing purposes, most pulps are bleached to a brightness level ranging from about 70 percent, which is somewhat creamy in appearance, to "full brightness" or maximum levels of between 88 and 94 percent.

Traditionally, mills that produce market pulp (i.e., pulp sold to other mills for papermaking) have had to meet high brightness standards based on the requirements of pulp buyers. It is not clear, however, to what extent market pulp bleached to lower brightness levels would be accepted. Brightness standards for market pulp are higher, for instance than most integrated mills require for their own paper products. Many integrated mills reportedly use pulp bleached to a level of 80 to 88 percent (depending on the source).

³ At least three different measurement techniques are in use around the world. Along with the regions where they are most widely used, these are: GE brightness (U.S.); Elephro brightness (Canada); and ISO brightness (Scandinavia). Throughout most of this report, brightness is reported using ISO measures, (most often used in the technical literature) unless otherwise indicated. All three are measured in a similar fashion, and there is usually little more than a single point difference between them on a scale of 0-100. As a general rule, the following applies: 92 GE = 91 Elephro = 90 ISO.

Pulp bleaching is performed using a variety of chemicals and process conditions in a series of stages known collectively as the bleaching sequence. Table 5-1 lists the common bleaching stages and the conditions under which they are carried out. The shorthand abbreviations are used universally in the industry to describe the bleaching sequence. For example, C represents a bleaching stage using elemental chlorine, E is an extraction stage using caustic, and so on.

Successive stages are needed in the bleaching sequence to break down and remove lignin that remains in the pulp following cooking, screening, and washing. Bonds between lignin and fiber are first broken in the bleaching stages through the use of chemicals such as elemental chlorine or chlorine dioxide. Then, in the extraction stage, the lignin is solubilized in caustic (sodium hydroxide) to facilitate its removal, and washed from the pulp. It is the removal of lignin that causes the loss of color, or pulp brightening. In the papermaking stages, additives such as titanium dioxide are used to make paper appear still whiter.

Bleaching chemicals are distinguished by the nature of their chemical activity and by their selectivity, i.e., their capacity to attack lignin while doing minimal damage to the cellulose fibers. Typically, early stages in a bleaching sequence are designed to dissolve and then extract the bulk of the lignin present in the brownstock. Because lignin concentrations in these stages are high, relatively non-specific chemicals like chlorine can be used without causing significant damage to the pulp. During later bleaching stages, when residual lignin concentrations are lower, more selective chemicals must be used. The emphasis then shifts from removal of lignin to brightening of the small remaining amount of lignin. Lignin removal and brightening stages are almost always separated by extraction stages, in which alkaline chemicals are used to solubilize and facilitate removal of the lignin from the pulp. The E₁ or first extraction stage is almost as important as the first chlorination stage. After chlorination and washing (but prior to extraction), approximately 30 to 50 percent of the chlorinated lignin is removed. Following extraction, a full 80 to 90 percent of the lignin will have been removed.

Common bleaching sequences used to attain full brightness on softwood kraft pulp include CEDED, CEHDED, or OCEDED. The first two of these begin with a chlorination stage. Chlorine is an aggressive oxidant, and is traditionally used in the first stage to dissolve as much of the residual lignin as possible. Chlorination is followed by alkaline extraction using caustic (NaOH). This neutralizes the pulp and facilitates removal of the dissolved lignin solids during washing. The first sequence finishes with a chlorine dioxide (ClO₂) bleaching/brightening stage, followed by alkaline extraction, and a final

TABLE 5-1

Summary of Bleaching Chemicals

Chemical Sequence	Shorthand	Symbol	Form	Process Conditions	Notes
Chlorine	C	Cl ₂	Gas dissolved in water, 2-5% chlorine on pulp	pH: 2 or lower Temp: 15-30 C	Effective, economical delignification. Can cause loss of pulp strength if used improperly.
Chlorine dioxide	D	ClO ₂	7 to 10 g/l ClO ₂ solution in water	pH: 3.5-5 Temp: 60-80 C	High brightness without pulp degradation. Must be made at mill site.
Alkaline extraction with sodium hydroxide	E	NaOH	5 to 10% NaOH solution	pH: 10-11 Temp: 60-80 C	Dissolves and removes reaction products from chlorination. Darkens pulp.
Hypochlorite (sodium or calcium)	H	NaOCl or Ca(OCl) ₂	approx. 40 g/l solution	pH: 11 (must be buffered due to release of HCl) Temp: 20-60 C	Easy to make and use. Generated onsite from chlorine and caustic. Can cause loss of pulp strength if used improperly. Linked to formation of chloroform.
Peroxide	P	H ₂ O ₂ or Na ₂ O ₂	2 to 5% solution	pH 10.5 Temp: 70-80 C	Easy to use. Low capital cost, but high chemical cost.
Hypochlorous acid	L	HClO	solution		Unstable
Nitrogen dioxide	N	NO ₂			Rarely used.
Hydrosulfite (sodium or zinc)	Y	Na ₂ S ₂ O ₄ or ZnS ₂ O ₄	solution or solid		Not commonly used.
Ozone	Z	O ₃	gas	pH 1.0 - 2.0	Acid conditions
Oxygen	O	O ₂	gas (for bleaching)	Temp: 90-120 C	Alkaline conditions
Mixtures of chlorine and chlorine dioxide (subscript indicates lower quantity chemical)	D _c or C _D	Cl & ClO ₂			Low cost, but used in large quantities. Equipment expensive.
Sequential addition of chlorine and chlorine dioxide	D-C or C-D	Cl & ClO ₂	solution		
Alkaline extraction reinforced with oxygen (O), sodium hypochlorite (H), or hydrogen peroxide (P)	E _O , E _H , E _P	NaOH & O ₂ , NaXX, or H ₂ O ₂	NaOH solution, reinforced with approx. 10 lbs O ₂ /ton pulp		addition of oxygen to the extraction stage to achieve further reductions in lignin

Source: Reeve (1987); OTA (1989).

bleaching/brightening with chlorine dioxide. In the second sequence (CEHDED), an alkaline hypochlorite stage is added following the first extraction stage; hypochlorite both brightens and solubilizes residual lignin. In the third example (OCEDED), the pulp is “prebleached” with oxygen before undergoing the traditional five stage chlorination-extraction process. As discussed above in Section 4.3, an oxygen delignification stage can reduce the kappa number of the pulp entering the chlorination stage, thereby reducing the amount of chlorine subsequently required.

The number of bleaching stages affects both the final brightness and the ability to consistently control final brightness levels. A five stage CEDED bleaching sequence, for example, can bleach a given pulp to a higher final brightness level, as well as ensure greater brightness consistency and stability, in comparison with a CEH process.

Table 5-2 shows the most common bleaching sequences at U.S. pulp mills, based upon the results of a 1990 EPA census. The most common sequences include CDE_OD , $DCDE_{OP}D$, $DCE_{OP}D$, CEDED, and CEH, although there are as many as 90 additional unique sequences in use at smaller numbers of facilities. Major trends in the industry in recent years have been: (1) elimination of the hypochlorite stage (to reduce chloroform formation), and (2) the replacement of some chlorine in the first bleaching stage with chlorine dioxide. Between the time of the 1985 EPA/Paper Industry’s 104-Mill Study and the 1990 EPA Industry Census, 33 mills indicated that they would implement or increase ClO_2 substitution, and an additional 39 facilities reported that their intentions to do so over the period 1990 to 1993 (EPA, 1991). This section continues with a description of chlorine dioxide substitution and a discussion of its pollution prevention potential.

5.2 CHLORINE DIOXIDE SUBSTITUTION

The use of chlorine dioxide (ClO_2) as a bleaching agent became widespread in the 1960s, though primarily in the latter stages of the bleach sequence (e.g., in the conventional CEDED sequence). Because it is more selective towards lignin than chlorine, ClO_2 is effective in removing the smaller amounts of lignin that remain following chlorination without degrading the cellulose. Chlorine dioxide also saw use in the 1960s in small fractions during the first bleaching stage to prevent pulp viscosity loss and associated strength losses (McDonough, 1992). In recent years, however, attention has focused on increasing the substitution rate of chlorine dioxide for chlorine in the first bleaching stage, due to its beneficial impacts

TABLE 5-2
Most Common Bleaching Sequences
at U.S. Kraft Mills^[a]

Bleach Sequence ^[b]	Number of Mills with Bleach Sequence
C-E-H	4
C-E-HE-D	3
C-EO-HE-H-DE	3
CD-E-D-E-D	4
CD-E-H-D	3
CD-E-HE-D-E-D	3
CD-EO-D	9
CD-EO-H-D	3
CD-EOP-D	3
DC-EOP-D	4
DCD-EOP-D	6

^[a] Bleaching sequences performed at three or more mills are listed. Approximately 90 other sequences are used at one or two mills for each sequence.

^[b] Key: C Chlorination
 E Extraction
 D Chlorine dioxide
 H Hypochlorite
 O Oxygen
 P Peroxide
 CD Chlorine dioxide substitution
 EO Oxygen added to extraction stage
 EOP . . . Peroxide and oxygen added to extraction stage

Source: EPA (1993).

on pulp and effluent quality. The replacement of up to 50-70 percent of the elemental chlorine in the first bleaching stage with chlorine dioxide is now an accepted practice for environmental improvement and has been widely adopted within the North American pulp and paper industry. Substitution of more than 50-70 percent of the chlorine with chlorine dioxide is commonly referred to as "high" substitution.

Chlorine dioxide substitution for elemental chlorine in the first bleaching stage can be as effective as traditional bleaching in producing high strength, high brightness pulps. At substitution rates of 50 to 70 percent, chlorine dioxide can actually improve the efficiency of the delignification process over conventional chlorine bleaching (McDonough, 1992). According to a recent survey of Canadian mills using chlorine dioxide substitution, at substitution rates of 25 to 75 percent pulp brightness is not significantly different than with chlorine bleaching. At substitution rates approaching 100 percent, however, the efficiency or pulp yield declines slightly (McDonough, 1992) and brightness limits are reported to be marginally lower (Pryke et al., 1992, cited in Reeve, 1993).

The pollution prevention potential of chlorine dioxide is related to the different ways it reacts with lignin in the pulp, in comparison with chlorine. Reactions of chlorine-based compounds with lignin fall into three categories: substitution, addition, and oxidation. The first two reactions result in the formation of chlorinated organics, however, while oxidative reactions generally lead to fragmentation of the lignin (Forbes, 1992). Compared to elemental chlorine, chlorine dioxide is more of an oxidative bleaching agent. As a result, chlorine dioxide substitution increases the proportion of oxidative reactions, and leads to reduced formation of chlorinated organic compounds.

On a pound for pound basis, ClO_2 is more expensive than Cl_2 , but this is offset by the fact that chlorine dioxide is considered to be 2.63 times more effective than Cl_2 on a weight basis. Consequently, less chlorine dioxide is needed to obtain the same bleaching effect.⁴ Recent analyses estimate that chlorine dioxide can cost approximately two to four times as much as elemental chlorine for equivalent oxidizing power (O'Reardon, 1992).

⁴ The actual equivalent bleaching power of chlorine dioxide over chlorine varies from about 2.5:1 up to 4:1.

Generation of Chlorine Dioxide

Once generated, chlorine dioxide is unstable and hence cannot be shipped. In addition, chlorine dioxide can only be stored for a limited period of time (6 to 24 hours). Because of these constraints, ClO_2 is always generated onsite at the mill. The principal feed material for ClO_2 generation is sodium chlorate (NaClO_3), which is produced using electrolysis technology, similar to that used in chlor-alkali production.⁵ The electrolysis of a sodium chloride solution generates chlorine gas, which is reacted with water to form hypochlorite. The hypochlorite is then oxidized to form sodium chlorate, which is crystallized and dried for shipping (SRI, 1989).

At the mill, chlorine dioxide gas is generated using various systems based on the reduction of sodium chlorate in the presence of a reducing agent. Table 5-3 summarizes most of the chlorine dioxide generating processes operated at North American pulp mills. The systems use a variety of reducing agents: sulfur dioxide (Mathieson process), methanol (Solvay, R8, and modern SVP processes), and sodium chloride (R2, R3, and SVP processes).⁶ 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 .

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 (McKetta, 1979). With the increasing rate of chlorine dioxide substitution, 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-LiteTM) 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 (Reeve, 1993).⁷ Some additional technologies have developed that recover or transform byproducts that cannot be used in the recovery cycle. For example, the R9TM process, which is linked to the R8 reactor, generates chlorine dioxide and sodium hydroxide with no byproducts. The

⁵ The chlor-alkali process applies electricity to a solution of sodium chloride and produces elemental chlorine (Cl_2) and caustic (NaOH) in a fixed ratio.

⁶ The R-series generators are produced by Sterling Chemical (formerly ERCO and Albright & Wilson, subsidiaries of Tenneco) and the SVP systems are made by Eka Nobel, Inc.

⁷ The R8 reactor also provides more generating capacity than the R3 using similar equipment. This factor has contributed to the high degree of upgrading occurring in the industry.

TABLE 5-3

Summary of Chlorine Dioxide Generation Processes

Process	Reaction Equation	Reducing Agent	Byproducts
Mathieson	$2\text{NaClO}_3 + \text{SO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + 2\text{NaHSO}_4$	SO_2	spent acid solution
Solvay	$2\text{NaClO}_3 + \text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + 2\text{H}_2\text{O} + \text{HCHO} + \text{Na}_2\text{SO}_4$	CH_3OH	spent acid solution
R2	$\text{NaClO}_3 + \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{ClO}_2 + 0.5\text{Cl}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	NaCl	spent acid and chlorine
R3/SVP	$\text{NaClO}_3 + \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{ClO}_2 + 0.5\text{Cl}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	NaCl	saltcake and chlorine
R6/Lurgi/Chemetics/Vulcan	$1)\text{NaCl} + 3\text{H}_2\text{O} \rightarrow \text{NaClO}_3 + 3\text{H}_2$ $2)\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}$ $3)\text{NaClO}_3 + 2\text{HCl} \rightarrow \text{ClO}_2 + 0.5\text{Cl}_2 + \text{NaCl} + \text{H}_2\text{O}$	HCl	none
R8/SVP-MeOH/SVP-Lite	$9\text{NaClO}_3 + 2\text{CH}_3\text{OH} + 6\text{H}_2\text{SO}_4 \rightarrow 9\text{ClO}_2 + 3\text{Na}_2\text{H}(\text{SO}_4)_2 + 0.5\text{CO}_2 + 1.5\text{HCOOH} + 7\text{H}_2\text{O}$	CH_3OH	acid saltcake

Source: Stockburger, 1992.

R6/Chemetics/Lurgi-style generators are integrated plants which generate sodium chlorate onsite from chlorine or sodium chloride, and create no byproducts. The quality of the chlorine dioxide generated from these integrated plants, however, is not as pure. Finally, Eka Nobel has recently introduced a process that uses hydrogen peroxide as a reducing agent instead of methanol, which provides further increases in capacity from the same equipment.

Equipment specifications (i.e., metallurgy) 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 also prevents the mill from recovering chemicals and recycling process water from the D-stages. Many pulp mills are now striving to close the process water loop in the bleaching plant. A closed water system lowers mills' 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 (i.e., the C-, E-, and D-stages) should be isolated and excluded from the rest of the closed system.

Chlorine dioxide substitution in the first bleach stage may be implemented in several ways, including: (1) addition prior to chlorine (denoted D_C), (2) addition after chlorine (C_D), or (3) in a mixture with chlorine ($\text{C}+\text{D}$). Of these, the most effective method, in terms of bleaching efficiency, is the addition of chlorine dioxide prior to chlorine (Teder and Tormund, 1990; Pryke, 1989). Unfortunately, this order of addition has been linked with higher rates of dioxin and furan formation (Berry et al., 1989).

5.2.1 Number of Installations

Chlorine dioxide use has increased dramatically in recent years, as it has been adopted as the first proven method for reducing the levels of dioxin in bleaching effluent. It is relatively easy to illustrate the increasing use of chlorine dioxide in bleaching, since over 90 percent of U.S. demand for sodium chlorate (the feedstock for chlorine dioxide production) is accounted for by the pulp and paper industry (SRI,

1991). Figure 5-1 shows the trend for apparent domestic consumption of sodium chlorate in the U.S. between 1955 and 1987.⁸ By 1987, annual consumption had risen to 499,000 tons. Recent estimates by API pegged the 1990 level of consumption at 670,000 tons per year and projected growth to 975,000 tons per year by 1995 (API, 1992). Other sources forecast growth of roughly 8 to 10 percent per year through 1995 (Bradley, 1991).

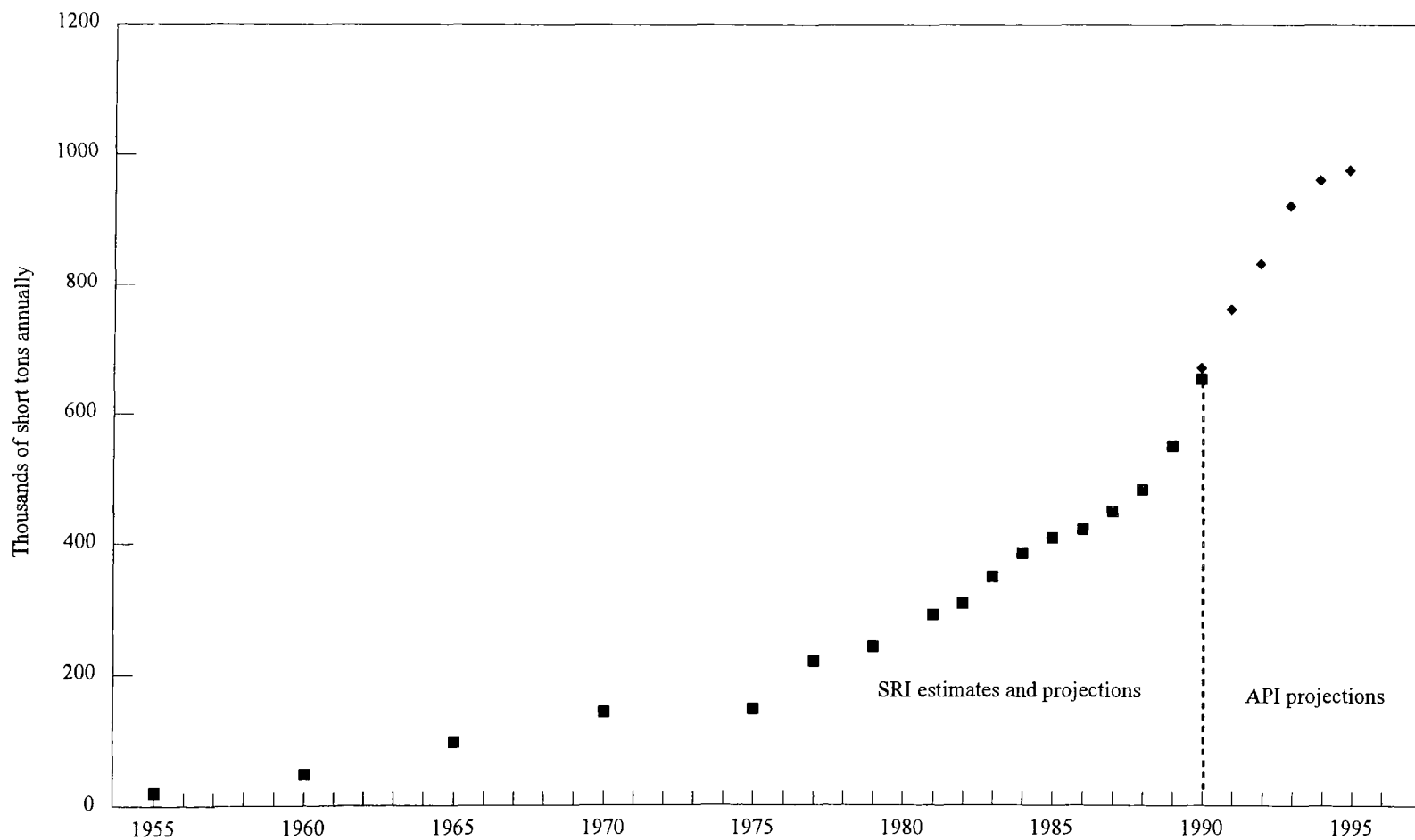
Table 5-4 shows the degree of chlorine dioxide substitution at U.S. mills in 1988, the most recent year for which data is available. As of mid-1988, chlorine dioxide substitution of 20 percent or greater was being practiced on only 16 of 165 bleaching lines. Since that time, however, it is apparent that the adoption of chlorine dioxide substitution has increased dramatically. Recent data suggests that Canadian bleach mills have extensively adopted chlorine dioxide substitution above 70 percent (Luthe et al., 1992 cited in McCubbin, 1993). A 1992 survey of Canadian pulp mills (Pryke et al., 1992) found that 87 percent of all Canadian bleached kraft pulp was produced using significant (25 to 75 percent) or 100 percent chlorine dioxide substitution. It is generally agreed that while U.S. mills have increased their use of chlorine dioxide, the percentage practicing "high" substitution is not as great as in Canada.

Market researchers Law, Sigurdson & Associates report that most bleached kraft mills now have chlorine dioxide generators and are currently using them 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).

While most mills currently have chlorine dioxide generating capacity onsite, further increases in production to enable higher substitution rates (and improved effluents) will require additional generating capacity, which will be expensive. Many mills are now at the point where they would have to make a significant capital investment to boost substitution any further. In fact, some companies, such as Weyerhaeuser, have declared that they will not invest additional money in chlorine dioxide generation. Further substitution at such mills will come through investment in non-chlorine technologies such as extended delignification, oxygen delignification, and peroxide stages. By reducing the overall bleaching chemical demands, these technologies will allow higher effective substitution rates using their existing ClO₂ capacity (McCubbin, 1992).

⁸ Apparent domestic consumption is calculated as production plus imports minus exports plus or minus year end-stock changes.

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



Source: SRI (1989 and 1991), API (1992).

TABLE 5-4
Levels of Chlorine Dioxide Substitution at
U.S. Kraft Mills, 1988

Percent Substitution	Number of Kraft Bleach Lines	Percent of Total	Cumulative Number	Cumulative Percent
over 50%	3	1.8%	3	1.8%
40 to 50%	3	1.8%	6	3.6%
30 to 40%	1	0.6%	7	4.2%
20 to 30%	9	5.4%	16	9.7%
10 to 20%	33	20.0%	49	29.7%
5 to 10%	41	24.8%	90	54.5%
less than 5%	16	9.7%	106	64.2%
0%	59	35.7%	165	100.0%
TOTAL	165	100%	--	--

Note: Since 1988 chlorine dioxide use in the industry has expanded considerably. Consumption for chemical pulp bleaching in 1988 was 483,000 short tons; in 1992 API projected that by 1993 consumption would rise to 920,000 tons. (See Figure 5-1)

Source: U.S. EPA (1990a).

According to a recent report, there are approximately 166 chlorine dioxide generators in North America, representing installed capacity of 3,194 short tons per day (Britt, 1992, cited in Stockburger, 1992). Table 5-5 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.

5.2.2 Costs and Economics

The capital cost of a 30 ton per day ClO_2 generating system has been estimated at \$2.8 million with an installed cost of \$5.7 million (Parkinson, n.d. cited in EPA, 1990). Engineering estimates prepared for the province of Ontario indicated a cost of \$100,000 to \$200,000 per daily tonne requirement or an average of \$3 to \$6 million (Ontario Ministry of the Environment, 1988). Still another estimate has placed the cost of equipment to convert sodium chlorate to chlorine dioxide at \$10 to \$20 million (Shariff, 1991).

Since most mills already operate their chlorine dioxide generating equipment to capacity, attempts to increase the substitution rate by generating more ClO_2 can involve investments of up to \$25 million. A Canadian study estimated the capital cost of expanding chlorine dioxide generating capacity at Ontario mills to be \$2 million to \$20 million per facility (Canadian dollars) with an average cost of about \$9 million (McCubbin et al., 1992). Additional investments may be required to upgrade the mixing equipment and controls at the chlorine dioxide addition point.

Under current chlorine and chlorine dioxide prices, the cost of substituting ClO_2 for Cl_2 may increase by as much as a factor of eight, as shown in the following calculations:

Cost of Cl_2	approx. \$45/ton or \$0.0225/lb
Equivalent oxidizing power of ClO_2 compared to chlorine	2.63
Cost of Cl_2 to replace 1 lb of ClO_2	$2.63 \times \$0.0225 = \0.06
Cost of sodium chlorate to produce 1 lb. ClO_2	\$0.30
Cost of reducing agent (methanol, acid, etc.) to produce 1 lb ClO_2	\$0.20
Total cost of generating 1 lb ClO_2	\$0.50
Ratio of cost of 1 lb ClO_2 to equivalent Cl_2	$\$0.50 \div \$0.06 = 8.3$

Source: Graves, 1993.

TABLE 5-5

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.

The economics of increased substitution have been explored in further detail in two recent analyses based on engineering costing of a hypothetical mill situation:

- An analysis presented at the U.S. EPA's Symposium on Pollution Prevention in the Manufacture of Pulp and Paper (McCubbin, 1993) compared the costs and environmental affects of alternative upgrades to an existing 1,000 tpd model mill (see Table 5-6). One of the options considered was an increase in 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 annual operating expenses would rise by \$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 (new generator among other things) and an increase in annual operating costs of \$7.1 million.

- A similar study by Brenner & Pulliam (1992) compared alternative bleaching technologies for a greenfield mill (new installation). Their 1000 tpd model mill was assumed to be practicing 30 percent substitution under the baseline scenario. Table 5-7 shows 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 5-8 provides yet another analysis of chlorine dioxide substitution costs. This table compares various levels of chlorine dioxide substitution with and without an oxygen delignification stage. For the baseline case of no chlorine dioxide substitution, chemical costs are estimated at \$10.83 per ton of pulp. Assuming oxygen delignification costs of \$5.30 per ton, at 70 percent chlorine dioxide substitution bleaching costs will be \$14.02 per ton, an increase of \$3.19.

These cost comparisons provide some rough estimates of the incremental costs for increasing chlorine dioxide substitution; the actual costs will be very site-dependent. All of these examples assume that under the baseline scenario the mills are not employing any alternative pulping technologies such as extended or oxygen delignification. The adoption of these technologies would reduce the kappa number of the pulp entering the bleach line and, therefore, reduce the quantity of chlorine dioxide needed in the bleaching stages.

TABLE 5-6

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 1000 tpd softwood kraft pulp mill. Bleach sequence is CD-E-D-E-D.

Source: McCubbin, 1992.

TABLE 5-7

**Cost and Environmental Comparison of Chlorine Dioxide Substitution
Greenfield Mill**

Parameter	Bleaching Scenario	
	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_DE₀DED.

Source: Brunner and Pulliam, 1992.

TABLE 5-8

**Impact of Chlorine Dioxide Substitution Levels
on Chemical Requirements and Costs**

Is Oxygen Delig- nification Installed	% ClO ₂ Subst.	Cl ₂ (tpd)	ClO ₂ (tpd)	Total Chemical (\$/ton)	O ₂ delig. (\$/ton)	Total (\$/ton)
1 No	0	41.69	0.00	\$10.83	\$0.00	\$10.83
2 No	10	37.52	1.59	\$11.38	\$0.00	\$11.38
3 Yes	50	10.65	4.05	\$7.16	\$6.30	\$13.46
4 Yes	60	8.52	4.86	\$7.44	\$6.30	\$13.74
5 Yes	70	6.39	5.67	\$7.72	\$6.30	\$14.02
6 No	70	12.51	11.10	\$14.67	\$0.00	\$14.67
7 Yes	100	0.00	8.11	\$8.56	\$6.30	\$14.86

Source: Devlin (1991); cited in Bettis (1991).

The cost of adopting increased chlorine dioxide substitution will also vary according to the condition and type of the existing generator. Pre-1970s equipment does not lend itself well to capacity expansions. To boost substitution rates, a new generator would be required. Much of the pre-1970s equipment, however, would probably be corroded and due for replacement. The newer design generators installed in the early 1980s (i.e., R3/SVP type) can be upgraded relatively inexpensively. According to McCubbin (1993), the capacity on these generators could probably be doubled for a few million dollars. Beyond that point, however, a new generator would be required, costing in the neighborhood of \$10 to \$20 million.

The capital and operation and maintenance (O&M) expenses for new chlorine dioxide systems will also vary depending upon the type of new capacity installed. Some of the newer integrated ClO_2 plants have a high capital cost, but reduced O&M expense. Power costs constitute the majority of the operating expense for integrated plants. In contrast, non-integrated chlorine dioxide generators, which rely on an external source of sodium chlorate, require less capital but incur higher O&M expenses (Stockburger, 1992). Note that the energy content of purchased sodium chlorate is high also, but that much of the energy is consumed in Canada, a major source of chlorate for U.S. mills.

The adoption of an oxygen/peroxide reinforced extraction stage (E_{OP}) following the first bleach stage can have a significant impact on the cost and effectiveness of chlorine dioxide substitution. Although an E_{OP} stage is more expensive than traditional caustic extraction, its contribution to delignification reduces the demands for chlorine dioxide in the final bleaching stages. This in turn frees up chlorine dioxide capacity for the first bleaching stage, hence, the substitution rate can be boosted without building new generating capacity. E_{OP} stages are very economical, thus most mills would adopt E_{OP} before making any other modifications. The cost of oxygen for extraction is cheaper than chlorine dioxide and the capital investment would be limited to roughly \$1 million. Similarly, increased competition and capacity have recently brought peroxide prices down significantly (from \$2.00 per kg three to four years ago to \$0.75 per kg today) (McCubbin, 1993).

5.2.3 Pollution Prevention Potential

A number of interrelated environmental issues are associated with higher levels of chlorine dioxide substitution. These are discussed below.

Impact on Effluent Quality

The amount of chlorinated organics formed during bleaching is proportional to the quantity of atomic chlorine consumed in the first bleaching stage. 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: (1) chlorine dioxide contains only one-half the atomic chlorine as elemental chlorine, and (2) less chlorine dioxide is needed, since it contains 2.63 times the oxidative power as elemental chlorine (McDonough, 1992). Overall, chlorine dioxide bleaching results in only one-fifth the amount of chlorinated organics as traditional chlorine bleaching (Forbes, 1992).

Brenner and Pulliam's study (1992) shows that shifting from 30 percent to 70 percent substitution would reduce chlorinated discharges and color, but would have little impact on BOD₅ (see Table 5-7). AOX in the bleach plant effluent would decline by 32 percent; color in the effluent would decline by 41 percent; but no improvement in BOD₅ would be seen. The study suggests, however, that at substitution rates above 70 percent improvements in BOD₅ could result.

McCubbin's (1993) analysis, which models the impacts of upgrading a hypothetical mill from an 11 percent substitution rate, suggests similar improvements in bleach plant effluent (see Table 5-6). Increasing substitution from 11 percent to a maximum of 30 percent (using E_{OP} and existing generating capacity) would reduce AOX to 3.4 kg per ton (a 36 percent decline) and possibly eliminate detectable dioxin and furan. Moving from 11 to 50 percent substitution reduces bleach plant effluent AOX levels from 5.3 kg per ton to 1.9 kg per ton (a 64 percent decline), reduces dioxin/furan levels from detectable to "marginally" detectable, and has no discernible affect on BOD. Increasing substitution from 11 to 100 percent reduces AOX from 5.3 kg per ton to 2.1 (a 60 percent decline), dioxin/furans would become non-detectable, and no improvements in BOD would be seen. Adding an oxygen/peroxide reinforced extraction stage following the 100 percent chlorine dioxide bleaching stage would further reduce AOX to 1.5 kg per ton (McCubbin, 1993).

Axegård (1987) investigated the relationship between the level of chlorine dioxide substitution and the amount of chlorinated phenolics in bleaching effluent. Chlorinated phenolics first increased slightly with the degree of substitution. Once a level of approximately 50 percent substitution was reached,

however, emissions decrease rapidly. This same study also measured AOX as a function of the degree of ClO_2 substitution but found a linear relationship. This illustrates the fact that under varying bleaching conditions the individual chlorinated organics may be found in different ratios. Given these findings, the choice of regulatory parameter could influence the selection of technology.

Impacts on Generation of Chloroform

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

Byproducts from Chlorine Dioxide Generation

Chlorine dioxide is generated by a variety of commercial processes, each of which produces some byproducts which may themselves have potential environmental impacts. The Mathieson process, for example, uses sulfur dioxide (SO_2) as a reducing agent and generates chlorine gas as a byproduct. Sulfur dioxide is either generated onsite by burning sulfur, or is shipped in. The R2, R3 and Hooker SVP processes use sodium chloride, and produce chlorine gas as a byproduct.⁹ Hypochlorite can also be produced as a byproduct in chlorine dioxide generators. At one time hypochlorite was used in the bleaching process, however, it is rapidly being abandoned at most kraft mills because of its impact on chloroform formation.

⁹ The byproduct chlorine produced by these reactors is quite dilute, and is not of a form suitable for pulp bleaching. Instead, the chlorine is absorbed in sodium hydroxide to convert it to hypochlorite. As noted elsewhere in this report, however, use of hypochlorite is being phased out in the industry.

At high 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 was in place. The impact of these discharges will vary depending on the quantities and the type of treatment practiced, however, in most situations it would simply act to neutralize acids. This possibility was considered in the study for Ontario, where the authors concluded "...we do not consider the discharge of unusable chlorine dioxide generator byproducts... to be of any environmental consequence." (Ontario Ministry of the Environment, 1988).

One further issue that has been discussed concerns the potential for formation of chlorates during ClO_2 bleaching. Axegård (1987) showed that higher levels of ClO_2 substitution increased the production of chlorates, a substance that has been found in Sweden to be toxic to certain types of algae (Rosemarin et al., 1990).¹⁰ Greenpeace (Kroesa, 1991) reports that although the impact of chlorates in North American waters has not been investigated, the Canadian industry (PAPRICAN) has claimed that they are not harmful to green algae such as are found in the Great Lakes. Chlorate can be converted to harmless chloride in a suitably operated biological treatment system.

Impacts on Energy

The adoption of higher levels of chlorine dioxide substitution has the potential to cause some shifting of energy consumption patterns in the industry. The generation of elemental chlorine is less energy intensive than all alternative bleaching chemicals except oxygen. Substitution of chlorine dioxide for chlorine would result in overall increases in energy consumption, although most of this would take place offsite. McCubbin's (1993) comparison revealed that the adoption of chlorine dioxide substitution has no effect on the mill's onsite energy consumption; however, offsite energy consumption (embodied in the purchased sodium chlorate) would increase by roughly 5.3 MW with 100 percent substitution (see Table 5-6). For perspective, a typical 1000 tpd pulp mill probably consumes 50 MW of electricity (McCubbin, 1993). The additional energy would be consumed during the offsite electrosynthesis of sodium chlorate. Since some 48 percent of the chlorate is imported from Canada (SRI, 1989), much of the energy consumption would be shifted from the United States to Canada.

¹⁰ At one time, sodium chlorate was used as a defoliant to remove the leaves from cotton and soybeans prior to mechanical picking (Kirk-Othmer, 1979).

5.2.4 Other Impacts

Potential Impacts on Chemical Markets

The increased substitution of chlorine dioxide for chlorine threatens to upset the traditional production balance between chlorine and sodium hydroxide (caustic soda). Conventional pulp bleaching has historically accounted for roughly 20 percent of the consumption of both of these products (TCI, 1990). Since the two chemicals are produced jointly by the chlor-alkali process in fixed ratios, declines in chlorine demand not accompanied by a corresponding decrease in caustic requirements could create chlorine surpluses or caustic shortages. The American Paper Institute (API) reports that demand for caustic in pulp bleaching is expected to decline by 7 percent from 1990 to 1995, versus declines in the demand for chlorine of roughly 35 percent (API, 1992). This forecasted imbalance within the pulp and paper industry may be slightly offset by increases in chlorine demand from other market segments.

Several processes are either currently available or under development that could help alleviate any potential imbalance. One technique involves producing caustic soda through the chemical conversion of soda ash and lime, which avoids chlorine as a byproduct. Major producers such as Tenneco Minerals, FMC Corporation, and Texas Gulf are currently manufacturing caustic soda in this manner (Busch, 1992). In some applications, including pulp bleaching, soda ash can also be used to replace caustic soda. This may help to buffer any caustic soda price increases precipitated by a drop in chlorine demand. Other processes are focussing on production of caustic soda at the mill, including production of caustic as a byproduct of chlorine dioxide generation.

On the chlorine side, attempts are being made to develop processes that can produce chlorine dioxide from chlorine. This would tend to stabilize chlorine demand. Eka Nobel of Sweden is working on an electrolytic process that, while promising, requires considerable onsite energy. Some of the integrated chlorine dioxide can reportedly operate using only chlorine as a feedstock (Stockburger, 1992). Increasing demand for chlorine derivative products such as polyvinylchloride (PVC) could also help to maintain balance in chlor-alkali markets.

Impacts on Safety

A further issue arising from chlorine dioxide substitution is safety concerns. Chlorine dioxide is very unstable and must be produced, stored, and used under controlled conditions. Decomposition can occur easily if the material becomes contaminated, particularly if there is exposure to oxidative materials. Concerns for workers have also been expressed because chlorine dioxide leaks reportedly cannot be detected as easily as chlorine (Kroesa, 1991). However, the track record over four decades of industrial use has been good.

5.3 SPLIT ADDITION OF CHLORINE CHARGE/IMPROVED pH CONTROL

The technique of splitting up the addition of chlorine in the C-stage follows from research by 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 (in the form of AOX). This is in contrast to other approaches that may emphasize reducing the total amount of chlorine used.

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

The control of pH in the chlorination stage has also been used as a means for influencing 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.

5.3.1 Number of Installations

Westvaco has implemented split chlorine addition at its bleached kraft mills at Luke (Maryland), Covington (Virginia), and Wickliffe (Kentucky). To our knowledge, no other pulp and paper companies have so far indicated they are experimenting with this technique.

5.3.2 Costs and Economics

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

5.3.3 Pollution Prevention Potential

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 (see Table 5-9). Mill trials have shown that fairly low levels of TCDD and TCDF (6 ppt in CE-stage pulp) can be obtained (Hise, 1989).

5.4 OXYGEN-REINFORCED EXTRACTION

The term oxidative extraction (or oxygen extraction) refers to the use of elemental oxygen in the first alkaline extraction stage (E_1) of a conventional bleaching sequence. In a conventional bleaching sequence, the extraction stage follows chlorination and completes the solubilization of chlorinated and oxidized lignin molecules, facilitating their removal. The addition of gaseous oxygen to the alkaline 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 (O'Reardon, 1992). Oxidative extraction has also been used to help mills cut back on hypochlorite, a more expensive and aggressive chemical and the one that is most associated with chloroform emissions.

TABLE 5-9

Effect of Split Chlorine Addition on
Formation of TCDD and TCDF
(ppt)^[a]

Method of Addition of Chlorine	2,3,7,8-TCDD	2,3,7,8-TCDF
One charge	31.7	338
Two charges	18.6	187
Three charges	14.8	100

^[a] As measured in pulp following chlorination and first extraction stages.

Source: Hise (1989).

When oxygen is used in extraction, the bleaching stage is denoted as E_O . Oxygen-enhanced caustic solutions can also be used as pretreatments prior to chlorination, however these are not discussed in this section. Addition of oxygen in the E_1 or subsequent extraction stages typically occurs at a 0.5 percent on pulp basis.

A recent development has been the conversion of E-stage equipment to operate with a pressurized pre-retention tube (Hastings et al. 1992). Savings of approximately 11 kg of active chlorine per ton pulp were obtained and AOX fell by approximately 0.5 kg per ton (Hastings et al., 1992).

Several integrated mills producing pulps with 80 to 85 percent ISO brightness have reportedly been able to convert to short sequence bleaching ($C_D E_O D$) following installation of an E_O stage (O'Reardon, 1992).

5.4.1 Number of Installations

Since its introduction in the late 1970s, oxygen extraction has been widely adopted in North America and elsewhere. In 1985 it was reported that 55 mills were using E_O stages (Reeve, 1985) representing capacity of around 15 million tpd. Since then, oxygen reinforcement has spread dramatically. Data for Canadian mills from 1987 indicated that 80 percent of bleach lines were using oxidative extraction (Ducey, 1987). A similar high percentage of U.S. mills are believed to have implemented oxidative extraction. Hastings et al. (1992) estimate that in 1992 mills representing close to 60 million tpd of the world's bleached pulp capacity had adopted E_O .

5.4.2 Costs and Economics

Costs of oxygen-reinforced alkali extraction will include the costs of oxygen mixing equipment, which can range from relatively minor to moderately expensive. According to Hastings et al. (1992), 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. Oxygen is added 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 normally applied. Hastings et al. (1992) also suggest that it may be

worthwhile to install an upgraded washer following this stage since it does perform a delignification role.

One source reported estimated costs for a 1983 installation at a 450 tpd mill at \$0.5 million (Ducey, 1984). These costs were reportedly more than offset by the savings in hypochlorite alone. Pryke (1985) reported on research by PAPRICAN that showed savings of 6 kg of hypochlorite and 4 kg of chlorine dioxide per ton of pulp in a CDEHDED sequence. Annual cost savings per mill of \$600,000 to \$800,000 were also reported, but these cost data are probably outdated. They serve to demonstrate, however, that the addition of oxygen to a traditional E-stage is normally economically attractive.

Conversion to a pressurized extraction E_o stage (Hastings et al., 1992) required installation of a pressurized pre-retention tube, a medium consistency pump, and an oxygen sparger (see Figure 5-2). Total costs of that project, including engineering and installation, were under \$2 million.

5.4.3 Pollution Prevention Potential

As explained in earlier sections, 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 benefit accrues if the extraction stage performs a delignification role and enables a reduction in chlorine use or an increase in chlorine dioxide substitution. Savings in active chlorine of about 2 kg per kg of oxygen charged will generally be observed (Hastings et al., 1992). In an atmospheric tower up to 4 kg of oxygen per tonne could be charged, while in a pressurized reactor up to 6 kg per tonne could be added. This results in a reduction in formation of chlorinated organics.

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, chloroform formation (Ducey, 1984). Hypochlorite bleaching stages are most closely associated with emissions of chloroform (Dallons et al., 1990). To the extent that oxidative extraction is used to replace hypochlorite, improvements in atmospheric emissions of chloroform should result.

5.5 PEROXIDE EXTRACTION

Peroxide (H_2O_2) is often combined with caustic in the E_1 extraction stage. In such bleaching sequences, the symbol E_p is used. As with oxidative extraction (E_o), the use of hydrogen peroxide has been found to promote additional removal of lignin during the extraction stage. The oxidative power of the peroxide can also perform some bleaching. The combination of these effects may enable the mill to reduce usage of chemicals either upstream, in the case of chlorine, or downstream, in the case of hypochlorite or chlorine dioxide. Peroxide and oxygen are often used together in the E_1 stage, i.e., E_{op} . Hydrogen peroxide is also being used in the high density storage chest as a brightening agent. In some cases, this is considered a safeguard against possible heat-related brightness reversion that may occur with higher rates of chlorine dioxide substitution, particularly for high brightness grades of pulp (Downs, 1990).

Hydrogen peroxide is produced via a process called anthraquinone autoxidation, which involves the reduction (hydrogenation) of alkyl anthraquinones to anthrahydroquinones. This product is then oxidized to yield hydrogen peroxide and the original alkyl anthraquinone. The hydrogen peroxide is extracted from the reaction solution with water, diluted to proper concentrations, and marketed as an aqueous solution.

Peroxide is produced offsite and shipped to the mill via tanker as a 70 percent solution in water. 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.

Webster (1990) described a strategy to achieve significant environmental and economic benefit from the use of peroxide, without increasing ClO_2 requirements. Using a C_pE_oDED mill as an example, the first step is to add peroxide 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_p -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.

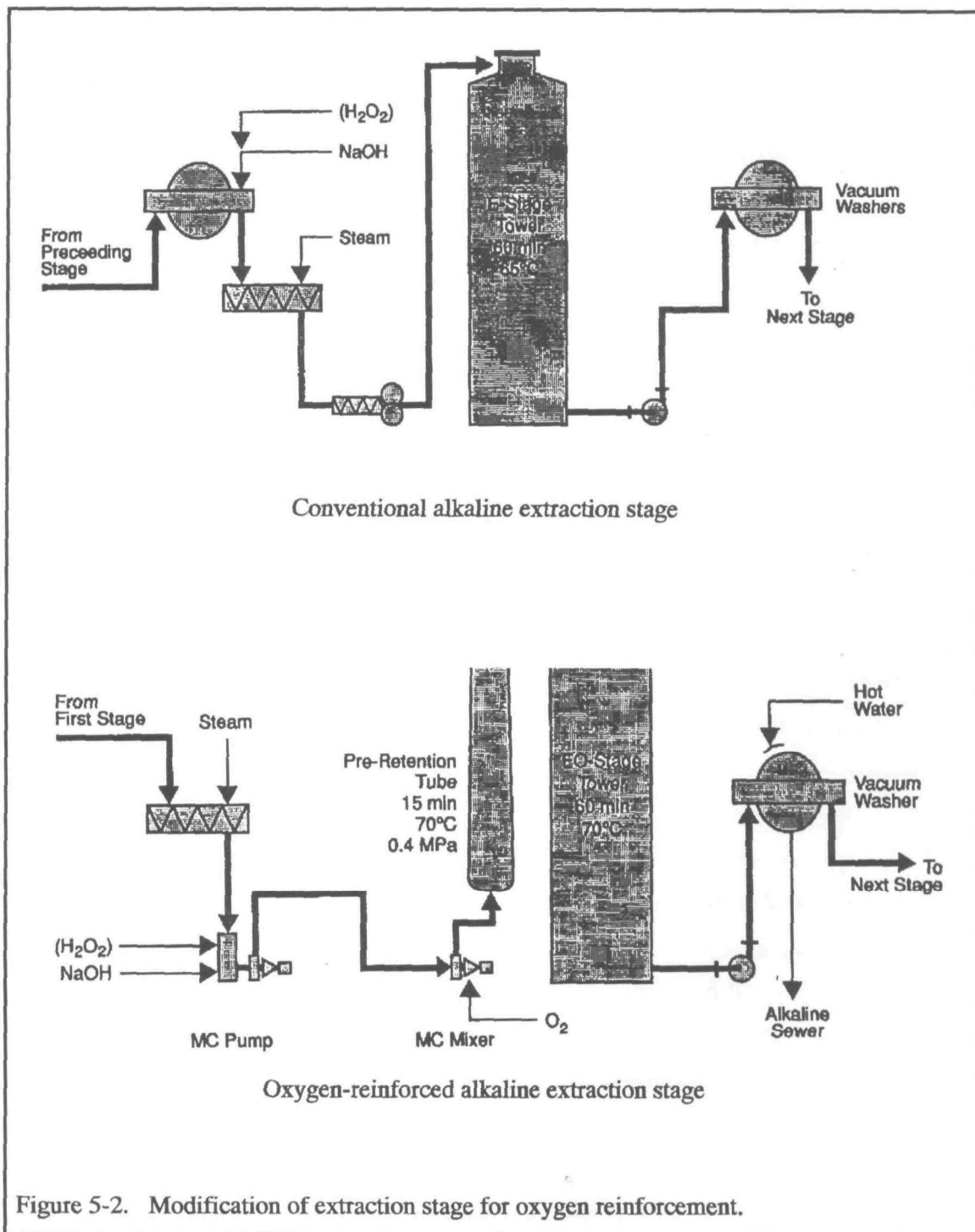


Figure 5-2. Modification of extraction stage for oxygen reinforcement.

Source: Hastings et al., 1992.

Recent mill trials using peroxide in the oxygen-reinforced E_1 stage and in subsequent extraction stages showed that at constant CE kappa number and chlorine dioxide consumption the use of elemental chlorine could be reduced by 30-40 percent (Anderson, 1992). Results from trials at five mills are shown in Table 5-10. In all of these trials, dioxin levels were reported as non-detectable. Peroxide extraction can also assist mills in moving to 100 percent ClO_2 substitution. Many mills encounter higher bleaching costs at 100 percent substitution due to the reduced delignification efficiency compared to lower ClO_2 substitution levels. Brightness ceilings may fall a little if oxygen delignification is used. Peroxide extraction can offset these disadvantages by reducing ClO_2 generating requirements and improving final brightness (Anderson, 1992).

Although more commonly used for brightening mechanical pulps, peroxide has been 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, full brightness sequence using ozone, e.g., OZEP. Full peroxide stages typically require 2.5 percent peroxide or more on pulp, 70°C or higher and a retention time of 2 to 4 hours. The brightening effect is increased as the time and temperature are increased but viscosity begins to drop. To protect the pulp, a prior chelation stage is crucial to ensure removal of metal ions that remain with the pulp as chlorine is removed from the sequence. The only kraft mill currently producing "full" brightness chlorine-free pulp is at Mönsterås, Sweden. The pulp produced is 88 percent brightness and is made from hardwood. The mill has not yet produced full market softwood pulps, but has announced plans to do so.

5.5.1 Number of Installations

The percentage of all bleach lines in North America using hydrogen peroxide in the extraction stage was estimated several years ago to be 25 percent (Ducey, 1987). Strunk (1990) estimates that 60 U.S. and Canadian mills use approximately 28,000 tpy of peroxide for enhanced extraction. At an average application rate of 0.25 percent by weight on pulp, he estimates that 11 million tons of pulp are bleached using peroxide. Walsh (1991b) reports a 30 percent increase in peroxide use in pulp and paper between 1989 and 1990, however its use is split between bleaching of kraft, mechanical, and secondary fibers, with about half of the U.S. consumption accounted for by kraft bleaching (Downs, 1990).

TABLE 5-10

**Impact of Use of Peroxide in Extraction Stages
on Chlorine Consumption and Substitution Rate**

Parameter	Mill A	Mill B	Mill C	Mill D	Mill E
Before					
Sequence	C _D E _O DED	C _D E _O HDED	C _D E _O DED	C _D E _O HDED	C _D E _O DED
BS Kappa	32	33	28	29	33
ClO ₂ Subst. (%)	6.9	8	6	30	30
Kappa factor	0.21	0.16	0.23	0.21	0.22
Brightness	91	90	91	90	90
After					
Sequence	C _D E _{OP} DE _P D	C _D E _{OP} (H)DE _P D	C _D E _{OP} DE _P D	C _D E _{OP} DE _P D	C _D E _{OP} DED
BS Kappa	32	33	28	29	
ClO ₂ Subst. (%)	27	18	12	47	33
Kappa factor	0.16	0.13	0.17	0.18	47
Brightness	91	90	91	90	0.17
					90
H ₂ O ₂ addition (%)	0.5	0.45	0.5	0.25	0.35
Cl ₂ decrease (%)	37	29	31	33	41

Source: Anderson (1992).

5.5.2 Costs and Economics

Capital costs of \$100,000 for storage tanks, mix tank, and piping have been cited as typical by Webster (1990). He notes that, compared to other options such as increased chlorine dioxide generating capacity, the costs are much lower. In terms of operating costs, the main impacts will be a change in overall chemical consumption. Peroxide application rates between 0.1 and 1.0 percent by weight on pulp (2 to 20 lbs per ton) have enabled mills to reduce their consumption of other bleaching chemicals. In most cases, however, the overall change in chemical costs has not been reported.

The price of hydrogen peroxide has dropped significantly in recent years. 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, the peroxide industry is far more cost competitive. Prices for peroxide have recently dropped from roughly \$2.00 per kg three or four years ago to \$0.75 per kg today (McCubbin, 1992). This drop in prices has meant that for most mills peroxide is less expensive than ClO_2 , to the extent that replacement is feasible.

Althouse (1988) reported that addition of peroxide to an oxidative extraction stage (i.e., E_{OP}) had enabled one mill to shorten the bleaching sequence from five to three stages and realize the following savings:

Electrical costs	\$1 to \$3 per ton of pulp or \$175,000 to \$525,000 per year;
Steam costs	\$3 to \$5 per ton of pulp or \$525,000 to \$875,000 per year;
Maintenance costs	\$2 to \$5 per ton of pulp or \$375,000 to \$875,000 per year.

The same source indicates that replacement of hypochlorite with peroxide can produce higher strength pulp, thereby reducing the need for chemical strength additives.

5.5.3 Pollution Prevention Potential

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. When measured at this point in the bleaching sequence, the term CEK number (chlorination-extraction kappa number) is used. In two cases reported by Walsh (1991a), CEK fell from 3.1 to 2.4 and from 4.1 to 3.0. This higher degree of delignification means that bleaching chemicals can be reduced 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.

In case 2 above, AOX and chloroform concentrations were reported before and after addition of peroxide to the extraction stage. In the CEHD sequence, AOX levels were 5.1 kg per ADMT and chloroform was measured at 0.352 kg per ADMT. In the modified CE_pHD sequence, AOX was reduced to 3.7 kg per ADMT (27 percent decrease) and chloroform to 0.178 kg per ADMT (49 percent decrease).

Webster (1990) has summarized recent mill trials using peroxide at various locations in the bleaching sequence. 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 all of these pollutants. 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.

Strunk (1990) presents data that shows the effect of peroxide addition to an oxygen reinforced extraction stage (E₀). The addition of oxygen to a conventional caustic extraction stage first lowered CEK number from 3.8 to 2.9. Peroxide addition at 0.4 percent reduced this further to 2.2, while peroxide at 0.8 percent reduced it to 2.0.

Hastings et al. (1992) report that active chlorine savings of about 2 to 3 kg of chlorine per kg of peroxide charged can be achieved through addition of 1-4 kg per adt peroxide in the E₁ stage, and that a further 3 to 5 kg chlorine per kg peroxide charged could be saved through addition of up to 2 kg per adt in the E₂ stage.

Impacts on Chloroform Generation

Hydrogen peroxide has been used successfully to partially or completely replace hypochlorite in the bleaching sequence. For mills that use hypochlorite, this should result in reduced atmospheric chloroform emissions. The effect on chloroform was observed in one case to have been reduced by 49 percent (Walsh 1991a).¹¹

Walsh (1991a) reported the impacts of peroxide extraction at three case study mills in terms of the bleaching chemical reductions obtained, including reductions in hypo:

Mill 1: A C_DE_HD bleaching sequence at a southern hardwood kraft mill was converted to C_D-E_P-D (e.g., replacement of hypochlorite with peroxide in the extraction stage). The substitution ratio was 1:3.5 peroxide for hypochlorite. Further, chlorine dioxide consumption in the D stage was reduced by 7.2 lb per ton.

Mill 2: A CEHD bleaching sequence at a northern blended softwood kraft mill was converted to CE_PHD (e.g., peroxide addition to extraction stage). Hypochlorite consumption fell by 1.4 pound for each pound of peroxide added, and chlorine dioxide requirements fell by 3.2 lb per ton.

Mill 3: A C_DEHD bleaching sequence at a southern pine kraft mill was converted to C_DE_PHD (e.g., peroxide addition to extraction stage). Hypochlorite consumption dropped by 50 percent.

The cost implications of these chemical substitutions were not reported.

Strunk (1990) reported the effects on pulp properties of peroxide and oxygen addition to the first extraction stage. Third stage pulp brightness (GE method) first rose from 72 to 79 when oxygen was added to the conventional caustic extraction stage. Peroxide addition at 0.4 percent raised brightness to 82, while peroxide at 0.8 percent achieved an 83 brightness.

5.6 ADDITIONAL TECHNOLOGY OPTIONS IN THE BLEACHING AREA

In addition to the major pollution prevention technologies discussed above, several further options should be mentioned. These may sometimes be adopted as part of the upgrades discussed above (as in

¹¹ In the case of dissolving pulp mills, substitution of peroxide for hypochlorite has not yet been fully demonstrated.

the case of improved chemical controls or mixing equipment), while in other cases these qualify more as water conservation measures or pollution control techniques than pollution prevention.

5.6.1 Improved Chemical Controls

The control of bleaching chemical application rates is vital to minimizing formation of chlorinated organics such as dioxins and furans. Excess chlorination will not only increase bleaching costs but will also lead to increased formation of these undesired byproducts. Upgraded instrumentation to monitor and control chemical application rates will help minimize chlorination rates to within acceptable ranges. Costs for improved chemical controls could range from \$150,000 to \$500,000, depending on the type of system installed.

5.6.2 Improved Chemical Mixing

The equipment used to mix chemicals with pulp is an important factor in controlling formation of chlorinated organics. The development of the high-shear mixer has resulted in greater consistency of chemical mixing, resulting in reduced potential for localized excess concentrations of chlorine-based chemicals. Pockets of excess chlorine or chlorine dioxide within the reactor vessel can lead to formation of additional dioxins and furans. Costs for improved mixing equipment could range from \$200,000 to \$500,000, depending on the size and type.

5.6.3 Jump-Stage, Counter-Current Washing

Reductions in effluent flows can be obtained in some cases by reusing the acid filtrates (from hypochlorite or chlorine dioxide stages) as dilution and wash water for the first bleaching stage. The technique also encompasses reuse of second extractions stage filtrates as dilution and wash water in the first extraction stage. The major impact of this technique, where applicable, will be on reduced effluent flows and water consumption. Some energy and steam savings will also result. These methods are included on most new mill installations or rebuilds, while costs for retrofits will be very site-specific.

SECTION FIVE REFERENCES

- Althouse, 1988. E.B. Althouse. "Hydrogen Peroxide Addition to EO Stages is Beneficial," *Pulp & Paper*, June 1988.
- Anderson, 1992. Ross Anderson. "Peroxide Delignification and Bleaching," Proceedings, *Nonchlorine Bleaching Conference*, Hilton Head SC, March 1992. Available from Miller-Freeman Publications, San Francisco.
- API, 1992. American Paper Institute. *Report on the Use of Pulping and Bleaching Chemicals in the U.S. Pulp and Paper Industry*, June 26, 1992. New York.
- Axegård, 1987. Peter Axegård. "Chlorine Dioxide Substitution Reduces the Load of TOCl," Proceedings, *1987 TAPPI Pulping Conference*, p. 105.
- Berry et al., 1989. R.M. Berry, B.I. Fleming, R.H. Voss, C.E. Luthe, and P.E. Wrist, "Toward Preventing the Formation of Dioxins During Chemical Pulp Bleaching," *Pulp & Paper Canada*, September, 1990, p. 48.
- Bradley, 1991. Rosemary F. Bradley. "Pulp Bleaching Agents and Technologies Substituting for Chlorine at North American Pulp Mills," *Chemical Industries Newsletter*, SRI International (Menlo Park, CA). September-October 1991.
- Britt, 1992. M.P. Britt. Personal communication, Vulcan Chemicals, Birmingham, AL, March 24, 1992. Cited in Stockburger, 1992.
- Brunner and Pulliam, 1992. Lee Brunner and Terry L. Pulliam. "A Comprehensive Impact Analysis of Future Environmentally Driven Pulping and Bleaching Technologies," Proceedings, *1992 TAPPI Pulping Conference*, Boston MA, November.
- Busch, 1992. Gretchen Busch. "Staying Power," *Chemical Marketing Reporter*, Special Report: Paper Chemicals '92, September 28, p.SR 9.
- Crawford et al., 1991. Robert J. Crawford, Victor J. Dallons, Ashok K. Jain, and Steven W. Jett. "Chloroform Generation at Bleach Plants With High Chlorine Dioxide Substitution and/or Oxygen Delignification," Proceedings, *1991 TAPPI Environmental Conference*, p. 305.
- Dallons et al., 1990. Victor J. Dallons, Dean R. Hoy, Ronald A. Messmer, Robert J. Crawford. "Chloroform Formation and Release From Pulp Bleaching," *TAPPI Journal*, June 1990, p. 91.
- Downs, 1990. Tim Downs. "Chemical Markets Remain Mixed as Paper Industry Slowdown Continues," *Pulp & Paper*, November 1990, p. 55.

SECTION FIVE REFERENCES (cont.)

- Ducey, 1984. Michael J. Ducey. "Oxidative Extraction at Halsey Mill Cuts Hypochlorite Consumption," *Pulp & Paper*, October 1984, p. 118.
- Ducey, 1987. Michael J. Ducey. "Pulp Bleaching Concerns Focus on ClO₂ Generation, Effluent Control," *Pulp & Paper*, June 1987, p. 89.
- EPA, 1993. U.S. Environmental Protection Agency. *Pulp, Paper, and Paperboard Industry - Background Information for Proposed Air Emission Standards*. Office of Air Quality Planning and Standards, Research Triangle Park, NC. Preliminary Draft. April 1993.
- EPA, 1991. *Preliminary Summary Report of Questionnaire Responses for Mills that Bleach Chemical Pulps*. Revised. (Mimeo.) CB/EAD/OST/OW, U.S. Environmental Protection Agency. Washington, D.C. October 31, 1991.
- Fleming, 1992. Bruce I. Fleming. "The Organochlorine Spectrum: Mills, Public Must Discern Toxic, Nontoxic," *Pulp & Paper*, April 1992, p.59-62.
- Forbes, 1992. David, R. Forbes. "Mills Prepare for Next Century with New Pulping, Bleaching Technologies," *Pulp & Paper*, September 1992, p. 79-90.
- Graves, 1993. Comments of David P. Graves on draft *Pollution Prevention Technologies for the Bleached Kraft Segment of the U.S. Pulp and Paper Industry*, U.S. EPA/OPPT, December 1, 1992. March, 1993.
- Hastings et al., 1992. "Current State of the Art of E/O, E/P, and E/OP Technologies," Proceedings, *Nonchlorine Bleaching Conference*, Hilton Head, SC, March 2-5, 1992. Available from Miller Freeman Publications, San Francisco.
- Hise and Hintz, 1989. Ronnie G. Hise and Harold L. Hintz. "Effect of Brownstock Washing on Formation of Chlorinated Dioxins and Furans During Bleaching," Proceedings, *1989 TAPPI Pulping Conference*.
- Kirk-Othmer, 1979. *Encyclopedia of Chemical Technology*, Vol. 5, 3rd edition. John Wiley & Sons.
- Kroesa, 1991. Renate Kroesa. "Chlorine Dioxide - An Overview," July 1991. (Greenpeace mimeo).
- Luthe et al., 1992. C.E. Luthe, P.E. Wrist, R.M. Berry. "An Evaluation of the Effectiveness of Dioxin Control Strategies on Organochlorine Effluent Discharges from the Canadian Bleached Chemical Pulp Industry," Proceedings *CPPA Spring Conference*, May, Jasper.

SECTION FIVE REFERENCES (cont.)

- McCubbin, 1993. McCubbin, Neil. "The Costs and Benefits of Various Pollution Prevention Technologies in the Bleached Kraft Pulp Industry," Proceedings, *International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper*, August 18-20, 1992, Washington, DC. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. EPA-744R-93-002. February 1993.
- McCubbin et al., 1991. Neil McCubbin, Howard Edde, Ed Barnes, Jens Folke, Eva Bergman, Dennis Owen. *Best Available Technology for the Ontario Pulp and Paper Industry*. Rep. ISBN 7729-9261-4, Ontario Ministry of the Environment, Toronto, Ontario.
- McCubbin, 1992. McCubbin, Neil. Telephone communication between Eric M. Sigler of ERG and Neil McCubbin, November 20.
- McDonough, 1992. Thomas, J. McDonough. "Chlorine to Disappear from Future Paper Industry Bleaching Sequences," *Pulp & Paper*, September, p. 61-71.
- McKetta, 1979. John J. McKetta (ed.). *Encyclopedia of Chemical Processing and Design. Vol 7: Catalyst Carriers to Chloralkali*. (Marcel Dekker: NY).
- O'Reardon, 1992. Dan. O'Reardon. "Review of Current Technology Vital to Bleach Plant Modernization Study," *Pulp & Paper*, April, p.124-129.
- Ontario Ministry of the Environment, 1988. *Kraft Mill Effluents in Ontario*. Municipal-Industrial Strategy for Abatement. March 1988.
- OTA, 1989. U.S. Congress, Office of Technology Assessment. *Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp*, OTA-BP-O-54 (Washington, D.C.: U.S. Government Printing Office, May 1989).
- Pryke, 1989. Douglas C. Pryke. "Chlorination-Stage Mixing Practices," *TAPPI Journal*, June 1989, p. 143.
- Pryke et al., 1992. Pryke, D.C., M Dumitru, R. Cunningham, and D.W. Reeve. "A Survey of Chlorine Dioxide Substitution in Bleached Kraft Mills in Canada," Proceedings, *Canadian Pulp and Paper Association Technical Conference*, May 14-16, 1992, Jasper Alta, Can.. Cited in Reeve, 1992.
- Pryke, 1985. Douglas C. Pryke. "Fraternity Gathers at the Chateau: The 1985 International Pulp Bleaching Conference," *TAPPI Journal*, August 1985, p. 145.
- Reeve, 1987. Douglas W. Reeve. "The Principles of Bleaching," Proceedings, *1987 TAPPI Bleach Plant Operations Seminar*.

SECTION FIVE REFERENCES (cont.)

- Reeve, 1993. Douglas W. Reeve. "The Emerging Technology of Chlorine Dioxide Delignification," Proceedings, *International Symposium on Pollution Prevention in the Manufacture of Pulp and Paper*, August 18-20, 1992, Washington, DC. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. EPA-744R-93-002. February 1993.
- Reeve, 1985. Douglas W. Reeve. "Worldwide E Installation Survey," *TAPPI Journal*, November 1985, p. 142.
- Rosemarin et al., 1990. Arno Rosemarin, Karl Johan Lehtinen, Mats Notini. "Effects of Treated and Untreated Softwood Pulp Mill Effluents on Baltic Sea Algae and Invertebrates in Model Ecosystems," *Nordic Pulp and Paper Research Journal*, February 1990, p. 83.
- Shapiro, 1992. Lynn Shapiro. "A Quality Quest," *Chemical Marketing Reporter*, Special Report: Paper Chemicals '92, September 28, p. SR 3-8.
- Shariff, 1991. Shalina Shariff. "New Challenges in Pulp and Paper," *Chemicalweek*, May 8, 1991, p. 36.
- SRI, 1989. *Chemical Economics Handbook Product Review: Sodium Chlorate*, SRI International, March.
- SRI, 1991. *Chemical Economics Handbook Product Review: Sodium Chlorate*, (online update). SRI International, October 1991.
- Stockburger, 1992. Stockburger, Paul. "What You Need To Know Before Buying Your Next Chlorine Dioxide Plant," Proceedings *1992 TAPPI Engineering Conference*, Boston, MA, September 14-17.
- Strunk, 1990. Willaim G. Strunk. "Kraft Bleach Plants Increase Use of Hydrogen Peroxide as Benefits Mount," *Pulp & Paper*, October 1990, p. 112.
- TCI, 1990. The Chlorine Institute. *Economic Impact of Dioxin Regulation on the Chloralkali Industry*. Prepared by Consulting Resources Corporation, November.
- Teder and Tormund, 1990. "What Happens During Sequential DC Bleaching?" Proceedings, *1990 TAPPI Pulping Conference*.
- Walsh, 1991a. Patricia Walsh. "Hydrogen Peroxide: Innovations in Chemical Pulp Bleaching," *TAPPI Journal*, January 1991, p. 81.
- Walsh, 1991b. Patricia Walsh, development manager for pulp and paper, Interlox Corp.; cited in *Chemical Marketing Reporter*, September 23, 1991, p. SR4.
- Webster, 1990. John Webster. "H₂O₂-Enhanced Bleaching Strategy Cuts TOCl Levels in Mill Effluent," *Pulp & Paper*, April 1990, p. 141.