Chapter 5

Technologies for Reducing Chlorinated Organics in Pulp Manufacture

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The bleaching plant is the major source of waterborne environmental pollutants produced by pulp and paper mills. As much as 40 percent of the biological oxygen demand (BOD), 25 percent of the suspended solids (SS), 70 percent of the color, and nearly all of chlorinated organic materials (TOC1) produced by pulp mills originate in the bleaching process. The amount and nature of bleach plant pollutants vary considerably among the bleaching sequences used, wood species, and pulping processes.

Water is used in large quantities in the bleaching process (averaging 20,000 to 30,000 gallons per ton of pulp produced, although modern mills use much less than this). In contrast to pulping chemicals, the bleaching chemicals are generally not recovered but are discharged as wastes after treatment.

Chlorination, often the first bleaching stage after pulping in many bleaching sequences, requires large volumes of water to dilute the unbleached pulp to a low consistency for subsequent bleaching (about 3 percent fiber by weight compared to water), and is therefore a major source of chlorine-contaminated water. Chlorination sometimes uses as much water as all of the subsequent bleaching stages combined. To reduce the amount of fresh water consumed, the chlorination filtrate is often recycled in the bleaching stage, or paper mill white water is used for dilution.

General hypotheses have been advanced to explain the possible occurrence of dioxins in pulp, paper, and mill wastes. If true, these hypotheses may suggest ways to reduce the amount of dioxins produced in pulp and paper manufacture. First, since lignin or wood extracts probably contain some dioxin precursors, the reduction of the amount of lignin exposed to chlorine in the bleach plant might reduce the volume available for dioxin formation. It is now believed that lignin may not be a major source of precursors as originally thought.

Second, by reducing the amount of chlorine used, or eliminating the use of chlorine bleach altogether, the formation of dioxins might be reduced or even eliminated.

Third, a recent discovery by the Pulp and Paper Institute of Canada that oil-based defoamers made with contaminated used oil may be the source of nonchlorinated precursors of dioxin and furan that become tetrachloro-p-dibenzodioxin (TCDD) and tetrachlorodibenzofuran (TCDF) with chlorination.[1] By using “cleaner” oil- or water-based defoamers (although water-based defoamers may not be effective in washing brownstock), this source of precursors can be eliminated.

Fourth, preliminary findings indicate that the formation of TCDD and TCDF can be reduced by modifying conventional chlorine bleach sequences. For instance, by applying chlorine gas in smaller, successive split charges rather than a single large charge, research has shown reductions in TCDD.[2] By carefully controlling the acidity (pH) of the unbleached pulp within an optimum range, TCDD has also been reduced. Applying chlorine bleach before the addition of chlorine dioxide (CD) tends to produce less TCDD than if chlorine and chlorine dioxide are mixed (CD) or if chlorine dioxide is applied separately before the addition of chlorine. TCDD and TCDF formation is also sensitive to the ratio of chlorine to lignin. The Swedish Pulp and Paper Research Institute has found that if chlorine additions are kept below 15 percent (chlorine to lignin), TCDD and TCDF can be kept to low levels.[3] These observations need verification.

Fifth, improvements in secondary biological waste treatment can further reduce the amount of fine, colloidal suspended solids on which TCDD and

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[1] R. H. Voss et al., “Some New Insights Into the Origins of Dioxins Formed During Chemical Pulp Bleaching, ’ *Canadian Pulp and Paper Association Environment Conference Proceedings,* Vancouver, B. C., Oct. 25-26, 1988, p. 31.

[2] Ronald B. Estridge and William Kraske, American Paper Institute, material presented at the OTA dioxin workshop, Washington, DC, Nov. 14-15, 1988.

[3] Knut P. Kringstad et al., ‘‘Bleaching and the Environment,’ *1988 Pulp Bleaching Conference,* Orlando, FL, June 5-9, 1988 (Atlanta, GA: TAPPI, 1988).

TCDF are transported.[4] Supplemental treatment with chemical coagulant, precipitant, absorbents, and perhaps destruction by ultraviolet light and chemicals could increase the efficiency of the existing waste treatment facilities. Further evaluation is needed on these options,

Should it prove necessary to reduce the amount of dioxins produced from pulp and paper manufacture for health or environmental reasons, one approach to consider is prebleaching technologies that would reduce the amount of lignin passing to the bleach plant. Another approach would utilize brightening technologies that reduce or eliminate chlorine gas from the bleaching sequence. The several options available to reduce the formation of TCDD, TCDF, and other chlorinated organics are not mutually exclusive and can be linked at stages throughout the pulping, bleaching, and waste disposal processes to achieve low levels of discharge.

Because of the pollution potential of chlorinated compounds and the volume of wastewater produced by chlorine bleaching, the chlorination stage is the focal point for efforts to control pollution resulting from the manufacture of pulp. There are several possible approaches to reducing the amount of dioxin and other chlorinated organics formed during chlorine bleaching:

- Delignify pulp to a further degree before bleaching
  - extended delignification
  - oxygen delignification
  - pretreatment with nitrogen (more lignin can be removed without fiber damage)
- Substitute other bleaching chemicals for chlorine
  - chlorine dioxide for part or all of the chlorine
  - hydrogen peroxide
  - alkaline extraction supplemented with oxygen and peroxide
  - ozone (precommercial)
- Modify chlorination procedures (more research needed)
  - optimize the acidity (pH) of the pulp
  - use smaller multiple charges of chlorine instead of one
  - apply chlorine first, then bleach with chlorine dioxide
- Remove known sources of precursors (e.g., contaminated defoamers or other additives, prewash pulp, etc.)
- Improve waste treatment systems (more research needed)
  - chemical coagulant
  - sorption or precipitation enhancers
  - destruction with ultraviolet light or chemicals
  - anaerobic treatment

Elimination of chlorine in the bleach sequence combined with internal recycling of process water aimed at developing an overall “pollution free” pulping system probably offers the best theoretical strategy for reducing the pollution from bleach plants over the long term, but because of practical limitations, it may not be commercially viable for sometimes

OXYGEN DELIGNIFICATION

Although the introduction of any chlorinated bleaching chemical (e.g., chlorine gas, sodium, or calcium hypochlorite), can generate some chlorinated organic compounds, chlorine gas used in the prebleaching stages of the bleaching sequence produces the largest amount (figure 5-1). Chlorinated organics produced by pulp mills contain small amounts of TCDD and TCDF (see ch. 2).[6] Their presence in pulp mill wastes is ascribed to chlorination in the bleach sequence although the precise chemical reactions and mechanisms that produce dioxins are not known. Other factors might also contribute to dioxin formation.

Ever since the connection was made between dioxin and the use of chlorine, the emphasis of those advocating process changes to reduce the formation of TCDD, TCDF, and other chlorinated organics has focused on oxygen delignification technology. The Swedish example has served as a demonstration of

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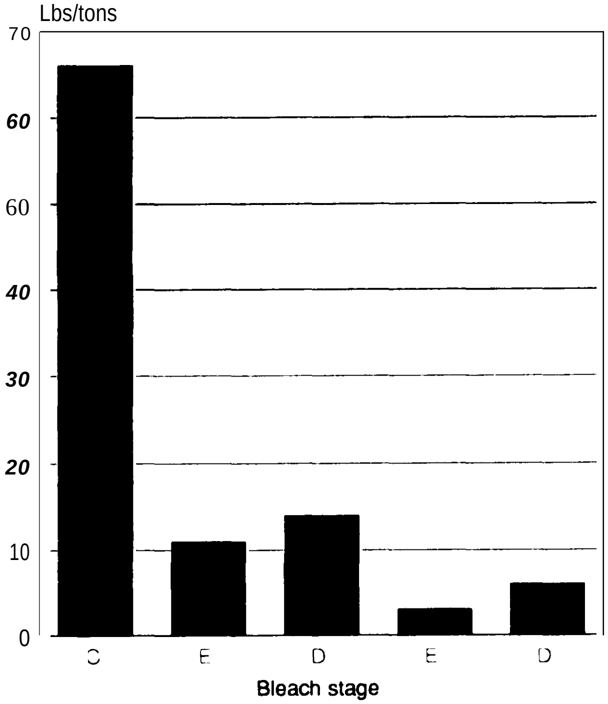
[4] U.S. Environmental protection Agency, *USEPA Bench Scale Wastewater Treatability Study Pulp and Paper Mill Discharges of 2378 -TCDD and 2378-TCDF: Proposed Interim Control Measures Interim NPDES Permit Strategy* (Westlake, OH: EPA Region 5, 1988), p. 17.

[5] Allan M. Springer, *Industrial Environmental Control: Pulp and Paper Industry* (New York, NY: John Wiley & Sons, 1986), P. 161.

[6] U.S. Environmental Protection Agency, *National Dioxin Study,* EPA/350-SW-87-025, August 1987, p. III-33.

Figure 5-l—Chlorinated Waste From Bleaching of Hardwood Pulp



SOURCE. Allan M. Springer, *Industrial Environmental Control; Pulp and Paper Industry* (New York, NY John Wiley& Sons, 1986), p. 166.

one method to reduce the amount of chlorine needed in the bleaching process. Sweden has encouraged the international move toward adopting oxygen delignification to solve the chlorine problem. It should not be overlooked that first, most of the bleached kraft mills in Sweden have already installed oxygen delignification at a considerable capital expense, and second, oxygen delignification is a Swedish technology largely manufactured in Sweden.

The effectiveness of oxygen delignification to reduce the amount of chlorine needed is well documented. It should be noted, however, that other technologies and process modifications are also available that can reduce the amount of dioxins produced, but none will reduce the amount of chlorine-based bleach needed to the degree that oxygen can. Conversion to oxygen delignification is not always the best solution. However, the substitution of oxygen bleaching for chlorination in prebleaching and brightening sequences is considered by some pulp and paper experts to be a technological trend that likely defines the future state-of-the-art in low-chlorine bleach plant design.

Effluent from oxygen bleaches, such as oxygen gas, ozone, or peroxides, can be recycled internally to destroy harmful byproducts that might be formed. Transition from conventional chlorine bleaching to oxygen delignification and bleaching has been faster in Scandinavian countries-particularly Sweden—than it has in the United States and Canada.[7] In Sweden, oxygen bleaching has been used in place of biological waste treatment that is commonly used in North America. Although oxygen delignification was developed in the Soviet Union, the process was commercialized in Sweden in the late 1960s and in the Union of South Africa in the early 1970s.

Early interest in oxygen delignification stemmed primarily from its ability to reduce pulp mill pollution. Substantial reductions in BOD, color, and chlorinated organics in the effluent can be realized, as well as savings in bleaching agents. Oxygen prebleaching may not significantly alter the kinds of chemicals formed (although this has not been determined with certainty), but, when properly conducted, it will probably generate smaller quantities of all these compounds.[8] Moreover, bleaching operations using oxygen do not normally call for a hypochlorite stage, as a result, little chloroform is released (other non-oxygen bleaching sequences also do not use hypochlorite stages, e.g., CEDED).

Chlorinated organics—not specifically dioxins—are major pollutants in the Baltic Sea. Nowhere in the United States have chlorinated organics presented the problems that have been experienced in the Baltic region. BOD has been the major environmental concern in the United States (U.S. standards for BOD were stricter than Sweden's); attempts to

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[7] Fifteen Swedish pulp mills manufacture bleached sulfate pulp. Nine mills currently use oxygen in the first prebleaching Stage of the bleaching sequence and two others have plans to install oxygen stages in the bleach sequence. Committee for the Gulf of Bothnia, Water Pollution Problems of Pulp and Paper Industries in Finland and Sweden, Naturvardsverket Rapport 3384, May 1987, p. 55.

[8] Knut Kringstad and Krister Lindstrom, "Spent Liquors From Pulp Bleaching," *Environmental Science and Technology, vol. 18, No. 8, 1984,* p. 246A,

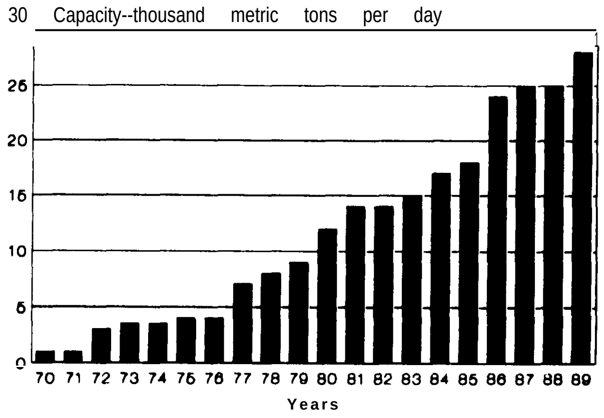
address this problem have relied on secondary biological waste treatment and internal changes in pulp mill processes.

With the exception of Sweden and Germany (Germany has no kraft mills), where environmental requirements have forced acceptance, economics have been a significant motivating factor in adoption of oxygen delignification technology. For instance, in Japan where oxygen delignification systems have recently gained acceptance, oxygen is cheap because it is produced as a byproduct of nitrogen recovery, which is needed in the manufacture of printed electronic circuits. At North American mills where oxygen delignification has been installed, waste improvements have been accompanied by economic benefits from shorter bleaching sequences and smaller and cheaper effluent treatment systems.

Oxygen delignification can cause degradation of the pulp and reduce paper strength. In 1963, this problem was reduced with the discovery that the addition of magnesium chemicals (e.g., magnesium carbonate or sulfate) can reduce or prevent degradation of cellulose fibers.[9] Oxygen delignification and bleaching produces pulp that compares favorably with conventional bleached pulps in most ways. Strength properties of oxygen pulps are slightly less than conventional pulps, but may be acceptable for some products if delignification by oxygen does not exceed about 40 to 50 percent of the pretreatment lignin level.[10] Experts differ as to the viscosity and strength of oxygen pulp compared to conventional pulp. Brightness stability for oxygen pulps is equal to or better than that of conventional pulps.

Since the construction of the first pulp mill to use oxygen delignification in 1970 at Enstra, South Africa, there has been a steady increase in the annual world production of oxygen pulps (figure 5-2). In 1988, world installed capacity was expected to exceed 10 million metric tons per year. About half the oxygen capacity is in Scandinavia and Europe, one-fifth is in North America, and one-fifth is in Japan. About 92 percent of the installed capacity of oxygen delignification systems is in kraft mills, and 60 percent is in bleached softwoods (table 5-l). The use of oxygen delignification is expected to expand worldwide as environmental standards are tightened and will likely accelerate even more if savings in the cost of bleach plant operations favor oxygen pulps.

Figure 5-2—World Production Capacity of oxygen-Delignified Pulp



SOURCE: Larry Tench and Stuart Harper, "Oxygen-Bleaching Practices and Benefits: An Overview," *TAPPI Journal*, November 1987, p. 57.

Capital cost of oxygen delignification systems is high. Cost estimates based on prior conversions from a conventional chlorine bleaching process to oxygen delignification range between $20 million and $30 million for an existing pulp mill with a capacity of 750 to 1,000 tons per day, depending on the need to modify supporting equipment, such as recovery boilers, evaporators, etc. If the mill required expansion of supporting equipment, such as evaporators and brownstock washers, the cost would escalate to $40 million to $50 million. If, in addition, the mill did not have sufficient reserve recovery boiler capacity, the additional liquor treatment required for oxygen delignification would raise the cost to ***$80*** million. However, if the mill did not require recovery modifications, costs may go as low as $8 million to $10 million.

The American Paper Institute estimates that if the 98 bleached chemical pulp mills in the United States that have not yet installed oxygen delignification equipment **(5** have already done so for a combined

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[9] I. Croon and D.H. Andrews, "Advances in oxygen Bleaching: 1, Demonstration of Its Feasibility and Scope, " *TAPPI Journal*, vol. 54, No. 2, p. 1893 *et seq.*

[10] Larry Tench and Stuart Harper, "Oxygen-Bleaching Practices and Benefits: An Overview, " *TAPPI Journal*, November 1987, p. 55.

total of 6,100 tons per day of oxygen pulp capacity). The total capital outlay to the U.S. industry would then be about $3 billion or $40,000 per daily ton of capacity to fit out the U.S. industry with oxygen systems (if capital costs were annualized and changes in operating costs were considered, the costs of oxygen delignification would be lower).

For greenfield construction of a new bleached chemical pulp mill using oxygen delignification, the capital cost of an oxygen system is more attractive. The capital cost of installing an oxygen delignification system in a mill of 1,000 tons per day capacity could be between $25 million to $35 million more than for conventional chlorine bleaching. The higher cost of oxygen delignification compared to conventional chlorine bleaching is part due to the cost of the oxygen generating plant ($1 2 million to $14 million), and part due to the need for larger recovery boilers.[11]

Oxygen Delignification Technology

The objective of chemical pulping is to reduce the amount of lignin carried forward with the brownstock pulp to the brightening stages of the bleach plant. The less lignin that prebleached pulp contains, the less bleaching that is required, Conventional kraft pulping, for example, produces pulp with a kappa number between 32 and 35. By subjecting conventional pulp to oxygen delignification, the kappa number may be reduced to 16 or 17.[12] This allows the use of a short bleaching sequence, since the amount of lignin to be bleached is reduced up to 50 percent. An even higher proportion of lignin can be removed from sulfite pulp. Oxygen delignification is considered to be an extension of the cooking process. With an oxygen bleached pulpit is possible to reduce the amount of chlorine gas bleach. With additional research and development, it may be possible to eliminate it altogether by using ozone, hydrogen peroxide, and/or chlorine dioxide.

Effluent from the oxygen delignification stage is disposed of by cycling it through the pulp mill chemical recovery cycle. If chlorine is used as a bleaching chemical, the effluents cannot be disposed of in the recovery plant because of the corrosiveness of chlorides and the difficulty in purging chlorides from a closed recovery cycle. White liquor, the same reagent that is used in the kraft pulping process, can also be used in the oxygen delignification process and then recycled through the recovery plant. Installation of an oxygen delignification unit may require that the capacity of the chemical and energy recovery plant be increased to accommodate the additional dissolved organic and inorganic chemicals.[13]

Several commercial oxygen delignification systems have been developed. They differ more in detail than in operating principles. These units are of two general types: 1) high consistency, and 2) medium consistency. Consistency refers to the amount of wood fiber in relation to the volume of solution in a reactor vessel. The higher the ratio of fiber to water, the higher the consistency. High consistency oxygen delignification systems use pulp slurries containing 20 to 32 percent fibers. Medium consistency is 10 to 15 percent fibers. At high consistencies, the pulp is more of a ‘‘fluff” than a fluid. The key to effective oxygen delignification systems is the ability to disperse oxygen finely enough to last for the necessary reaction *time.* This cannot be done efficiently with pulp consistencies of less than 6 percent because of energy considerations.

Differences among the oxygen delignification systems are mainly in the design of the reaction vessel and associated pumping and gas handling equipment. In general, the capital equipment cost is lower for a medium consistency system than for a high consistency system.[14] On the other hand, the consumption of oxygen and alkali is somewhat higher for medium consistency oxygen delignification. Medium consistency systems require a longer retention time than high consistency reactors to achieve the same degree of delignification, therefore capacity for medium consistency units must be larger to maintain the same rate of production. Medium consistency oxygen stages are often used to

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[11] Ronald J. Slinn, vice president, American Paper Institute, personal correspondence, August 1988. Cost data supplied by the industry have not been verified with other sources.

[12] Croon and Andrews, op. cit., note 9, p. 1896.

[13] Springer, op. cit., note 5, p. 172.

[14] Kamyr, inc., *Oxygen Delignification*, bull. No. KGDI8OI-WN1O87 (Glens Falls, NY: 1987), p. 11.

Table 5-1—Oxygen Delignification Systems Installed Worldwide

Company	Location	Startup	Sequence	Capacity a.d. metric tons/day	Medium or high consistency	Hardwood or softwood
KRAFT						
Scandinavia						
Billerud	Gruvoen, Sweden	1972	OC$_D$EDED	500	HC	SWD
Munksjo	Aspa, Sweden	1973	OC$_D$EDED	380	HC	SWD
Stora Kopparberg	Skutskaer, Sweden	1977	OC$_D$EDED	650	HC	SWD
MoDoCell	Husum, Sweden	1977	OC$_D$EDED	1,000	HC	SWD
Norrlands Skogsagares Cellulosa	Vallvik, Sweden	1978	OC$_D$EDED	600	HC	SWD
Stora Kopparberg	Skutskaer, Sweden	1978	OC$_D$EDED	650	HC	SWD
Svenska Cellulosa	Oestrand, Sweden	1980	OC$_D$EDED	1,000	HC	HWD/SWD
Sodra Skogsagarna	Monsteras, Sweden	1981	OC$_D$EDED	1,000	HC	HWD/SWD
Kopparfors	Norrsundet, Sweden	1983	OC$_D$E$_O$OD	1,000	HC	SWD
			OC$_D$E$_P$DE$_P$D		MC	
Fiskeby	Skaerblacka, Sweden	1986[a]	OC$_D$E$_O$DD	510	MC	HWD/SWD
Sodra Skogsagarna	Moerrum, Sweden	1989[a]		420	MC	SWD
		1989[a]		700	MC	HWD
				8,410		
Europe and U.S.S.R.						
Cellulose d'Aquitaine	St. Gaudens, France	1973	OCEDED	500	HC	HWD
ZCP	Kwidzyn, Poland	1978	OC$_D$EHD	600	HC	SWD
UST	Illimsk, USSR	1979	OD$_C$EHDED	800	HC	SWD
Zellstoff	Pols, Austria	1984	OD$_C$EDED	630	MC	SWD
V/O Prommash	Svetogorsk, USSR	1985	ODEDED	455	MC	HWD
				2,985		
Africa and South America						
Sappi	Enstra, S. Africa	1970	ODED	200	HC	SWD
Sappi	Enstra, S. Africa	1978	ODED	500	HC	HWD
Sappi	Ngodwana, S. Africa	1985	OD/CED	575	HC	SWD
Suzano de Papel e Celulose	Suzano, Brazil	1989[a]		1,365	MC	HWD
				2,640		
North America						
Chesapeake	West Point, VA	1972	C$_D$OD	550	HC	HWD
Eddy Forest Products	Espanola, Ontario	1977	OC$_D$E$_O$HD	500	HC	SWD
Eddy Forest Products	Espanola, Ontario	1980	OC$_D$EHD	500	HC	HWD
Union Camp Corp.	Franklin, VA	1981	OCED	800	HC	HWD
Procter & Gamble	Oglethorpe, GA	1980	OD/CD$_O$D	1,000	HC	SWD
Union Camp Corp.	Eastover, SC	1984	OC$_D$ED	650	HC	HWD/SWD
Consolidated Paper	Wisconsin Rapids, WI	1980	OC$_D$E$_O$D	450	MC	HWD
Champion Internat'l	Pensacola, FL	1986	OC$_D$E$_O$D	730	MC	HWD
Champion Internat'l	Pensacola, FL	1987	OC$_D$E$_O$D	560	MC	SWD
				5,740		

Table 5-1—Oxygen Delignification Systems Installed Worldwide—Continued

Company	Location	Startup	Sequence	Capacity a.d. metric tons/day	Medium or high consistency	Hardwood or softwood
Japan						
Daishowa	Shiraoi	1975	OCEHD	550	HC	HWD
Jujo Paper	Kushiro	1975	OH	600	HC	SWD
Taio Seishi Paper	Mishima	1984	OD/CE$_O$HE[e]	665	MC	HWD
Oji Paper	Tomakomai	1985	OH	550	MC	SWD
Chuetsu Pulp Kogyo.K.K.	Sendai	1986	OCH$_P$HE$_P$D	550	MC	HWD/SWD
Taio Seishi Paper	Mishima	1986	OCEHDD	525	MC	SWD
Daishowa	Suzukawa	1986		620	MC	SWD
Oji Paper	Ebetsu	1986	OD/CEHD	650	MC	HWD/SWD
Daishowa	Shiraoi	1986		400	MC	HWD
Hokuetsu Paper	Niigata	1986	OCEHD	480	MC	HWD
Kishu Paper	Shingu	1987[a]	OCEHD			
				5,590		
SULFITE						
Hunsfos	Hunsfos, Fed. Rep. of Norway	1979	OCEHH	130	HC	WD WD
Bayrische Zellstoff	Kelheim, Fed. Rep. of Germany	1979	OEDH or OE$_P$H	160	HC	SWD
Rauma-Repola	Rauma, Finland	1983	OCEDH	450	MC[b]	SWD
Celpak	Paskov, Czechoslavakia	1984	OC$_D$ED	660	HC	SWD
Hannoversche Papierfabriker	Alfeld-Gronau, Fed. Rep. of Germany	1986	OCEH	250	MC[b]	SWD
PWA Wa	Mannheim, Fed. Rep. of Germany	1986	PO$_S$-PO$_A$-HH[c]	185	MC	SWD
Flambeau Paper	Wisconsin, USA	1987[a]	OH	200	MC[b]	HWD
				2,035		
SPECIALTY						
Peterson & Son	Moss, Norway	1975		140	MC	SWD[d]
Korsnas Marma	Korsnas, Sweden	1984		100	MC	HWD/SWD[d]
				240		

[a] Under construction

[b] Atmospheric reactor

[c] PO$_S$ = acid peroxide/oxygen
PO$_A$ = alkaline peroxide oxygen

[d] High-yield polysulfide

[e] Screen rejects

SOURCE: Larry Tench and Stuart Harper, "Oxygen-Bleaching Practices and Benefits: An Overview, *Tappi Journal*, November 1987, p. 56

achieve 35 to 40 percent delignification. Both medium and high consistency bleaching systems require efficient washing of the oxygen bleached pulp to prevent carry over of the dissolved organics into the bleaching system.

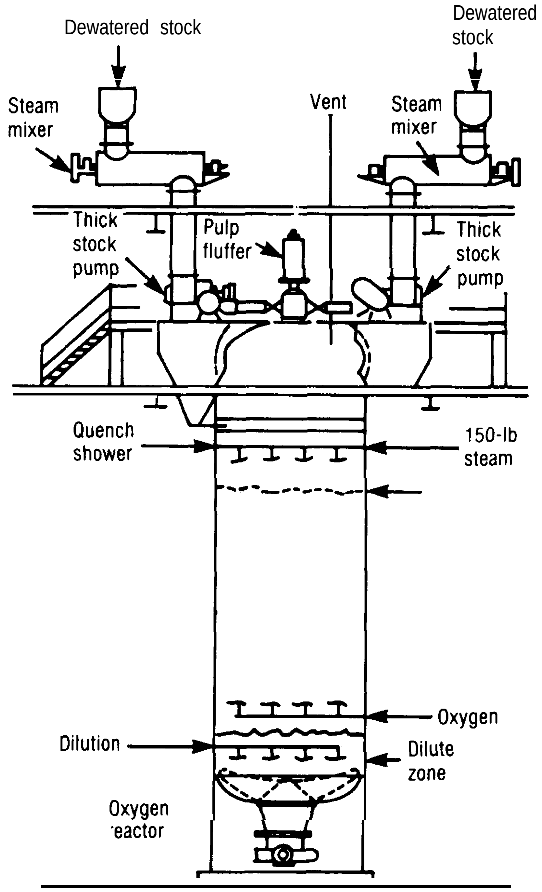
Medium consistency oxygen delignification causes less degradation of the wood fibers than high consistency systems, but because of the slower rate of delignification it is more difficult to delignify to very low kappa numbers using medium consistency. Two-stage medium consistency oxygen systems have been proposed to overcome this problem.[15] Medium consistency may have several other advantages over high consistency processes, such as:

- Massive dewatering equipment is not needed.
- Loss in pulp strength is about one-third.
- Magnesium salt protectors are not needed.
- Use of oxygen is reduced by one-fourth.
- Almost no carbon monoxide is produced.
- Little danger of explosion from gas accumulations.[16]

High Consistency Systems

High consistency oxygen delignification systems can produce high brightness pulps up to 90+ GE with supplemental bleaching, In the high consistency processes well-washed brownstock pulp, that is dewatered after discharge from the digester to 28 to 32 percent consistency, is treated with alkali (oxidized white liquor) and magnesium salts (a protector or inhibiter) in a mixer, it is then fluffed and fed into an oxygen reactor (figure 5-3). The pulp is heated with pressurized steam (90 to 120 'C) and oxygen gas is injected into the bottom of the reactor. The atmosphere in the reactor is maintained at about 80 percent oxygen. Gases produced by oxidation of the lignin are purged to avoid combustion. The oxygenated pulp is washed after discharge from the reactor before being sent to the bleach plant.

Figure 5-3—High Consistency Oxygen Delignification Stage



SOURCE: Adapted from Kenneth E. Smith, "Oxygen Bleaching System Operating Wall at Union Camp's Franklin Mill," *Pulp & Paper*, October 1982.

Medium Consistency Systems

The steps for preparing the brownstock for oxygen treatment that are used in the medium consistency process are similar to those used for high consistency oxygen delignification. Pulp consistency is adjusted to between 10 and 15 percent. Magnesium salts may or may not be added to the pulp depending on the selected procedure. Oxygen gas is dispersed throughout the pulp mixture, and steam is added to bring the mixture to a temperature of about 100 "C before it is injected at the base of the oxygen reactor (figure 5-4). The mixing of the

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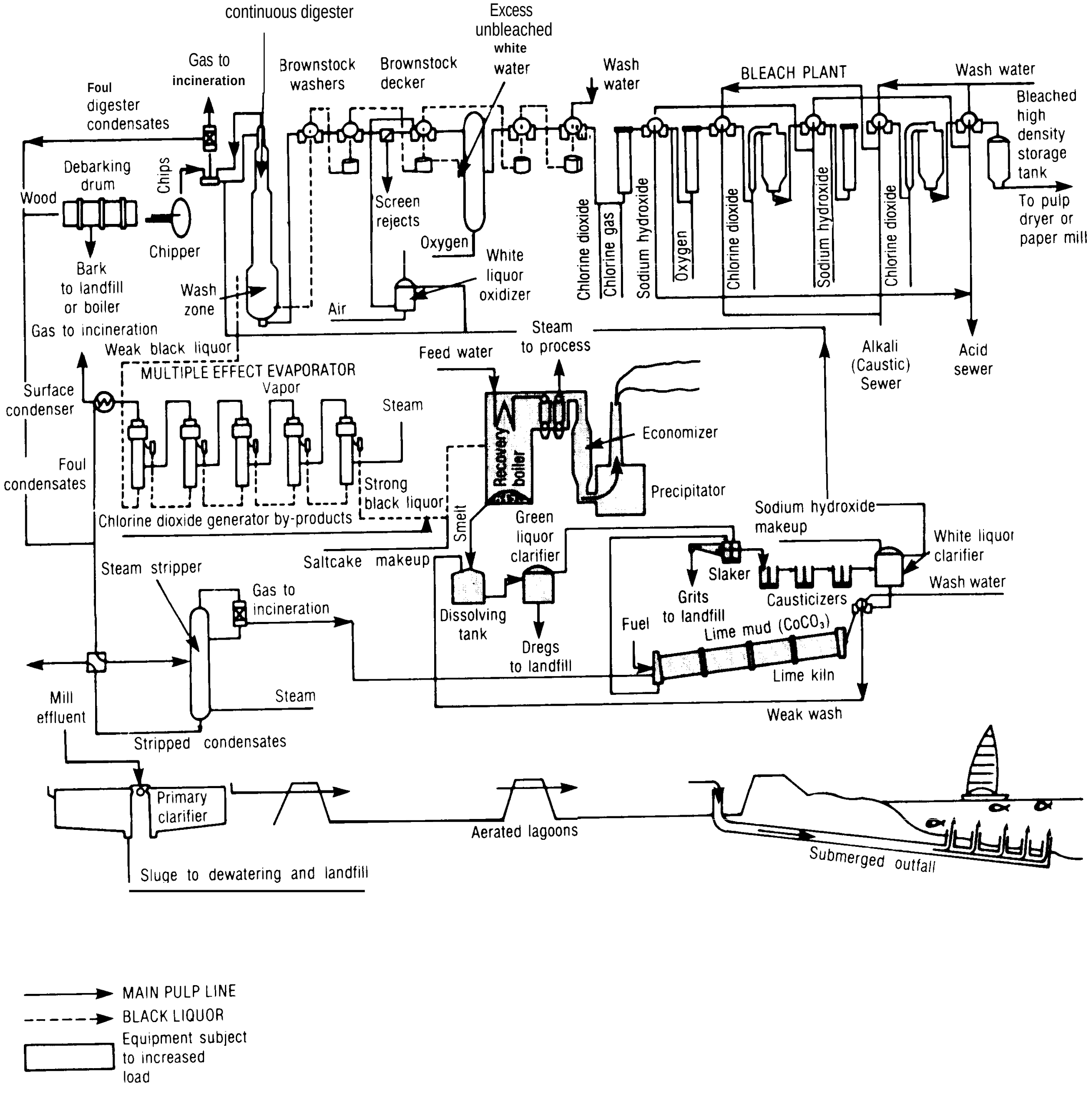
[15] Ibid., p. 12,

[16] Michael D. Meredith and Joseph M. Bentvelzen, ''oCO&The Bleach Sequence of the '80s,' 1984 *Oxygen Delignification Symposium* (Atlanta, GA: TAPPI Press, 1984), p. 112.

Figure 5-4-Oxygen Delignification System Installed in a Bleached Kraft Pulp Mill



SOURCE: Environment Ontario, *Stopping Water Pollution At Its Source* (Toronto, Ont: Ministry of the Environment, 1988).

oxygen and steam with the pulp prior to transport to the reactor is the major difference in materials handling between the two systems. Reaction begins immediately, and about half the oxygen is consumed in the first 2 minutes. The oxygenated pulp is normally retained in the reactor for 45 to 60 minutes.

Effects of Oxygen Delignification on Pollutant Loads

The processes and conditions under which dioxins are formed during pulping, bleaching, and brightening are not well known. Dioxins are usually formed in small quantities, and the conditions leading to their formation are poorly understood. Heat, light, and catalytic action have been shown to stimulate the conversion of chlorinated precursors to dioxins.[17] Chlorine makes up about 44 percent of a TCDD molecule. Lignin is a complex polymer containing many resin acid, fatty acid, and phenolic derivatives that could serve as precursors for the formation of dioxins in the presence of chlorine under appropriate physiochemical conditions. Other non-lignin components (e.g., extractives, nonchlorinated dioxins, and catachols), may also be precursors of TCDD or TCDF.

Impco Division of Ingersoll-Rand, an equipment manufacturer that produces oxygen delignification systems, claims that oxygen treatment of prebleached pulp before a short chlorination brightening sequence significantly reduces the pollution load in kraft mill effluents compared to the most common five-stage bleach sequence CEDED (table 5-2). Similar results are reported from prebleach oxygen delignification using a chlorine-chlorine dioxide first stage bleach sequence (C_DE_oD) compared with a long bleach sequence (CDEoDED) without oxygen pretreatment (table 5-3). Furthermore, the total amount of chlorinated phenolic compounds formed in the bleaching process decrease considerably as a result of oxygen delignification (figure 5-5). The phenolic compounds released from conventional and oxygen-delignified pulps are lower in quantity but probably do not differ much in composition compared to those produced from conventional pulp,[18] To the extent that phenolic compounds may be linked with the production of TCDD, this may indicate that oxygen delignification could reduce the amounts of phenolic precursors present in the pulp.

Limited data are available that directly relate the reduction of TCDD and TCDF to oxygen delignification. There is substantial evidence that oxygen delignification can reduce the amount of waste chlorinated organics produced, as well as reduce BOD and COD (chemical oxygen demand), and can significantly reduce effluent color. Few analyses have been made of dioxin in effluents and pulps from oxygen-treated pulps. The Swedish Pulp and Paper Research Institute recently published some preliminary information on the effects of oxygen delignification on dioxins and furans.

Sweden's experience with oxygen delignification and appropriate bleaching sequences show that the release of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF)[19] in kraft pulp mill effluents can be reduced to relatively low levels (table 5-4). Similar reductions in PCDD and PCDF have been recorded in prebleached oxygen pulps. Conventionally bleached softwood pulps contained levels of PCDD and PCDF of between 9 and 29 ppt; oxygen pulps contained between 0.2 and 5 ppt (expressed as TEQ-toxic equivalents) .20 A similar sample of bleached pulp from five U.S. kraft mills without oxygen delignification averaged 13 ppt TCDD and 93 ppt TCDF (TEQ about 22 ppt, within the range of Swedish mills reported above).[21] One U.S. mill with a softwood oxygen delignification line and a short bleaching sequence including chlorine dioxide (C_D) in the first bleaching stage reports no detectable levels of TCDD in either bleached pulp or effluent.[22]

Extended Delignification

Alkaline digestion (cooking) and oxygen delignification are both aimed at reducing the amount of lignin in the wood pulp before it is brightened in the bleach plant. Therefore, oxygen is considered an

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[17] U.S. Environmental Protection Agency, *Dioxins*, EPA-600/2-80-197 (Cincinnati, OH: EPA Industrial Research Laboratory, 1980).

[18] U. Germgard et al., ''Oxygen Bleaching and Its Impact on the Environment,'' *1984 Oxygen Delignification Symposium* (Atlanta, GA: TAPPI Press, 1984), p. 101.

[19] PCDD and PCDF include TCDD and TCDF as well as other related isomers.

[20] Kringstad et al., op. cit., note 3, pp. 2-3.

[21] U.S. Environmental Protection Agency, *U.S. EPA/Paper Industry Cooperative DioxinScreeningStudy,* EPA-440/1-88025 (Washington, DC: *1988)1* p. 76.

[22] U.S. Environmental Protection Agency, op. cit., note 4, p. 1.

Table 5-2—Effluent Characteristics of Oxygen-Treated Bleached Pulp and Pulp Bleached by the Common Chlorinated Bleach Processes[a] (pounds per ton)

Bleach sequence	BOD_5	COD	Color	CL-
CEDED	10-39	80-90	180-250	60-70
OCED	10-15	40-50	30-50	30-40
Percent Difference	45-55	45-50	80-85	35-55

[a] Based on 50 percent delignification.

SOURCE: Ingersoll-Rand, Oxygen *Delignification Technology. An Update* (Nashua, NH: Ingersoll-Rand, 1986), p. 4.

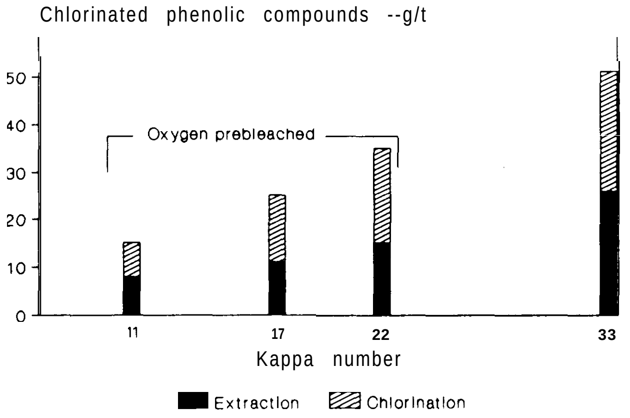
Table 5-3-Effluent Characteristics for Softwood Kraft Pulps With and Without Oxygen Delignification[a] (kg/metric ton)

Bleach Sequence	BOD^5	COD	Color	TOCL
C_DE_ODED	15-21	65-75	200-300	5-8
OC_DE_OD	8-11	30-40	80-120	3-4
Reduction (Percent)	40-50	45-55	60-75	35-50

[a] Oxygen stage reduction in kappa number 4550 percent.

SOURCE: Larry Tench and Stuart Harper, "Oxygen Bleaching Practices and Benefits An Overview," *TAPPI Journal*, November 1967, p. 56.

Figure 5-5—Phenolic Compounds Formed With and Without Oxygen Bleaching



SOURCE. U Germard et al., "Oxygen Bleaching and Its Impact on tha Environment," *1984 Oxygen Delignification Symposium* (Atlanta, GA. TAPPI Press, 1984), p 101.

extension of the cooking process. Retaining the pulp in the digester for a longer period and exposing it to a modified time-temperature-alkaline cycle can reduce the amount of lignin retained in the brownstock. There is a practical limit to the amount of cooking that can be done without dissolving the desired components of the wood fiber and reducing the pulp yield. A balance, therefore, between cooking and other delignification processes must be used.

A combination of extended cooking—sometimes called ''modified" cooking—and oxygen delignification has been used to achieve kappa numbers between 10 and 12 for unbleached pulp.[23] Others believe that kappa numbers as low as 7 can be achieved without loss of pulp strength.[24] With prebleached pulps of such low lignin content, it may be technically possible to eliminate the use of chlorine in the bleaching process altogether.

The standard kraft cooking procedure generally yields softwood pulp with kappa numbers between 30 and 35. Oxygen delignification can reduce the standard prebleached pulp to 16 to 20, although commercial practice is typically limited to 20 kappa because of strength considerations. Extended cooking plus oxygen treatment can produce pulps with kappa numbers between 7 and 12. By starting the kraft cook at a relatively low concentration of alkali

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[23] Stig Andtbacka, '' Low Kappa Pulping Followed by Oxygen Deli unification, *Australian Pulp and Paper Industry Technical Association Journal*, March 1986, p. 129.

[24] Kamyr, Inc., *Kamyr Continuous Cooking Plus Modified Continuous Cooking Plus Medium Consistency Oxygen* (Glens Falls, NY: date unknown).

Table 5-4-Emissions of PCDD and PCDF (expressed as TEF)[a] in Receiving Waters From Swedish Pulp Mills With and Without Oxygen Delignification

	Pulp	Bleaching process	Production (tons/yr)	TEF (g/yr)
Without oxygen delignification				
1	softwood	(C_{95}+ D_5) (E()) H D	300,000	2-5.8
	Hardwood	(C_{95}+D_5) (E_O) H D E D		
2	softwood	C (E-O) H D (E_P) D	125,000	0.7
	Hardwood	(C_{10}+D_{90}) E D E D		
With *oxygen delignification*				
3	*softwood*	*O (C_{85}+D_{15})* E D E D	160,000	0.4
	Hardwood	O (C_{70}+D_{15}) E D E D	160,000	
4	Softwood	O(C_{85}+D_{15}) (E_O) D D	75,000	0.7
	Hardwood	O (C_{70}+D_{15}) (E_O) D D		
5	softwood	O (C_{85}+D $_{15}$) (E_O) D E D	235,000	0.1
	Hardwood	O (C_{70}+D_{I5}) (E_O) D E D	85,000	

[a] TEF is the "Toxicity Emission Factor" according to G. Eadon as discussed in J.S Bellini and D.G. Barnes, *Toxicology* and *Industrial Health*, vol. 1, No. 4, 1985, p 235.

SOURCE: Knut P. Kringstad et al., addendum 10 "Bleaching and the Environment," *1988 International Pulp Bleaching* Conference, Orlando, FL, June 5-9, 1988 (Atlanta, GA: TAPPI, 1988), pp. 2-3.

and lengthening the retention period, low-lignin pulps are produced with comparable strength to pulps containing more lignin that are produced by standard cooking methods.

Extended delignification can be either a batch process or a continuous process. Continuous modified cooking digesters have been developed by Kamyr, Inc. and others, which split the white liquor (alkali) charge and introduce it into different points in the impregnation and cooking stages and at the base of the reactor (figure 5-6).

As its name implies, extended delignification requires a longer cooking time than standard pulping, While standard kraft pulp is cooked for 1 to 3 hours, extended delignification, including impregnation (steeping) and cooking, may require over 4 hours.[25] Initial concentration of alkali in the cooking liquor is about half of that used in the standard cook. By the end of the cook, however, about 2 percent more alkali is used in the extended process than in the standard. Pilot tests have shown that pulp lignin concentration at the end of extended delignification may be 40 to 60 percent of that contained in standard pulp.

Pretreatment of Oxygen Pulps With Nitrogen Dioxide (PRENOX)

Laboratory experiments and pilot plant studies have demonstrated that treatment of pulp with a combination of nitrogen dioxide and oxygen prior to oxygen delignification can also reduce the lignin in prebleached pulps.[26] Nitrogen dioxide has been shown to promote more selective delignification in the oxygen delignification stage, thus resulting in less damage to the fiber.[27] The upper limit of delignification for most softwood kraft pulps is considered to be about 50 to 55 percent for oxygen treatment. Delignification to these limits, however, causes fiber degradation. To avoid this, oxygen delignitication is generally reduced to about 40 to 45 percent. By using PRENOX before the oxygen stage, delignification rates of about 75 percent (kappa number 8-10) may be possible to achieve.[28]

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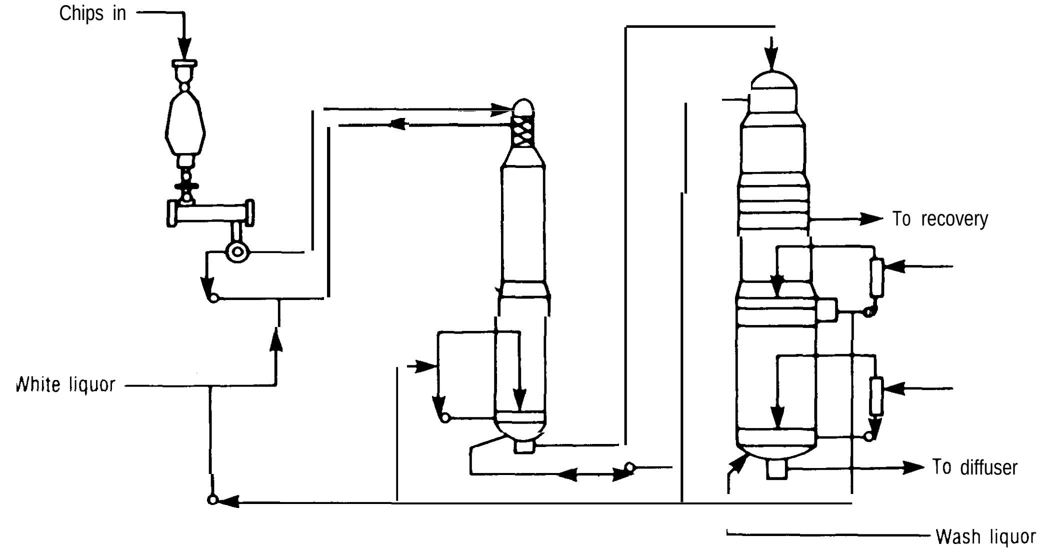
[25] Andtbacka, op. cit., note 23, p. 130.

[26] Rolf Brannland et al., "Oxidation of Pulp With NO_2/O_2 Prior to Oxygen Delignification—A Novel Process With Potentially Less Pollution,' S-93E; 04/87 2000 MarknadsRadct, Reprinted by Sunds Defibrator, May 1986.

[27] D. Lachenal and C. DE Choudens, "High Efficiency Oxygen and Peroxide Delignification, ' *Cellulose Chem. Technol., vol. 20,* p. 557,

[28] Bryan L. Sorensen, ''New Bleach Plants: A Review of Present State of the Art, *1987 Bleach P/ant Operations Seminar* (Atlanta, GA: TAPPI Press, 1987), p. 183.

Figure 5-6-Continuous Digester for Extended Delignification



SOURCE: Stig Andtbacka, "Low Kappa Pulping Followed by Oxygen Delignification," *Australian Pulp and PaPar* Industry *Technical Association* Journal, March 1986, p.130.

Soda-Anthraquinone/Oxygen Pulping

Although the kraft pulping process efficiently produces pulps with unmatched quality and may be used with any wood species, there are continuing efforts to develop a pulping system that eliminates sulfur chemicals from the pulping process because of the odor and environmental concerns. The most expensive capital investment in a kraft pulp mill is the chemical recovery plant. A soda-anthraquinone plant requires a similar recovery plant to that of a conventional system, however, the odor control equipment used in conventional mills is not needed.

The soda process was a forerunner of the kraft process.[29] Its major drawbacks are low pulp yields and inferior pulp quality that result from long cooking times, high temperatures, and the strong solution of sodium hydroxide needed to produce bleachable grade pulps.

The addition of small amounts of anthraquinone (AQ) to the pulping liquor are effective in accelerating the soda pulping process and improving pulp yields. Anthraquinones have also been used with kraft pulping, but a larger amount of the expensive chemical must be used to be effective and residual amounts of AQ can interfere with the chemical recovery plant. Furthermore, AQ is regulated by the Food and Drug Administration, and only small residual amounts are permitted in finished products.

Laboratory experiments with a two-stage soda/AQ-oxygen-sodium hydroxide delignification of hardwood has produced pulp of kappa numbers between 10 to 12 with about 5 percent higher pulp yields than comparable kraft pulp. Lignin content of softwoods pulped (kappa number 20) by the two-stage process did not match those of the hardwood pulp, however.[30] Researchers found that to avoid fiber degradation, the soda cooking must be stopped at a high kappa number and the remainder of delignification done with oxygen.

DISPLACEMENT BLEACHING

There is no difference between the chemistry of displacement bleaching and that used in conventional bleaching, only in the efficiency of the mass

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[29] Hutch Holton, * 'Softwood Pulping: A Major New Process, " *Pulp& Paper Canada, vol. 78,* No. 10, October 1977, p. 19.

[30] Y.C. Tsai, H-m. Chang, and J.S. Gratzl, ''Optimization of Soda-AQ/Oxygen Pulping Of Southern pine, '' 1984 *Oxygen Delignification Symposium* (Atlanta, GA: TAPPI Press, 1984), p. 31.

transfer.[31] When bleaching chemicals are displaced through a pulp mat, the fibers are continually exposed to highly concentrated bleaching chemicals, therefore bleaching is very rapid.

Displacement (sometimes referred to as "dynamic") bleaching is generally conducted in a multistage displacement tower (figure 5-7). Filtrate withdrawn at each stage is supplemented with makeup chemicals and reused. Unbleached pulp moves sequentially upward, while white liquor moves downward through the bleaching column. Displacement bleaching uses a minimum of water, thus reducing the amount of waste effluent and enabling the recycling of bleaching chemicals. The system is suited for use in a "closed-mill" configuration (see above).

Any water soluble bleaching chemical, including chlorine gas, can be used in displacement bleaching. Softwood and hardwood pulps of 86 to 88 GE brightness have been produced by displacement systems.[32] Displacement bleaching technology has produced mixed results. Although it requires more chemicals, and causes corrosion and scaling problems in some instances, displacement bleaching is still considered promising.

CLOSED-CYCLE BLEACHED PULP MILL

During the past 20 years the concept of a closed-cycle pulp mill that could significantly reduce the amount of waste effluents has received some attention. The closed-cycle concept involves:

- reducing the amount of water consumed by using filtrate as wash water,
- cycling the spent bleaching chemicals to the chemical recovery plant, and
- recovering the salts introduced into the recovery system for either re-use in manufacturing the bleaching chemicals or for disposal (figure 5-8).

By closing the water cycle of a bleached kraft mill, the demand for heat is reduced and considerable energy savings can result. Excess heat produced in the process is disposed of as low-grade waste heat into cooling waters. A closed-cycle mill bleach plant might use only 3,900 gallons per air-dry ton of pulp produced, while an average North American Mill would use 20,000 gallons.[33] A mixture of chlorine dioxide and chlorine gas is substituted for pure chlorine in the first bleaching stage to avoid reducing the pulp strength during the high-temperature-chlorination (60 °C).[34]

Pulp manufacture and bleaching, being chemical processes, obey the general principles of chemical combination and mass balance, In a mill in which water and all chemicals are recycled, all of the chemicals must be kept in proper balance or either an excess or shortage of bleaching chemicals will occur. An excess of certain chemicals, particularly sodium chloride (common salt), can contribute to corrosion of the recovery boiler. Some of the recovered salt can be reused to produce chlorine dioxide, but the excess must be disposed of. Corrosion-resistant materials and careful chemical control have largely overcome these problems.

The Great Lakes Paper Co. at Thunderbay, Ontario, installed the first closed-cycle mill in 1977, but the process has not been successful, and the mill is not now operating in the closed-cycle mode. Severe operating problems have been encountered which have resulted in abandoning the process. If these problems could be overcome by further development, the closed-cycle concept might reduce the cost of biological waste treatment, reduce energy costs, increase fiber yield, decrease water usage, and reduce chemical costs.

It is possible that some variation of the closed-cycle bleached kraft mill concept could be developed to incorporate oxygen delignification, extended delignification, or displacement bleaching, thus avoiding some of the problems encountered with conventional bleaching sequences.

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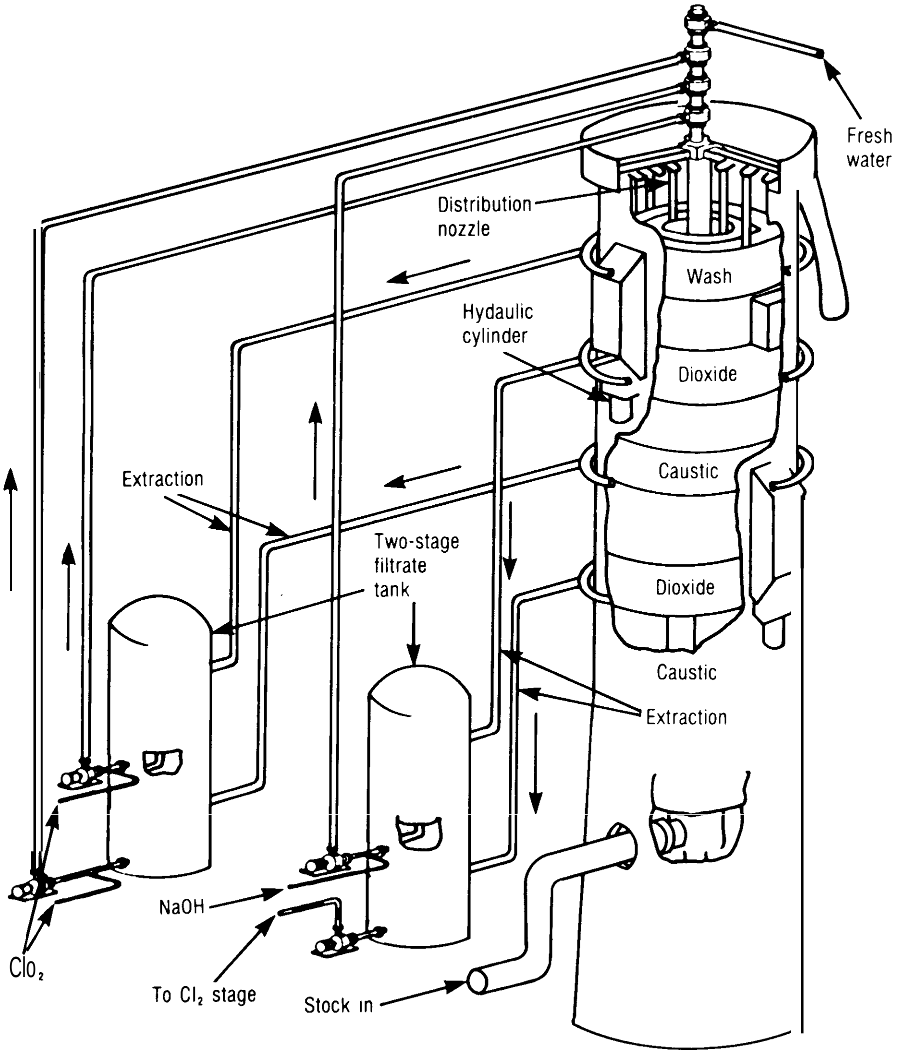
[31] Johan Gullichsen, "Displacement Bleaching, " *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 276.

[32] Springer, op. cit., note 5, p. 170.

[33] W. Howard Rapson, "The Closed-Cycle Bleached Kraft Pulp Mill," *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 415.

[34] Springer, *op.* cit., note 5, p. 129.

Fgaure 5-7-Multistage Displacement Bleach System Single Tower Bleach Plant Showing an EDED Wash Sequence

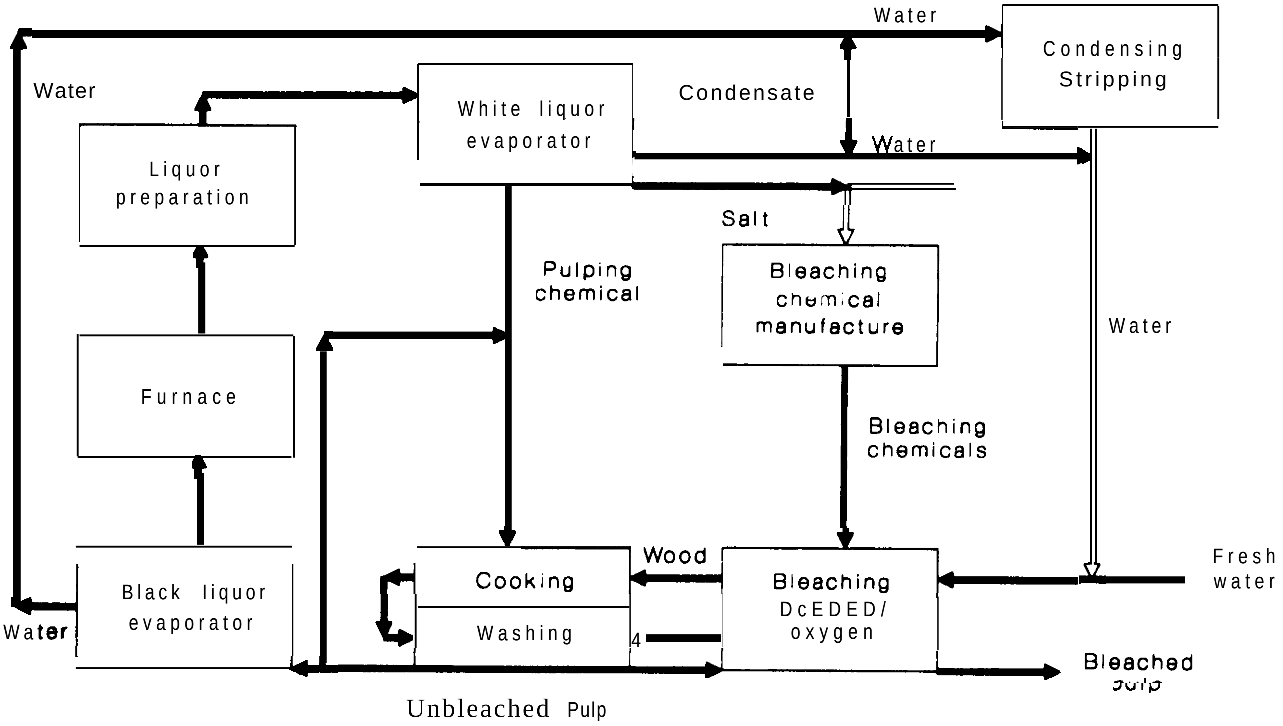


SOURCE: John Gullichsen, "Displacement Bleaching," *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979). p 288.

WASTE-OUTLET TREATMENT TECHNOLOGIES

Several physical and chemical treatments have been developed to cleanse pulp and paper effluents. Waste treatment processes include resin separation and ion exchange; use of chemicals such as aluminum oxide, metallic ions, lime, amines, and ozone; adsorption by wood; biological treatments such as enzymes and bacteria; filtration systems such as activated charcoal; membrane separation; and ultrafiltration, irradiation, and reverse osmosis. It is technically feasible, but extremely costly, to clean pulp-mill wastes to the purity of drinking water. In judging the economics of waste treatment systems, the cost of the exotic waste treatment technologies is generally compared with the cost of secondary biological treatment, which is the U.S. industry standard for removing most foreign materials other than color.

Figure 5-8—Closed-Cycle Bleached Kraft Pulp Mill



SOURCE: W. Howard Rapson, "The Closed-Cycle Bleached Kraft Pulp Mall," *The Bleaching of Pulp—Third Edition* (Atlanta, GA: TAPPI Press, 1979), p. 414.

The effectiveness of any waste treatment system is related to the internal processes used for delignifying and brightening the pulp. The load on the waste treatment plant can be reduced by using some of the technologies discussed above, e.g., oxygen delignification, soda-AQ pulping, or displacement bleaching. Use of bleaching sequences including oxygen, chlorine dioxide, hypochlorite, peroxide, or ozone can also change the nature of the treatable wastes. Waste treatment and pulping and bleaching technologies, therefore, may be considered as an integral system that can be balanced to achieve the desired performance standards.

Theoretically, the optimum way to make waste treatment a less costly venture is to integrate it into the manufacturing process. Benefits can then be gained from conservation of raw material, fibers, additives, energy, and water. Cost analyses of internal controls v. external controls generally show that internal modifications may be less capital intensive.[35] On the other hand, external pollution control does not interfere with established manufacturing processes and provides flexibility for a range of operating conditions and exigencies. Realistically, successful control probably requires a combination of both.

Color and solids are the first targets for cleanup of the pulp waste stream as it leaves the mill outlets. Untreated pulp-mill effluents are generally of a deep mahogany color. Most of that color is derived from the bleaching process, and most of that is from the caustic extraction process after the first bleaching stage. Most of the color is attributable to lignin in the waste effluent. Lignin is resistant to biodegradation,

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[35] H. Gehm, *State-of-the-Art Review of Pulp and Paper Waste Management*, EPA Technology Series EPA-R2-73-184 (Washington, DC: U.S. Government Printing Office, 1973), p. 32.

and secondary biological treatment plants remove only 30 percent or less of the color component.[36]

Primary Treatment of Suspended Solids

Suspended solids in the waste stream consist of bark, fiber, fillers, clay, and coloring agents. These are removed by sedimentation, flotation, and screening. Grit chambers, screens, and chemicals are used as sediment clarifiers to remove grit. Removal of suspended solids and grit currently constitute primary (first stage) treatment of pulp and paper mill waste.

Secondary Biological Treatment

Removal of suspended solids in the first stage is generally followed by biological waste treatment that is principally aimed at reducing the BOD of treated water. Secondary biological treatment has little effect on effluent color, but it may significantly reduce levels of toxic pollutants .37 As its name implies, biological treatment relies on the assimilation and conversion of potential pollutants in the waste effluent by bacteria, fungi, algae, and other living organisms. Since biological treatment relies on the physiological processes of living plants and animals to reduce the pollution load, the second stage of waste treatment is similar to farming-the plants and animals must be kept healthy, productive, and reproducing. In order to promote biological activity, adequate air and nutrients must be provided to the biota.

Biological treatment can remove 80 to 95 percent of the BOD. Research has shown that chlorinated bleach plant derivatives are more difficult to degrade by biological processes than nonchlorinated wastes. Several biological treatment systems are currently used to treat pulp mill waste (e.g, oxidation ponds, activated sludge, and aerated basins). Emerging biological treatment technologies include: rotating biological surfaces, fixed-film activated sludge, aerated activated carbon, and deep tank aeration.

Bench-scale wastewater treatability studies conducted by EPA indicated that the addition of alum or lime can remove more than 95 percent of TCDD and TCDF in bleach plant wastewater by improving the recovery of suspended sediments to which they adhere. Use of chemical treatments would probably require additional clarification and sludge dewatering facilities at most mills. The application of a non-ionic polymer to an oxidation pond reduced TCDD and TCDF to less than detectable levels.[38]

Oxidation Ponds

Oxidation ponds or basins depend primarily on surface exchange with the atmosphere for aeration, although some oxygen may be supplied photosynthetically by aquatic plants. Large surface areas are generally needed to provide sufficient air to maintain biological activity, therefore oxidation ponds tend to be large and shallow. Since the rate of biological activity increases with temperature, oxidation ponds work best in warmer southern climates. Oxidation ponds are relatively inexpensive, require little mechanical equipment, produce little secondary waste products that must be disposed of, and in emergencies can serve as temporary impoundments should an accidental discharge of harmful chemicals occur in the mill. Racetrack-shaped oxidation ditches are sometimes used to eliminate the primary clarification stage. Oxidation ditches require mechanical aeration because of the smaller water surface and perform more like an extended aeration activated sludge process than like a conventional oxidation pond system.

Oxidation basins are frequently equipped with aerators to increase the rate of biological activity (aerated stabilization basins). Nitrogen and phosphorous fertilizers are sometimes added if the waste stream is nutrient deficient. These supplemental treatments can reduce the retention time in the oxidation pond to 8 to 10 days in order to reduce BOD to a low level. The addition of mechanical aerators increases the cost of oxidation ponds, but they are generally cheaper than activated sludge systems.

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[36] Springer, op. cit., note 5, p. 182.

[37] C.C. Walden and J.C. Mueller, *Investigation of the Effect of BOD Reduction Systems on Toxicity*, CPAR Rept. No. 150-1 (Ottawa, Ont: Canadian Forest Service, 1973).

[38] U.S. Environmental Protection Agency, op. cit., note 4, P. 9.

Activated Sludge

Activated sludge treatment systems are often used where space limits the use of oxidation ponds. An adaptation from sanitary sewage treatment, activated sludge is a high-rate biological process that can reduce waste treatment retention time to 3 to 8 hours. The biological mass that is produced in the aeration stage of the treatment process is separated in a secondary clarifier and the active biological components are returned to the process, thus further accelerating biological activity.

Activated sludge systems are flexible and can be adapted to treat a wide range of wastes. However, these systems cannot withstand shocks from emergency mill releases nearly as well as oxidation ponds, and the biological balance of the process is more sensitive to chemical and biological perturbations. The capital and operating cost of activated sludge systems are generally twice as great as aerated ponds.

The pulp and paper industry is the largest user of pure oxygen-activated sludge (UNOX) technology, with 16 plants in operation in 1986.[39] Pure oxygen systems can remove 87 to 97 percent of BOD. The process has several advantages over conventional activated sludge systems such as, smaller aeration tanks required better tolerance to "shock loading," and better sludge settling. A buildup of carbon dioxide at some UNOX plants has raised concern about the potential toxicity to fish. Retention time in pure oxygen systems is about 3 to 4 hours.

Two-stage activated sludge systems, such as the Zurn Attisholz process, using two oxygen levels sequentially with high recycling rates can reduce BOD 95 percent and the process is very stable. Cost of the two-stage process may be slightly less than with conventional activated sludge.[40] There is some evidence that the two-stage oxygen activation process is more efficient in reducing toxicity of kraft wastewater.[41]

New or Developing Treatment Technologies

A number of of coagulant that remove color have been tested. Although several are effective, e.g., alum, ferric sulfate, sulfuric acid, activated carbon, etc., they are expensive. Lime is the least costly precipitation agent, and can be reclaimed in a kraft mill by oxidizing in the lime kiln. Pretreatment of waste effluents with enzymes before precipitation with lime can increase efficiency, as can the additions of magnesium sulfate.

Fungi have also been used to remove color from wastewater. White rot fungus *(Phanerochaete chrysosporium burds)* can metabolize the lignin responsible for most of the color of wastewaters. It can also eliminate toxic chlorinated and halogenated compounds from the waste stream, including dioxins.[42] Although the process (MYCOR) is economical, the fungi culture cannot sustain itself and may collapse, thus it must constantly be recultured.

Conventional ion exchange resins have not proven technically successful in removing color from pulping and bleaching wastes, but specialized synthetic resins seem promising. Resins are sensitive to overloading from suspended solids and contaminants that reduce their effectiveness, thus they have been used primarily on both small waste streams and isolated output from the chlorination and first extractive stages of the bleaching sequence. Ion exchange resins have thus far found only limited use in the pulp and paper industry. Activated carbon, because of its large adsorption surface area, is an effective scrubbing agent. The charcoal process has been used commercially, but its high cost and regeneration requirements make it less attractive. The efficiency of membrane processes is considered good, but their costs remain high.

Rotating Biological Surface

A new developing technology, rotating biological surfaces (RBS), involves rotating polyethylene discs alternately through the wastewater and into the air as they rotate on a shaft. The process is analogous to the

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[39] Springer, op. cit., note 5, p. 240.

@Ibid,, p. 242.

[41] Waste Water Technology Center, *An Assessment of Kraft Bleachery Effluent Toxicity Reduction Using Activated Sludge*, EPS 4-WP-77-3 (Ottawa, Ont: Environment Canada, 1977).

[42] U.S. Environmental Protection Agency, *National Dioxin Study*, EPA/530-SW-87-025 (Washington, DC: 1987), p. Vi-2.

simple "trickle filter' where wastewater is percolated through a porous medium exposed to air in the interstices. RBS usually operates in three stages, and removal of up to 90 percent of the BOD has been achieved with this technology. Efficiency of the process is proportional to the surface area of the discs, rotation speed, and submergence depth of the discs. Application of RBS is probably limited to small- or medium-size pulp mills because of costs in scaling the equipment to large volumes. In smaller operations the cost of RBS is about the same as the activated sludge process. Although pilot-scale testing of RBS has shown promise for removing BOD and toxicity, mill-scale studies have encountered operating difficulty .[43]

Innovations in Activated Sludge Technology

High-Rate, Fixed-Film Activated Sludge— Solid particles (e.g., clays, sand, or calcium carbonate) added to activated sludge systems can improve sludge settling and prolong solids retention. Calcium carbonate has been particularly effective because of its buffering capacity with regard to acid components in the waste effluent. The particles develop a fixed-film growth, allowing a high level of biological growth to develop on the expansive particle surfaces. Preliminary studies indicate that nearly all of the solids can be retained in the system except a small amount that is lost with the treated water, Most of the solids are lost through the respiratory processes as carbon dioxide and water.

The oxitron process is a variation of the fixed-film activated sludge system. Effluent, free of suspended solids, is fed to a fluidized bed of sand through which pure oxygen is injected. Biological growth develops around the sand particles, finally causing them to rise in the fluidized bed where they are selectively removed. The sand is later cleaned of the growth and returned to the fluidized bed. Tests of the process show it to be efficient and compact, but it is unable to tolerate any solids in the wastes to be treated. The oxitron system is best suited for large waste volumes of 2 to 3 million gallons daily. There are no commercial installations in service, but new technologies may utilize elements of the process.

Aerated Activated Carbon Filter—Experiments have shown that due to its immense surface area activated charcoal is an efficient filter medium. Coarse granular charcoal placed in a filter bed has been shown to be effective in removing contaminants from waste effluent. To keep the system aerobic, air is pumped through the filter bed. The system is tolerant of excessive suspended solids, but the capital and operating costs are likely to be high. While the system has been used on sanitary wastes, there has been limited operating experience in the pulp and paper industry.

Captor System—An English innovation, the Captor System is similar to the conventional diffused-aeration activated sludge process, but it encapsulates the biological growth in small polyurethane sponges. With the biomass contained in the sponges, the treated effluent is discharged through a screen sized to retain the impregnated sponges. Sponges are cleaned for reuse by squeezing through a wringer. Developers claim that a secondary clarifier is not needed, therefore the plant size may be reduced by about 20 percent from that of a conventional activated sludge plant. The Captor System has been used for municipal wastes, but it is not certain that this treatment would be sufficient to meet U.S. water standards. It may prove useful in upgrading existing overloaded biological treatment systems.

Deep Tank Aeration-Deep tank aeration increases the amount of time that air is in contact with the waste effluent. As its name implies, the process uses a deep tank or deep shaft as an aeration chamber. This eliminates the need for a secondary clarifier but still requires a floating clarifier. Deep aeration occupies less space than conventional activated sludge systems and is capable of handling emergency ''shock' loads from the paper mill.

Anaerobic Treatment

Anaerobic waste treatment is neither new, nor innovative. However, with reduced water usage by many of the modem pulp mills, there has been a general increase in the potency of the pollution load, and anaerobic treatment is being reconsidered as a means to improve waste treatment. Anaerobic systems are well suited for treating high-strength waste,

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[43] U.S Environmental Protection *Agency, Development Document for Effluent Limitations Guidelines and Standards for the Pulp, Paper, and Paperboard and the Builders' Paper and Board Mills: Point Source Categories,* EPA 440/1-82/025 (Washington DC: 1982), p. 342.

but with modifications such as, attached-film and expanded bed reactors, it may also be possible to treat low-strength waste anaerobically as well.

Anaerobic (absence of oxygen) decomposition is a microbial process, which is primarily dependent on bacteria. Unlike aerobic processes (e.g., activated sludge and oxidation ponds to which air is supplied) anaerobic processes depend on bacterial action that obtains oxygen from sulfate and nitrate ions in the waste stream. When applied in the pulp and paper industry, anaerobic treatment is generally used as a waste pretreatment before release to the aerobic stages of the treatment process. Anaerobic systems are sensitive to imbalances in the ambient waste, but the process is durable and can be applied to a wide range of waste effluents. High temperatures are needed to reduce treatment time, long startup periods are required, odor emissions can be significant, and there is difficulty in achieving low BOD levels with anaerobic decomposition.