# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

*A tool for understanding environmental decisions related to the pulp and paper industry*

## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS

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## OVERVIEW OF EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS

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## Introduction

Wood pulp is usually bleached to increase its brightness. In some cases, however, pulps are bleached to improve other properties, such as the ability to absorb water – an important property for tissue and paper towels. Wood products operations do not undertake bleaching.

Until the early 1990s, most pulp was bleached with chlorine. Since then, most mills have stopped using gaseous (also called elemental) chlorine for bleaching. The newer bleaching processes, known as elemental chlorine free (ECF) processes (or process chlorine free, PCF, if they are used on recovered fiber), produce far fewer chlorine-containing chemicals and have virtually eliminated a number of chlorinated chemicals of concern, including dioxin.

Figure C1 below shows the reduction in chlorinated organic compounds [measured by the AOX (adsorbable organic halides) test] over time.

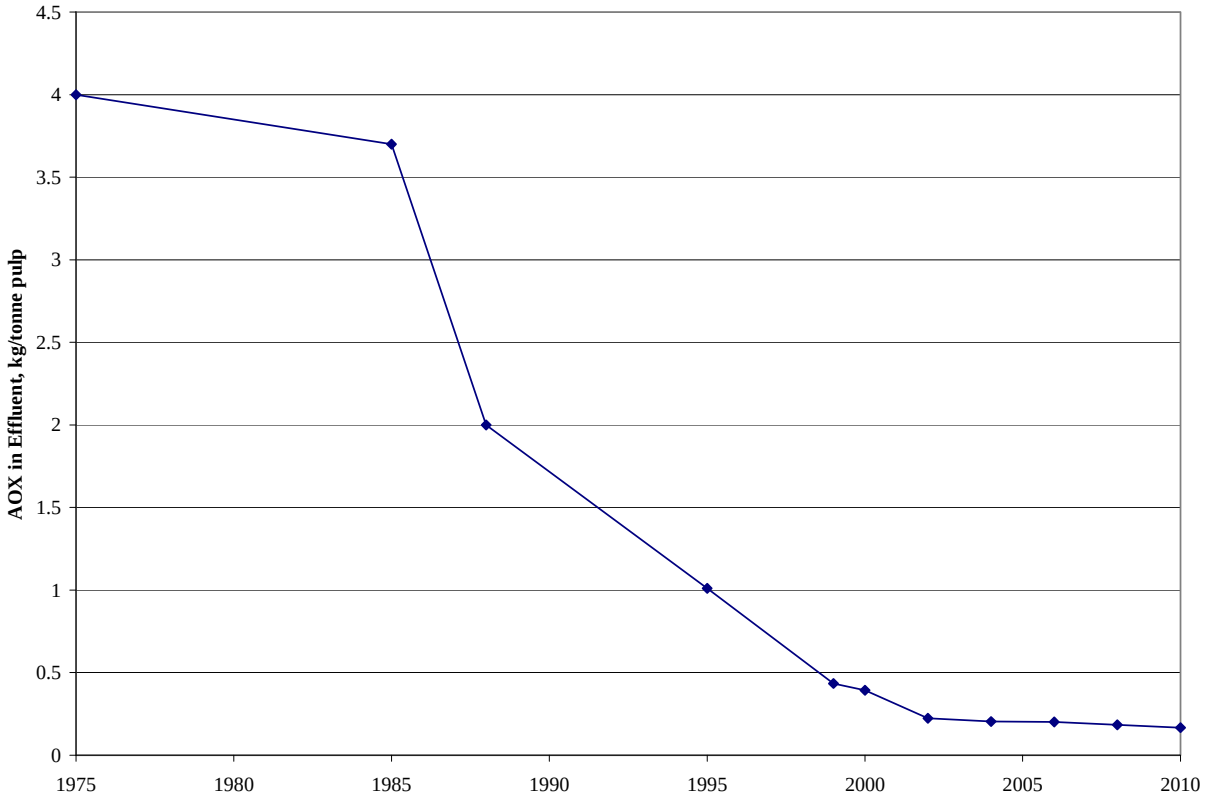


**Figure C1. Reduction in Adsorbable Organic Halides (AOX) over Time (Source: NCASI 2012; AF&PA 2012)**

To make further reductions beyond this, the bleach plant cannot be considered in isolation from the rest of the mill. Some of the approaches for further reducing the use of chlorine-based bleaching agents involve additional removal of lignin during pulping. Others involve using recovered bleach plant wastewaters (also called filtrates) for washing of unbleached pulps, an approach that sends organochlorine compounds to the mill's pulping liquor recovery process where they are burned. The recovery process, however, is sensitive and must be closely controlled to prevent safety and corrosion problems.

Whether these types of measures can be used at a mill to further reduce organochlorine chemical discharges will depend upon a host of site-specific factors, including existing mill equipment configurations and capacity, wood species pulped, and product quality concerns. Opportunities will be greatest for newly constructed mills or those undergoing significant modernization.

Below is more detailed information on pulp bleaching and the chemicals that can be formed during bleaching.

## References

American Forest and Paper Association (AF&PA). 2012. *2012 AF&PA sustainability report*. Washington, DC: American Forest and Paper Association.

National Council for Air and Stream Improvement (NCASI). 2012. File information.

## History of the Organochlorine Issue in the Pulp and Paper Industry

As far back as the 1970s, the paper industry was responding to concerns about the use of chlorophenolic slimicides in paper production and the contamination of the wastepaper supply with polychlorinated biphenyls (PCBs). These activities, however, were prelude to another unsuspected consequence of the industry's manufacturing practices.

A defining moment for the industry was the 1986 association of elemental chlorine-based bleaching with the presence of dioxins, most notably the specific dioxin compound 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). That association would spawn more than a decade of technical studies, governmental scrutiny and rulemaking, and judicial action.

The industry worldwide would subsequently abandon elemental chlorine bleaching (using $Cl_2$) in deference to elemental chlorine free bleaching (ECF), enhanced ECF (EECF) involving oxygen delignification and/or extended cooking, and, to a much lesser extent, totally chlorine free (TCF) bleaching. The dynamics of this transition in North America are illustrated in Figure C2.

Bleaching practices for mechanical pulps did not typically involve use of chlorinated compounds and, hence, dioxins and other organochlorines were not an issue. The use of sodium hypochlorite for bleaching recycled fiber was implicated in the release of chloroform from bleach plant vents and wastewaters. For that reason, it is rarely used today. Though use of sodium hypochlorite in mechanical pulping is not regulated, any use of chlorine and chlorine dioxide at these facilities in the U.S. is subject to controls mandated by the provisions of 1998 regulations adopted to control emissions of hazardous air pollutants from pulp and paper industry sources. The same is true for secondary fiber.

The U.S. Environmental Protection Agency ultimately published effluent limitations effectively requiring the termination of the use of elemental chlorine for pulp bleaching. EPA's decision reflected recognition that ECF would be sufficient to accommodate water quality concerns and that to go further would impose capital cost requirements that would be financially debilitating to a large segment of the industry. Water quality improvements following ECF application have led to a widespread decline in the number of receiving streams downstream of paper mills that were characterized as impaired due to the presence of dioxins.

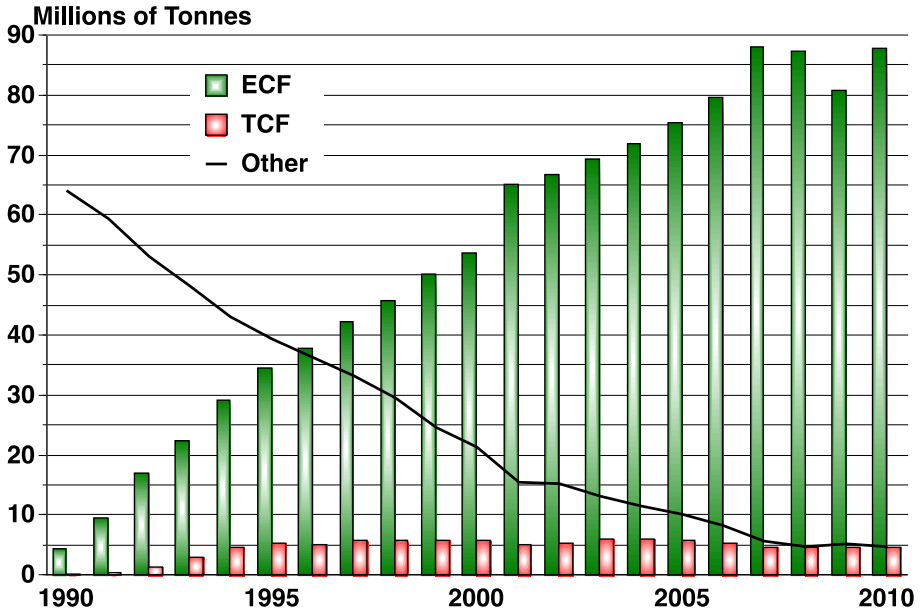


**Figure C2. World Bleached Chemical Pulp Production: 1990-2010**
**(AET at http://www.aet.org/science_of_ecf/eco_risk/2010_pulp.html)**

## Effects of Decreased Release of Chlorinated Compounds

### *General Overview*

In parallel, a number of companies, particularly in Europe, elected to go beyond ECF bleaching to find potential market opportunities with TCF processes and secure the process advantages associated with TCF and enhanced ECF technology. Among those advantages are reduced raw waste loads, smaller energy requirements, and a greater water economy that accompanies mill modernization programs. Achieving a sustained effluent-free bleach plant has remained elusive though, even with TCF bleaching.

Xerox, a prominent distributor of cut-sheet paper, has assembled a sustainability reference guide in which the company addresses aspects of bleaching options in the life cycle of paper (Xerox 2008). Views expressed about TCF and ECF bleaching reflect that company's perception of the co-benefit and trade-off balance.

> *"In comparison with elemental chlorine-free (ECF) pulps, the environmental benefits of totally chlorine-free processes (TCF) are now minimal. The main advantage of a TCF process is that process waters can continue to be circulated for a longer period of time. Thus, water consumption is usually less than in conventional chlorine bleaching. Because the TCF process does not use chlorine, it does not produce chlorine residuals in wastewaters. However, the replacement of chlorine gas with ECF chlorine dioxide has significantly decreased the amount of harmful chlorine residuals from chlorine bleaching. The result is that the differences between the TCF and ECF processes are now very small from an environmental point of view. The overall quality of the production process and equipment is a far more significant factor in environmental loading than the bleaching sequence."* (p. 12)

The complete replacement of elemental chlorine with chlorine dioxide virtually eliminates the formation and release of the most environmentally significant chlorinated organic compounds. Going further by complete replacement of all chlorine-based bleaching agents with oxygen-based chemicals would, in addition, preclude the generation of bleaching-related organochlorines. Certain pulping practices (e.g., extended cooking) and oxygen delignification can work alongside either ECF or TCF bleaching to reduce the organics sent to the bleach plant, thus reducing bleach chemical application rates. Of additional consequence to organochlorine release, as well as other environmental co-benefits, is the availability of capacity to manage pulp washing and bleach plant filtrates within the confines of the chemical recovery system. The bleach plant is not isolated from the balance of the mill. As a result, available options for organochlorine reduction are constrained by capabilities of the existing manufacturing infrastructure and potential product quality impacts. The challenges associated with reducing use of chlorinated compounds therefore go well beyond changes in bleaching chemicals, and can involve modifications to other areas of the pulp mill.

## References

Xerox Corporation. 2008. *Xerox and paper: A sustainability reference guide*. http://www.xerox.com/downloads/usa/en/s/sustainabilityRef_XE_sngl__rev_LR.pdf

## PCBs and Chlorophenolic Slimicides

Nearly 40 years have passed since the pulp and paper industry responded with its first major campaign to address the inadvertent presence of chlorinated compounds in its products and wastewater discharges. At that time, the 14-year use of polychlorinated biphenyls (PCBs) in the manufacture of carbonless copy papers that began in 1957 was implicated as a source of PCBs in Lake Michigan and other receiving streams. The problem was made all the more pervasive by virtue of the subsequent recycling of office papers containing the PCB-laden carbonless forms.

Responsible manufacturers reacted by adopting operating procedures to isolate carbonless carbon papers from the rest of their furnish, thus minimizing the PCBs in their products and effluents. Data collected by NCASI in 1981 affirmed that both food-grade and non-food-grade packaging materials, made from a variety of wastepapers, had declined in PCB content. Moreover, treatment systems installed during the 1970s in the U.S. further reduced the PCB concentration levels in mill discharges to non-detectable levels.

One would now expect that the likelihood of finding PCBs in mill wastes due to recycling of old carbonless copy paper has declined dramatically since almost all of the old paper that contained PCBs has been purged from files. Because this has been an issue of diminishing importance, there has been little effort to collect recent monitoring data, but a study by NCASI in the early 1990s found that levels of PCBs in post-1989 effluent samples from 11 deinking mills effluents were below detectable levels 99% of the time (NCASI 1994). Though environmental releases no longer persist, the legacy of that earlier era does. The removal of sediments from Midwest rivers that became repositories of PCBs historically discharged by deinking mills is a continuing enterprise costing hundreds of millions of dollars.

By 1980, the industry also recognized the wastewater implications of its use of slimicides containing pentachlorophenol (PCP) and trichlorophenol (TCP). That practice is no longer undertaken, both through voluntary elimination and by U.S. regulation in 1982. A number of European countries followed suit in banning pentachlorophenol for this use.

## References

National Council [of the Paper Industry] for Air and Stream Improvement, Inc. (NCASI). 1994. *PCB and TCDD/F levels in effluents from deinking mills producing fine paper or tissue and toweling*. Technical Bulletin No. 671. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

## Chlorinated Dioxins and Other Bleaching-Related Organochlorines

Industry bleaching technologists had held the view that conditions associated with pulp bleaching would not support the formation of dioxins. Indeed, available analytical data in the early 1980s supported that contention. By the end of the decade, however, there could be no doubt that elemental chlorine-based bleaching did, in fact, promote the formation of dioxins that subsequently emerged in product, effluent, and wastewater sludges in minute but environmentally significant quantities. Organochlorines, a term referring to an array of chlorine-based organic compounds including dioxin and furan, were also present in notable quantities.

In 1983, EPA analysis of several paper mill sludges in Maine failed to identify a presence of 2,3,7,8-TCDD at detection levels ranging from 85 to 340 parts per trillion (ppt). Subsequent work carried out under the auspices of the Maine Department of Environmental Protection had the benefit of lower analytical limits of detection. That information, which became available in 1985, showed levels ranging from the limit of detection up to 51 ppt.

Responding to public concern over dioxin contamination at Times Beach, Love Canal, Jacksonville and other sites, the U.S. Congress in 1983 directed EPA to conduct a National Dioxin Study to determine the extent of contamination nationwide. In the concluding phase of that work, the agency reported that

- a previously unsuspected possible source of 2,3,7,8-TCDD contamination in some areas appeared to be certain types of pulp and paper mill discharges;
- levels of 2,3,7,8-TCDD as high as 414 ppt were measured in sludges from mills using a molecular chlorine ($Cl_2$)-based bleaching process; and

- mills using a molecular chlorine ($Cl_2$) bleaching process were being investigated by EPA, the states, and the paper industry to determine the source of contamination within the mills.

The investigation carried out over the latter half of 1986 became known as the "Five Mill Study." The work was conceived as a screening study intended to discern the source of dioxins and their subsequent apportionment in treated and untreated wastewater streams, as well as sludges. Significantly, the study showed that the bleach plant was the most significant source of TCDD and related compounds, and that molecular chlorine use was a major factor influencing their formation.

More intensive NCASI investigation would follow in 1988 and 1999 at an additional 22 mills. It was learned that production of TCDD and TCDF occurred mostly in the chlorination stage of bleaching and that the amount increased with elemental (molecular) chlorine ($Cl_2$) use and the quantity of precursors in the unbleached brownstock. Whether the reduction of elemental chlorine use was achieved by high chlorine dioxide ($ClO_2$) substitution or use of oxygen delignification made little difference, as neither showed the presence of dioxin and furan that was present in mills bleaching with elemental chlorine. At the same time, NCASI managed a comprehensive inventory of dioxin releases from all 104 U.S. chemical pulp bleaching lines that practiced chlorine-based bleaching in an EPA study cooperatively supported by the industry (NCASI 1990).

Concern about organochlorine compounds was not confined to the United States and Canada. Developments in northern Europe actually predated those in North America. In 1982, the Swedish EPA commissioned the Environment-Cellulose project that has since been described as a "triggering factor for a worldwide discussion on the role of chlorinated organics in bleached pulp mill effluents." Early investigation in that program found deformities and adverse impacts on the reproductive health of fish in the vicinity of the discharge of poorly treated effluent from a mill employing chlorine bleaching. The effects were correlated with concentrations of chlorinated compounds, because both declined with distance from the mill.

Harrison (2002) has chronicled the events that followed. Among participants at early public meetings where Environment-Cellulose investigators presented their findings was the staff of Greenpeace Sweden. Greenpeace International subsequently decided in 1986 to launch an international pulp and paper campaign supported by full-time staff in several countries. For its part, the Swedish EPA in late 1987 began to seek limits on bleach mill discharges of AOX and adopted a long-term goal of eliminating discharges of chlorinated discharges. The U.S. EPA's National Dioxin Study results released in September 1987 further reinforced the Swedish regulatory action and provided further impetus to the Greenpeace initiative. The significance of the latter for the Swedish industry was the stimulation of chlorine-free paper markets in continental Europe – Germany in particular. The Swedish industry had initially sought to discredit the Environment-Cellulose studies and opposed the imposition of site-specific AOX limits in mill permits. By 1990, Swedish companies found competitive advantage in European market demands for "chlorine free" paper. The Beca AMEC report on Arauco Valdivia summarizes the situation at the time.

> *"When in the early 1990s the Scandinavian kraft mills started employing Totally Chlorine Free (TCF) bleaching, the main driver was the possibility to take advantage of the developing market for chlorine-free bleached pulp and paper primarily in Germany, but also Sweden, the Netherlands, Switzerland and Austria. Initially TCF pulps were paid a premium compared to conventionally bleached kraft pulp. An additional driver was the expectation that it would be feasible to recycle bleach plant effluents to the chemical recovery system for incineration, thereby reducing the effluent load."* (Beca AMEC 2006, p. 42)

Government action in North America took a more protracted path. In the United States, the release of the National Dioxin study in September 1987 launched a series of regulatory developments that would extend over a period longer than 10 years. That was in part attributable to a legal/judicial framework conducive to citizen intervention and the due process associated with development of regulatory requirements configured around the uniform application of technology-driven standards. A cacophony of environmental activism, science, pseudo-science, politics, and judicial action characterized the period. It was a time of

high drama that included environmental activist demonstrations that sometimes bordered on the sensational and allegations of cover-up and collusion between the industry and government, even the intrigue of an insider informant dubbed “Deep Pulp.” Notable milestones included:

- April 30, 1990: EPA announces its intent to develop regulations to reduce dioxin contamination in waterways and soil caused by the manufacture of chlorine-bleached pulp and paper.
- December 17, 1993: EPA proposes best available technology (BAT) effluent treatment standards based upon complete substitution of chlorine dioxide for use of elemental chlorine in bleaching and the application of oxygen delignification and/or extended cooking – known as “Option B” during the regulatory development process.
- July 15, 1996: EPA announces that available data justifies that “Option A,” incorporating 100% substitution of chlorine dioxide for use of elemental chlorine in bleaching (*without* oxygen delignification and/or extended cooking), should be given equal weight with the originally proposed Option B as a possible basis for BAT effluent limitations.
- November 14, 1997: EPA announces that final rules will establish effluent limitations based on ECF bleaching, i.e., 100% chlorine dioxide substitution (Option A). Option B served as the basis for new source performance standards.
- April 15, 1998: Final rules are published, with most mills expected to comply by April 2001.

In opting to require the equivalent of 100% $ClO_2$ substitution (known as “complete substitution” or elemental chlorine free (ECF) bleaching), as opposed to the more demanding Option B, the Agency took a position that “the additional cost of oxygen delignification was difficult to justify because it would result in only 1 gram of reduction of dioxin while costing the industry $1 billion.” That decision has been characterized as precedent-setting. Foster (1999) observed that the “regulation of dioxin emissions from paper mills appears to entail the first explicit recognition of the issue of diminishing returns by agencies regulating health and safety issues” (p. 56).

The 10-year window over which regulations were developed was not an idle time for the industry. Early NCASI scientific effort carried out on behalf of the industry sought to characterize the risk of a) communication and personal care products, b) food packaging, and c) food contact products. That work demonstrated that no significant risk accompanied the use of, or exposure to, paper products (Sullivan, LaFleur, and Gillespie 1989). U.S. Food and Drug Agency (FDA) appraisals at the time also concluded that no significant risks were associated with milk cartons, in part recognizing the changes already being made in the industry’s production processes.

In 1991, EPA reported having collected data that demonstrated that 64 facilities had made substantial changes to their bleach plant operations conducive to reduced dioxin formation. Cited changes included

- increased substitution of chlorine dioxide ($ClO_2$) for chorine ($Cl_2$) in the chlorination stage of the bleaching process;
- modernization and improvement in controlling chlorine bleaching; and
- increased use of hydrogen peroxide to enhance the extraction stages of the bleaching process.

Between 1990 and 1994, 29 oxygen delignification systems were installed in addition to the 11 installed in the 1980s, a proliferation rate described as dramatic, given the significant capital cost and engineering required within that short time frame. Information assembled by the Paper Task Force shows that in 1994, nearly one-fourth of bleached kraft pulp production in the U.S. was bleached with either ECF or enhanced ECF technology. Oxygen delignification and/or extended cooking employed in conjunction with conventional bleach sequences comprised an additional one-third.

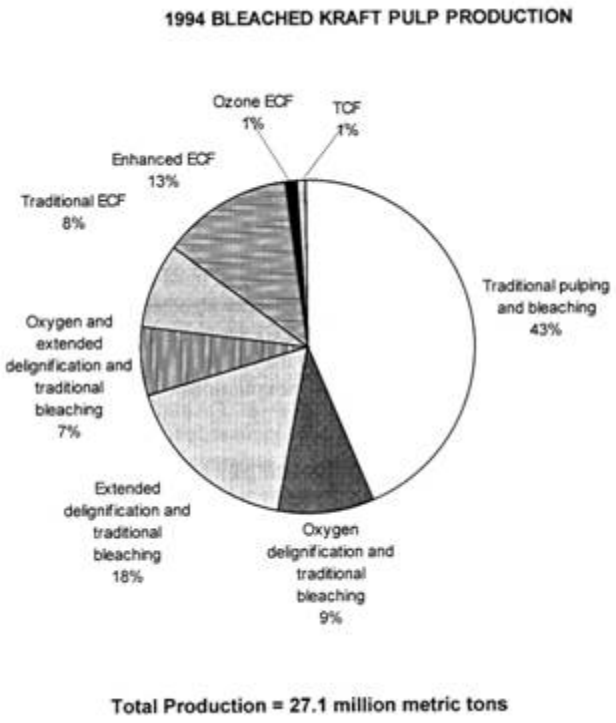


**Figure C3. 1994 Bleached Kraft Pulp Production (Source: Paper Task Force 1995)**

This commitment to responsibly address an environmental issue is apparent in the spike in the industry's water quality-related capital expenditures by U.S. pulp mills between 1987 and 1994 (see Figure C4 below). Over three-fourths of these capital expenditures between 1986 and 2001 were expended prior to the finalization of the effluent standards in 1998. In total, the industry in the U.S. undertook the largest water quality-related capital expenditure since the installation of biological wastewater treatment in the 1970s.

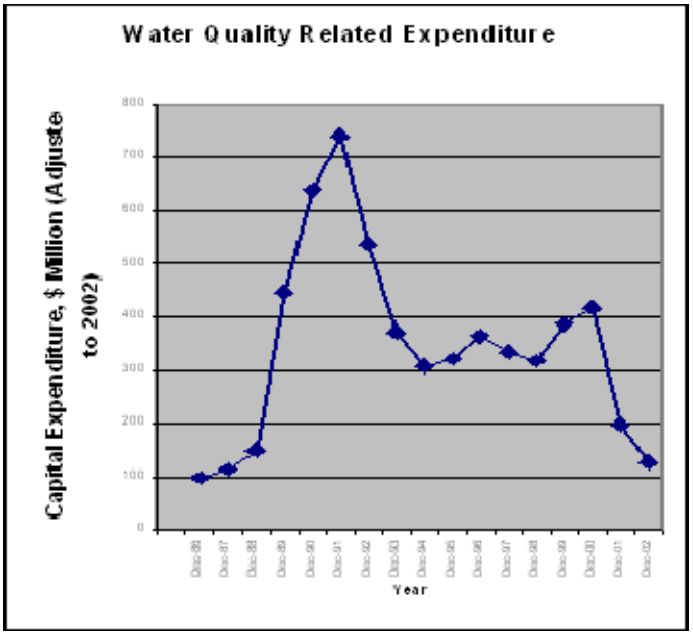


**Figure C4. Water Quality-Related Expenditures (Data from NCASI 2003)**

Sonnenfeld (1999) presents a view of industry thinking over this period.

> *"Even with some grumbling by firms, there was broad consensus among most parties that the industry had to change process-technologies, moving away from use of elemental chlorine. There were disagreements about "how much" and "how fast," but not about "whether," to adopt cleaner production processes and technologies. Leading producers and the industry associations which represent them conceded the shift to elementally chlorine-free (ECF) pulping technologies. Debate remains over the merits, costs and benefits of conversion to totally chlorine-free (TCF) processes, even while research continues on development of totally effluent-free (TEF) pulp manufacturing, which would have the effect, coveted by firms and regulators, of freeing the industry from locational restrictions with regard to its waste stream"* (p. 27).

## References

Beca AMEC Ltd. 2006. *Study report for review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia*. Prepared at the request of Resource Planning and Development Commission, Tasmania. Melbourne: Beca AMEC Ltd. http://s3.amazonaws.com/zanran_storage/www.aet.org/ContentPages/2827017.pdf

Foster, J.L. 1999. *The dead hand of environmental regulation: The causes and implications of regulatory rigidity; and the benefits and requirements of greater adaptability* or *Why regulations cannot adapt to new science, new technology, new economic conditions or changing policy priorities*. Report for The Center for Environmental Initiatives and MIT Consortium on Environmental Challenges. http://dspace.mit.edu/bitstream/handle/1721.1/1679/deadhand.pdf?sequence=1

Harrison, K. 2002. Paper trails: Environmental regulation in a global economy. Prepared for presentation at the Annual Political Science Association, Boston, August 2002.

National Council [of the Paper Industry] for Air and Stream Improvement, Inc. (NCASI). 1990. *An intensive study of the formation and distribution of 2,3,7,8-TCDD and 2,3,7,8-TCDF during the bleaching of kraft pulps*. Technical Bulletin No. 591. New York: National Council of the Paper Industry for Air and Stream Improvement, Inc.

National Council [of the Paper Industry] for Air and Stream Improvement, Inc. (NCASI). 2003. *A survey of pulp and paper industry environmental protection expenditures–2002*. Special Report No. 03-07. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

Paper Task Force 1995. *Environmental comparison of bleached kraft pulp manufacturing technologies*. White Paper No. 5. http://calculator.environmentalpaper.org/documents/1626_WP5.pdf

Sonnenfeld, D.A. 1999. *Social movements and ecological modernization: The transformation of pulp and paper manufacturing*. Berkeley, CA: Unniversity of California, Institute of International Studies. http://escholarship.org/uc/item/3zc0r2km

Sullivan, M., LaFleur, L., and Gillespie, W. 1989. Risks associated with potential dioxin exposure through consumption of coffee brewed using bleached pulp-based filters. *Chemosphere* 19 Nos. 1-6, 873-876.

## Wastewater and Water Quality Impacts Associated with Pulp Bleaching

The aftermath of the 1986 association of elemental chlorine bleaching with the release of dioxins brought scrutiny to the industry's impact on receiving streams and aquatic life. In 1990, there were 30 fish consumption advisories for dioxin downstream of U.S. bleached pulp mills. This reflected a judgment by state officials that dioxin contamination levels posed a health risk to sport and subsistence fishermen, as well as the general public, who catch and consume locally caught fish.

Since 1990, changes in bleaching technology, specifically the replacement of chlorine with chlorine dioxide during the first stage of pulp bleaching, have reduced dioxin discharges to a point where they cannot be detected in routine effluent monitoring tests. As a result, tissue concentrations in fish in the receiving waters downstream of those mills have decreased substantially. These decreases have allowed many of the former fish consumption advisories to be rescinded. By the end of 2004, there had been a 90% decrease in the number of dioxin advisories downstream of pulp and paper mills in1990 (AET 2005). See the "Discharge to Water" section of this tool for further information.

## References

Alliance for Environmental Technology (AET). 2005. Eco-system recovery: Lifting of fish consumption advisories for dioxin downstream of U.S. pulp mills - 2005 update. http://aet.org/reg_market_news/press_releases/2005/Eco051.html

## How and Why Is Pulp Bleached?

**Recycled Fiber -** Bleaching of "secondary" (recycled) fiber can have three functions: brightening (decolorization of lignin and contaminants), color stripping (removal of papermaking dyes), and delignification (removal of lignin). Currently, popular bleaching chemicals for recycled pulp are the oxidant hydrogen peroxide and the reductant sodium hydrosulfite. Another reducing agent of choice is formamidine sulfinic acid (FAS). Peroxide is presently the most common oxidizing agent for bleaching deinked pulp. It can be effective with both chemical and mechanical pulp fibers, and it may be used alone or in sequence with a reducing agent. As in the case of mechanical pulps, a chelating agent such as DTPA (diethylenetriamine pentaacetic acid) is needed to minimize catalytic decomposition from metal ions. The most common reducing agent for bleaching deinked pulp is sodium hydrosulfite. Hydrosulfite can be effective with both chemical and mechanical pulp fibers, and it may be used alone or in sequence with an oxidizing agent. FAS is an alternative reducing agent. It, too, can be effective with both chemical and mechanical pulp fibers.

**Mechanical Pulps** - Bleaching agents are applied to mechanical pulps for the purpose of brightening through decolorizing lignin while the lignin is retained with the final pulp, in contrast to chemical pulp bleaching in which lignin removal is desired. Bleaching of mechanical pulps is done with one or both of two chemical agents, hydrogen peroxide (an oxidant) and sodium hydrosulfite (a reductant). Alkaline peroxide bleaching dissolves some of the wood components, resulting in a yield loss of 1.5% to 3%. Hydrosulfite bleaching does not result in significant yield loss. Peroxide bleaching requires that the amounts of certain metals, especially manganese and iron, be controlled to prevent wasteful decomposition of the peroxide and potential compromises in pulp yield and quality. Transition metal control is typically accomplished by pretreating the pulp to remove the metals through the application of a metal chelating agent such as DPTA.

**Chemical Pulps -** Chemical pulp bleaching involves the application of chemicals to remove the remaining lignin, to brighten the pulp, and to decolorize dirt and shives (very small wood slivers) that contaminate the stock while, at the same time, protecting the cellulose fraction from significant degradation (NCASI

2003). Chemical pulping can remove most of the lignin and extractives from pulp (ca. 98%), but the residual lignin is often darker than the original lignin (see Figure C5) and imparts a brown color to the pulp (Dence and Reeve 1996). Beyond imparting a dark brown color to unbleached pulp, residual lignin can inhibit some optimum physical and optical properties of cellulosic products such as brightness, absorptivity, printability, and color stability. Achieving these properties requires that residual lignin be removed or decolorized through the application of chlorine-based and/or oxygen-based bleaching agents and subsequent extraction with caustic (NCASI 2004).


**Figure C5. Illustration Showing the Degree of Color Removal during Pulp Bleaching (http://www.chmltech.com/pulppaper_files/pulp%20bleaching.jpg)**

Several modifications to conventional pulping, known collectively as extended cooking, have enabled pulps with reduced lignin content to be produced prior to the bleach plant. Oxygen delignification is another technology that is used extensively to lower the residual lignin content prior to the bleach plant. Both extended cooking and oxygen delignification processes achieve their results by enabling more of the lignin to be dissolved and sent to the chemical recovery process via countercurrent pulp washing rather than to the sewer via the bleach plant filtrates. All totally chlorine free (TCF) bleached market kraft mills use some form of modified cooking and/or oxygen delignification to minimize the lignin content of the pulp entering the bleach plant (Stratton, Gleadow, and Johnson 2005).

## References

Dence, C.W. and Reeve, D.W. (eds). 1996. *Pulp bleaching principles and practice*. Atlanta, GA: Tappi Press.

National Council for Air and Stream Improvement, Inc. (NCASI). 2003. *Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s*. Technical Bulletin No. 860. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2004. Pulp bleaching systems. Chapter 8 in *Environmental resource handbook for pulp and paper mills*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Stratton, S., Gleadow, P., and Johnson, A. 2005. Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s. *Water Science & Technology* 50(3): 183-194.

## What Chemicals Are Used in Pulp Bleaching?

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 first extraction stage is almost as significant as the first bleaching stage in terms of lignin removal (USEPA 1993). Taken together, these two stages can account for some 90% of the lignin removal, as well as corresponding wastewater COD, color, and chlorinated organic matter.

The various bleaching chemicals, their functional role, and the symbols used to identify them in bleach sequence representations are summarized in Table C1.

**Table C1. Chemicals Used in Pulp Bleaching (Source: http://www.paperonweb.com/bleach.htm)**

| Bleaching Chemical | Chemical Formula | Bleaching Stage Abbreviation | Role in the Bleaching of Pulps |
|---|---|---|---|
| Chlorine | $Cl_2$ | C | Elemental chlorine ($Cl_2$) is an effective delignifying agent. As it breaks lignin bonds, it adds chlorine atoms to the lignin degradation products, thus producing significant amounts of chlorinated organic material. |
| Chlorine Dioxide (Some $ClO_2$ generation methods may concurrently produce small amounts of chlorine.) | $ClO_2$ | D | Chlorine dioxide ($ClO_2$) is a highly selective chemical that can both delignify and brighten pulp. It oxidizes lignin, but does not add chlorine atoms onto lignin fragments. Small amounts of elemental chlorine and other chlorine compounds formed during the chlorine dioxide bleaching process can react with degraded lignin to form chlorinated organic compounds. |
| Sodium Hydroxide (extraction stage) | NaOH | E | Used to remove colored components from partially bleached pulps that have been rendered soluble in dilute warm alkali solution. |
| Sodium Hypochlorite | NaOHCl | H | Sodium hypochlorite (NaOHCl) is an inexpensive delignifying agent formed by mixing elemental chlorine with alkali at the mill. |
| Hydrogen Peroxide | $H_2O_2$ | P | Hydrogen peroxide ($H_2O_2$) is mainly used to brighten pulps in the final bleaching stages. It may also be used within an alkaline (sodium hydroxide) extraction stage. Peroxide is often used at the end of a conventional bleaching sequence to prevent the pulp from losing brightness over time. Preferred for mechanical and recycled fiber. |
| Ozone | $O_3$ | Z | Ozone ($O_3$) is an effective delignifying agent and brightens the pulp as well. Ozone is an extremely powerful oxidizing agent and must be applied in a manner that minimizes cellulose degradation |
| Sodium hydrosulfite | $Na_2S_2O4$ | Y | Reductive bleaching; good for recycled fibers |

**Table C1. Continued**

| Bleaching Chemical | Chemical Formula | Bleaching Stage Abbreviation | Role in the Bleaching of Pulps |
|---|---|---|---|
| Oxygen | $O_2$ | O | Oxygen removes lignin and modifies other coloring components. In oxygen delignification that precedes bleaching, the pulp is treated with oxygen in a pressurized vessel at elevated temperature in an alkaline environment. It may also be used within an alkaline (sodium hydroxide) extraction stage. |
| EDTA or DPTA (Chelating Agents) | | Q | Used to control the brightness restricting and reversion effects of iron salts and other heavy metals in the pulp. |
| Formamidine sulfinic acid (FAS) | $(NH_2)_2CSO_2$ | F | Formamidine sulfinic acid (FAS), also called thiourea dioxide, may be used to obtain higher brightness for peroxide-bleached recycled fiber. |

## References

United State Environmental Protection Agency (USEPA). 1993. *Pollution prevention technologies for the bleached kraft segment of the U. S. pulp and paper industry*. EPA/600/R-93/110. Washington, DC: United States Environmental Protection Agency. http://www.p2pays.org/ref/02/01128/01128.pdf

## The Names of Different Bleaching Sequences

Mill bleaching processes have been often characterized on the basis of a) the extent to which they have eliminated the use of chlorine-based bleaching agents and b) the extent to which bleach plant filtrates are recycled or otherwise discharged as wastewater.

1. **Elemental chlorine-based bleaching** historically involved the use of elemental chlorine in the first bleaching stage, often augmented with minor amounts of chlorine dioxide.
   Illustrative Bleach Sequence: C/D E D E D. This type of bleaching is not practiced to a significant extent in North America, and has largely been replaced with ECF bleaching.

2. **Traditional ECF bleaching** involves complete substitution of elemental chlorine with chlorine dioxide. Careful process control is required to prevent conversion of chlorine dioxide into elemental chlorine during the pulp delignification process.
   Illustrative Bleach Sequence: D $E_{OP}$ D $E_P$ D.

3. **Enhanced ECF bleaching** involves reducing the lignin content of pulps prior to bleaching with either extended cooking or oxygen delignification. Both extended cooking and oxygen delignification processes enable more of the dissolved lignin to be sent to the chemical recovery process via countercurrent pulp washing rather than to the sewer via the bleach plant filtrates. Subsequent bleaching is through an ECF sequence.
   Illustrative Bleach Sequences: O D $E_{OP}$ D *or* O Z $E_{OP}$ D.

4. **Low effluent ECF (can also be used as a component of TCF bleaching)** involves recirculation of filtrates, at times to a substantial degree, from various bleaching stages back through the mill chemical recovery system for eventual burning in the recovery furnace. The potential for implementing this type of bleaching is limited by the mill's ability to manage the related build-up of non-process elements (e.g., manganese).
   Illustrative Bleach Sequence: O D $E_{OP}$ D *or* O Q P $E_{OP}$ P P.

5. **TCF bleaching** replaces all chlorine-based bleaching agents with oxygen-based bleaching agents, typically oxygen, ozone, and hydrogen peroxide. For wood pulp, extended cooking and/or oxygen delignification prior to bleaching is a prerequisite.
   Illustrative Bleach Sequence: O Q P $E_{OP}$ P P.

6. **Processed Chlorine Free (PCF) bleaching** denotes 100% use of oxygen-based chemicals in lieu of chlorine-based bleaching agents for the brightening or bleaching of recycled fiber.
   Illustrative Bleach Sequences: P *or* Y *or* P-Y.

The predominance of bleaching sequences that use combinations of some or all of the major bleaching agents (chlorine dioxide, peroxide, oxygen, and ozone) has rendered the terms ECF and TCF inadequate to characterize the current state of the art of kraft pulp bleaching.

# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

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## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON WATER USE

### Overview

Pulp bleaching is usually accomplished in sequential stages using a combination of chemicals. It is common for the pulp to be washed between stages to remove spent chemicals, dissolved lignin, and other soluble products. After use, this wash water is discharged and represents the bulk of the effluent discharge from the bleach plant and is often a significant part of total mill discharge. Partial or complete counter-current circulation of wash water (i.e., circulation from latter stages to earlier stages) is a common water conservation practice.

### More information

Impact of reuse and recycle of bleach plant filtrates

Conventional reduction of bleach plant chemical and water requirements

Barriers to recovery of bleach plant filtrates


# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON WATER USE

## Impact of Reuse and Recycle of Bleach Plant Filtrates

The notion of a "zero-effluent bleach plant" has been the Holy Grail of environmentally motivated process changes sought at bleached chemical pulping operations. Among the benefits giving impetus to that quest are

1. reducing the volume of mill process water requirements and the associated hydraulic load on wastewater management systems;
2. reducing the organic load imposed on wastewater treatment operations and subsequent discharges to receiving streams; and
3. eliminating the discharge of chlorinated organic compounds.

The accumulation of chloride ions in mill processes can be a key obstacle to reusing bleach plant filtrates. Thus, eliminating the use of chlorine-based bleaching agents is often perceived to be the most direct path to collectively achieving these ends by virtue of enabling greater recirculation of bleach plant filtrates. Chlorine-based bleaching agents, however, are not the only source of troublesome chloride ions that accumulate in recirculated process streams, nor are chlorides the only inorganic substances that can be problematic in closed water systems. The progressive closure of bleach mill water systems, regardless of bleach sequence, invites a number of operational issues:

1. the increased concentrations of organic and inorganic compounds resulting in increased corrosion, scaling, and deposition within the bleach plant and other mill areas;
2. the accumulation of dissolved solids that cause a considerable increase in the consumption of bleaching chemicals;
3. difficulty in reaching target brightness, particularly for peroxide bleached pulps;
4. variable pulp quality, particularly for TCF pulps;
5. increased likelihood of precipitation of calcium oxalate ($CaC_2O_4$), calcium carbonate ($CaCO_3$), and barium sulfate ($BaSO_4$); and
6. the possibility that additional evaporation plant capacity and additional recovery boiler capacity may have to be installed (STFI 2003 as cited in AMEC 2006).

Of particular interest here is the extent to which the closure of mill water systems impacts bleaching chemistry in ways that affect pulp bleachability or increase chemical requirements.

For elemental chlorine free (ECF) mills, the prime concern associated with bleach plant filtrate recirculation has been the build-up of chloride in the chemical recovery cycle, with secondary concerns related to pulp quality and mill operability. For totally chlorine free (TCF) mills, however, the prime concern has been pulp quality (strength and brightness) with secondary concerns in operability, and potassium and chloride build-up in the recovery system. Both ECF and TCF bleach plant closure can cause operating difficulties with increased chemical consumption, poorer pulp quality, and challenges in minimizing deposition and scaling on equipment (AMEC 2006).

Currently, ECF effluents can be recycled to chemical recovery, but only when there is provision made for increased chloride removal from the chemical recovery system. This, as might be expected, is due to the build-up of chloride ions ($Cl^-$) and in some cases potassium (K). Given that TCF bleach effluents contain virtually no chloride, the problems associated with chloride are less than those in ECF bleaching, but in general, increased purging is also required due to accumulation of other dissolved substances that are problematic (Gleadow et al. 1996).

Both ECF- and TCF-based bleaching strategies are compatible with a high degree of system closure. With the development of new technologies and the concept of alkaline stage recovery, ECF is being seen by some as the more compatible. The main reason is that chlorine dioxide bleaching is less sensitive to the build-up of organics and metals in highly closed water recycle circuits compared to ozone and peroxide bleaching. Based upon current knowledge, the degree of closure in TCF operations can be only partial, whereas ECF mills are more likely to operate fully closed. There are, however, no bleach plants in papergrade bleached kraft mills that operate fully closed on a continuous basis.

Much of the technology development associated with kraft mill bleach plant closure has involved extensive water use reduction and has been accompanied with a concurrent need for understanding and managing the impact of contaminant build-up in mill water systems. This has meant focusing on mitigating undesirable consequences such as scale deposits, corrosion, loss of bleaching efficiency, increased evaporative loads, reduced production capacity, and loss of operational flexibility. These issues have caused many companies to reconsider the role of process closure in minimizing effluent impacts. In many cases, the optimal solution has been found to be a high degree of closure, down to 15 $m^3$/ton, coupled with external biological treatment of the remaining process effluent (Stratton, Gleadow, and Johnson 2005).

## References

AMEC Ltd. 2006. *Study report for review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia*. Melbourne: Beca AMEC Ltd. http://s3.amazonaws.com/zanran_storage/www.aet.org/ContentPages/2827017.pdf

Gleadow, P.L., Vice, K., Johnson, A.P., Sorenson, D.R. and Hastings, C.R. (1996). Mill applications of closed cycle technology. In *Proceedings of the 1996 TAPPI International Non-Chlorine Bleaching Conference*. Atlanta, GA: Tappi Press.

Stratton, S., Gleadow, P., and Johnson, A. 2005. Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s. *Water Science & Technology* 50(3): 183-194.

Swedish Pulp and Paper Research Institute (STFI). 2003. *Ecocyclic pulp mill – "KAM" – Final report 1996–2002*. KAM Report A100. Stockholm: Swedish Pulp and Paper Research Institute.


# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON WATER USE

## Conventional Reduction of Bleach Plant Chemical and Water Requirements

***Bleach Plant Water Use and Internal Recirculation:*** A bleach plant consists of a series of three to six stages in which the pulp is chemically treated and then washed to remove spent bleaching chemicals and dissolved pulp components. Typically, the stages are sequenced as an alternating series of bleaching and extraction stages. In a bleaching stage, the pulp is treated with chemical bleaching agents. In an extraction stage, chemicals (usually sodium hydroxide that is sometimes fortified with oxygen and peroxide) are added to neutralize the chemical reactions and the acidity of the pulp prior to the next bleaching stage. An extraction stage is not required in all cases. In most mills, the resulting filtrates are not chemically compatible with kraft mill recovery systems, and are sent to the mill sewer. Therefore, the bleach plant provides an important purge of inorganic components from the wood pulp and for chloride ions resulting from chlorine or chlorine dioxide use.

In the typical elemental chlorine free (ECF) bleach sequence (Figure C6), there is extensive recirculation of filtrates within the bleach plant. Filtrates are always reused within a bleach plant stage for dilution of pulp entering the stage, at the end of the reactor, and in the washer vat. Filtrates used for pulp washing are used in countercurrent fashion on washers upstream with respect to the direction of pulp flow. Generally, filtrates from the latter stages of a bleach plant may be reused in their entirety, whereas filtrates from the initial stages contain materials that interfere with bleaching and so are reused sparingly, if at all, for pulp washing. Filtrates are used on the stage immediately upstream (“direct”), on a stage of similar chemistry two or more stages upstream (“jump stage”), or a combination of both (“jump stage split flow”) (Histed and Nicolle 1973).

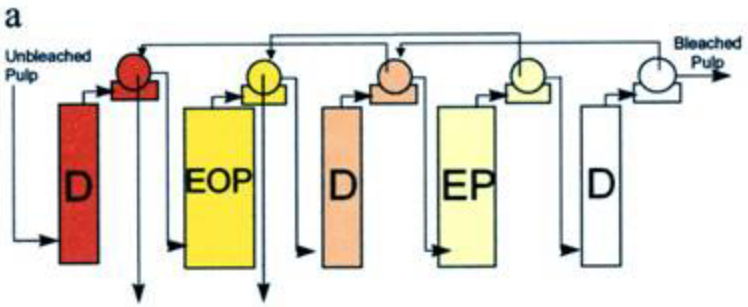



**Figure C6. Typical Elemental Chlorine Free Bleaching Sequence**

Filtrate recirculation within the bleach plant results in reduced fresh water consumption and bleach plant effluent flows; however, it does not lead to a reduction of specific emissions like AOX and COD on a mass basis (e.g., kg/ADt) (AMEC 2006).

***Reducing Bleach Plant Chemical and Water Requirements:*** There are process modifications that can be undertaken to reduce the chlorine dioxide requirements in the bleach plant. Many ECF sequences attempt to take full advantage of the power of oxygen-based (oxygen and peroxide) chemicals. The fortification of caustic extraction with oxygen and/or peroxide is one example. Although an $E_{OP}$ extraction stage, for example, is more costly than traditional caustic extraction, its contribution to delignification

reduces the demands for chlorine dioxide in subsequent bleaching stages. That reduction translates into less generation of organochlorines.

More dramatic reductions accompany pulping modifications that, in combination with 100% $ClO_2$ substitution in bleaching, have come to be known as “enhanced ECF.” Both extended cooking (EC) and oxygen delignification (OD) achieve their results by enabling more of the lignin to be dissolved and sent to the chemical recovery process as opposed to the waste treatment plant in bleach plant filtrates. These processes result in reductions in COD, BOD, and color, to the extent that the additional dissolved organic substances are captured and destroyed in the recovery furnace. Another important outcome is that bleaching can be achieved using less chlorine dioxide in the first bleaching stage. The amount of AOX formed in bleaching is primarily determined by the amount of atomic chlorine applied to the pulp in the first bleaching stage.

It is rare that the application of oxygen delignification allows the use of reduced wash water flow in the first bleaching stage, but there is the opportunity for benefit where the additional pulp delignification prior to bleaching allows for the elimination of one or more bleaching stages. This is illustrated with the sequence in Figure C7 below, when compared to a conventional five-stage $D(E_{OP})D(E_P)D$ sequence.

The capture of OD wash waters or other bleach plant filtrates for subsequent processing in the chemical recovery cycle does not inherently result in reduced mill wastewater volumes. That outcome depends in part upon the availability of existing recovery capacity and the extent of adverse process implications that accrue to increased concentrations of unpurged contaminants that cycle up in tighter process water systems. Mills that employ extended cooking and/or oxygen delignification do, however, demonstrate lower bleach plant flows than mills with conventional pulping (USEPA 1997). Thus there is, in practice, a correspondence between lower discharges of organochlorines and lower water use where enhanced ECF is employed.

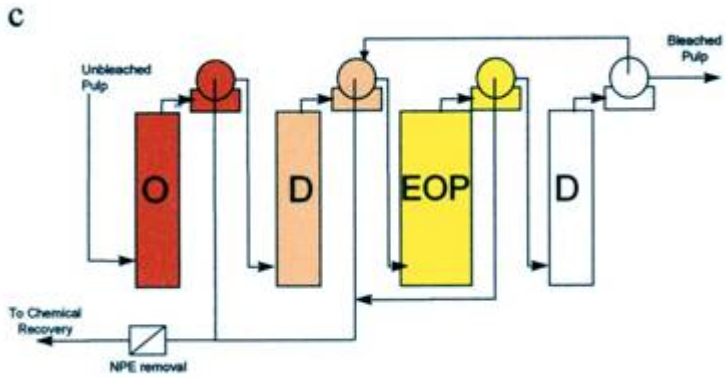



**Figure C7. Typical Elemental Chlorine Free Bleaching Sequence following Oxygen Delignification**

EPA attributes that trend, in part, to the tendency for mills to undertake other significant water conservation measures when installing OD and EC capability, as well as any possible gains associated with the reduction of bleaching stages that accompanies OD and EC application. In any case, extended cooking and oxygen delignification can significantly reduce bleach plant effluent loads from kraft mills that have adopted either or both of these now widely practiced technologies (Stratton, Gleadow, and Johnson 2005). See Table C2 below.

**Table C2. Production-Normalized Kraft Bleach Plant Flow Rates[a] (Source: Stratton, Gleadow, and Johnson 2005)**

| Type of Mill[b] | Hardwood Lines | | Softwood Lines | |
|---|---|---|---|---|
| | Average ($m^3$/kkg) | No. of Lines | Average ($m^3$/kkg) | No. of Lines |
| Mills Without EC or OD | 24.7 | 12 | 37.1 | 13 |
| Mills With EC and/or OD | 19.7 | 4 | 24.7 | 12 |
| TCF Mills | 11.6 | 1 | 18.3 | 7 |

[a] The average flow rates presented in this table were derived from bleached papergrade kraft mills.
[b] EC = extended cooking, OD = oxygen delignification, TCF = totally chlorine-free bleaching.

Barriers exist that limit filtrate recycle, regardless of whether ECF or TCF bleaching sequences are employed. The reliance of TCF bleaching on oxygen-based bleaching agents minimizes the formation of organochlorines and also allows greater opportunity for filtrate recovery and reuse, to the extent that chloride concentration buildup is the dominant impediment to filtrate recovery and use. However, the use of totally chlorine free bleaching chemicals requires an extensive removal of the metals (such as manganese, iron, and copper ions) from the pulp due to their negative impact on the peroxide bleaching. This removal and subsequent purging from the system is usually done using a chelating treatment, as shown by the Q-stage in Figure C8 below, or using an acid wash of the pulps.

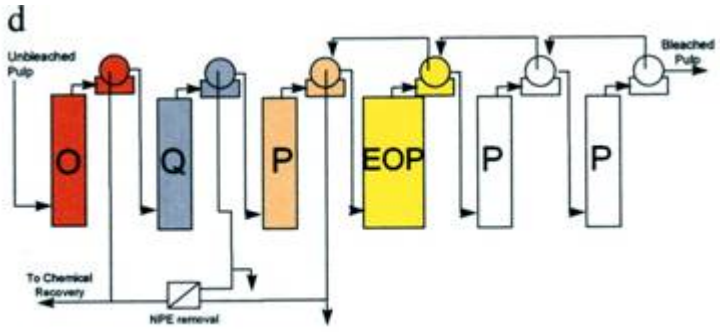



**Figure C8. Typical Totally Chlorine Free Bleaching Sequence**

## References

AMEC Ltd. 2006. *Study report for review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia*. Melbourne: Beca AMEC Ltd. http://s3.amazonaws.com/zanran_storage/www.aet.org/ContentPages/2827017.pdf

Histed, J.A. and Nicolle, F.M.A. 1976. Water reuse and recycle in the CDEHDED bleach sequence. *Tappi Journal* 59(3): 75-77.

Stratton, S., Gleadow, P., and Johnson, A. 2005. Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s. *Water Science & Technology* 50(3): 183-194.

United States Environmental Protection Agency (USEPA). 1997. *Supplemental technical development document for effluent limitations guidelines and standards for the pulp, paper, and paperboard category subpart B (bleached papergrade kraft and soda) and subpart E (papergrade sulfite)*. EPA-821-R-97-011. Washington, DC: U.S. Environmental Protection Agency, Engineering and

Analysis Division, Office of Science and Technology.
http://water.epa.gov/scitech/wastetech/guide/pulppaper/upload/1997_12_12_guide_pulppaper_jd_stdd-v4a.pdf


# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON WATER USE

## Barriers to Recovery of Bleach Plant Filtrates

***Reducing Bleach Plant Filtrate Discharges:*** Water is critical to operating an effective bleach plant. In a conventional open bleach plant, all water entering the bleach plant is discharged as wastewater or exits with the pulp.

Bleach plant filtrates are extensively recirculated within the bleach plant. An essential prerequisite for further filtrate recovery is volume reduction. The amount of water required in the fiberline and recovery systems of kraft mills is small relative to the volumes generated in most bleach plants. For this reason, recovery and use of a significant fraction of bleach plant effluent requires that bleach plant water use be minimized (Stratton, Gleadow, and Johnson 2005).

Reducing bleach plant water use must be done carefully. Extensive recycling of water in the pulp washing and bleaching process increases the concentrations of dissolved organics reaching the bleach plant with the unbleached pulp, so some increase in bleaching chemical usage is expected to occur. In addition, dissolved organic matter initially solubilized in the bleach plant is carried back into the first stage of bleaching through normal pulp washing inefficiencies. These organics consume bleaching chemicals, reducing their efficiency and effectiveness, especially for ozone and peroxide (NCASI 2003). The primary means of mitigating the effect of organic matter on bleach chemical use is efficient washing, especially after oxygen delignification. In this regard, the performance of pulp washing equipment is the most important consideration (NCASI 2003).

***Filtrate Recovery and Reuse:*** Progressive bleach plant closure involves collection of filtrates for use elsewhere in the fiberline, kraft recovery system, or some external recovery process. Recovery of bleach plant filtrates is not easy to accomplish, and the impacts can be substantial. These impacts arise from the fact that filtrate recovery represents a simultaneous loss of capacity to purge contaminants and gain of new material inputs to the recovery system (Stratton, Gleadow, and Johnson 2005).

Both elemental chlorine free (ECF) and totally chlorine free (TCF) mills recycle alkaline filtrates. It is likely a little easier for TCF mills to recycle alkaline filtrates, due to the lower chloride levels in these filtrates. There are, however, demonstrated technologies that have been successfully applied in a number of mills for controlling chloride levels in the kraft recovery system (AMEC 2006).

An approach at some mills involves recovery of extraction stage filtrate by routing it to the post-oxygen washers. Recovering filtrates in this manner may either increase the evaporative load or reduce washing effectiveness, or a combination of both, unless other water conservation measures are implemented in the fiberline. The volume of filtrates that can be recovered via the fiberline is, however, limited by the existing washing and evaporation capacities in a given mill (NCASI 2003). Therefore, existing mills would be constrained by their existing capital intensive infrastructure.

Recycling of acidic filtrates is rarely practiced. It is likely easier to recycle acidic filtrates in ECF mills, since in TCF mills the build-up of metals results in ineffective bleaching. Both ECF and TCF mills must overcome calcium (Ca)- and possibly barium (Ba)-based scales associated with acid filtrate recycle (AMEC 2006). Apart from chlorides, the buildup of dissolved substances in closed water systems can pose obstacles to mill operability and product quality, when using either type of bleaching sequence.

***Accumulation of Non-Process Elements (NPEs):*** Partial closure of the bleach plant (and other mill systems) leads to increased concentrations of organics (dissolved wood compounds) and inorganics, often called non-process elements (NPEs). Raw materials, especially wood, water, and makeup chemicals, are important sources of NPEs. NPEs are often classified according to the kinds and locations of impacts they have (NCASI 2003).

1. Chlorides and potassium have adverse impacts on recovery furnace operation, and contribute to increased corrosion in digesters, evaporators, and recovery boilers.
2. Calcium and barium can form scale deposits in the bleach plant and at locations where acidic bleaching filtrates are recovered.
3. Manganese, iron, and copper consume certain bleaching chemicals and the subsequent degradation products can cause pulp strength losses.
4. Silicon and aluminum form scale deposits on heat transfer surfaces.

In addition to increased consumption of bleaching chemicals, the efficiency of chelation in a Q-stage in removing transition metal ions is reduced by extensive system closure (STFI 2003 as cited in AMEC 2006).

A key to successful recovery and recycle of bleach plant effluent, therefore, is management of non-process elements. Controlled purges are required for chloride, potassium, sulfur, phosphorus, silica, aluminum, calcium, magnesium, manganese, and iron (Axegård et al. 2003) and a variety of technologies are available to manage the impacts of NPEs (NCASI 2003).

The challenges in managing the problems with increased concentrations of organic and inorganic compounds (i.e., the need for their control and removal) is the same as or greater than in TCF bleaching relative to ECF bleaching. This is because NPEs have a greater impact on pulp quality and brightness in TCF bleaching. In some mills, the build-up of metal levels (particularly manganese (Mn)) due to filtrate recycle is so high that $H_2O_2$ bleaching, an important part of any TCF sequence, loses effectiveness and this makes strength and brightness targets unobtainable. Bleaching with $ClO_2$ is not subject to this limitation (AMEC 2006). Experience with alkaline effluent recovery shows ECF-based sequences would likely be more effective because chlorine dioxide is more selective and is less sensitive to carryover of organics and transition metals.

## References

AMEC Ltd. 2006. *Study report for review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia*. Melbourne: Beca AMEC Ltd. http://s3.amazonaws.com/zanran_storage/www.aet.org/ContentPages/2827017.pdf

Axegård, P., J. Carey, J. Folke, P. Gleadow, J. Gullichsen, D. Pryke, D. Reeve, B. Swan, and V. Uloth. 2003. Minimum-impact mills: Issues and challenges. In *Environmental impacts of pulp and paper waste streams*, ed. T. Stuthridge, M.R. van den Hueval, N.A. Marvin, A.H. Slade, and J. Gifford. Pensacola, FL: SETAC Press.

National Council for Air and Stream Improvement, Inc. (NCASI). 2003. *Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s*. Technical Bulletin No. 860. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Stratton, S., Gleadow, P., and Johnson, A. 2005. Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s. *Water Science and Technology* 50(3): 183-194.

Swedish Pulp and Paper Research Institute (STFI). 2003. *Ecocyclic pulp mill – "KAM" – Final report 1996–2002*. KAM Report A100. Stockholm: Swedish Pulp and Paper Research Institute.

# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

***A tool for understanding environmental decisions related to the pulp and paper industry***


## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON ENERGY USE

### Overview

For purposes of broad comparison, bleaching practices may be categorized on the basis of their tendency to generate organochlorine compounds. Though an oversimplification, it is convenient to progressively categorize them as conventional, elemental chlorine free (ECF), enhanced ECF, and totally chlorine free (TCF). Conventional bleaching is associated with the use of elemental chlorine, whereas enhanced ECF precedes bleaching with extended cooking and/or oxygen delignification. Each has a different energy profile that can be significantly influenced by site-specific conditions.

### More information

Energy consumption for different bleaching configurations

Importance of unbleached pulp lignin content

Electricity to make bleaching chemicals

Energy efficiency of different bleaching sequences


# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON ENERGY USE

## Energy Consumption for Different Bleaching Configurations

Energy consumption within these various general configurations is a function of

1. the extent to which unbleached pulp is delignified prior to bleaching;
2. the chemical configuration of the subsequent bleaching sequence;
3. the magnitude of bleaching sequence-related chemical requirements;
4. process heat requirements;
5. electricity required for pumping and mixing among and within the various bleaching stages; and
6. electrical energy required for the production of bleaching chemicals.

The latter two items, when combined, are particularly prominent. Taken together, they represent from one-third to one-half of a mill's total electrical requirements. Considering the bleach plant alone, elemental chlorine free (ECF) bleaching sequences applied to similar unbleached pulps tend to be more attractive than totally chlorine free (TCF), when considering total electricity requirements for chemical manufacture and bleach plant operation. Differences as great as 50% have been estimated. Such comparisons, however, are highly sensitive to the estimates of electricity required for the manufacture of the major bleaching chemicals used. From an electrical energy standpoint, ECF sequences are typically more efficient than TCF sequences for delignifying pulps in the bleach plant.

Energy requirements among the various categories of bleaching are seldom compared in isolation from considering the extent to which pulps are delignified prior to bleaching. In their appraisal of bleached kraft manufacturing technologies, the Paper Task Force (1995) tabulated information comparing the energy profiles of alternative bleach sequences, presented in Table C3 below.

Factors that dominate the energy footprint are a) the extent to which unbleached pulps are delignified prior to bleaching, and b) the chemical agents chosen for the bleaching sequence.

In their analysis, the Paper Task Force (1995) concludes that enhanced ECF bleaching processes require significantly less total energy input than either conventional bleaching or traditional ECF processes. Taking into account potential energy credits, enhanced ECF bleaching consumes 36% less energy than conventional chlorine bleaching and 47% less than the traditional ECF sequence. The lowest energy inputs are associated with the low effluent ECF and TCF processes. However, relative to an enhanced ECF sequence, energy input varies less than 10% for filtrate recovery enabled by either a low effluent ozone ECF process, a low effluent ozone TCF process, or an enhanced ECF process with chloride purge (BFR). Folke et al. (1996) offer a broader perspective:

> *"The progression from the highest to the lowest energy-consuming sequences is not smooth, reflecting the variations from mill to mill. In practice there is considerable variation between bleach plants using identical bleaching sequences. The authors have seen data where consumption of bleaching chemicals differed by well over 25% in substantially identical bleach plants producing competitive products from similar wood using identical bleaching sequences. The reasons are primarily differences in operating skills, which in turn depend heavily upon management equipment, the quality of training and the supervision of process operators, and the skills of maintenance personnel. In many cases, these differences outweigh the advantage of one bleach sequence over the other with respect to energy efficiency and effluent quality."*

They go on to say:

*"Bleaching sequences based on peroxide generally result in lower energy demand than those based on ozone, which are in turn more energy efficient than those based on chlorine dioxide. However, mill operating conditions, product specifications and operator skills can have just as much an effect on energy consumption. The agenda is thus not whether to use ECF or TCF as the choice of bleaching sequence, but rather to modernize the pulping operation itself."*

**Table C3. Estimates of Energy Usage and Savings for Different Pulping Processes for 90 GE Brightness Softwood Pulp (millions of Btu/air-dried metric ton of pulp) (Source: Paper Task Force 2005)**

| | Bleaching Process | $C_{50}D_{50}EDED$ | D(EO)DED | OD(EO)D | OZ(EO)DD | OZQPZP | OD(EO)D + BFR |
|---|---|---|---|---|---|---|---|
| **Energy Input** | Energy to manufacture chemicals[1] | 7.6 | 10.2 | 5.0 | 5.0 | 3.6 | 5.4 |
| | Direct equipment power[2] | 0.9 | 0.9 | 1.3 | 1.5 | 2.2 | 1.3 |
| | Process steam[3] | 4.4 | 4.4 | 3.8 | 3.1 | 3.8 | 3.8 |
| **Energy Credit** | Recovery steam credit[4] | 0.0 | 0.0 | -1.6 | -2.7 | -2.7 | -2.7 |
| | Water supply credit[5] | 0.0 | 0.0 | -0.3 | -0.3 | -0.3 | -0.3 |
| | Effluent treatment credit[6] | 0.0 | 0.0 | -0.1 | -0.2 | -0.2 | -0.2 |
| **Energy Balance** | **TOTAL ENERGY INPUT** | 12.9 | 15.5 | 10.2 | 9.6 | 9.6 | 10.6 |
| | **TOTAL ENERGY CREDITS** | 0.0 | 0.0 | -2.0 | -3.1 | -3.1 | -3.1 |
| | **NET ENERGY REQUIRED** | 12.9 | 15.5 | 8.2 | 6.5 | 6.5 | 7.5 |

NOTE: The energy data include the transmission losses associated with generating electricity at a utility; thus 1 kilowatt hour of electricity equals 10,500 Btu of energy.
[1] Energy required to make the bleaching chemical.
[2] Running power consumed by the bleach plant equipment.
[3] Process steam energy required (converted into kWh/metric ton).
[4] Credit for recovery boiler steam used (assuming that O-stage solids are recovered for O(CD)ED and ODED cases, and O-, Z- and E-stage solids are recovered for the OZQPZP case).
[5] Water supply energy credit based on reduced deep well pumping.
[6] Effluent treatment energy credit based on reduced BOD treatment requirements in an aerated lagoon.

## References

Folke, J., Renberg, L., and McCubbin, N. 1996. Environmental aspects of ECF vs. TCF pulp bleaching. In *Environmental fate and effects of pulp and paper mill effluents*, 681-691. Boca Raton: St. Lucie Press.

Paper Task Force. 1995. White Paper No. 5. *Environmental comparison of bleached kraft pulp manufacturing thechnologies*. http://c.environmentalpaper.org/documents/1626_WP5.pdf


# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON ENERGY USE

## Importance of Unbleached Pulp Lignin Content

Kappa number is a measure of the amount of lignin remaining in pulp. The higher the kappa number value, the higher the use of bleaching chemicals required to brighten the pulp.

The kappa numbers of pulps leaving the digester are typically about 30 for softwoods and 20 for hardwoods in bleached kraft mills that employ conventional cooking methods. Several modifications to conventional cooking, known collectively as extended cooking (EC), have enabled kappa numbers to be further reduced in the digester in ways that minimize yield and strength losses. Kappa numbers associated with EC are about 20 for softwoods and about 14 for hardwoods.

Oxygen delignification (OD) is another technology that is used extensively to lower the residual lignin content prior to the bleach plant. The technology is more selective than most extended cooking processes. Lignin reductions of approximately 50% are achievable with OD, resulting in softwood kappa number in the 14-18 range.

Some mills use both extended cooking and oxygen delignification to achieve very low kappa number pulps prior to bleaching, producing pulps with kappa number values in the range of 10-12, perhaps even lower. Deterioration of pulp strength properties is the limiting obstacle for kappa number reduction prior to the bleach plant.

More recent strategies have been focused away from obtaining the most delignification possible in the digester and toward optimizing the fiberline as a whole based on economic, quality, and environmental factors. In these strategies, oxygen delignification plays a larger role because it can provide more selective lignin removal with less yield loss than extended cooking (Stratton, Gleadow, and Johnson 2005).

An EU appraisal of the kappa number reduction capabilities of the various pulping related technologies is summarized in Table C4.

**Table C4. Kappa Numbers Currently Achieved after Different Technologies Used (Source: IPPC 2001)**

| Delignification Technology | Hardwood | Softwood |
|---|---|---|
| Conventional Cooking | 14 - 22 | 30 - 35 |
| Conventional Cooking and Oxygen Delignification | 13 - 15 | 18 - 22 |
| Extended Cooking | 14 - 16 | 18 - 22 |
| Extended Cooking and Oxygen Delignification | 8 -10 | 8 - 12 |

TCF bleaching requires a low incoming kappa number (10-12) for the pulp to attain full brightness and good strength properties because of the power of the bleaching chemicals and fiber degradation during bleaching. A final pulp brightness of 89% ISO is achievable with TCF bleaching without yield loss. A larger amount of residual lignin remains in TCF bleached pulp than in ECF bleached pulp and this residue has to be stabilized to minimize yellowing after production. ECF bleaching can be done on a pulp with a higher kappa number (IPPC 2001).)

Data tabulated by Axegård et al. illustrates the significance of unbleached pulp kappa number to the electrical energy embodied in the production of bleaching agents.

**Table C5. Approximate Costs and Use of Electrical Energy for Bleaching Chemicals Consumed in Different Bleaching Sequences (Source: Axegård et al. 2003)**

| Post Oxygen Kappa Number | Bleaching Sequence | Bleaching Chemical Cost (USD/ptp) | Electrical Energy Requirements to Produce Bleaching Chemicals (ptp)[a] | |
|---|---|---|---|---|
| | | | kWh | kWh/Kappa |
| 18 | (C85+D15)($E_O$)DED | 22 | 160 | 9 |
| 18 | D($E_{PO}$)DD | 31 | 260 | 14 |
| 8 | D($E_{PO}$)DD | 22 | 150 | 19 |
| 8 | QPZP | 25 | 96 | 12 |

Based on laboratory bleaching of oxygen-delignified softwood kraft pulp bleached to ISO-brightness 90%.
[a] Hydrogen peroxide is assumed to be generated from hydrogen produced by electrolysis of water.

The tabulation shows a 42% dividend in chemical energy accompanying the 55% kappa number reduction for a D(EPO)DD bleach sequence. The 36% energy reduction for the TCF sequence relative to the ECF sequence on the low kappa number pulp is also noteworthy.

## References

Axegård, P., J. Carey, J. Folke, P. Gleadow, J. Gullichsen, D. Pryke, D. Reeve, B. Swan, and V. Uloth. 2003. Minimum-impact mills: Issues and challenges. In *Environmental impacts of pulp and paper waste streams*, ed. T. Stuthridge, M.R. van den Hueval, N.A. Marvin, A.H. Slade, and J. Gifford. Pensacola, FL: SETAC Press.

Integrated Pollution Prevention and Control (IPPC). 2001. *Reference document on best available techniques in the pulp and paper industry*. http://eippcb.jrc.ec.europa.eu/reference/BREF/ppm_bref_1201.pdf

Stratton, S., Gleadow, P., and Johnson, A. 2005. Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s. *Water Science & Technology* 50(3): 183-194.


# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON ENERGY USE

## Electricity to Make Bleaching Chemicals

The electricity requirements, reported by a number of sources, necessary to produce the major chemicals used in bleach plants are summarized in Table C6.

**Table C6. Electrical Energy Requirements for Production of Chemicals in Bleach Plants (kWh/kg)**

| Chemical | Formula | McIlroy and Wilczinsky 1999 | Laxén and Henricson 1996 | Folke et al. 1996 | Dence and Reeve 1996 | Paper Task Force 1995 |
|---|---|---|---|---|---|---|
| Chlorine | $Cl_2$ | 3 | | 1.6 | 2.3 – 2.6 | 1.37* |
| Sodium hypochlorite | NaOCl | | | 3.5 | | |
| Chlorine dioxide | $ClO_2$ | 9.25[a] | 8.9 | 11 | | 9.8 |
| Sodium Hydroxide | NaOH | 2.8[b] | 1.8 | 1.8 | 2.0 – 2.3 | 1.37* |
| Ozone | $O_3$ | 19.9[c] | 10 | 14 | 13.4[d] | 11.9 |
| Oxygen, cryogenic | $O_2$ | 1.15 | | 2.8 | 3 | |
| Oxygen, PSA/VSA[e] | $O_2$ | 0.4 | 0.4 | 2.8 | 2.65 | 0.39 |
| Hydrogen peroxide | $H_2O_2$ | 0.75 | 0.61 – 3.85[f] | 3.5 | | 1.69 |

[a] Based upon the R8 process.
[b] Based upon the use of oxidized white liquor (OWL) in the oxygen delignification stage and fresh caustic in extraction stages for the ODEopDED bleaching sequence.
[c] Ozone, 13 wt % $O_3$ in $O_2$.
[d] From Gottlieb et al. (1994), Ozone, 6 wt % $O_3$ in $O_2$, Electricity cost includes power of gas recycle system, $O_3$ generator power, and power for cooling needs (chilled water and cooling tower).
[e] A mill using only $O_2$ in the Eo stage would have cryogenic oxygen delivered on site. A mill with oxygen delignification would likely have a pressure swing absorption (PSA)/vacuum swing absorption (VSA) plant on site.
[f] The lowest estimate is based upon $H_2$ production by steam reforming, a slightly higher value is obtained using methanol cracking, and the highest estimate is based upon $H_2$ production by electrolysis.
* The reasons for this value being low are not known.

Electricity requirement estimates reported by these published reference papers vary considerably for the primary ECF bleaching chemical $ClO_2$, and the primary TCF bleaching chemicals, $O_3$ and $H_2O_2$. As much could be said for sodium hydroxide, which is common to both bleaching concepts. The relative cost and energy advantages of alternative bleach sequence configurations warrant scrutiny with regard to underlying estimates of electricity required for chemical manufacture.

**$ClO_2$ Manufacture**: Chlorine dioxide ($ClO_2$) is the primary bleaching chemical used worldwide for final delignification and brightening of chemical pulps. Most mills in North America use purchased sodium chlorate to generate $ClO_2$ on site. The primary methods of generating $ClO_2$ at pulp mills are the Sterling R8/R10 process and similar Eka SVP-MeOH process. In 1992, 76% of the installed $ClO_2$ capacity in

North America used one of these processes, where sodium chlorate is reduced to chlorine dioxide with methanol acting as the reducing agent (Stockburger 1992). The electrical energy required to produce chlorine dioxide is large (8.9 – 11.0 kWh/kg) because of the large energy requirements for the production of sodium chlorate. For example, in the R8 process, approximately 97% of the energy required to produce $ClO_2$ is a result of the energy requirements to produce sodium chlorate. McIlroy and Wilczinsky's estimate of 9.25 kWh/kg is based upon the R8 process (McIlroy and Wilczinsky 1999); other authors do not specify a generation process.

**Ozone**: Ozone is produced by passing oxygen through a corona discharge, which has large electrical requirements (10.0 – 19.9 kWh/kg). With current technology, ozone yields from oxygen are low (6 to 13 wt. %). The differences in $O_3$ electricity requirements among the authors tabulated above are most likely due to the concentrations of ozone being produced. It is known that the concentration of ozone production from oxygen is a function of applied voltage (Dence and Reeve 1996). The value reported by Gottlieb et al. (1994) of 13.4 kWh/kg is based upon an ozone production facility at a pulp mill and includes the most information regarding ozone production and auxiliaries.

**Caustic and Chlorine**: Sodium hydroxide and chlorine are commercially produced by the chloralkali process, which involves the electrolysis of sodium chloride solution with the anode and cathode separated by a membrane. For commercial production of sodium hypochlorite, the membrane is simply removed. Since the molecular weights of chlorine gas and sodium hypochlorite are similar, 71 and 74 respectively, their cost on a kg basis should be similar as well. It is unclear why there is a large difference in electricity requirements between chlorine gas and sodium hypochlorite reported by Folke et al. (1.6 kWh/kg vs. 3.5 kWh/kg respectively).

It is has been reported that a chloralkali process with multi-layered membranes, zero gap, and cathode coatings has achieved a power consumption of 2000-2300 kWh/ton of sodium hydroxide at current densities of 2-4 $kA/m^2$. This translates to 2.3-2.6 kWh/kg of $Cl_2$ (Dence and Reeve 1996), values similar to the McIlroy and Wilczinsky reported value of 3.0 kWh/kg. McIlroy and Wilczinsky's values of 3.0 and 2.8 kWh/kg for $Cl_2$ and NaOH are deemed representative because they are in fair agreement with the values reported elsewhere (Dence and Reeve 1996) and they consider the use of oxidized white liquor (OWL) as the alkali source for $O_2$ delignification. The Paper Task Force (1995) value for caustic seems irregular, in comparison to these other reported values.

## References

Dence, C.W. and Reeve, D.W. (eds). 1996. *Pulp bleaching principles and practice*. Atlanta, GA: Tappi Press.

Folke, J., Renberg, L., and McCubbin, N. 1996. Environmental aspects of ECF vs. TCF pulp bleaching. In *Environmental fate and effects of pulp and paper mill effluents*. 681-691. Boca Raton: St. Lucie Press.

Gottlieb, P.M., W.E. Nutt, S.R. Miller and T.S. Macas. 1994. Mill experience in high-consistency ozone bleaching of southern pine pulp. *TAPPI Journal* 77(6): 117–124.

Laxén, T., Henricson, K. 1996. Energy efficiency in ECF and TCF bleaching. *Pulp & Paper Canada* 97(1): 58-62.

McIlroy, D. and J. Wilczinsky. 1999. Chemical pulp mills. Chapter 5 in *Energy cost reduction in the pulp and paper industry: A monograph*, ed. P.N. Williamson. Montreal: Pulp and Paper Research Institute of Canada (Paprican).

Paper Task Force. 1995. White Paper No. 5. *Environmental comparison of bleached kraft pulp manufacturing thechnologies*. http://c.environmentalpaper.org/documents/1626_WP5.pdf

Stockburger, P. 1992. What you need to know before buying your next chlorine dioxide plant. In *Proceedings of the 1992 Tappi Engineering Conference*, 1085-1091. Atlanta, GA: Tappi Press.


# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON ENERGY USE

## Energy Efficiency of Different Bleaching Sequences

Summing the energy content required to produce all chemicals used in the bleach plant allows a comparison of bleaching chemical electrical costs among various bleaching sequences. Comparisons of bleaching energy efficiency are best made among bleaching sequences with similar starting kappa number, final brightness value, and wood furnish.

Within the bleach plant, electrical energy is primarily used for chemical mixing and pumping of stock and filtrates. It is on the order of 30 kWh/ADt per bleaching stage (Dence and Reeve 1996).

Electricity demand in the bleach plant represents roughly 15% of the total electricity requirements at bleached kraft market pulp mills.

NCASI staff compared a number of laboratory bleaching studies reported in the literature to compare the electricity requirements of ECF, ECF-lite (ECF bleaching with low chlorine dioxide doses and increased use of oxygen or ozone), TCF, and chlorine-based (for a historical perspective) bleaching sequences. ECF-lite bleaching sequences are bleaching sequences using less than 10 kg/ODMT of chlorine dioxide (Chirat and Lachenal 1999). Only literature sources with complete measured chemical charge information were used. The bleach sequences examined and their reference sources are listed in Table C7. For complete chemical charge information, the reader is referred to the individual literature references shown in the last column of the table.

Electricity requirements for a number of chemicals used in the bleach plant were not considered in the electricity calculations. TCF sequences use chelants such as EDTA or DTPA for chelation of transition metals prior to hydrogen peroxide and ozone bleaching, and use magnesium sulfate ($MgSO_4$) in hydrogen peroxide bleaching as a bleach agent stabilizer. Many mills also use $MgSO_4$ to minimize pulp degradation in oxygen delignification stages. These costs were not considered and are expected to be small. Sulfuric acid is commonly used in both ECF and TCF sequences for pH control. The electrical costs of sulfuric acid addition were not considered because of its low cost and because sulfuric acid addition numbers are often not reported in the literature.

The overall electrical requirements for TCF sequences are quite dependent upon the estimated ozone and hydrogen peroxide electricity requirements. If the values of 13.4 kWh/kg and 0.75 kWh/kg for ozone and hydrogen peroxide, respectively, are used (the lower range for these chemicals), TCF sequences are comparable to ECF sequences for electricity requirements if only the electricity needs for the bleaching chemicals are considered. That trend is shown in Figure C9.

The chlorine-based sequences fall in the same range as ECF sequences. Even though chlorine gas is less expensive to produce than chlorine dioxide, chlorine-based sequences, in general, require higher sodium hydroxide charges in subsequent extraction stages, increasing their overall electrical requirement.

TCF sequences tend to have more bleaching stages than ECF sequences. If an average value of 30 kWh/ADmt per bleaching stage (for pumping and mixing) is factored into the calculation, ECF sequences have lower electrical consumption, as shown Figure C10.

The difference appears more dramatic if values for the electrical energy required to produce ozone and peroxide are taken from the upper end of their reported range. If values of 19.9 kWh/kg and 3.5 kWh/kg for ozone and hydrogen peroxide, respectively, were used (the higher range for these chemicals), TCF sequences, on average, would appear to require 50% more electricity than ECF sequences. That outcome is represented in Figure C11. Figure C12 incorporates the additional electrical power required for pumping and mixing.

To the extent that electrical energy efficiency is sought in the bleaching of kraft pulps, ECF bleaching would generally appear to be the option of choice, especially in comparison with longer TCF sequences, although there are exceptions. The overall energy efficiency of bleached kraft pulp production, however, requires integrated consideration of prior delignification accomplished in pulping.

## Table C7. Bleach Sequences from Literature Used in the Electricity Calculations

| Bleaching Sequence | Classification | Pulp Type | Kappa into Bleach Plant | Final Brightness (ISO %) | Reference |
|---|---|---|---|---|---|
| $C_DEHDED$ | C, lab | Northeastern softwood kraft pulp | 25.3 | 90.3 | Histed & Nicolle 1976 |
| CEDED | C, lab | Softwood kraft pulp | 25 | 85 | Ruhanen & Dugal 1982 |
| $C_DEDED$ | C, lab | Black spruce kraft pulp | 30.6 | 90.6 | Liebergott et al. 1984 |
| $C_DE_ODED$ | C, mill | Eucalyptus | 17 | 90.5 | Walsh et al. 1999 |
| $C_DE_ODED$ | C, mill | Softwood kraft pulp | 21.3 | 91.4 | Wilson et al. 1999 |
| D(EP)DED | ECF, lab | $O_2$ delignified softwood and hardwood kraft pulp | 12.1 | 90.1 | Rautonen et al. 1996 |
| D(EP)DED | ECF, lab | | 12.1 | 90.0 | Rautonen et al. 1996 |
| DEDED | ECF, lab | | 13.2 | 89.1 | Rautonen et al. 1996 |
| DEDED | ECF, lab | | 18.4 | 89.4 | Rautonen et al. 1996 |
| OD(EOP)DD | ECF, lab | Eucalyptus | 18.2 | 90.0 | Colodette et al. 1999 |
| (OQ)(OP)(ZE)DD | ECF-lite, lab | Eucalyptus | 18.2 | 90.0 | Colodette et al. 1999 |
| $DEoD_1ED_2$ | ECF, lab | $O_2$ delignified softwood kraft pulp | 12.7 | 88.4 | Toven & Gellerstedt 2003 |
| DEOQ(PO) | ECF-lite, lab | | 12.7 | 87.5 | Toven & Gellerstedt 2003 |
| $(DZ)EoD_1ED_2$ | ECF-lite, lab | | 12.7 | 87.5 | Toven & Gellerstedt 2003 |
| (DZ)EoQ(PO) | ECF-lite, lab | | 12.7 | 87.7 | Toven & Gellerstedt 2003 |
| DEopD | ECF, mill | Hardwood | 19 | 90.4 | Pryke et al. 1999 |
| DEopD | ECF, mill | Softwood | 34 | 88.7 | Pryke et al. 1999 |
| DEopD | ECF, mill | Hardwood | 7.5 | 90+ | Herbert 1999 |
| DEopDD | ECF, mill | Softwood | 14 | 90+ | Herbert 1999 |
| QOQPZPP | TCF, lab | $O_2$ delignified softwood and hardwood kraft pulp | 7.2 | 89.4 | Rautonen et al. 1996 |
| QOQZQPZP | TCF, lab | | 7.2 | 90.6 | Rautonen et al. 1996 |
| QOQPZP | TCF, lab | | 9.1 | 89.6 | Rautonen et al. 1996 |
| QPZPZP | TCF, lab | | 12.1 | 88.8 | Rautonen et al. 1996 |
| QZPZP | TCF, lab | | 12.1 | 88.5 | Rautonen et al. 1996 |
| QPZPZP | TCF, lab | | 13.2 | | Rautonen et al. 1996 |
| QPQZPZP | TCF, lab | | 18.4 | 89.5 | Rautonen et al. 1996 |
| QOQPZPZPP | TCF, lab | | 18.4 | 88.2 | Rautonen et al. 1996 |
| QOQZQPZP | TCF, lab | | 18.4 | 88.9 | Rautonen et al. 1996 |
| QOQZPZP | TCF, lab | | 18.4 | 89.0 | Rautonen et al. 1996 |
| (OQ)(OP)(ZQ)(PO) | TCF, lab | Eucalyptus | 18.2 | 90.0 | Colodette et al. 1999 |
| Z(EO)Q(PO) | TCF, lab | Softwood kraft | 30 | 89.2 | Ni & Ooi 1996 |

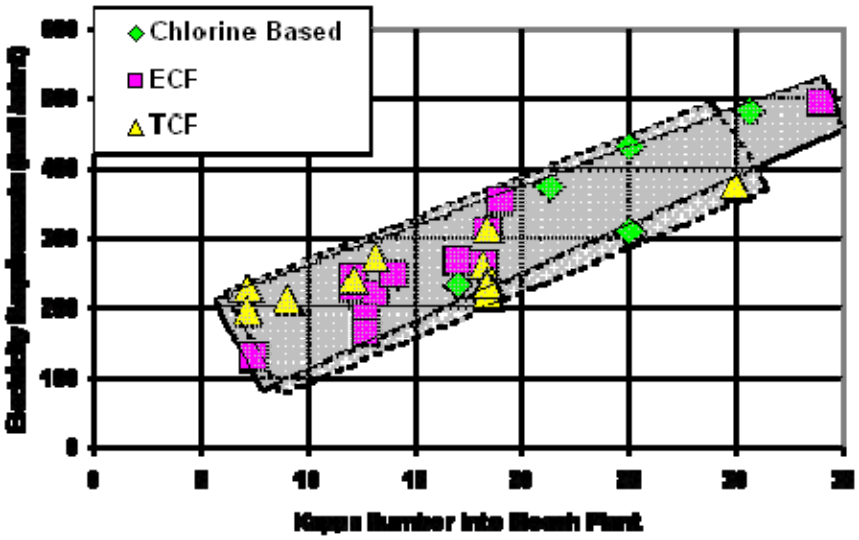



**Figure C9. Electrical Energy Requirements for Bleaching Sequences When Only Considering Electricity Required for Chemical Production and Lower Electricity Values for $O_3$ and $H_2O_2$**
[Dotted quadrangle encapsulates TCF sequences; solid quadrangle encapsulates ECF sequences]

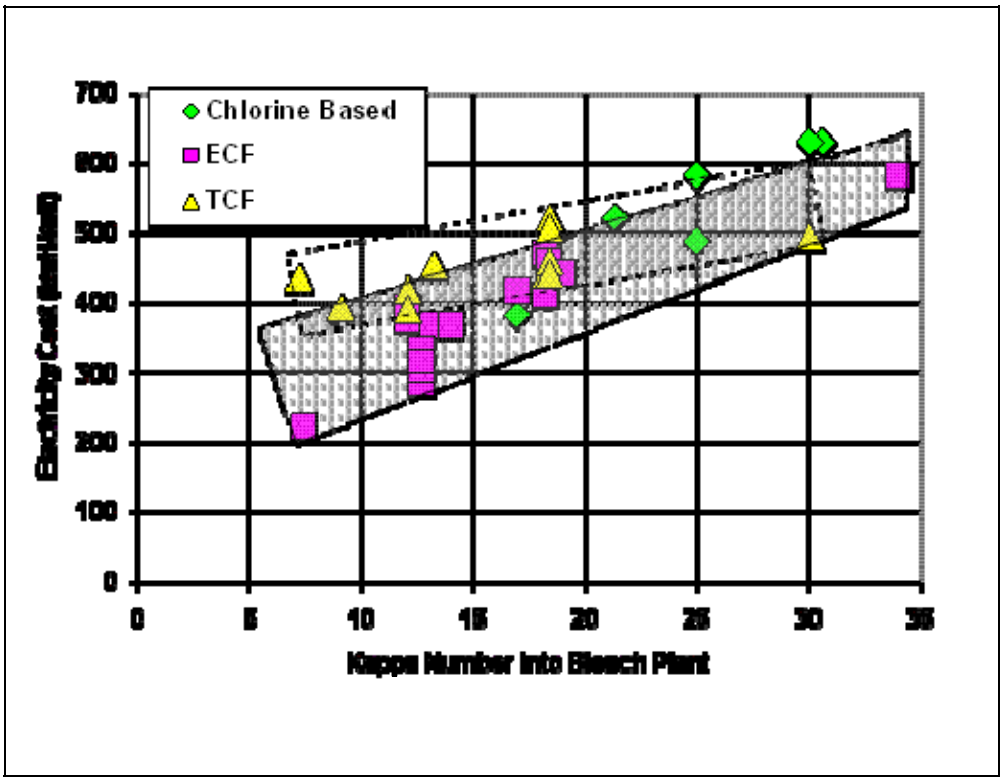



**Figure C10. Electrical Energy Requirements for Bleaching Sequences When Including Electricity Required for Stage Pumping and Mixing and Using Lower Electricity Values for $O_3$ and $H_2O_2$**
[Dotted quadrangle encapsulates TCF sequences; solid quadrangle encapsulates ECF sequences.]

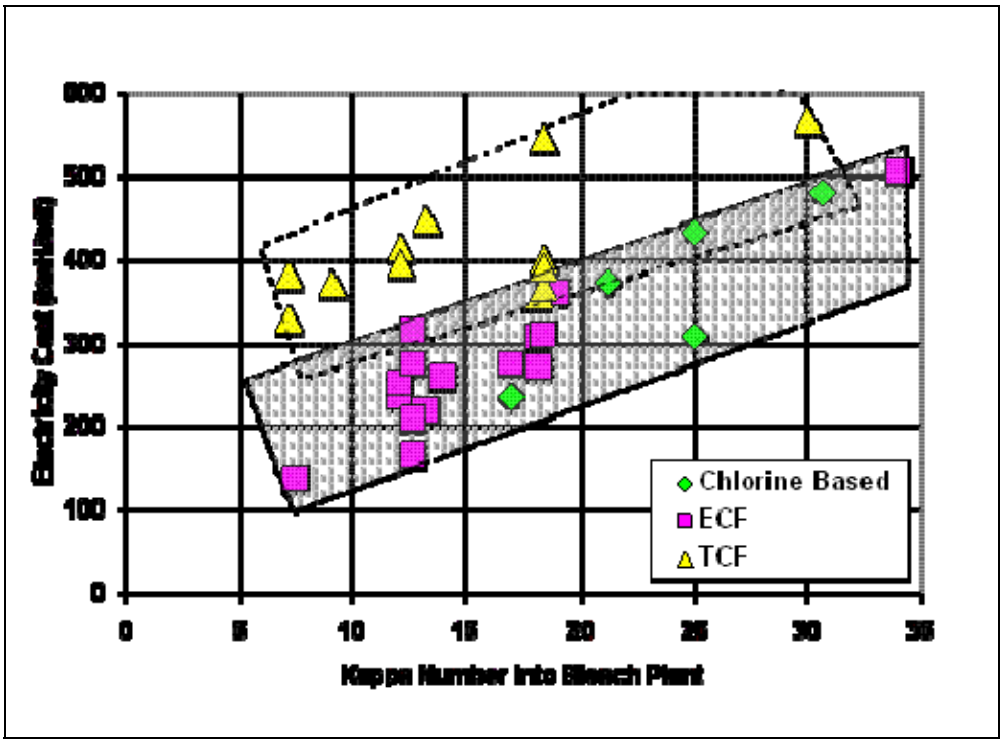



**Figure C11. Electrical Energy Requirements for Bleaching Sequences When Only Considering Electricity Required for Chemical Production and Higher Electricity Values for $O_3$ and $H_2O_2$**
[Dotted quadrangle encapsulates TCF sequences, Solid quadrangle encapsulate ECF sequences.]

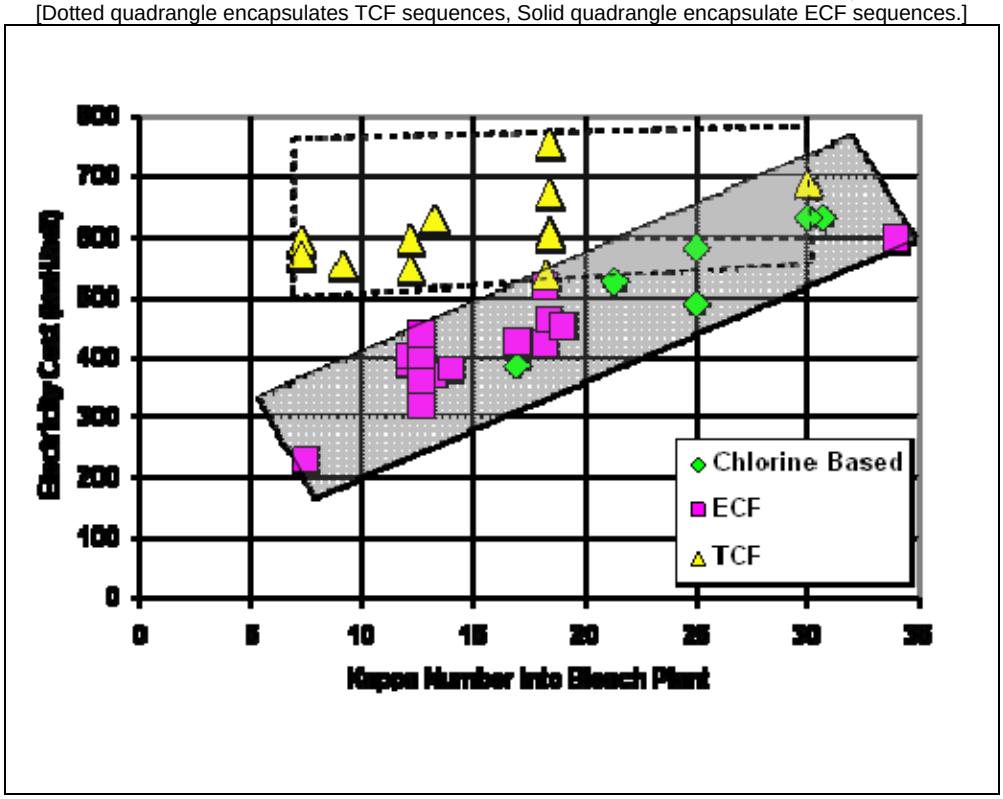



**Figure C12. Electrical Energy Requirements for Bleaching Sequences When Including Electricity Required for Stage Pumping and Mixing and Using Higher Electricity Values for $O_3$ and $H_2O_2$**
[Dotted quadrangle encapsulates TCF sequences, Solid quadrangle encapsulate ECF sequences.]

## References

Chirat, C. and Lachenal, D. 1999. Brushing up on bleaching techniques. *Pulp and Paper International* 41(10):41-43.

Colodette, J. L., Gomide, J. L., Argyropoulos, D. S., Robles, Y.A.M., Almeida, J. M., Mehlman, S. K., deBrito, A.G.H. 1999. Effect of pulping processes on bleachability with ECF, Z-ECF and TCF bleaching. *Appita Journal* 52(5): 368-374.

Herbert, S. 1999. ECF bleaching of hardwood and softwood at Alberta-Pacific Forest Industries Inc. In *Elemental chlorine free bleaching, A TAPPI Press anthology of published papers*, 44-49. Atlanta, GA: TAPPI Press.

Histed, J.A. and Nicolle, F.M.A., 1976.Water reuse and recycle in the CDEHDED bleach sequence. *Tappi Journal* 59(3): 75-77.

Liebergott, N., van Lierop, B., Garner, B.C., and Kubes, G.J. 1984. Bleaching a softwood kraft pulp without chlorine compounds. *Tappi Journal* 67(8):76-80.

Ni, Y. and Ooi, T. 1996. Laboratory study on bleaching softwood kraft pulp by a totally chlorine free process including the novel ozone bleaching. *Tappi Journal* 79(10): 167-172.

Pryke, D.C., Farley, B., and Wolf, A. 1999. Implementation of ECF bleaching at Mead Paper Co., Chillicothe, Ohio. In *Elemental chlorine free bleaching, A TAPPI Press anthology of published papers*, 33-43. Atlanta, GA: TAPPI Press.

Rautonen, R., Rantanen, T., Toikkanen, L, and Malinen, R. 1996. TCF bleaching to high brightness – Bleaching sequences and pulp properties. *Journal of Pulp and Paper Science* 22(8):J306-J314.

Ruhanen, M. and Dugal, H.S. 1982. First-stage bleaching of softwood kraft pulp with peroxide, instead of chlorine. *Tappi Journal* 65(9):107-110.

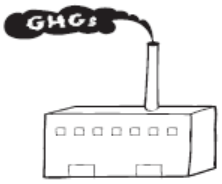
Toven, K. and Gellerstedt. G. 2003. Structural changes of softwood kraft lignin in oxygen delignification and prebleaching. In *Proceedings of the 10th international symposium on wood and pulping chemistry*, Vol. 2, 340-435. Yokohama, Japan, June 7–10, 1999. Atlanta, GA: Tappi Press. http://www.chemeng.ntnu.no/research/paper/Publications/1999/iswpc99-toven.pdf

Walsh, P.B., Hoyos, M., and Seccombe, R.C. 1999. Practical mill experience with the use of hydrogen peroxide reinforced extraction stages to reduce and/or eliminate the use of elemental chlorine in hardwood kraft pulps for AOX reduction. In *Elemental chlorine free bleaching, A TAPPI Press anthology of published papers*, 75-79. Atlanta, GA: TAPPI Press.

Wilson, R., Swaney, J., Pryke, D.C., Luthe, C.E., and O'Connor, B.I. 1999. Mill experience with chlorine dioxide delignification. In *Elemental chlorine free bleaching, A TAPPI Press anthology of published papers*, 105-113. Atlanta, GA: TAPPI Press.

# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

***A tool for understanding environmental decisions related to the pulp and paper industry***




GREENHOUSE GASES

## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON GREENHOUSE GAS EMISSIONS

### Overview

The co-benefits and trade-offs between reductions in organochlorines and greenhouse gas emissions are associated with the impacts on energy use. If changes in energy use are associated with changes in the amounts of fossil fuels being burned, the effects on greenhouse gas emissions will resemble those on energy consumption, with the specific impacts being dependent on the type of fossil fuel being affected. If the changes in energy consumption affect only biomass energy, there will be no significant effect on greenhouse gas emissions.

# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

***A tool for understanding environmental decisions related to the pulp and paper industry***

WOOD USE

## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON LAND AND WOOD USE

### Overview

Wood represents one of the primary costs associated with production of chemical pulps, so it is crucial to use wood in the most efficient manner possible. In kraft pulping, it takes about 2.3 dry kg wood to produce 1 dry kg fully bleached pulp, a yield of about 43%. The 57% yield loss occurs primarily during cooking (pulping) and to a lesser extent during bleaching, as the lignin and other non-fibrous wood components are removed and the pulp is brightened.

### More information

Pulp yield for ECF and TCF pulps

Effects of pulping on wood requirements

Effectiveness of chlorine-based vs. oxygen-based bleaching

WOOD USE

# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON LAND AND WOOD USE

## Pulp Yield for ECF and TCF Pulps

While the loss of some amount of fiber in cooking and bleaching is unavoidable, overall yield can be maximized by limiting the degree of cooking, maximizing the use of bleaching chemicals that selectively react with residual lignin, and by limiting the number of bleaching stages. In general, modern elemental chlorine free (ECF) mills tend to use wood more efficiently than totally chlorine free (TCF) mills due mostly to the strong preference of chlorine dioxide to react with residual lignin relative to fibers. TCF mills generally cook pulp to a greater extent before the bleach plant (i.e., lower kappa number), rely on less selective oxidants such as oxygen, ozone and peroxide, and require more bleaching stages than ECF mills. Technologies have been developed to mitigate yield differences between ECF and TCF processes, though these add cost and complexity to mill operations.

Cooking is designed to intentionally dissolve the non-fibrous components, primarily lignin, which are subsequently removed by washing the pulp. During the cook some fibers are also dissolved and a certain amount of such loss is unavoidable. Parthasarathy (1997) points out that a linear relationship exists between yield and the kappa number domain between 20 and 85, but that below 20, reductions in pulp yield can be precipitous.

In a conventional bleached kraft mill, cooking is terminated at a level that maximizes lignin removal, fiber strength, and overall yield. Residual lignin is then removed and the pulp is brightened in a series of bleaching stages in which chemicals are reacted with the pulp followed by washing. Lower kappa number pulps are necessary for TCF bleaching, especially if peroxide is used early in the bleaching sequence. TCF bleach plants are believed to require incoming kappa numbers below fifteen, and preferably below twelve.

Current TCF sequences are likely to have lower yields than ECF sequences when the bleach sequences have the same incoming bleach plant kappa and final brightness target. Very few literature data are available, however, to enable direct comparison of yields between ECF and TCF bleaching sequences.

In 1994, Fleming and Stone advanced a number of observations on the effects of TCF bleaching on pulp quality, including yield:

- Evidence is beginning to suggest that low kappa number pulping and TCF bleaching produce lower yields of bleached pulp compared with ECF bleaching of pulps with kappa numbers of more than 20.
- Besides the yield losses caused by low kappa pulping, the literature indicates that TCF bleaching produces more yield loss than ECF bleaching.
- Pulp strength also deteriorates as kappa number is decreased in cooking. Strength loss begins below 22 kappa number in the conventional cooking of softwood….and 18 to 20 kappa number is considered the optimum operating region.
- If environmental considerations force digester kappa numbers and bleaching technology into regions where strength loss occurs, then a higher percentage of the low-yield TCF pulp must be added to the paper furnish to maintain the strength of the sheet. It decreases the amount of mineral filler, high-yield pulp, or secondary fiber that can be included and consequently further increases the amount of fresh wood that must be used to produce one ton of paper.

Over a decade later (2006), AMEC carried out a comprehensive review of ECF and TCF bleaching processes. Among their findings were observations related to pulp yield:

- The level of delignification in cooking, the cooking process [type], and oxygen delignification determine the final pulp yield.
- The yield loss in bleaching is in the range 1-3% (on wood) and is most likely independent of whether an ECF or TCF sequence is employed.
- There is a tendency for increased yield loss if either alkaline peroxide or ozone bleaching are carried out, particularly in the bleaching of hardwood pulps.
- Because TCF bleached pulps tend to have lower oxygen-delignified pulp kappa number, they have a lower overall bleached yield than ECF bleached pulps.

## References

AMEC Ltd. 2006. *Study report for review of ECF and TCF bleaching processes and specific issues raised in the WWF report on Arauco Valdivia*. Melbourne: Beca AMEC Ltd. http://s3.amazonaws.com/zanran_storage/www.aet.org/ContentPages/2827017.pdf

Fleming, B. and Sloan, T. 1994. Low Kappa cooking, TCF bleaching affect pulp yield, fiber strength. *Pulp & Paper* December. http://www.risiinfo.com/db_area/archive/p_p_mag/1994/9412/94120111.htm

Parthasarathy, V.R. 1997. Shift in pulping, bleaching strategy yields better resource utilization. *Pulp & Paper* March. http://www.risiinfo.com/db_area/archive/p_p_mag/1997/9703/focus3.htm

# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON LAND AND WOOD USE

## Effects of Pulping on Wood Requirements

Reducing the environmental impact of pulp bleaching has focused attention on reducing the lignin content (as measured by kappa number) of brownstock pulps so that less work remains to be done in the bleach plant. The basic advantage of pre-bleaching kappa number reduction technologies is that more of the lignin is dissolved, captured, and combusted in the recovery furnace and less is discharged from the bleach plant.

Kappa number reduction prior to bleaching can be achieved by extended cooking and/or the use of oxygen delignification technologies (NCASI 2003). The extent to which extended cooking can be practiced has been constrained by pulp yield and quality requirements, but has been increased by a number of modifications to kraft pulping technology (McDonough 1992). Oxygen delignification involves reacting the cooked and washed pulp with oxygen under alkaline conditions. Further lignin removals of 50% and greater can be accomplished, but are limited due to potential for loss of pulp strength.

There are numerous possible variations in the application of these technologies, either individually or in sequence. Each seeks to compensate for one or more disadvantages of the other, yield being among them. At the risk of oversimplification, oxygen delignification is more selective (i.e., toward lignin removal) than conventional bleaching which, in turn, is more selective than pulping (McCubbin 1997). The importance of selectivity to pulp yield is illustrated in Figure C13.

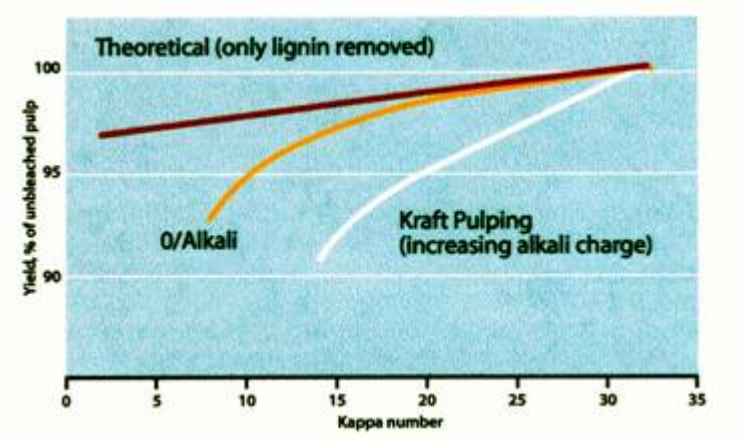



**Figure C13. Yield Loss Related to Kappa Number for Different Delignification Approaches (Source: Saldivia 2002)**

The diagram displays yield loss as delignification proceeds beyond the kappa associated commonly with conventional pulping. The greater selectivity of oxygen extends delignification without the loss of fiber that accompanies doing so with conventional pulping practice. Yet oxygen delignification also reaches a point where fiber loss accelerates as delignification progresses. The art lies in optimizing the deployment of pulping and other delignification approaches in ways that reduce fiber loss, preserve pulp properties and reach kappa number levels suitable for the bleaching sequence that follows.

Modified cooking procedures have been used to obtain softwood kraft pulps with low kappa numbers, and reports claim good strength retention even down to a kappa number of 10 in some cases. This low kappa number enables TCF bleaching sequences to reach high brightness levels (Fleming and Sloan 1994). However, the potential yield loss suffered in achieving such low kappa numbers compared to conventional values of 25-30 can be significant. Options for maximizing pulp yield while delignifying to low kappa number include pulping to 25-30 kappa number, followed by two-stage oxygen delignification (Axegård et al. 2003).

## References

Axegård, P., J. Carey, J. Folke, P. Gleadow, J. Gullichsen, D. Pryke, D. Reeve, B. Swan, and V. Uloth. 2003. Minimum-impact mills: Issues and challenges. In *Environmental impacts of pulp and paper waste streams*, ed. T. Stuthridge, M.R. van den Hueval, N.A. Marvin, A.H. Slade, and J. Gifford. Pensacola, FL: SETAC Press.

Fleming, B. and Sloan, T. 1994. Low Kappa cooking, TCF bleaching affect pulp yield, fiber strength. *Pulp & Paper* December. http://www.risiinfo.com/db_area/archive/p_p_mag/1994/9412/94120111.htm

McCubbin, N. 1997.Yield improvements possible with $O_2$ delig, digester modifications. *Pulp & Paper* June 1997. http://www.risiinfo.com/db_area/archive/p_p_mag/1997/9706/feat2.htm

McDonough, T.J. 1992. *Bleaching scenarios for the year 2000*. IPST Technical Paper Series No. 439. http://smartech.gatech.edu/bitstream/1853/2152/1/tps-439.pdf

National Council for Air and Stream Improvement, Inc. (NCASI). 2003. *Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s*. Technical Bulletin No. 860. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Saldivia, M.A.G. 2002. Oxygen delignification in two stages. *Fiber & Paper* 4(3):26-29. http://www.metso.com/MP/marketing/Vault2MP.nsf/BYWID2/WID-060906-2256E-5044D/$File/FibPap3_02%20PORTAL.pdf?openElement

WOOD USE

# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON LAND AND WOOD USE

## Effectiveness of Chlorine-based vs. Oxygen-based Bleaching

In his primer on the bleaching of chemical pulps, Ragauskas has compared the basic properties of bleaching agents in terms of a high (H), medium (M), and low (L) effectiveness (Ragauskas n.d.).

| | Efficiency[a] | Reactivity[b] | Selectivity[c] | Dirt Removal[d] | Environmental Implications |
|---|---|---|---|---|---|
| **Chlorine** | H | H | H | H | H |
| **Chlorine Dioxide** | H | M | H | H | M |
| **Oxygen** | L | L | M | M | L |
| **Peroxide** | L | L | H | L | L |
| **Sodium Hypochlorite** | M | M | M | H | H |
| **Ozone** | H | H | M | L | L |

[a] the degree to which a bleaching agent's oxidizing power is used in desirable, lignin-degrading reactions
[b] the fraction of the residual lignin that the bleaching agent is practically capable of removing
[c] the degree to which the bleaching agent can remove lignin without dissolving or damaging the other components of the fiber, cellulose and hemicellulose
[d] the ability to remove dirt particles, a very important characteristic benefited by slower lignin reaction time

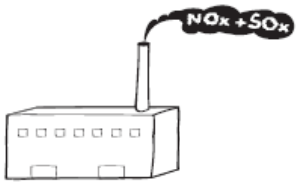
The comparison illustrates why there was historical preference for elemental chlorine, apart from its environmental implications, and shows the advantage enjoyed by chlorine dioxide relative to oxygen-based bleaching agents.

## References

Ragauskas, A. n.d. Basics of bleaching chemical pulps. IPST-Ga Tech. http://www.ipst.gatech.edu/faculty_new/faculty_bios/ragauskas/technical_reviews/Basics%20of%20Pulp%20Bleaching.pdf

# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

***A tool for understanding environmental decisions related to the pulp and paper industry***




EMISSIONS TO AIR

## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON EMISSIONS TO AIR

### Overview

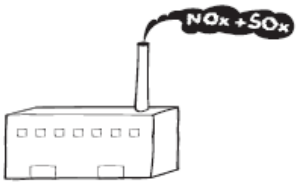
Emissions of certain air pollutants from chemical pulp bleaching operations are affected by the choice of bleaching chemicals, and the industry's shift from chlorine bleaching to elemental chlorine free (ECF) bleaching has altered emission profiles. Emissions of chlorine ($Cl_2$) are essentially eliminated when molecular chlorine use for bleaching is curtailed with ECF. Emissions of chlorine dioxide ($ClO_2$), while controlled, are likely to be slightly higher with ECF due to the increased generation and use of the chemical. Chloroform ($CHCl_3$), a by-product formed when pulp is bleached with hypochlorite or chlorine, is generated in much smaller quantities when chlorine dioxide is used in place of the former chemicals. Emission reductions for chloroform of greater than 99% have resulted from the application of ECF bleaching and elimination of chlorine and sodium hypochlorite from the bleaching sequence.

Emissions of volatile organic compounds (VOCs) and substances classified as hazardous air pollutants (HAPs) come into play where oxygen delignification is used as the pathway to enhanced ECF and totally chlorine free (TCF) bleaching sequences, as significant increases in methanol emissions accompany oxygen delignification.

### More information

Emissions associated with pulp bleaching

Emission levels and controls regulatory backdrop




EMISSIONS TO AIR

# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON EMISSIONS TO AIR

## Emissions Associated with Pulp Bleaching

Chemical pulp mills have shifted away from chlorine bleaching with a resulting increased use of oxygen and chlorine dioxide in the bleaching sequence. Greater use of these chemicals has led to increased emissions of carbon monoxide, a by-product of bleaching with oxygen or chlorine dioxide. Furthermore, because some chlorine dioxide is made using methanol as a reducing agent, increased use of chlorine dioxide leads to higher methanol emissions from chlorine dioxide manufacturing, methanol storage, and from bleaching operations.

Progression of bleaching sequences toward enhanced elemental chlorine free (ECF) and totally chlorine free (TCF) sequences opens up other opportunities for increased emissions. These are associated with oxygen delignification and water conservation measures that drive recirculation of mill process streams. These emissions include an array of hazardous air pollutants that are subject to emission controls. Methanol is principal among them.

ECF mills that seek to reduce water use by recycling a portion or all of their bleach plant effluent may also find substantial increases in gaseous hydrochloric acid (HCl(g)) emissions (Adams 1994). This is due to increased chloride accumulation within the kraft recovery cycle and the subsequent release of chloride associated with HCl(g) emissions from the recovery furnace. The prospect also exists that mills that recover the pulp and bleach plant filtrates jointly may find increased emissions of combustion-related dioxins (Paper Task Force 1995). (Note that dioxins originating in combustion processes have greater degrees of chlorine substitution and are thus up to 1,000 times less toxic than the TCDD species most often associated with molecular chlorine bleaching, discussed elsewhere within this section of the Tool.)

Mechanical pulp bleaching and recovered fiber brightening systems typically use chemicals such as hydrogen peroxide, sodium hydrosulfite or, for recycled pulps, formamidine sulfinic acid (FAS) or hypochlorite. Of these, sodium hypochlorite is the only chemical that contains chlorine. Chloroform is the only important chlorinated compound known to be generated and emitted when hypochlorite is used for brightening. The use of peroxide, hydrosulfite, or FAS in place of hypochlorite for recovered fiber brightening would eliminate the production of chloroform.

The most prominent emissions generally associated with pulp bleaching are, therefore

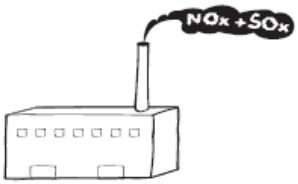
- chlorine and chlorine dioxide,
- carbon monoxide,
- chloroform,
- methanol, and
- other miscellaneous hazardous air pollutants.

Within the United States, emissions of chlorine, chloroform, methanol and other designated hazardous air pollutants (HAPs) are regulated to a level consistent with the application of Maximum Achievable Control Technology (MACT). Carbon monoxide emitted from bleach plant sources would be subject to scrutiny during site-specific permitting, unlike carbon monoxide emissions from mill combustion sources that are subject to criteria pollutant emission standards.

## References

Adams, T.N. 1994. *Overview of closed-cycle technology for kraft pulping and bleaching*. Project F017. Report to the Member Companies of the Institute of Paper Science and Technology. https://smartech.gatech.edu/xmlui/bitstream/handle/1853/511/F017_001_02211994.pdf

Paper Task Force 1995. *Environmental comparison of bleached kraft pulp manufacturing technologies*. White Paper No. 5. http://c.environmentalpaper.org/documents/1626_WP5.pdfhttp://www.edf.org/documents/1626_WP5.pdf




# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON EMISSIONS TO AIR

## Emission Levels and Controls Regulatory Backdrop

**Bleach Plant:** Bleaching system standards for the U.S. are illustrated in Figure C14.

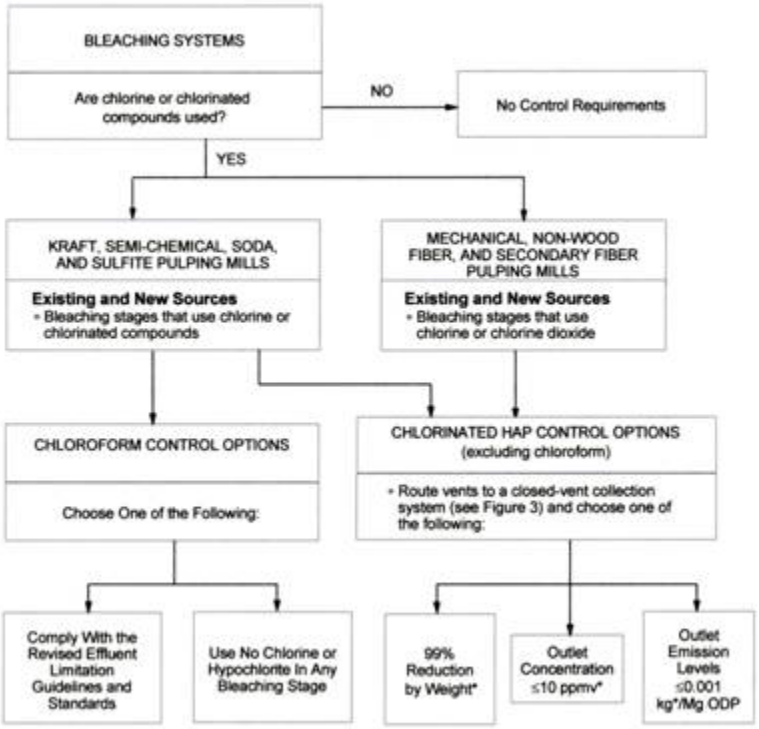



**Figure C14. U.S. Environmental Regulatory Standards for Bleach Plants (Source: USEPA 1997)**

U.S. emission standards promulgated in 1998 for chemical pulping require the collection and treatment of all vent gases from the bleaching stages where chlorinated compounds are applied. Treatment to remove chlorine and other gaseous hazardous air pollutants (HAPs) containing chlorine (other than chloroform) is necessary. A mill can demonstrate compliance with the treatment portion of regulation using any one of three alternatives:

- reducing the total chlorinated HAP mass in vent streams by 99% or more, measured as chlorine, using a control device (e.g., a scrubber), or
- reducing the total chlorinated HAP emission concentration (excluding chloroform) to 10 ppmv or less exiting a treatment/control device, or
- reducing the total chlorinated HAP mass emission rate to 0.001 kg total HAP (excluding chloroform) per tonne ODP.

Similar requirements exist for mechanical pulping and secondary fiber mills where chlorine or chlorine dioxide is used.

Chloroform emissions from chemical pulp bleaching are addressed by eliminating use of chlorine and sodium hypochlorite in bleaching sequences.

Emissions from bleach plant sources are commonly treated using scrubbers, typically packed towers. Scrubbing mediums include chilled water, caustic, extraction stage filtrate, sodium bisulfite, weak wash from the kraft recovery causticizing system, hydrosulfite, and white liquor. The effectiveness of these scrubbers is dependent on their design and choice of scrubbing medium. The control efficiency for both chlorine and chlorine dioxide is typically 95% or greater, and achieving greater than 99% efficiency is not uncommon. Thus, while it is likely that in replacing chlorine with chlorine dioxide overall industry emissions of chlorine have decreased and chlorine dioxide emissions have increased, the change in the mass of emissions is small because source controls are very effective.

**Oxygen Delignification Sources:** Regulations in the U.S. require the collection and treatment of the vent gases from blow tanks, washers, filtrate tanks, and intermediate stock chests that are part of an oxygen delignification system. The specified level of treatment is at least 98% for all gaseous organic "hazardous air pollutants," although demonstrating 98% efficiency for methanol alone is sufficient. Most mills with oxygen delignification systems meet this requirement by ducting the vent gases into a high volume low concentration (HVLC) gas system and introducing the collected gases to a boiler or recovery furnace as combustion air (NCASI 2004).

## Bleaching of (Virgin) Chemical Pulps

Until the 1990s, most chemical pulp mills used chlorine and chlorine dioxide to bleach pulp, and some mills also used hypochlorite. The discovery that dioxin can be formed when chlorine is used to bleach chemical pulps led to changes in the chemicals used for pulp bleaching. The most notable change was the elimination of chlorine and hypochlorite in favor of chlorine dioxide in the sequence, known as elemental chlorine free (ECF) bleaching. This conversion also led to the increased use of oxygen and hydrogen peroxide in the bleaching sequence. Complete elimination of all chlorine compounds in pulp bleaching in favor of oxygen and peroxide is termed totally chlorine free (TCF) bleaching.

Air emissions from bleaching that are known to be affected by use of the various bleaching chemicals include chlorine, chlorine dioxide, chloroform, carbon monoxide, and methanol.

**Chlorine** and chlorine dioxide emission points include bleaching tower vents, bleach plant washer and filtrate tank vents, and the chlorine dioxide generator. Uncontrolled bleach plant emissions of chlorine and chlorine dioxide range from 0 to 10.42 lb/ADTP and from 0.03 to 25.5 lb/ADTP, respectively (NCASI 1991). Uncontrolled emissions from chlorine dioxide generators range from 0.04 to 24 lb $Cl_2$/ton $ClO_2$ generated and from 0.2 to 6.12 lb $ClO_2$/ton $ClO_2$ generated (NCASI 1991).

**Chloroform** is a by-product of bleaching with hypochlorite, chlorine and, to a much lesser extent, chlorine dioxide. Oxygen, peroxide, or other non-chlorinated bleaching chemicals do not produce chloroform. Figure C15 has been derived from various NCASI studies. It shows the magnitude of chloroform generation from a typical bleach line using chlorine and hypochlorite relative to a typical line using only chlorine dioxide (ECF). Liquid effluents are included because chloroform in effluent would likely be released to air during wastewater treatment. Chloroform releases from the bleach plant directly to air are of a similar magnitude to effluent loads for these bleaching methods. As is apparent in the figure, 99.5% of the reduction in chloroform emissions has been achieved through implementation of ECF bleaching. The remaining 0.05% reduction could be achieved through TCF bleaching. TCF bleaching is not known to generate chloroform.

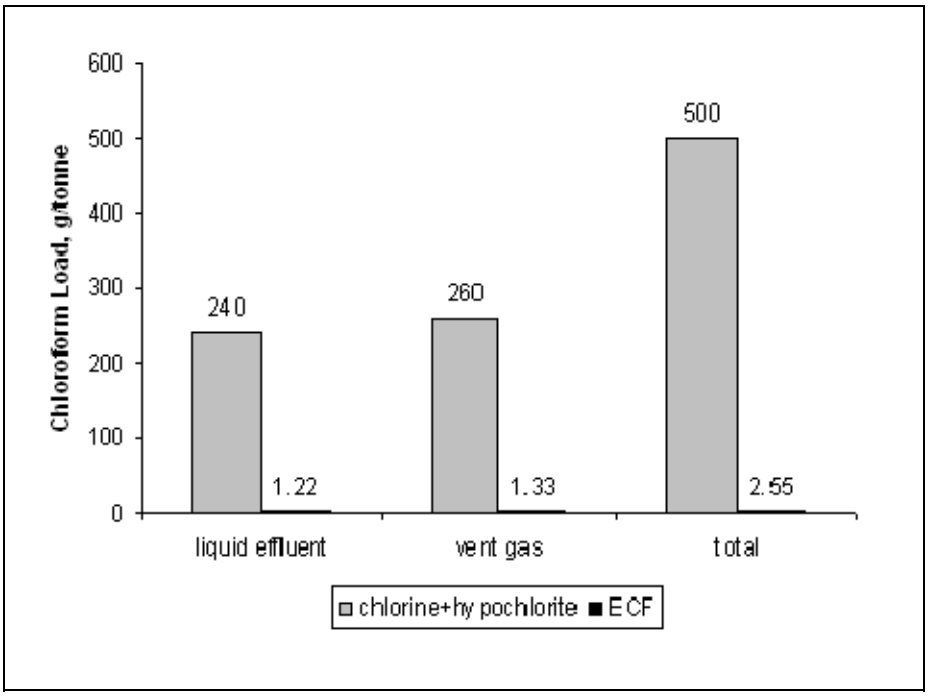



**Figure C15. Chloroform Load from Chlorine + Hypochlorite and Chlorine Dioxide (ECF) Bleaching of Kraft Pulp**

**Carbon monoxide** is formed by the use of oxygen in pulping and bleaching, as well as by chlorine dioxide use in bleaching (Dence and Reeve 1996). Increases in the use of both process chemicals as replacements for chlorine have resulted in increased emissions of carbon monoxide, though at some U.S. mills increases due to the use of oxygen delignification may be offset by the use of vent gas control devices.

The mechanisms by which carbon monoxide is formed are not well understood and thus, it is not known whether elimination of chlorine dioxide (for TCF sequences) and expanded use of oxygen and peroxide in the bleaching sequence would result in an increase in carbon monoxide emissions from bleaching.

**Methanol** is formed in pulping and bleaching (Dence and Reeve 1996). Liquid methanol is also used as a raw material by some mills in the process of generating chlorine dioxide. Emissions of methanol associated with the manufacture and use of chlorine dioxide would be expected to increase as more chlorine dioxide is used to replace chlorine in the bleaching sequence. The relationship between methanol emissions and the increased use of chlorine dioxide and oxygen for bleaching is not straightforward. Data suggest that emissions will be similar for chlorine-based and ECF bleaching (Dence and Reeve 1996). Methanol emission data from TCF sequences are not available but would likely be equal to, or greater than ECF emissions.

Methanol is also prominent among the hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) emitted from oxygen delignification systems common in enhanced ECF and TCF systems, with the release points shown in Figure C16.

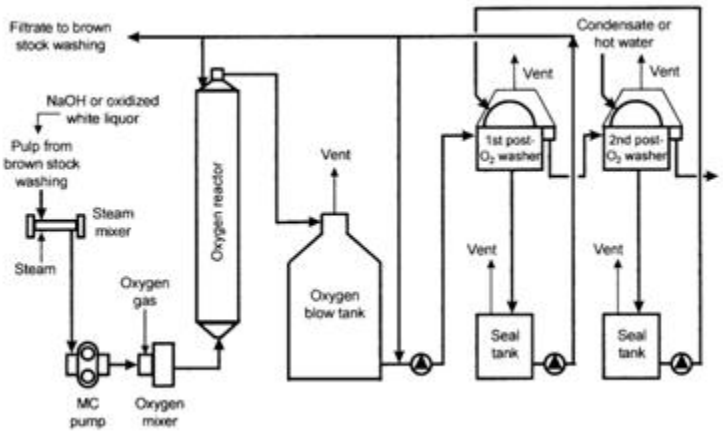



**Figure C16. Oxygen Delignification-Related VOC Release Points**

**Volatile Organic Compounds** (VOCs): In mills that practice oxygen delignification, volatile organic compounds present in the incoming pulp slurry, oxidized white liquor, and washer shower water can be released in vent gases from the blow tank, washer hood, washer filtrate tank, and pulp storage tank. The amounts of these compounds present in the various process liquids will depend upon the water reuse practices of the mill, particularly if condensates are used on the post-oxygen washers (NCASI 2008). Data assembled by the Paper Task Force (Table C8) are illustrative.

**Table C8. VOC Emissions from Bleached Kraft Mill Sources (Source: Paper Task Force 1995)**

| | VOC Emissions | Pulp Mill Sources, (lb C/ODTP) |
|---|---|---|
| **Conventional Case**[a] | Pulping | 1.11 |
| | Bleaching | 0.31 |
| | Chemical Recovery | 0.97 |
| | **Total** | **2.39** |
| | | |
| **Traditional ECF** | Pulping | 1.11 |
| | Bleaching | 0.03 |
| | Chemical Recovery | 0.97 |
| | **Total** | **2.11** |
| | | |
| **Enhanced ECF**[b,c] | Pulping | 1.11 |
| | Bleaching | 0.68 (0.15) |
| | Chemical Recovery | 0.96 |
| | **Total** | **2.92 (2.24)** |
| | | |

[a] Conventional case employs 50% chlorine dioxide substitution.
[b] Bleaching sources include the oxygen delignification system and the bleach plant.
[c] Values in parentheses include emissions from an oxygen delignification system that used fresh shower water.

Though enhanced ECF may be beneficial from the standpoint of organochlorine generation, these data indicate that uncontrolled VOC emissions will be greater than those for traditional ECF. Moreover, VOC emissions from the oxygen delignification system and bleaching sources in enhanced ECF bleaching are more than four times greater when condensates are used in lieu of fresh water.

**Other Hazardous Air Pollutants**: In 1995, the Paper Task Force assembled data collected by NCASI that quantified uncontrolled emissions of hazardous air pollutants (HAPs) from major bleached kraft mill non-combustion sources. The data are summarized in Table C9.

### Table C9. HAP Emissions from Bleached Kraft Mill Sources (Source: Paper Task Force 1995)

| | HAP | Pulp Mill Sources, (lb/ODTP) | Bleach Plant Sources, (lb/ODTP)[a,b] | Ratio of Bleach Plant to Pulp Mill Sources |
|---|---|---|---|---|
| **Conventional Case[c]** | Methanol | 2.18 | 0.52 | 23.8% |
| | Acetaldehyde | 0.08 | 0 | 0.0% |
| | Formaldehyde | 0.02 | 0 | 0.0% |
| | Chloroform | 0.13 | 0.12 | 92.3% |
| | **Total** | **2.54** | **0.68** | **26.7%** |
| | | | | |
| **Traditional ECF** | Methanol | 1.912 | 0.25 | 13.1% |
| | Acetaldehyde | 0.085 | 0.003 | 3.5% |
| | Formaldehyde | 0.019 | 0 | 0.0% |
| | Chloroform | 0.021 | 0.011 | 52.4% |
| | **Total** | **2.132** | **0.27** | **12.7%** |
| | | | | |
| **Enhanced ECF** | Methanol | 2.932 (2.182) | 1.27 (0.52) | 43.3% (23.8%) |
| | Acetaldehyde | 0.128 (0.094) | 0.047 (0.012) | 36.7% (12.7%) |
| | Formaldehyde | 0.021 (0.020) | 0.002 (0.00) | 9.5% (0.0%) |
| | Chloroform | 0.013 (0.014) | 0.002 (0.002) | 15.4% (14.3%) |
| | **Total** | **3.193 (2.402)** | **1.329 (0.54)** | **41.6% (22.5%)** |
| | | | | |
| **Low Effluent TCF** | Methanol | 2.338 | 0.135 | 5.8% |
| | Acetaldehyde | 0.111 | 0.029 | 26.1% |
| | Formaldehyde | 0.041 | 0.021 | 52.2% |
| | Chloroform | 0 | 0 | 0.0% |
| | **Total** | **2.596** | **0.158** | **6.1%** |

[a] Bleach plant sources include the oxygen delignification system and the bleach plant.
[b] Values in parentheses include emissions from an oxygen delignification system that used fresh shower water.
[c] Conventional case employs 50% chlorine dioxide substitution.

Chloroform and methanol have both been previously discussed. Reduced reliance on chlorine and chlorine dioxide results in less chloroform generation. However, reductions are small in going beyond 100% chlorine dioxide substitution.

For traditional and enhanced ECF sequences, methanol represents greater than 92% of HAP emissions. Methanol content of the evaporator condensates used as wash water on the final stage of post-oxygen washing is the most important factor affecting oxygen delignification system HAP emissions (NCASI 2008). The second most prevalent HAP is acetaldehyde, which contributes about 3% of the total HAPs, on average.

What most distinguishes the low effluent TCF sequence in the assembled data is the mill use of bleach plant filtrate in the first oxygen washer. It suggests that use of TCF sequence filtrates can result in lower HAP emissions than use of condensates.

### Brightening of Mechanical and Chemi-Mechanical Pulps

Mechanical and chemi-mechanical pulps are typically bleached (brightened) using peroxide and/or sodium hydrosulfite or other non-chlorine containing chemicals (Dence and Reeve 1996). Thus, bleaching of these pulps does not produce chlorinated by-products.

### Brightening of Recovered Fiber

Brightening of most recycled pulps is accomplished with either sodium hypochlorite or non-chlorine based chemicals such as hydrogen peroxide, sodium hydrosulfite or formamidine sulfinic acid (FAS) (Dence and Reeve 1996). Mills that do not use hypochlorite or other chlorine-containing chemicals for brightening are said to operate process chlorine free, or PCF.

**Chloroform** is produced as a by-product of brightening with hypochlorite. The generation of chloroform in recovered brightening stages using hypochlorite is similar in magnitude as that associated with hypochlorite bleaching of virgin pulps ranging between about 0.12 and 1.2 kg/air dry metric ton (ADMT) of pulp (Dence and Reeve 1996). A portion of this chloroform would be emitted in bleach plant vents and the remainder with bleach plant wastewater sent for treatment. Elimination of hypochlorite from the brightening system in favor of peroxide or other non-chlorine containing brightening agents would eliminate most or all generation of chloroform.

**Carbon Monoxide** is produced when hydrogen peroxide is used as a brightening agent. Conversion of hypochlorite brightening to peroxide brightening would be expected to result in increased industry emissions of carbon monoxide.

## References

Dence, C.W. and Reeve, D.W. (eds). 1996. Pulp bleaching principles and practice. Atlanta, GA: Tappi Press.

National Council [of the Paper Industry] for Air and Stream Improvement, Inc. (NCASI). 1991. Bleach plant chlorine and chlorine dioxide emissions and their control. NCASI Technical Bulletin No. 616. New York: National Council of the Paper Industry for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2004. Pulp bleaching systems. Chapter 8 in *Environmental resource handbook for pulp and paper mills*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2008. *Summary of industry experience with odor minimization at wastewater treatment plants*. Technical Bulletin No. 949. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Paper Task Force. 1995. *Comparison of kraft, sulfite, and BCTMP manufacturing technologies for paper*. White Paper No. 12. http://c.environmentalpaper.org/documents/1632_WP12.pdf

United States Environmental Protection Agency (USEPA). 1997. *Summary flow diagrams of the pulp and paper MACT standard (40 CFR Part 63, Subpart S)*. Research Triangle Park, NC: United States

Environmental Protection Agency, Waste and Chemical Processes Group, Emission Standards Division. http://www.epa.gov/ttn/caaa/t3/reports/pp1_flo.pdf

# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

***A tool for understanding environmental decisions related to the pulp and paper industry***


## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON DISCHARGE TO WATER

### Overview

Apart from eliminating the formation of the most environmentally significant dioxins and chlorinated phenolic compounds to less than measurable levels, the replacement of elemental chlorine with chlorine dioxide at North American pulp and paper mills also provides significant reduction in other chlorinated substances and effluent color. Quantifiable levels of 2,3,7,8-tetrachlorodibenzofuran (TCDF) are now rare, and 2,3,7,8-tetrachlorodibenzodioxin (TCDD) cannot be detected in routine effluent monitoring tests. Oxygen-demanding substances in mill effluent, typically measured as biochemical oxygen demand (BOD) and (COD), are more influenced by the extent of delignification prior to bleaching rather than by the bleach plant configuration itself.

### More information

Wastewater and water quality impacts associated with pulp bleaching

Wastewater pollutants other than organochlorine compounds

Organochlorine compounds in wastewater


# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON DISCHARGE TO WATER

## Wastewater and Water Quality Impacts Associated with Pulp Bleaching

The aftermath of the 1986 association of elemental chlorine bleaching with the release of dioxins brought scrutiny to the industry's impact on receiving streams and aquatic life. In 1990, there were 30 fish consumption advisories for dioxin downstream of U.S. bleached pulp mills. This reflected a judgment by state officials that dioxin contamination levels posed a health risk to sport and subsistence fishermen, as well as the general public, who catch and consume locally caught fish.

Since 1990, changes in bleaching technology, specifically the replacement of chlorine with chlorine dioxide during the first stage of pulp bleaching, have reduced dioxin discharges to a point where they cannot be detected in routine effluent monitoring tests. As a result, tissue concentrations in fish in the receiving waters downstream of those mills have decreased substantially. These decreases have allowed many of the former fish consumption advisories to be rescinded. By the end of 2004, there had been a 90% decrease in the number of dioxin advisories downstream of pulp and paper mills since 1990 (AET 2005). See Figure C17. As of 2012, there were six remaining dioxin advisories downstream of pulp and paper mills.

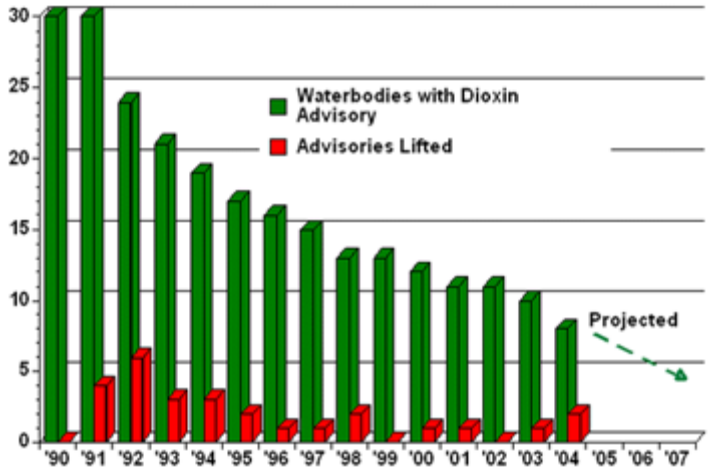



**Figure C17. Dioxin Advisories Downstream Of Pulp Mills (Source: AET 2005)**

Nowhere was the industry's role in the dioxin contamination of aquatic life more rigorously examined than in the state of Maine. In 1997, the Maine legislature enacted a statute prohibiting bleached pulp mill discharges of dioxins into receiving waters of the state. Paper mill compliance with that requirement was to be demonstrated by a statistical comparison of fish tissue (or surrogate) samples collected below the mill's wastewater outfall and samples collected from an upstream location unaffected by the mill's discharge. In 2003, after consultation with an expert review panel, Maine Department of Environmental Protection settled on an approach involving three species: white sucker, smallmouth bass, and caged mussels. Judgments were to be made with application of uniform statistical methods and on the basis of a

preponderance of the evidence. All bleached kraft mills in Maine successfully achieved the demonstrations required by the original law.

These outcomes support U.S. Environmental Protection Agency statements made at the time the agency issued rules requiring what had already been well underway within the industry – the installation of ECF bleaching technology. In a November 1997 announcement, EPA observed that "today's rule will eliminate, over time, all dioxin-based fish advisories that have been attributed to the mills, particularly benefiting subsistence fishers who depend primarily on fish for food" (USEPA 1997).

Though there may be reasons to suggest going beyond elemental chlorine free (ECF) bleaching, addressing the issue that first gave the industry its dioxin visibility is no longer among them.

Apart from eliminating the formation of the most environmentally significant dioxins and chlorinated phenolic compounds to less than measurable levels, the replacement of elemental chlorine with chlorine dioxide also provides significant reduction in other chlorinated substances and effluent color. Even quantifiable levels of TCDF are now rare. Oxygen-demanding substances, typically measured as BOD and COD, are more influenced by the extent of delignification remaining to be accomplished in bleaching, thus giving advantage to greater degrees of delignification during pulping. Where circumstances permit, more extensive use of oxygen-based bleaching agents in lieu of chlorine-based agents create additional opportunity for filtrate recirculation and further reduction in pollutant contributions to wastewater. TCF bleaching eliminates the formation of chlorinated compounds during bleaching.

Some substances liberated during bleaching resist biological degradation and are only partially removed in biological treatment systems. Among them, color is least affected by conventional wastewater treatment practices. However, conventional wastewater treatment practices are generally effective in conditioning bleached pulp mill effluents to accommodate receiving stream water quality needs.

## References

Alliance for Environmental Technology (AET). 2005. Eco-system recovery: Lifting of fish consumption advisories for dioxin downstream of U.S. pulp mills - 2005 update. http://aet.org/reg_market_news/press_releases/2005/Eco051.html

United States Environmental Protection Agency (USEPA). 1997. EPA eliminates dioxin, reduces air and water pollutants from nation's pulp and paper mills. Press Release November 14, 1997. Washington, DC: United States Environmental Protection Agency. http://yosemite.epa.gov/opa/admpress.nsf/b1ab9f485b098972852562e7004dc686/cec7ccca2be74f2e8525654f00682f23?OpenDocument


# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON DISCHARGE TO WATER

## Wastewater Pollutants Other Than Organochlorine Compounds

Effluent quality is commonly judged on the basis of such aggregate characteristics as biochemical oxygen demand (BOD), chemical oxygen demand (COD), and color. Each reflects a measured effect of a combination of constituents, and not the concentration of one specific substance.

- **Biochemical Oxygen Demand (BOD)** measures the capacity of an effluent to biochemically consume dissolved oxygen from receiving waters. The numerical subscript denotes the number of days over which oxygen consumption is measured, typically five days. $BOD_5$ figures prominently among effluent limitations regulated in North America. $BOD_7$ is regulated in some areas of Europe.
- **Chemical Oxygen Demand (COD)** is a measure of the amount of chemically oxidizable compounds in effluent when exposed to a strong chemical oxidant. Unlike BOD, it captures substances that are not readily degraded in natural ecosystems. COD regulation is common in Europe, but not in North America.
- **Color** is a visual characteristic that, for comparisons here, is driven by the presence of lignins, tannins, resins, and high molecular weight lignin degradation products formed during bleaching and pulping. Effluent color is principally attributable to pulping liquor losses and filtrates from the first two stages of bleaching.

The character of wastewater streams from bleaching is influenced by a number of site-specific factors. Among them are wood type, bleaching sequence, chemical usage, bleaching stage temperature, pH, type of pulp washer, and efficiency of pulp washing between stages. Thus, any generalizations that are offered must be tempered with that understanding.

**Oxygen-Demanding Substances:** Pulp bleaching is one of the major contributors to effluent BOD and COD at bleached kraft mills. Pulp mill liquor losses are another, but there are estimates that suggest as much as one-half of the COD at a typical bleached kraft mill can originate in pulp bleaching (Johansson and Fletcher 1994). BOD and COD levels will be roughly proportional to pulp yield loss during bleaching (Ragauskas n.d.).

**Color:** Use of oxygen delignification or extended cooking can reduce color loads from conventional bleaching by 50% or more. Color is also observed to decrease with increasing levels of chlorine dioxide substitution. In fact, substitution of chlorine dioxide for chlorine in the first bleaching stage can reduce the color in bleach plant effluents by 50 to 80% compared to bleaching at 0% substitution. At mills with both oxygen delignification and/or extended cooking and high or complete substitution bleaching, bleach plant color loads between 50 and 100 lb/ADTP are not uncommon (NCASI 2004b).

**Delignification and Chemical Recovery Impact**: The process of pulping and bleaching involves the removal of lignins that otherwise bind and color cellulose fibers. Nearly all of the work involved in delignification is accomplished during the pulping process. Residual lignins that remain, as well as other colored substances, are subsequently removed or brightened during bleaching. Once removed, all of these substances represent a source of BOD, COD, color, and other chemical reaction products that are of environmental significance. The challenge is minimizing the loss of these wood extractives and chemical reaction products into the mill wastewater streams.

The kraft chemical recovery process provides a ready vehicle by which substances that are removed in pulping are captured and destroyed in a closed cycle with a potential gain in energy. To that end, it is useful to accomplish as much delignification as possible in the pulping process prior to bleaching. Extended cooking and/or oxygen delignification that often precede ECF bleaching accomplish just that. Greater delignification in pulping leaves smaller amounts of substances to be removed during bleaching where they contribute to BOD, COD, and color discharged with bleach plant filtrates. See Table C10.

**Table C10. Illustrative Effect of Delignification on Effluent Properties of a Softwood Kraft Bleach Plant (Source: Gullichsen 1991)**

| | Kappa Number | $BOD_7$ (kg/t) | COD (kg/t) | Color (kg Pt/t) | AOX (kg/t) |
|---|---|---|---|---|---|
| Standard Kraft | 30 | 16 | 80 | 200 | 7 |
| Extended Cooking | 24 | 14 | 60 | 150 | 4.8 |
| Oxygen Delignification | 18 | 12 | 50 | 120 | 3.5 |
| Extended Cooking and Oxygen Delignification | 14 | 9 | 39 | 100 | 2.8 |

As a generalization, BOD, COD, color, and AOX discharged with bleach plant filtrate tend to be roughly proportional to the lignin content of the pulp entering the bleach plant. (Kappa number is an indirect measure of the lignin content of the pulp.)

**Filtrate Recovery Impact:** Further gains in pollutant reduction are possible to the extent that delignification products extracted from pulps during bleaching can also be incorporated into the chemical recovery process. The use of oxygen-based bleaching agents in the initial stages of bleaching, where the bulk of BOD, COD, and color are produced, promote that opportunity. As shown in Figure C18, use of ozone in the initial bleaching sequence allows filtrates from both the Z and $E_{OP}$ stages to be routed to the chemical recovery system, given their alkaline nature.

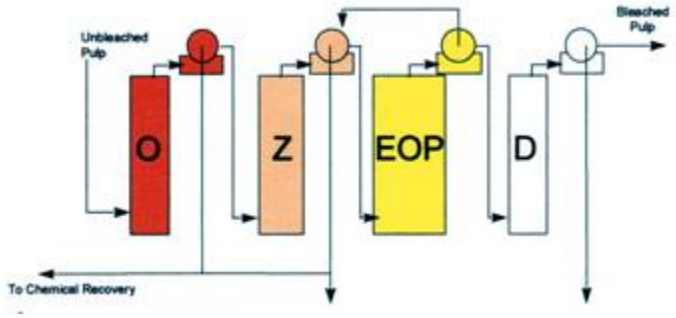



**Figure C18. Bleaching Sequence Showing Alkaline Filtrate Recovery**

The potential benefit of doing this has been demonstrated with the 1992 application of a similar ozone bleaching sequence at the Union Camp mill in Franklin, Virginia. The estimated benefits relative to a prior CEDED sequence is captured in Table C11.

**Table C11. Relative Reduction in Environmental Releases with Ozone-Based vs. Chlorine-Based Bleaching Sequences (Source: http://www.p2pays.org/ref/10/09430.htm)**

| | CEDED Sequence | OZEOD Sequence | Reduction, % |
|---|---|---|---|
| Volume of Effluent, $m^3$/AD Tonne | 55.1 | 7.5 | 86 |
| $BOD_5$, kg/AD Tonne | 16 | 1.8 | 89 |
| COD, kg/AD Tonne | 65 | 5.6 | 91 |
| Color, kg/AD Tonne | 185 | 3.5 | 99+ |
| AOX, kg/AD Tonne | 5.7 | 0.076 | 98 |

The reductions in environmental releases that can accrue with combined use of oxygen delignification and ozone as the first bleaching stage are dramatic. Indeed, there is little further gain to be had with total replacement of chlorine-based bleaching agents and the recovery of the remaining filtrate.

There are, of course, pragmatic limitations on the extent to which filtrates can be recovered; these are addressed more fully in the Water Use section of the Chlorinated Compounds Tab of this Tool. Among them is the need for adequate evaporator and recovery furnace capacity. Moreover, ozone is an aggressive bleaching agent and recognition must be made of its potential to degrade cellulose fiber. Pulp fed to the ozone reactor must have a sufficiently low lignin content to allow full bleaching with a reasonable ozone application (NCASI 2003).

**Wastewater Treatment:** Before release into the environment, bleach plant wastewaters are typically subjected to biological treatment in combination with wastewater streams from the balance of the mill. BOD, COD, and color vary in their responsiveness to such treatment. Drawing upon the data tabulated previously, Gullichsen estimated the corresponding treated effluent contribution that might accompany high rate biological treatment, as summarized in Table C12.

**Table C12. Illustrative Effect of Biological Treatment on Effluent Properties of a Softwood Kraft Bleach Plant (Source: Gullichsen 1991)**

| | Kappa Number | $BOD_7$ (kg/t) | COD (kg/t) | Color (kg Pt/t) | AOX (kg/t) |
|---|---|---|---|---|---|
| | | | | | |
| Standard Kraft | 30 | 2.4 (85%) | 45 (44%) | 180 (10%) | 3.9 (44%) |
| Extended Cooking | 24 | 2.2 (84%) | 36 (40%) | 130 (13%) | 2.2 (54%) |
| Oxygen Delignification | 18 | 2.0 (83%) | 31 (38%) | 100 (17%) | 1.9 (46%) |
| Extended Cooking and Oxygen Delignification | 14 | 1.7 (81%) | 27 (31%) | 85 (15%) | 1.3 (54%) |

(The values in parentheses represent the percentage removed with treatment.)

As might be expected, high degrees of removal are reflected for BOD, given that the characteristic high molecular weight lignin degradation products are not appreciably biodegradable within the time frame of most wastewater treatment processes. Some of these products may adsorb to biological solids and be removed via sludge wasting or settling (NCASI 2004a).

**Chelants**: It is common practice to use a chelating stage to remove metal ions prior to brightening mechanical pulps with hydrogen peroxide. An alkaline peroxide stage in a kraft mill bleach plant is almost always preceded by an acidic chelating stage that includes washing. Chelants tie up metal ions in solution, making them much less reactive during bleaching.

TCF mills may have higher levels of nitrogen due to use of chelants, and conflicting data exist on the extent to which the nitrogen in chelants is biodegradable (NCASI 2003). EDTA, a prominent chelant, is non-toxic to mammals at environmental concentrations, but there is some concern about its potential to remobilize toxic heavy metals out of sediments and its biodegradability. Membrane systems and alkaline biological treatment schemes have been suggested as a means of reducing the disposal of filtrates from EDTA chelating stages into the environment (IPPC 2001).

## References

Alliance for Environmental Technology (AET). 2005. Eco-system recovery: Lifting of fish consumption advisories for dioxin downstream of U.S. pulp mills - 2005 update. http://aet.org/reg_market_news/press_releases/2005/Eco051.html

Gullichsen, R. 1991. Process internal measures to reduce pulp mill pollution load. *Water Science and Technology* 24 (3-4): 45-53

Integrated Pollution Prevention and Control (IPPC). 2001. Reference document on best available techniques in the pulp and paper industry. http://eippcb.jrc.ec.europa.eu/reference/BREF/cak_bref_1201.pdf

Johansson, N.G., and Fletcher, D.E. 1994. Optimization of bleaching sequences in order to help meet environmental regulation. In *Proceedings of the 1994 TAPPI international non-chlorine bleaching conference*. Atlanta, GA: TAPPI Press.

National Council for Air and Stream Improvement, Inc. (NCASI). 2003. *Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s*. Technical Bulletin No. 860. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2004a. *Effluent treatment systems and water quality issues. Chapter 11 in Environmental resource handbook for pulp and paper mills*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI). 2004b. Pulp bleaching systems. Chapter 8 in *Environmental resource handbook for pulp and paper mills*. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

Ragauskas, A. n.d. *An introduction – Overview: Environmental aspects, bleaching kraft pulps*. IPST-Georgia Tech Technical Review. http://www.ipst.gatech.edu/faculty/ragauskas_art/technical_reviews/Environmental.pdf

United States Environmental Protection Agency (USEPA). 1997. EPA eliminates dioxin, reduces air and water pollutants from nation's pulp and paper mills. Press Release November 14, 1997. Washington, DC: United States Environmental Protection Agency. http://yosemite.epa.gov/opa/admpress.nsf/b1ab9f485b098972852562e7004dc686/cec7ccca2be74f2e8525654f00682f23?OpenDocument

# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

***A tool for understanding environmental decisions related to the pulp and paper industry***


## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON DISCHARGE TO WATER

### Organochlorine Compounds in Wastewater

The generation and release of certain water pollutants from chemical pulp bleaching operations are affected by the choice of bleaching chemicals, and the industry's shift from chlorine bleaching to ECF bleaching has altered wastewater characteristics.

**Chlorinated organic by-products** of chemical pulp bleaching that are the most toxic and recalcitrant to wastewater treatment are chlorinated dioxins and furans and highly chlorinated phenolic compounds. These compounds can be produced during elemental chlorine bleaching of chemical pulps, but their presence at measurable levels is virtually eliminated in ECF bleaching.

The reduction in chlorinated organic by-products from use of chlorine dioxide occurs because, as the chlorine dioxide substitution level increases, the amount of chlorine available to react with lignin and other organic compounds decreases. Moreover, elemental chlorine and chlorine dioxide differ fundamentally in the way they chemically react with lignin in unbleached pulp. Compared to elemental chlorine bleaching, AOX, a measure of total chlorinated organic material, is reduced by 90% or more with ECF bleaching. Greatest reductions in chlorinated substances accompany practices that reduce the quantities of lignin in pulps prior to ECF bleaching sequences. TCF bleaching would eliminate the generation of chlorinated compounds in the bleach plant.

**Chloroform**, a by-product formed when pulp is bleached with sodium hypochlorite or chlorine, is generated in much smaller quantities when chlorine dioxide is used in place of the former chemicals. Emission reductions for chloroform of greater than 99% have resulted from the application of ECF bleaching and elimination of chlorine and hypochlorite from the bleaching sequence.

Mechanical pulp bleaching and recovered fiber brightening systems typically use chemicals such as hydrogen peroxide, sodium hydrosulfite or, for recycled pulps, formamidine sulfinic acid (FAS) or sodium hypochlorite. Of these, hypochlorite is the only chemical that contains chlorine. The use of peroxide, hydrosulfite, or FAS in place of hypochlorite for recovered fiber brightening would eliminate the production of chlorinated organic compounds.

### Bleaching of (Virgin) Chemical Pulps

The characteristics of wastewater from a bleached chemical pulp mill are highly influenced by bleaching operations because a large portion of the wastewater produced at a mill originates from bleaching operations. Compounds that derive from bleaching operations and that are known to be affected by the use of the various bleaching chemicals include dioxin (2,3,7,8-TCDD) and furan (2,3,7,8-TCDF), substituted chlorinated phenolic compounds, chloroform, and adsorbable organic halides, or AOX (a measure of total chlorinated organic material).

**Dioxin and furan** were shown to be unintended byproducts of chemical pulp bleaching with chlorine in the 1980s. With respect to pulp bleaching, the specific compounds produced were limited to 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and tetrachlorodibenzofuran (2,3,7,8-TCDF). Extensive measurement of effluents from ECF bleach plants shows that measurable levels of 2,3,7,8-TCDD are not found and that 2,3,7,8-TCDF is only very rarely found at quantifiable levels (USEPA 2006). TCF bleaching eliminates any possibility that these compounds might be formed at levels below analytical detection limits.

**Chlorinated phenolic compounds** of concern with respect to toxicity and resistance to biological treatment include the highly substituted phenolics. These include the tri-, tetra-, and penta-substituted phenols, catechols, and guaiacols. Of these, 13 compounds are predominant, and some were shown to be generated during the chlorine bleaching of chemical pulps. Extensive measurement of effluents from ECF bleach plants shows that these compounds are only very rarely detected at quantifiable levels (EPA 2006). TCF bleaching eliminates any possibility that these compounds might be formed at levels below analytical detection limits.

**Chloroform** is a by-product of bleaching with sodium hypochlorite, chlorine, and to a much lesser extent, chlorine dioxide. Chloroform is not known to be produced by oxygen, peroxide, or other non-chlorinated bleaching chemicals. Figure C19 shows the magnitude of chloroform generation associated with a typical bleach line using chlorine and hypochlorite and a typical line using only chlorine dioxide (ECF). Chloroform loads from TCF mills would be zero.

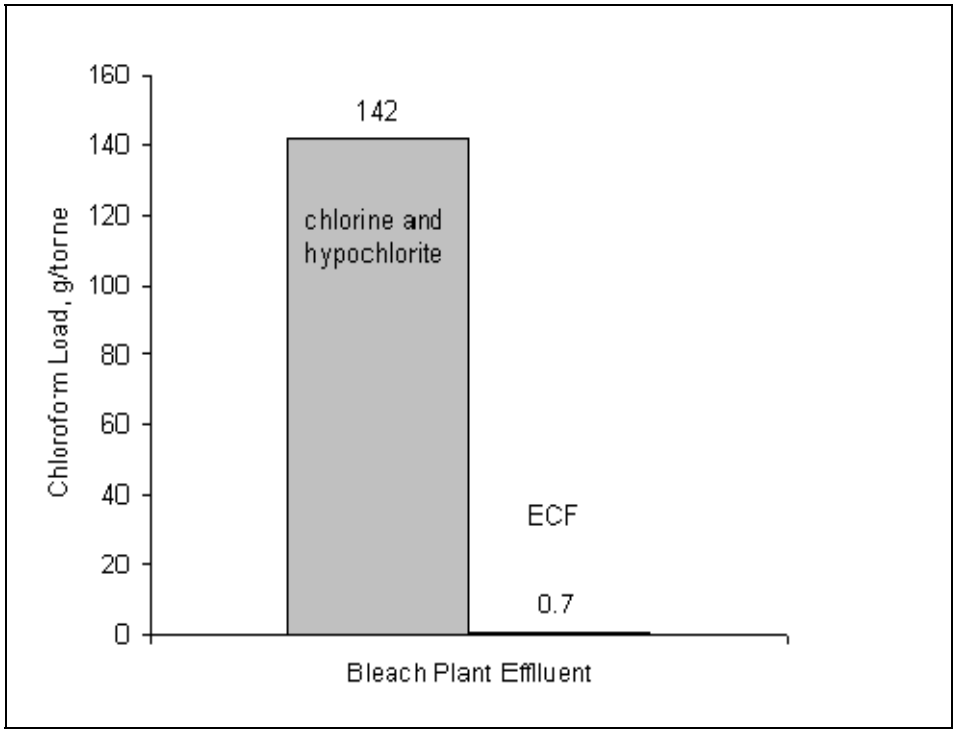



**Figure C19. Chloroform Load from Chlorine + Hypochlorite and Chlorine Dioxide (ECF) Bleaching of Kraft Pulp (Source: USEPA 1997)**

As is apparent in the figure, 99.5% of the reduction in chloroform emissions is achieved through implementation of ECF bleaching. The remaining 0.5% reduction could be achieved through TCF bleaching.

**AOX** is a measurement parameter representing the amount of chlorinated organic material present in wastewater. The chemistry of bleaching with chlorine is such that a portion of the chlorine attaches to organic structures in wood, resulting in chlorinated organic compounds. The chemistry of chlorine dioxide in bleaching is quite different from that of chlorine, resulting in much lower levels of chlorinated organic material and thus much lower AOX. TCF bleaching does not produce AOX.

For both chlorine and chlorine dioxide bleaching, the amount of AOX formed is related to the charge (addition rate) of chlorine or chlorine dioxide in the early bleaching stages. Hardwood pulps require lower chemical charges to achieve a given brightness relative to softwood pulp and thus produce less AOX. Similarly, the use of oxygen delignification and/or extended cooking prior to pulp bleaching of hardwood or softwood reduces the need for chemicals in the subsequent bleaching stages and thus reduces the amount of AOX generated.

AOX is partially treatable in biological wastewater treatment systems yielding effluent loads that are 50 to 70% lower than bleach plant loads. Some of the removal takes place within the mill due to chemical reactions when waste streams are mixed.

Figure C20 shows the estimated loads of AOX in biologically treated effluents at mills using various bleaching sequences.

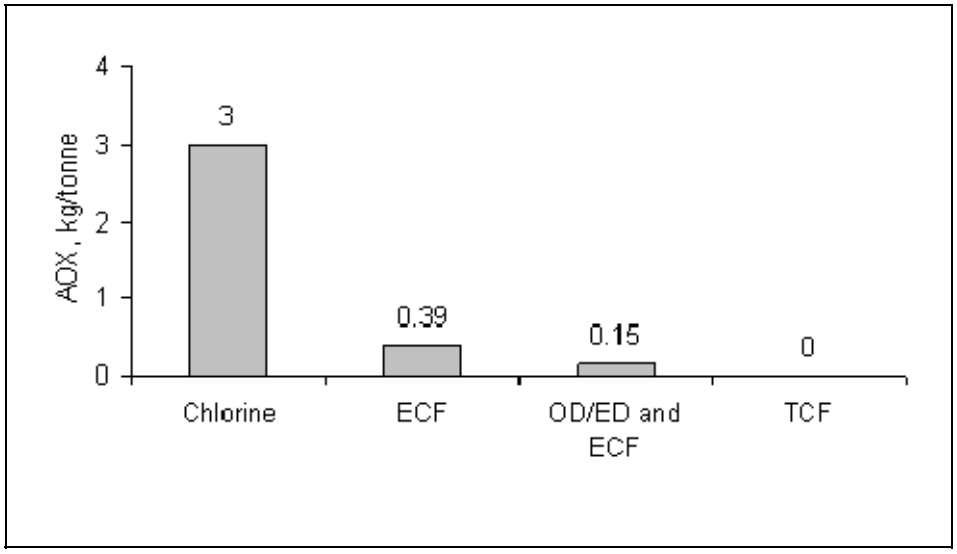



**Figure C20. AOX Loads in Treated Effluents from Softwood Bleaching Sequences (Source: USEPA 1997)**

## Bleaching of Mechanical and Chemi-Mechanical Pulps

Mechanical and chemi-mechanical pulps are typically bleached (brightened) using sodium peroxide and/or sodium hydrosulfite or other non-chlorine containing chemicals (Dence and Reeve 1996). Thus, bleaching of these pulps does not produce chlorinated by-products.

## Brightening of Recovered Fiber

Brightening of most recycled pulps is accomplished with either sodium hypochlorite or non-chlorine based chemicals such as hydrogen peroxide, sodium hydrosulfite, or formamidine sulfinic acid (FAS) (Dence and Reeve 1996). Mills that do not use hypochlorite or other chlorine-containing chemicals for brightening are said to operate process chlorine free, or PCF.

**Chloroform** is produced as a by-product of brightening with sodium hypochlorite. The generation of chloroform in recovered fiber brightening stages using hypochlorite is similar in magnitude to that associated with hypochlorite bleaching of virgin pulps; ranging between about 0.12 and 1.2 kg/air dry metric ton (ADMT) of pulp (Dence and Reeve 1996). A portion of this chloroform would be emitted in

bleach plant vents and the remainder with bleach plant wastewater sent for treatment. Elimination of hypochlorite from the brightening system in favor of peroxide or other non-chlorine containing brightening agents would eliminate most or all generation of chloroform.

**Dioxins and highly chlorinated phenolics** are not commonly measured at recovered fiber operations. The chemistry of formation of these compounds in kraft pulp bleaching provides little reason to expect that these compounds are formed in hypochlorite bleaching (NCASI 2001). Measurements of treated effluents for dioxins and furans at mills in the 1990s showed 2,3,7,8-TCDD to be below analytical minimum levels in all cases and 2,3,7,8-TCDF to occur only very rarely and this was likely due to the presence of the compound in the recovered paper supply (NCASI 1994). Conversion to process chlorine free (PCF) brightening processes may provide some assurance that dioxins and highly chlorinated phenolics are not discharged, but given the low or non-detectable levels in treated effluents, it is not possible to quantify the reduction that might be achieved.

AOX can be formed in sodium hypochlorite brightening of recovered fiber. Loads from recovered fiber brightening systems or treated final effluents from such mills, however, have not been widely measured and reported. Use of PCF brightening would not lead to AOX generation and thus, conversion from hypochlorite bleaching would be expected to result in a reduction of AOX discharged with treated effluents.

## References

Dence, C.W. and Reeve, D.W. (eds). 1996. *Pulp bleaching principles and practice*. Atlanta, GA: Tappi Press.

National Council [of the Paper Industry] for Air and Stream Improvement, Inc. (NCASI). 1994. *PCB and TCDD/F levels in effluents from deinking mills producing fine paper or tissue and toweling*. Technical Bulletin No. 671. Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

National Council for Air and Stream Improvement, Inc. (NCASI) 2001. *Factors that affect chloroform, AOX, chlorinated phenolic compounds, TCDD, and TCDF in kraft mill ECF bleach plant effluents - A Literature review*. Technical Bulletin No. 819, Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.

United States Environmental Protection Agency (USEPA). 1997. *Supplemental technical development document for effluent limitations guidelines and standards for the pulp, paper, and paperboard category subpart B (bleached papergrade kraft and soda) and subpart E (papergrade sulfite)*. EPA-821-R-97-011. Washington, DC: U.S. Environmental Protection Agency, Engineering and Analysis Division, Office of Science and Technology. http://water.epa.gov/scitech/wastetech/guide/pulppaper/technicalsupp.cfm

United States Environmental Protection Agency (USEPA). 2006. *Final report: Pulp, paper, and paperboard detailed study*. EPA-821-R-06-016. Washington, DC: United States Environmental Protection Agency, Engineering and Analysis Division, Office of Water. http://water.epa.gov/lawsregs/lawsguidance/cwa/304m/upload/2006_12_27_guide_304m_2006_pulp-final.pdf

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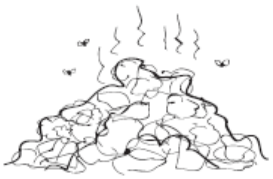


SOLID WASTE

## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON SOLID WASTE

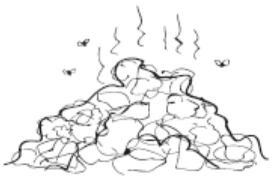
### Overview

Reducing the use of chlorine-containing compounds in pulp bleaching reduces the amounts of chlorinated materials in mill solid wastes, especially in the residuals from mill wastewater treatment plants. The improvements that occurred when the industry converted from chlorine bleaching to elemental chlorine free (ECF) bleaching were dramatic. Since the transformation to ECF bleaching, the amounts and types of chlorinated chemicals that remain in industry solid wastes are well within ranges suitable for using the materials beneficially in a wide variety of ways.

### More information

Wastewater residuals

Purging residuals from the process



SOLID WASTE

# EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON SOLID WASTE

## Wastewater Residuals

In 1999, a review of the dioxins and furans in pulp mill wastewater treatment plant residuals found that, on a TEQ basis, the levels in municipal wastewater treatment plant residuals were more than an order of magnitude greater than the average for ECF mill wastewater treatment plant residuals (Wiegand, Thacker, and Miner 1999). (TEQ stands for “toxic equivalents” and it sums all of the dioxins and furans on the basis of their relative toxicity).

## References

Wiegand, P., Thacker, W., and Miner, R. 1999. Effluent quality at kraft mills that use complete substitution bleaching. *TAPPI Journal* 82(4): 135-144.

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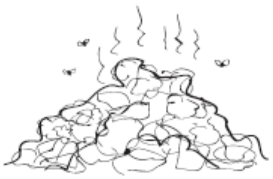

SOLID WASTE

## EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON SOLID WASTE

### Purging Residuals from the Process

The buildup of chlorides and non-process elements is a major obstacle to closing the bleach plant by reusing bleach plant filtrates in the pulping liquor cycle. For that reason, various alternative approaches have been proposed and used to purge substances that otherwise accumulate in the process and adversely affect either process chemistry and/or equipment integrity. Substances of consequence other than chlorides include potassium, calcium, barium, manganese, and iron.

Candidate technologies for isolating unwelcome filtrate contaminants into more concentrated waste streams include membrane filtration for alkaline stage organic compounds, ion exchange resins for metals, precipitation, and evaporation. Creative schemes for using some of these concentrated residues have been contemplated, but treatment and/or incineration, and producing residual ash, are the more readily available alternatives. Spent ion exchange resins would also require disposal.

A chloride removal process (CRP) and metals removal process (MRP) have had application in Champion International's Canton, North Carolina mill (now Evergreen Packaging) since 1995. The mill's patented bleach filtrate recycle (BFR$^{TM}$) process uses oxygen delignification and elemental chlorine free (ECF) bleaching (ODEopD), with recycle of bleach plant filtrate to the recovery system. The process has enabled recirculation of the initial D- and E-stage filtrates. In this case, contaminant concentrates containing potassium, chlorides and scale-forming alkaline earth minerals are sent to sewer (NCASI 2003).

Discarding a portion of the particulate catch of the recovery furnace electrostatic precipitator has been more commonly pursued to maintain suitable liquor levels of chloride and potassium. The recausticizing system also provides an outlet where precipitated contaminants emerge with the discarded dregs.

Progressive recirculation of the acid stage filtrates of ECF bleach sequences into the chemical recovery/recausticizing system is a means of reducing untreated wastewater organochlorine levels. It is also a means of adding to the burden of process contaminants that will require removal and potentially contribute to additional manufacturing solid waste.

### References

National Council for Air and Stream Improvement, Inc. (NCASI). 2003. *Pulp mill process closure: A review of global technology developments and mill experiences in the 1990s*. Technical Bulletin No. 860. Research Triangle Park, NC: National Council for Air and Stream Improvement, Inc.