**Meeting the Challenge of “No-Effect” Pulping and Bleaching**

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**Are Pulp and Paper Mills Environmentally Safe?**

Pulp and paper mills today are cleaner, more efficient and more environmentally safe than ever. A recent study from Sweden on the effluents from modern pulp mills confirmed that “it is clearly possible to meet high environmental demands while producing high-quality bleached kraft market pulp.”

Even so, changing marketplace requirements and new environmental concerns and regulations challenge the industry as never before. New advances in technological capabilities will make possible even further advances.

"No effect" is optimal. The goal of the pulp and paper industry is to continue to find technologies that meet customer demands, are economically viable and are environmentally acceptable. This goal has been described variously as having “no effect,” “minimum impact,” “zero effluent,” “effluent-free” or “closed system” operations.

While all human activity impacts the environment in one way or another, this vision embraces the concept of continuous improvement toward an optimal goal.

**Chlorine Dioxide is a Positive Step**

The use of chlorine dioxide as a bleaching agent is one step toward that goal. It is a very effective chemical with several advantages over chlorine. It is more "selective" and thus more gentle to wood fibers. Smaller amounts of it are needed to achieve the same quality of finished product. And, it produces 90 percent fewer byproducts of the type that may bioaccumulate in aquatic environments. Thus, chlorine dioxide is a positive step on the way to “no-effect” operations.

**More Research**

While the move to chlorine dioxide and other technologies is being accomplished relatively quickly, technologies that represent the next generation, including ozone, enzymes and peroxy acids, are still in the developmental stage. Extensive design and engineering will be necessary to incorporate the latest scientific advances.

Since many interconnected technologies are needed in pulp and papermaking operations, changes in one process often impact the performance of others. Consequently, one change often leads to many. Enormous resource commitments of time and capital are essential for most changes.

Weyerhaeuser is committed to continually implementing new and better systems, chemicals and equipment — moving ever closer to the optimal goal of a "no-effect" mill.

*Glossary of terms on back page.*

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Bleached pulp is key to the quality and performance characteristics of many everyday products.
How White Paper is Made

Cellulose is the Building Block

Cellulose fibers from trees have been used to make paper for several thousand years. Paper made in China 2000 years ago came from the soft inner bark of the mulberry tree. Today, wood and wood derivatives are still the primary source of cellulose fibers.²

To make paper, wood must first be pulped; its primary components must be broken down and separated from each other. These elements are cellulose, hemicellulose, lignin and resins.

Second, some of these components must be removed from the pulp. This is accomplished through several different stages of highly controlled washing and bleaching.

White paper is made by removing the lignin and the resins.

Why It's Important to Remove Lignin

Lignin impairs certain qualities that are important in white paper. Lignin and resins inhibit the ability of cellulose fibers to bond to each other. Paper that retains some level of lignin, like newsprint, is less strong than paper without lignin.

Paper with a higher lignin content is also less white because lignin is naturally tan colored. Pure white (“bright”) paper is made from pulp that has had nearly all of the lignin and resins removed.

What Determines How Paper is Made?

A product's intended use, customer and environmental requirements, available technology and tree species are among the factors that determine how paper is made. These vary by product.

Paper Products Are a Blend of Fiber Types

<table>
<thead>
<tr>
<th>Process and Fiber Type</th>
<th>Hygienic Products</th>
<th>Printing and Writing</th>
<th>Corrugated Containers</th>
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Softwood has long fibers (good for strength and bulk). Hardwood has short fibers (good for opacity and printability).

Each product has a different set of pulping and bleaching requirements.

For some products, bleaching is unnecessary. The paper for brown grocery bags and shipping cartons is perfectly acceptable unbleached.

For other products, bleaching is essential. It ensures purity in hygienic, surgical or food applications. It provides long-term resistance to discoloration for papers used in books and other documents. And it helps ensure that colors printed on photographic and printing papers are brilliant and true.

Where do the cellulose fibers come from?

In the United States, wood and recovered paper products provide the cellulose fibers needed for paper.²

- 30% from wood scraps from sawmills
- 25% from recovered wastepaper
- 45% from pulpwood trees*  

*Pulpwood trees are specifically planted, harvested and replanted in a continuous cycle to supply a sustainable supply of wood fiber.
PULPING FUNDAMENTALS

THERE ARE TWO WAYS TO MAKE PULP

There are two basic types of pulping processes, mechanical and chemical, with chemical being by far the most common.

Mechanical pulping grinds the wood into pulp. This abrasive action damages the cellulose fibers significantly. Though weakened, these fibers are suitable for some kinds of paper, such as newsprint.

For paper requiring more strength and flexibility, such as most printing and writing papers, chemical pulps are necessary. In chemical pulping, the integrity of the fibers is retained. Consequently, they form strong, flexible, interfiber bonds.

Today, 90 percent of all chemical pulp is made by the sulfate, or kraft, process.

WHAT DOES CHEMICAL PULPING DO?

Chemical pulping accomplishes two objectives: separates — as well as removes — the cellulose fibers from most of the other wood components (lignin, resins). No pulping process does this job completely, so further processing with bleaching chemicals is necessary for many products.

THE CHEMICALS ARE RECOVERED

In chemical pulping, wood chips are cooked under pressure and high temperatures with chemicals such as sodium sulfide and sodium hydroxide. These are then washed from the pulp with water and cycled through the recovery system where they are regenerated for reuse.

There are two clear environmental benefits to this process. First, 97 to 98 percent of the pulping chemicals can be recycled and regenerated.

Second, energy (in the form of steam and electricity) is produced from the extracted lignin during the process of recovering the chemicals. Chemical pulp mills today are essentially self-sufficient in energy, often producing a surplus of electricity.

ADVANCED PULPING TECHNOLOGIES

One of the principal aims of pulping research is to find ways to increase the amount of lignin removal during pulping. Technologies that remove more and more lignin prior to bleaching reduce the amount of chemicals needed during bleaching.

Recent technological advances — such as modified cooking (extended delignification) and pre-bleaching with oxygen — can remove 75 to 80 percent more residual lignin than traditional pulping can. This reduces the amount of bleaching chemicals by an equivalent 75 to 80 percent without sacrificing quality.

ADDING TO THE RECOVERY SYSTEM

These modifications, however, also create new demands on the recovery system, so other changes become necessary. In particular, the largest piece of equipment, the recovery boiler, may require extensive improvements to avoid decreased production capacity and increased costs.

Evolving Pulping Technologies

Remove Greater Amounts of Lignin

Recent advances in washing, pulping and oxygen prebleaching technologies have significantly increased lignin removal. Chemicals required for bleaching are reduced by an equivalent amount.

Note: Not result of combining the processes is not additive.
**BLEACHING FUNDAMENTALS**

**BLEACHING COMPLETES THE PULPING PROCESS**

To preserve the integrity of the cellulose fibers while producing the highest-quality, whitest pulps, further processing is required. Pulping alone cannot remove all of the lignin without damaging fibers and impairing strength as well as yield.

Bleaching is necessary for many products. Among them are those that must be absorbent and pure, such as products used for personal hygiene. Bleached pulp is required for papers that are expected to hold up well in storage and for papers that will not yellow or turn brittle. It is also essential for photographic paper or any paper for which high-quality color reproduction is required.

**BLEACHING IS DONE IN A SERIES OF STAGES**

Typically, three to five distinct stages and five or more different chemicals are needed to bleach pulp. Each stage involves different chemicals and a different set of conditions (such as time, temperature, pressure and chemical concentration). The process is carefully controlled and highly interconnected to minimize water, chemical and energy resources.

Following each chemical treatment, the pulp is washed to remove residual lignin and unreacted chemicals.

Bleaching sequences have been modified with advances in technology. More effective chemical usage and more efficient systems result from the modifications.

**BLEACHING CHEMICALS ARE "SELECTIVE"**

Compared with pulping chemicals, bleaching chemicals are highly "selective." They remove lignin without further weakening the wood fibers. Since they are more effective, they are needed in smaller amounts than the less-selective pulping chemicals.

Oxygen towers operate under high pressure and temperature and require special (inert) metallurgy. Oxygen and other bleaching chemicals are not readily interchangable.

The Evolution of Bleaching Chemicals: A Worldwide Perspective

![Relative Amounts of Bleaching Chemicals](chart)

Source: Croon Consult, Stockholm, Sweden 1991

**NOTE:** Bleached pulp production growth averages about 2 percent per year.

Peroxide use includes bleaching of mechanical as well as chemical pulps.

Progress in technology and equipment design allows for continuous improvement in the types and amounts of bleaching chemicals.
CHLORINE DIOXIDE REDUCES ENVIRONMENTAL IMPACTS

HOW CHLORINE WORKS

Pulp and papermakers have historically used chlorine and related compounds in the bleaching process. In combination with alkaline extraction, chlorine breaks down lignin molecules. These smaller molecules are soluble and are washed out and biologically treated in the effluent treatment system.

With chlorine bleaching, about 10 percent or less of the chlorine becomes molecularly bound to the lignin, forming chlorinated organics.\(^5\)

Pulp bleached without chlorine is often called ECF — or elemental chlorine-free. This means that chlorine compounds, but not chlorine by itself is used. Pulp bleached without any chlorine compounds is called TCF — or totally chlorine-free.

CHLORINE DIOXIDE IS MORE EFFECTIVE

While chlorine dioxide contains the word “chlorine,” it is a very different chemical with different characteristics and by-products.

Chlorine dioxide is the most effective bleaching chemical in use today. It is over 2\(\frac{1}{2}\) times more effective than chlorine at removing unwanted lignin molecules from pulp.\(^6\) Consequently, a smaller amount of chlorine dioxide is needed to produce the same quality and quantity of pulp.

Because it is a more “selective” chemical, chlorine dioxide is also less damaging to wood fibers than chlorine. This selectivity is so great it can be described as “surgical.”

FEWER CHLORINATED ORGANICS

Chlorine dioxide oxidizes lignin with minimal formation of chlorinated organics. It produces about one-tenth of the chlorinated organics that are produced in bleaching with chlorine.\(^7\)

Chlorine dioxide also produces far fewer chlorinated organics of the type that are highly chlorinated and biopersistent. Compared with chlorine, the difference is a 90 percent reduction.\(^8\)

ECF IS A STEP

Chlorine dioxide-production capacity can be installed or increased more readily than other major modifications, producing immediate results. It is an important step toward the optimal goal of “no effect.”

It is not, however, an inexpensive endeavor. It is approximately eight times more expensive to produce than is chlorine. Costly production equipment is also required.\(^6\)

<table>
<thead>
<tr>
<th>Chlorine</th>
<th>Chlorine Dioxide</th>
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<td>Less expensive</td>
<td>2(\frac{1}{2}) times more effective</td>
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<tr>
<td>10% becomes chlorinated organics</td>
<td>Greater molecular selectivity</td>
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<td></td>
<td>Produces lower AOX</td>
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<td>1% becomes chlorinated organics</td>
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Chlorine dioxide offers some distinct advantages over chlorine.

Three or more bleaching stages are needed to complete the bleaching process. Each stage requires different conditions of time, temperature, pressure and chemical dosage.
THE RECOVERY CYCLE

RECOVERY IS THE GOAL

Recovering and reusing chemicals is a goal of the pulp and paper industry. Recovery decreases costs, lessens environmental impacts and produces energy as a by-product. A typical recovery cycle is 97 to 98 percent efficient. And modern chemical pulp mills produce more energy than they consume.

Ideally, all or nearly all of the bleaching and pulping chemicals could be recovered for reuse. This would virtually eliminate the need for effluent treatment.

Today only pulping chemicals are fully recoverable. Some bleach effluents are too corrosive and cannot currently be recycled. Instead, they are biologically treated to reduce by-products and eliminate their toxicity.

The pulp and paper industry is researching technologies that will accomplish more recovery. Some that have been successfully integrated into the system include modified cooking (extended delignification), oxygen pre-bleaching and high-efficiency washing. Other technologies, such as ozone, are in active development.

Wood chips

The range of typical components is species-dependent:
- 40-50% Cellulose
- 25-39% Hemicellulose
- 18-31% Lignin
- 2-3% Resins

Effluents are released after treatment

Bleach-plant effluent consists of water, dissolved wood resins, lignin fragments and spent chemicals. This effluent undergoes mechanical and biological treatment, typically lasting up to 30 days.

Effluent-treatment systems reduce or eliminate three principal by-products: total
Incorporation of the latest technologies has allowed Weyerhaeuser to make continuous progress toward "no-effect" mills. suspendsed solids (TSS), oxygen-consuming substances (measured as BOD or COD), and chlorinated organic substances (measured as AOX). They also greatly reduce or eliminate potential toxicity to aquatic organisms.

Scientific research indicates that very low concentrations of these by-products can be safely released into the aquatic environment. (Some chlorinated organics already occur naturally in rivers and oceans).

**Meeting U.S. Clean Water Act Requirements**

Today's pulping and bleaching effluents meet the stringent requirements outlined in the U.S. Clean Water Act. Our optimal goal of "no effect" will call for further water purification. Membrane technology, chemical post-treatment and other advanced biological treatment systems are potential options. Finding the right system is an important part of meeting the goal.
**CHLORINE IN THE ENVIRONMENT**

**CHLORINE OCCURS NATURALLY**

Both chlorine and biologically formed chlorinated organics occur naturally in the environment. Oceans, rivers and peat bogs are major sources of organic chlorine compounds. The Atlantic Ocean, for example, is estimated to produce 100 million tons of chloroform each year.

**NATURAL PROCESSES ELIMINATE CHLORINATED ORGANICS**

Regardless of their origin, under certain conditions (for example, in sediments and sludge), natural anaerobic bacteria react with these compounds, effectively eliminating them. This process is called biodehalogenation.

**NOT ALL CHLORINATED ORGANICS ARE THE SAME**

In general, the number of chlorine atoms in chlorinated organic molecules determines the degree of toxicity. The more chlorine atoms, the more bio-persistent the compound, and the more potential for toxicity.

Bleaching with chlorine produces some molecules with three or four chlorine atoms; bleaching with chlorine-dioxide predominantly produces molecules with only one or two chlorine atoms.

**WITH ADVANCES IN TECHNOLOGY, AOX IS DECREASING**

**AOX DOES NOT MEASURE TOXICITY**

AOX is a broad term that combines all types of chlorinated organics into one number. It measures the total amount of chlorine bound to organic compounds. It does not distinguish between compounds that bioaccumulate and those that don't. An AOX measure by itself, then, does not relate directly to toxicity or ecological impact.

**WHAT IS EOCI?**

Extractable organic chlorine, called EOCI, is that fraction of AOX that is extractable in a non-polar solvent. It represents about 1 to 3 percent of the AOX.

Of the EOCI, about 10 percent may contain compounds that most readily bioaccumulate and are considered potentially most toxic and persistent. Of those, the lipophilic organic compounds are the most likely to bioaccumulate in the fatty tissue of animals.

The compounds that are of most concern are polychlorinated organics with three or more chlorine atoms per molecule. Dioxin, with four chlorine atoms per molecule, is one such compound.

**EOCI IS REDUCED WITH CHLORINE DIOXIDE**

EOCI is reduced tremendously when bleaching is done with chlorine dioxide, rather than chlorine. Other advances, including extended delignification, oxygen delignification, and optimized washing and mixing techniques, have also helped in reducing the formation of chlorinated organics.

Effluent-treatment systems typically eliminate about half of the chlorinated organics produced in bleaching. Effluent-treatment systems typically eliminate about half of the chlorinated organics produced in bleaching. 11

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DIOXIN HAS BEEN VIRTUALLY ELIMINATED

Under certain conditions, bleaching with chlorine can produce minute levels of dioxins. When this was discovered, in 1985, the pulp and paper industry immediately launched extensive research to determine how dioxin was being formed and to find ways to eliminate it.

Substitution of chlorine dioxide for chlorine, along with pulping, mixing and washing modifications, has helped the industry to significantly reduce dioxin levels. Today, Weyerhaeuser has virtually eliminated dioxin formation in its processes.

Continuous technological improvement is made possible through ongoing scientific research.

Efficient removal of lignin and pulping or bleaching chemicals demands high-performance washing. These counterflow washers help ensure that the bleaching process is kept to a minimum.
MODIFICATIONS ARE NOT SIMPLE
Modifications to any part of the pulping and bleaching process can impact the whole system. It’s not as simple as substituting one chemical for another, or one process for another.

State-of-the-art pulp and papermaking is an extremely complex process, involving a series of complicated, interconnected chemical and/or mechanical processes. Proposed system modifications first require detailed analysis and modeling to determine their overall impacts.

COSTLY INVESTMENTS
According to a recent report in Forbes magazine, U.S. papermakers have spent $100 billion modernizing and building new plants since 1980. The industry invests more on plant and equipment per dollar of sales than any other industry. Modifications can range from $25 million to more than $300 million per plant.

Experience shows it generally takes up to three years for design and construction of modified mills.

CHANGES MUST MEET FUTURE DEMANDS
With these kinds of investments, any modifications must be right “the first time.” They must satisfy current, as well as future, product, environmental and customer requirements.

New technologies must be proven technologies. They must undergo thorough testing and analysis in pilot projects before they can be expanded to commercial use. And care must be taken that improvements in one area of emissions (for example water effluents) do not create new problems in other areas (for example, in air quality or solid waste). Risks must be minimized and opportunities must be maximized.

CURRENT TECHNOLOGIES RECOVER MORE
Extended delignification and oxygen prebleaching are allowing effluents that formerly were treated and discharged to be recovered and reused. Bleaching research is focused on developing new technologies that will allow for the recycling of even more chemicals — essentially all bleach plant effluents.

Chlorine dioxide is an effective bridge to new technologies. Ozone and other promising bleaching technologies, including peroxy acids and enzyme treatments, are on the horizon. As they, and other technologies, become technically and economically viable, they will be incorporated into the bleaching process. The vision of “no-effect” mills is today being realized.
Weyerhaeuser is committed to continuous improvement in environmental performance. This will be accomplished through a steady transition to new and improved technologies.

Weyerhaeuser welcomes the challenge of meeting customer and environmental requirements with safe, efficient and cost-effective processes and equipment.

Pulp and paper mills today are cleaner, more efficient and more environmentally safe than ever. Pulping and bleaching effluents meet the stringent requirements of environmental regulations such as the Clean Air Act and the Clean Water Act. Additionally, these modern mills save fossil fuels by producing their own energy.
GLOSSARY

AOX (adsorbable organic halogen) — “Adsorbable” refers to a physical attachment to a surface; “organic” is a carbon compound; and “halogen” refers to either fluorine, chlorine, bromine or iodine.

alkaline extraction — Removal of lignin activated by oxidative bleaching agents with sodium hydroxide (alkali).

bioaccumulate — The tendency to accumulate in living organisms.

biologically chlorinated — Naturally occurring organic compounds containing one or more chlorine atoms.

bio-persistent compounds — Compounds that are broken down or excreted slowly by the metabolism of complex organisms.

cellulose — A natural polymer of glucose units that constitutes the chief component of the cell walls of plants.

cellulose — A substance consisting of two or more different chemical elements.

chlorinated organics — Carbon compounds with chlorine atoms.

delignification — The removal of lignin from wood.

ECF (elemental chlorine-free) — Refers to pulp that has been bleached without the use of chlorine gas.

enzyme — A complex protein that catalyzes (promotes) specific biochemical reactions.

EOCl (extractable organic chlorine) — Compounds containing carbon and chlorine that are soluble in a non-polar solvent.

hemicellulose — Non-cellulosic wood carbohydrates.

highly chlorinated — Chemical compounds that have numerous chlorine atoms.

lignin — The substance that provides stiffness to plant tissues, making them woody.

lipophilic — Fat soluble.

membrane technology — Advanced filtration technology based on osmotic pressure.

non-polar solvent — Any of a class of organic liquids that are insoluble in water.

organics — Chemical compounds derived from carbon compounds.

ozone — A form of oxygen containing three, rather than two, oxygen atoms.

peroxy acids — Organic compounds that contain a high proportion of reactive oxygen atoms.

residual lignin — That lignin which remains after wood chips have been pulped.

“selective” chemicals — The molecular structure of some chemicals predisposes them to react to other chemicals in particular, selective ways.

“spent” chemicals — Used chemicals that have been depleted of their original properties (ability to react to other compounds).

TCF (totally chlorine-free) — Refers to pulp that has been bleached without the use of chlorine compounds.

TOCl (total organic chlorine) — Compounds containing carbon and chlorine.

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