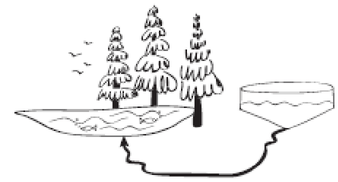
ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

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



DISCHARGES TO WATER

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.

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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.

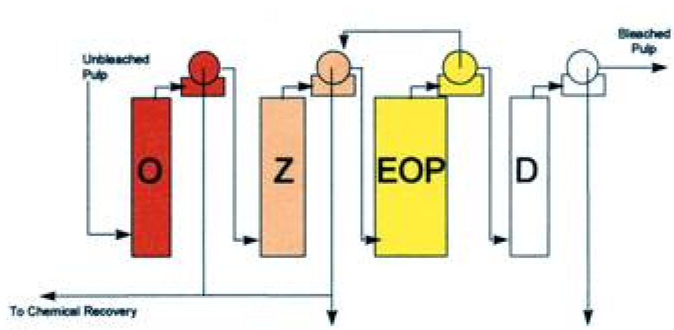

Figure C18. Bleaching Sequence Showing Alkaline Filtrate Recovery

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.

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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).

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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).

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