

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

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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% ClO₂ 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.

	Hardwood Lines		Softwood Lines	
Type of Mill ^b	Average	No of Linco	Average	No of Linco
	(пі /кку)	NO. OF LINES	(пт/ккд)	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

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

^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

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